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Nickel(II)-Catalyzed Direct Olefination of Benzyl Alcohols with Sulfones with the Liberation of H_2

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Contents

1. General Information

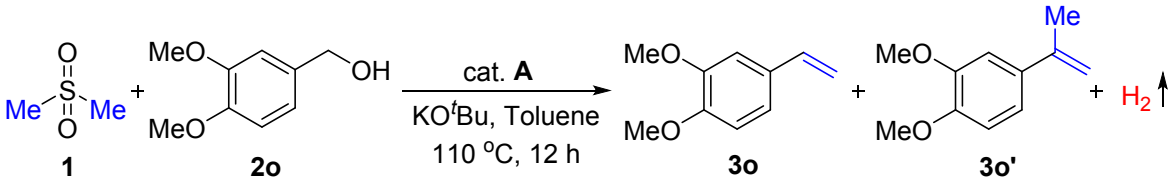
All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone and followed by distilled under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (SilicycleSiliaflash F60 (230-400 mesh). ^1H NMR (400 or 500 MHz), $^{13}C\{^1H\}$ 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 7.26 for ^1H (chloroform-d), δ 77.2 for $13C\{^1H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained 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). HPLC analysis was performed on Agilent Technologies 1260 Infinity with UV detector.

2. Experimental Section

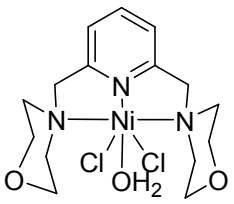
All the nickel complexes were prepared based on previously reported procedure.[1]

2.1 Reaction Optimization

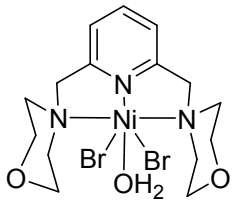
Table S1. Optimization of reaction condition.[a]



Entry	Reaction conditions	Yield of **3o** & **3o'** (%)[b]
1	$NiCl_2$ used as [Ni] source	32 (7)
2	$NiBr_2$	38 (6)
3	$NiCl_2(PMe_3)_2$	47 (8)
4	$Ni(Cp^*)_2$	52 (12)
5	Standard conditions	76 (2)
6	Catalyst B	72 (6)
7	K_2CO_3 instead of KO*t*Bu	n.r.
8	Na_2CO_3 instead of KO*t*Bu	n.r.
9	Cs_2CO_3 instead of KO*t*Bu	n.r.
10	KOH instead of KO*t*Bu	61 (8)
11	1,4 dioxane used as solvent	n.r.
12	n-octane used as solvent	71 (6)
13	rt	n.r.
14	at 80 °C	62 (5)



(**A**)



(**B**)

[a]Reaction conditions: **1** (0.5 mmol), **2o** (0.5 mmol), cat.[Ni] (3 mol%), KO*t*Bu (0.55 mmol), and toluene (1 mL), 110 °C, 12 h. [b]Isolated yields. n.r. = no reaction.

Optimization studies on the direct olefination are summarized in Table 1. We began our investigation using dimethyl sulfone (DMS) (**1**) as a model substrate and (3,4-dimethoxyphenyl)methanol (**2o**) as a coupling reagent in the presence of $NiCl_2$ (3 mol %), and KO*t*Bu (1.1 equiv) as a base in refluxing toluene for 12 h to yield the expected product **3o** in 32% isolated yield (Table S1, entry 1). Under similar conditions other nickel salts were also examined and gave moderate yield of the olefinic product (Table S1, entries 1-4). Interestingly, by employing NNN-Ni(II) complexes **A** and **B** under optimal conditions, the product **3o** was obtained in 76% and 72% yield, respectively (Table S1, entries 5-6). Notably, the liberated hydrogen gas was detected on gas chromatography and quantified.

Significantly, no dehydrogenative olefination was observed in the absence of Ni-catalyst. Other bases such as Cs_2CO_3, KOH, and K_2CO_3 gave poor results under standard reaction conditions (Table S1, entry 7-9). Next the effect of solvent under our Ni-catalyzed conditions was performed, and found that the reaction proceeds efficiently in toluene compared to other solvents and affording **3o** in good yield (Table S1, entry 11-12). By lowering the temperature, we have obtained the product **3o** in lower yield (Table S1, entry 13-14).

2.2 General procedure for the nickel-catalyzed olefination of alcohols

To an oven-dried 10 mL screw-capped vial, catalyst **A** (3 mol%), sulfone **1** (0.5mmol), alcohol **2** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated slowly under reduced pressure maintaining the water bath temperature 23 ^oC. The solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

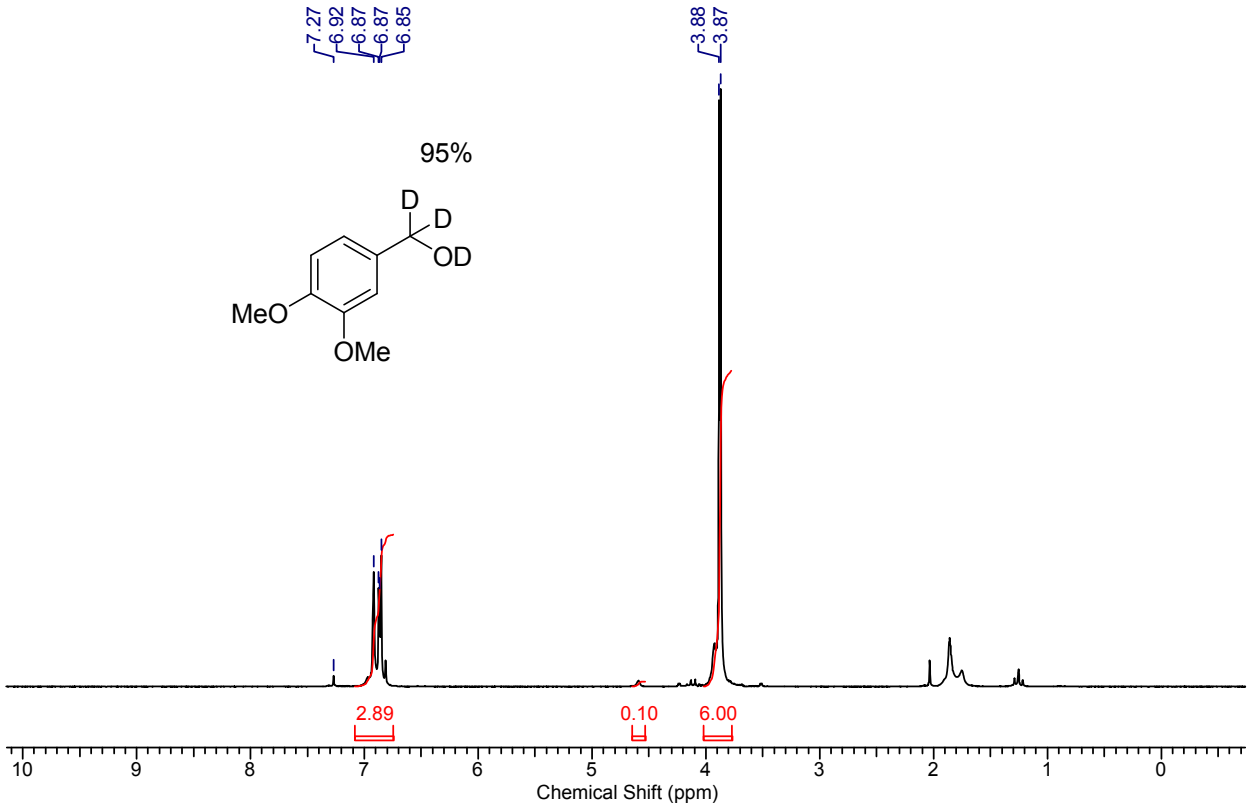
2.3 General procedure for the demethylation of 9

To an oven-dried 10 mL screw-capped vial, (*E*)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (0.5 mmol) in CH_2Cl_2 (2 mL) under argon was treated with BBr_3 (5 equiv) at 0 ^oC. The solution was warmed to room temperature and stirred for 5 h followed by the slow addition of water (4 mL) and further stirring for 30 min. Then, CH_2Cl_2 was evaporated under reduced pressure and the water phase was extracted with EtOAc (3×5 mL). The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using MeOH/CH_2Cl_2 as an eluting system to afford **10**.

3. Mechanistic studies

3.1 Synthesis of [D_3]-2o

To an oven-dried 10 mL screw-capped vial, Ru-MACHO (3 mol%), 3,4-dimethoxybenzyl alcohol **2** (0.1 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), deuterium oxide (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 130 °C for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

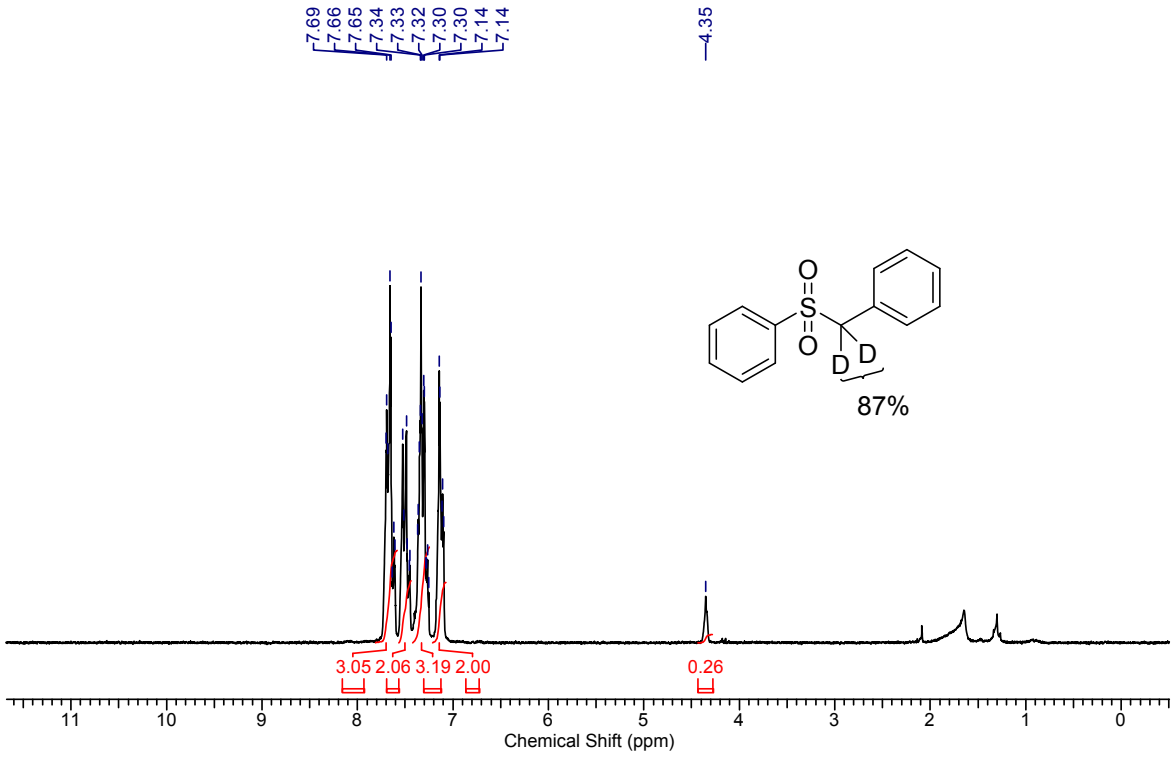


^{1}H NMR of [D_3]-2o

3.2 Synthesis of deuterated sulfone [D2]-4

To a solution of the benzyl phenyl sulfone (0.5 mmol) in THF (6 mL) containing DBU (5 equiv.) was added deuterium oxide (1 mL, 99.9 at % D). The mixture was stirred in a closed vial at room

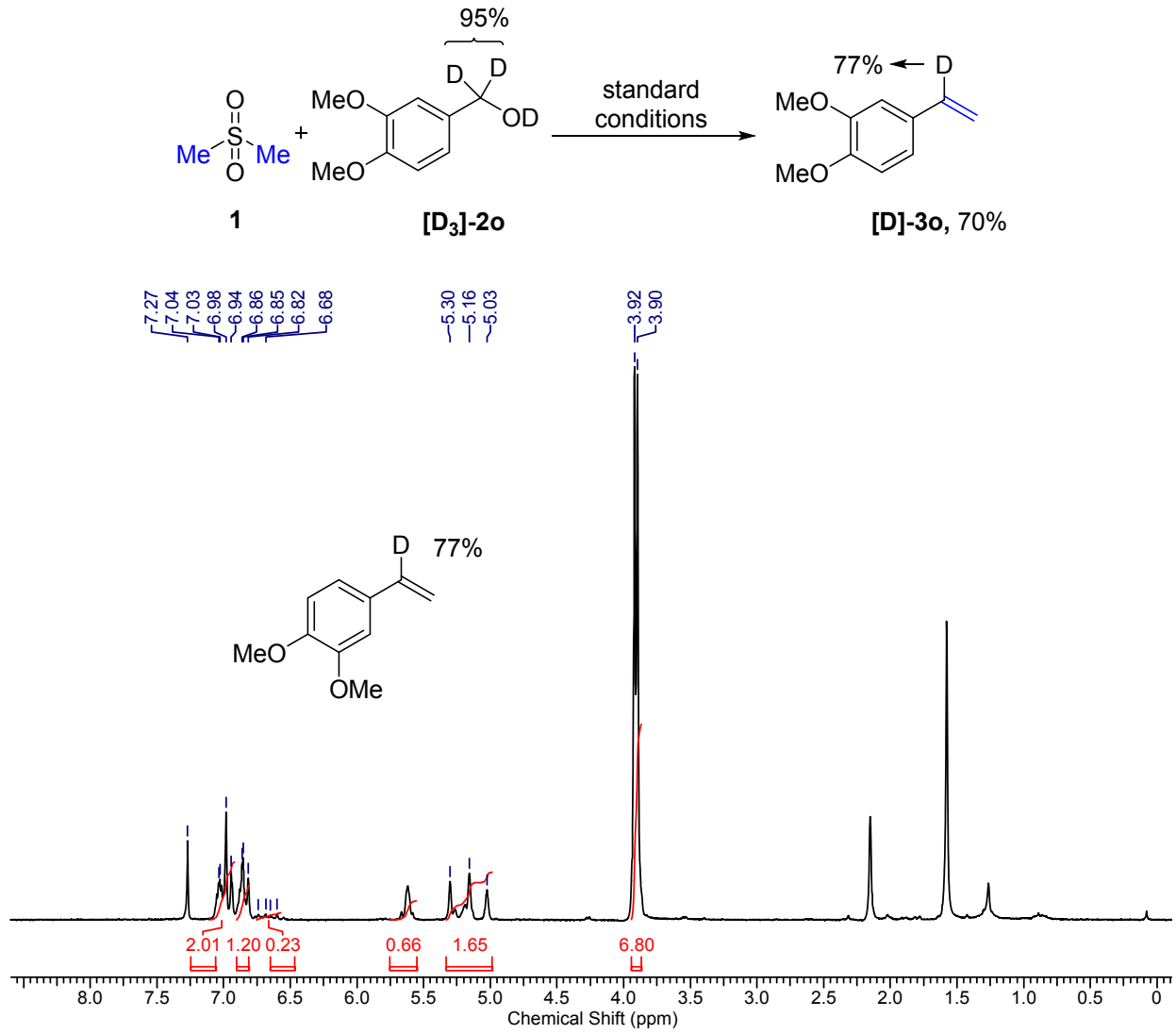
temperature for 18 h. To the mixture was added ethyl acetate (2 mL) and three times washed with 1N HCl (5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure and the compound was use directly used for further reaction.



^{1}H NMR of Deuterated sulfone [D2]-4

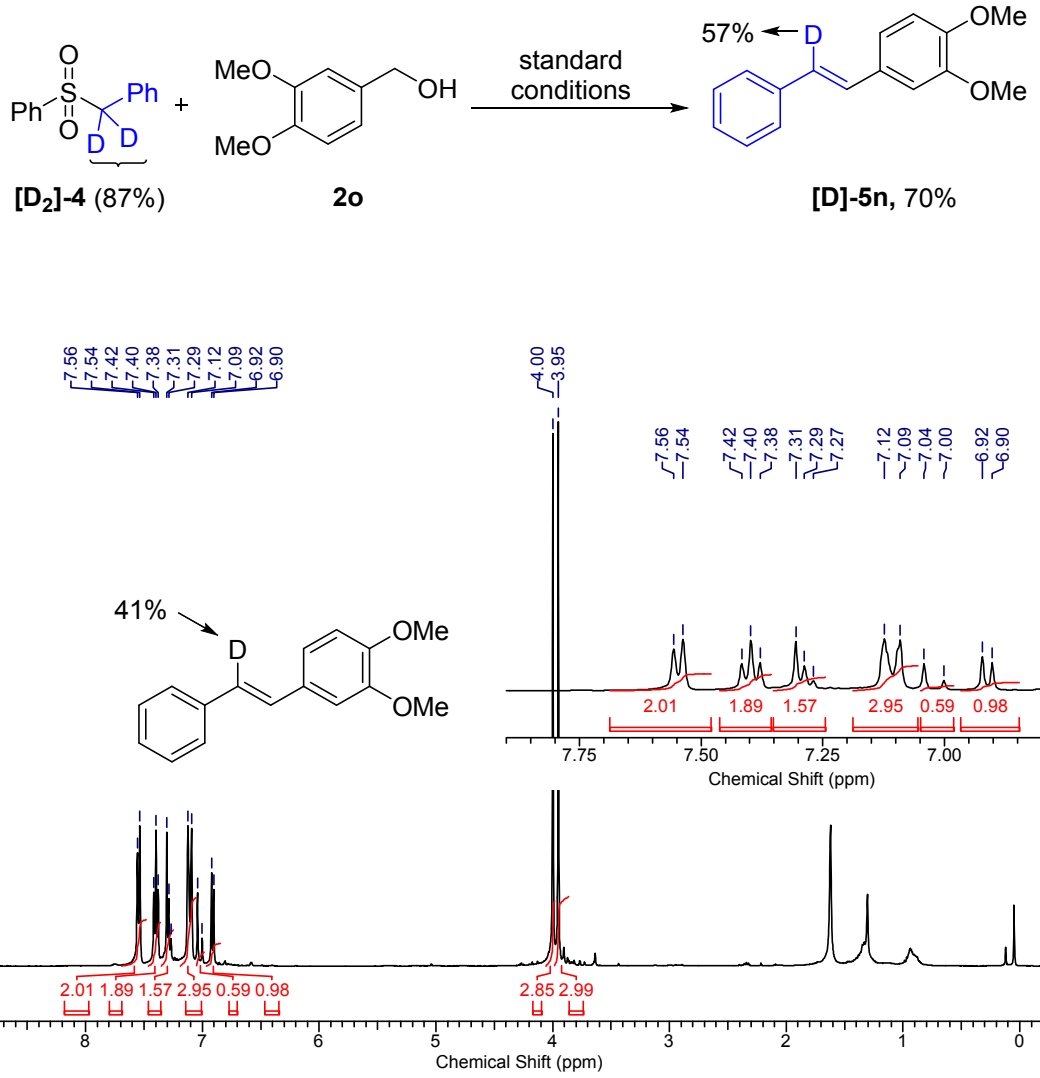
3.3 Deuterium labelling experiments

a) To an oven-dried 10 mL screw-capped vial, complex **A** (3 mol%), dimethyl sulfone **1** (0.5 mmol), 3,4-dimethoxy benzyl alcohol [**D_3**]-**2o** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.



1H NMR of [D]-3o

b) To an oven-dried 10 mL screw-capped vial, complex **A** (3 mol%), benzyl phenyl sulfone [**D_2**]-**4** (0.5mmol), 3,4-dimethoxy benzyl alcohol **2o** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

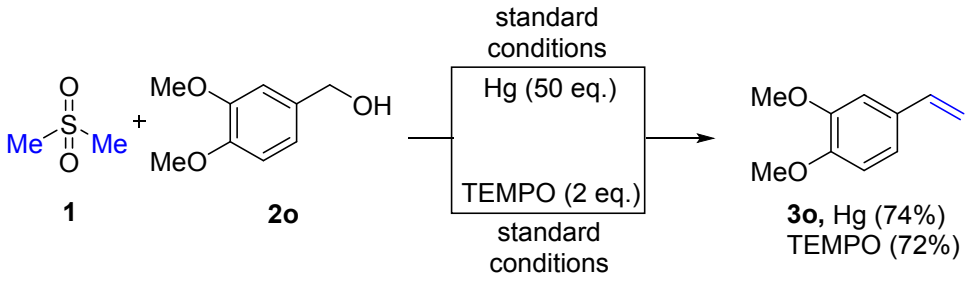


^{1}H NMR of [D]-5n

3.4 Reaction in presention of Hg and TEMPO

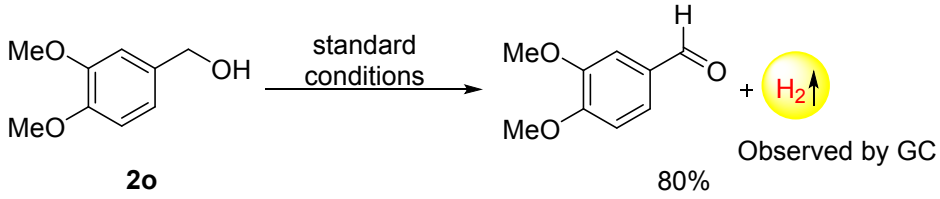
To an oven-dried 10 mL screw-capped vial, complex **A** (3 mol%), dimethyl sulfone **1** (0.5 mmol), 3,4-dimethoxy benzyl alcohol **2o** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), Hg (50 equivalent with respect to catalyst) or TEMPO (2 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated

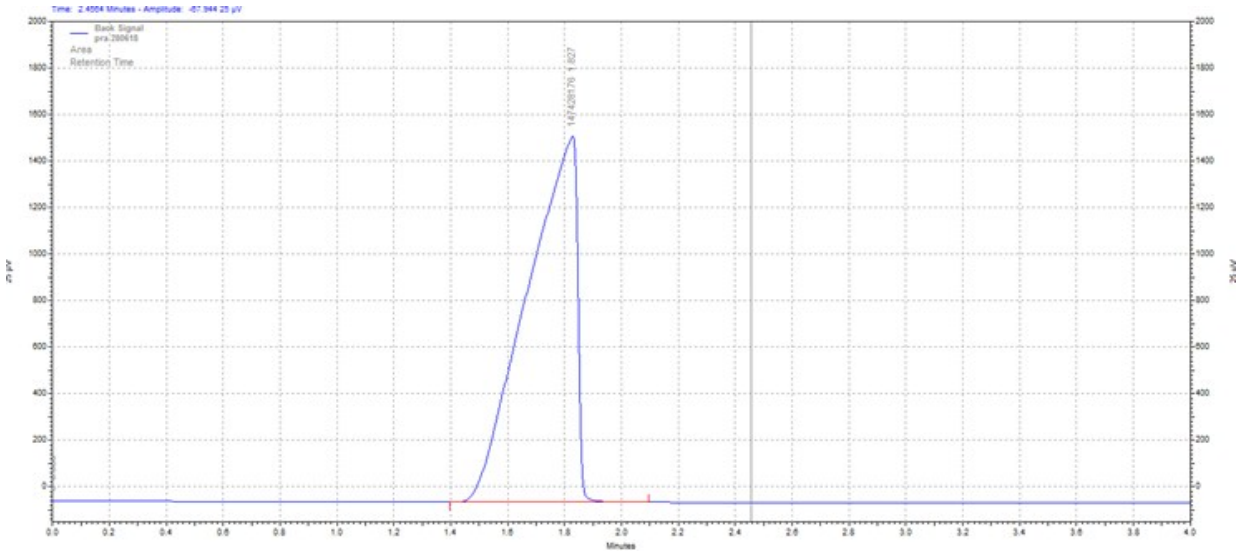
under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.



3.5 Qualitative analysis of hydrogen gas and aldehyde intermediate

To an oven-dried 10 mL screw-capped vial, complex **A** (3 mol%), 3,4-dimethoxybenzyl alcohol **2o** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the gaseous mixture was analysed on GC (TCD detector) which showed the formation of dihydrogen.



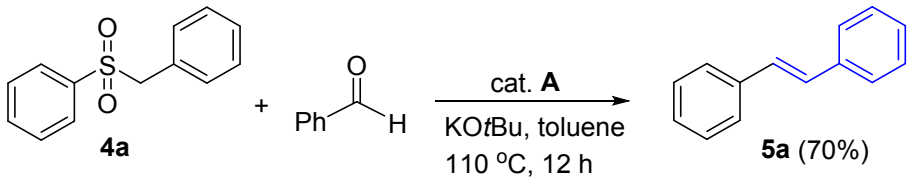


GC spectra of H_2

3.6 Control experiments

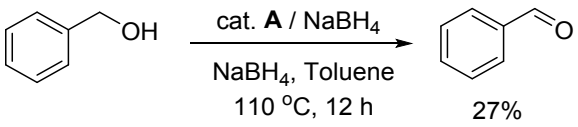
(a) Reaction with aldehyde:

To an oven-dried 10 mL screw-capped vial, complex **A** (3 mol%), benzyl phenyl sulfone **4a** (0.5 mmol), benzaldehyde (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.



(c) Dehydrogenation of alcohol by *in situ* generated Ni-H species

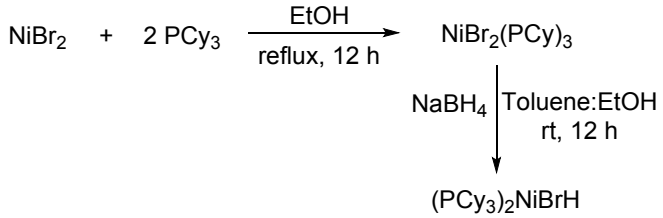
To an oven-dried 10 mL screw-capped vial, catalyst **A** (3 mol%), benzyl alcohol (0.5 mmol), sodium borohydride (3 mol%), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was submitted for GC and GC-MS.



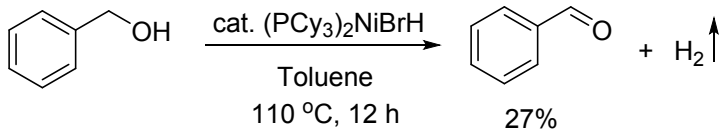
(d) Preparation of Ni-complexes and dehydrogenation of benzyl alcohol

Based on the literature reported procedure, the $PCy_3)_2NiBr_2$ complex was prepared (*J. Chem. Soc. A* **1971**, 152-154). The $(PCy_3)_2NiBrH$ complex was obtained as yellow solid (decomposes very

fast in solvent). Characterization data are in agreement with the literature reported data (*ISRN Inorg. Chem.* **2013,** 1-13; Melting point = 152 ^{o}C (decomposed).

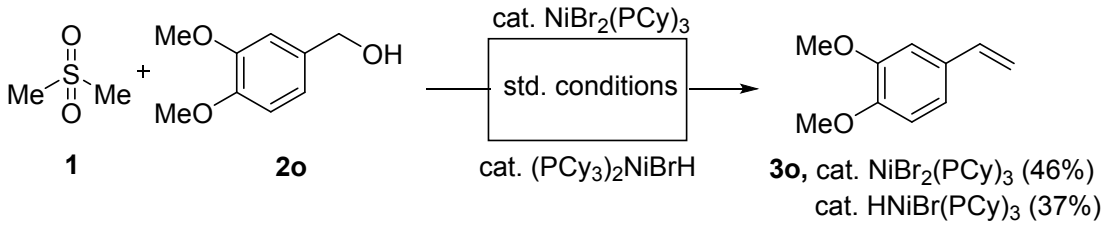


To an oven-dried 10 mL screw-capped vial, $PCy_3)_2NiBrH$ (5 mol%), 3,4-dimethoxybenzyl alcohol **2o** (0.5 mmol), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the gaseous mixture was analysed on GC (TCD detector) which showed the formation of dihydrogen and gave the corresponding aldehyde in 23% yield.



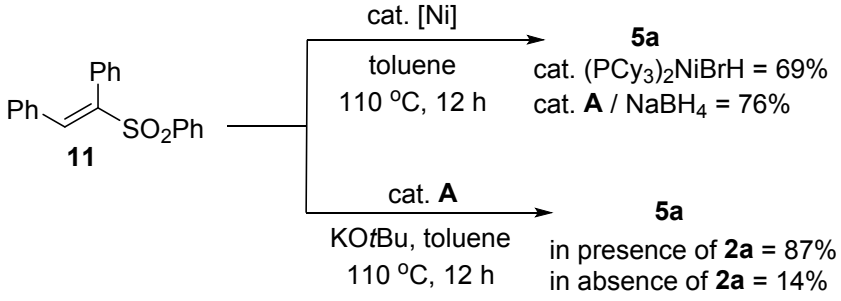
(e) Direct olefination reaction catalysed by $PCy_3)_2NiBr_2$ or $PCy_3)_2NiBrH$ complexes

To an oven-dried 10 mL screw-capped vial, $PCy_3)_2NiBr_2$ (5 mol%) or $PCy_3)_2NiBrH$ (5 mol%), sulfone **1** (0.5mmol), alcohol **2** (0.5 mmol), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated slowly under reduced pressure maintaining the water bath temperature 23 ^{o}C. 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.

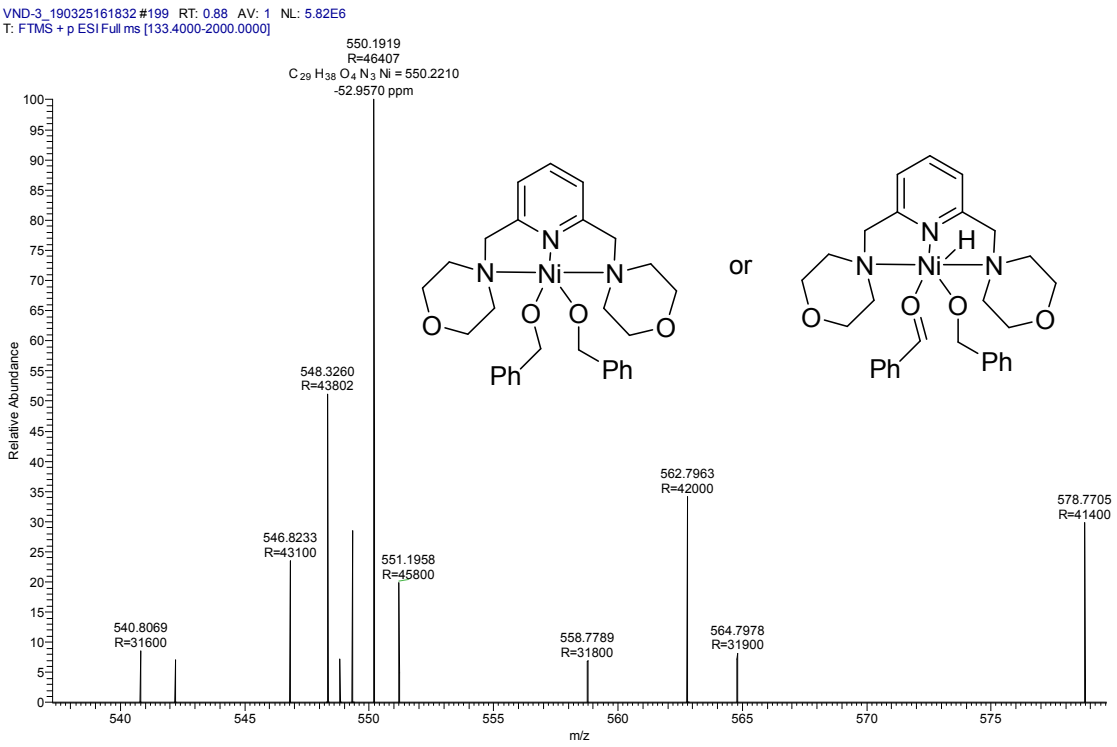


(f) Reaction with vinyl sulphone (11):

To an oven-dried 10 mL screw-capped vial, (complex **A** (3 mol%) + KO*t*Bu (0.55 mmol, 1.1 equivalent) or 5 mol% of $PCy_3)_2NiBrH$ or complex **A** (3 mol%) + 3 mol% of $NaBH_4$), (*E*)-(1-(phenylsulfonyl)ethene-1,2-diyl (**11**, 0.5mmol), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 12 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was submitted for GC and GC-MS.



3.7 Detection of intermediates by HRMS: To an oven-dried 10 mL screw-capped vial, catalyst **A** (0.5 mmol), benzyl alcohol (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at reflux for 4 h. Then, the reaction mixture was submitted for HRMS.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C 29 H 38 O 4 N 3 Ni = 550.2210
-52.9570 ppm
548.3260
R=43802
546.8233
R=43100
551.1958
R=45800
540.8069
R=31600
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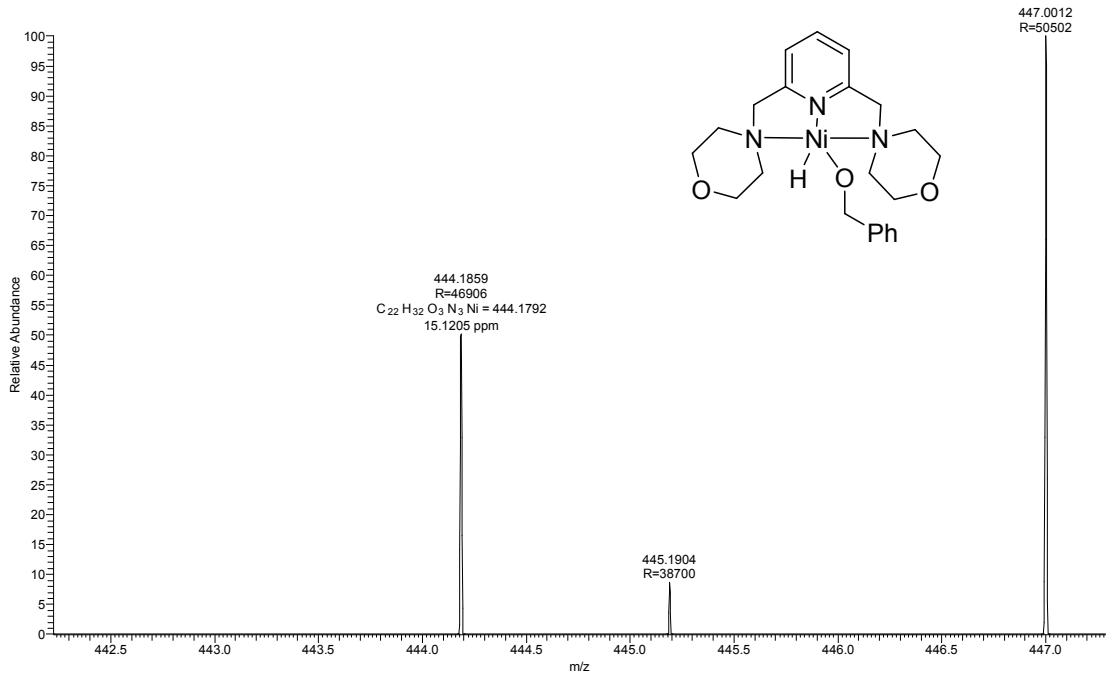
578.7705
R=41400
or
Relative Abundance
m/z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R=50502
444.1859
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C 22 H 32 O 3 N 3 Ni = 444.1792
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445.1904
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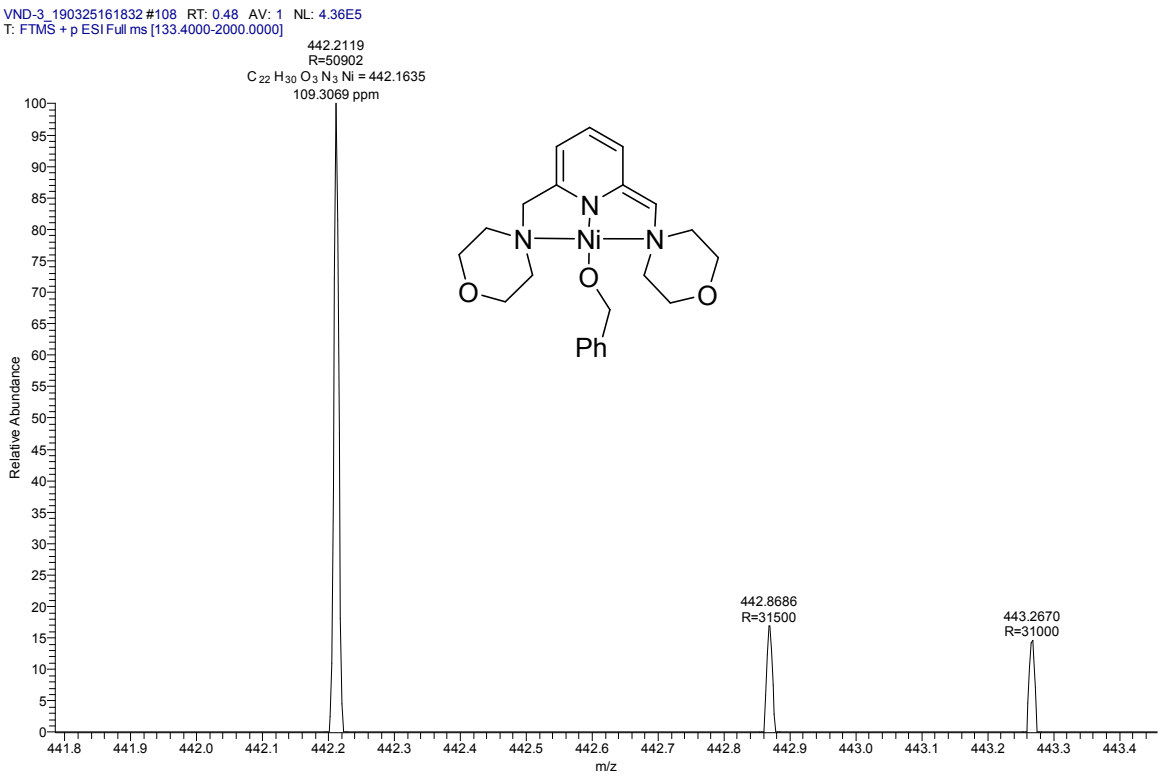
Relative Abundance
m/z



HRMS analysis of reaction mixture

3.8 Kinetics analyses

The progress of the reaction studied with the kinetic analyses and revealed that the olefination reaction is first order with respect to sulfone and catalyst, and fractional order in alcohol and the base concentration.

Rate-order determination

The initial rate method was used to determine the rate order of the olefination reaction with respect to various components of the reaction. The data of the concentration (mmol) vs time (min.) plot was fitted to linear using origin pro 8. The slope of the linear fitted curve represents the reaction rate. The order of the reaction was determined by plotting log(rate) vs log(conc.) of that particular component.

3.8.1 Rate order determination with respect to benzyl alcohol (2a)

To determine the order of the olefination reaction on **2a**, the initial rates at different initial concentrations of **2a** were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

To an oven dried 15 mL screw cap pressure tube, benzyl phenyl sulfone (0.216 mmol, 1 eq.), Ni catalyst (0.0108 mmol, 5 mol%), KO^{t}Bu (0.216 mmol, 1 eq.), mesitylene (0.216 mmol, 1 eq.) as an internal standard, specific amount of **2a** and toluene (1.95 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2 mL. The reaction mixture was kept for stirring at 140°C (bath-temperature). At regular intervals (10 min, 20 min, 30 min, 40 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (mmol) vs time (min.) plot (**Figure S1**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of **2a** was given in (**Table S1**) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S2**) to determine the order of reaction with respect to benzyl alcohol.

Table S1. Rate of the olefination reaction at different initial concentration of (**2a**).

Experiment	**Amount of 2a (gm)**	**Initial concentration of 2a (mmol)**	**Initial rate [mmol/min]× 10^{-4}**
1	0.012	0.108	1.74
2	0.023	0.216	3.09
3	0.035	0.324	5.012
4	0.047	0.436	7.24

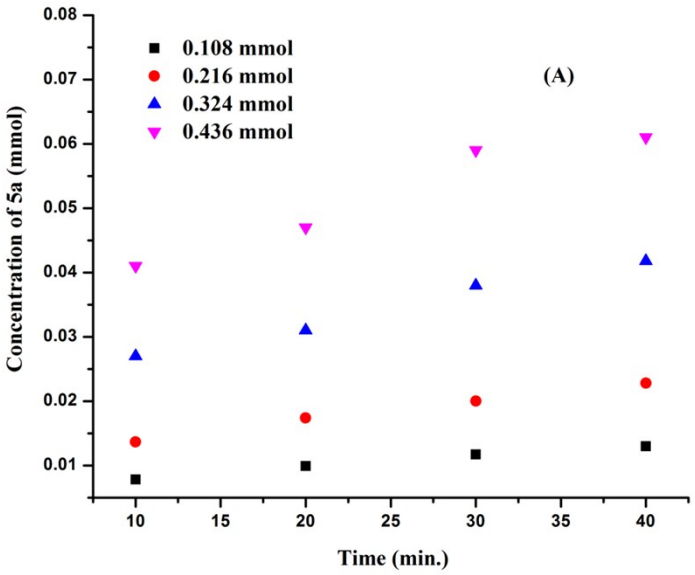


Figure S1. Concentration *vs* time plot at various concentrations of (**2a**).

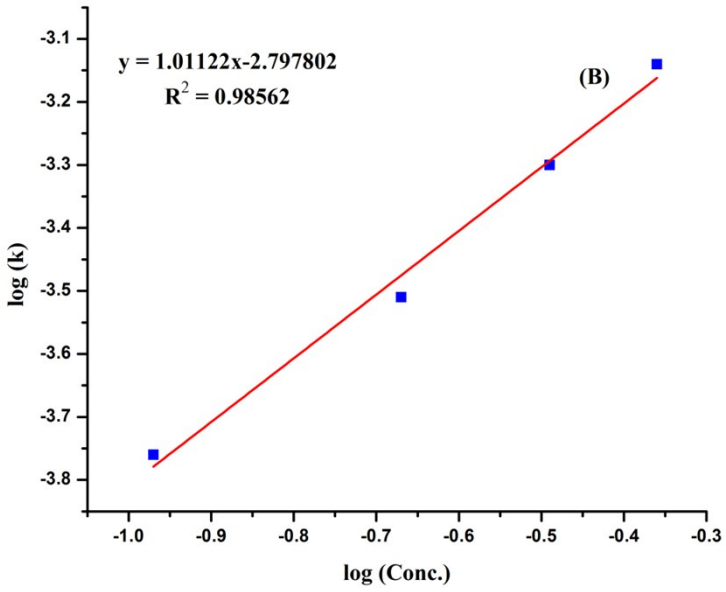


Figure S2. log(rate) *vs* log(conc.) graph of (**2a**).

3.8.2 Rate order determination with respect to benzyl phenyl sulfone (4a)

To an oven dried 15 mL screw cap pressure tube, benzyl alcohol (0.216 mmol, 1 eq.), Ni catalyst (0.0108 mmol, 5 mol%), KO^{t}Bu (0.216 mmol, 1 eq.), mesitylene (0.216 mmol, 1 eq.) as an internal

standard, specific amount of **4a** and toluene (1.95 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2 mL. The reaction mixture was kept for stirring at 140°C (bath-temperature). At regular intervals (10 min, 20 min, 30 min, 40 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (mmol) vs time (min.) plot (**Figure S3**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of **4a** was given in (**Table 2**) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S4**) to determine the order of reaction with respect to benzyl phenyl sulfone.

Table S2. Rate of the olefination reaction at different initial concentration of (**4a**).

Experiment	**Amount of 4a (gm)**	**Initial concentration of 4a (mmol)**	**Initial rate [mmol/min]× 10^{-4}**
1	0.025	0.108	1.74
2	0.050	0.216	2.55
3	0.075	0.324	3.63
4	0.10	0.436	3.98

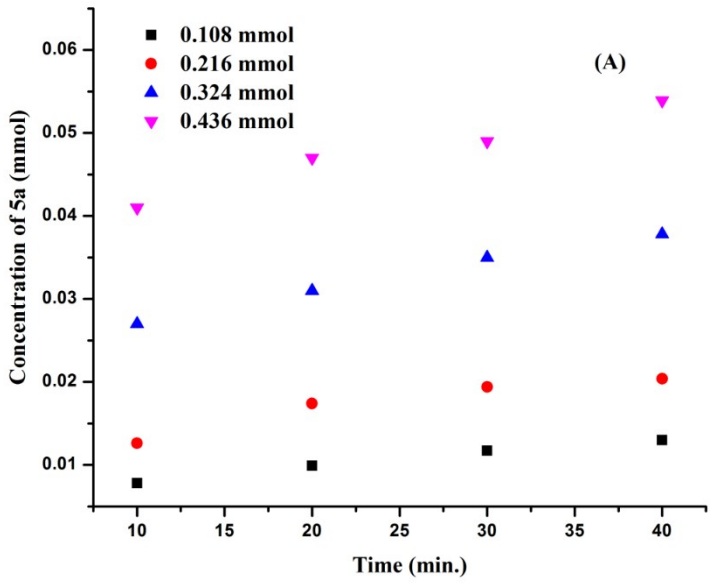


Figure S3. Concentration *vs* time plot at various concentrations of (**4a**).

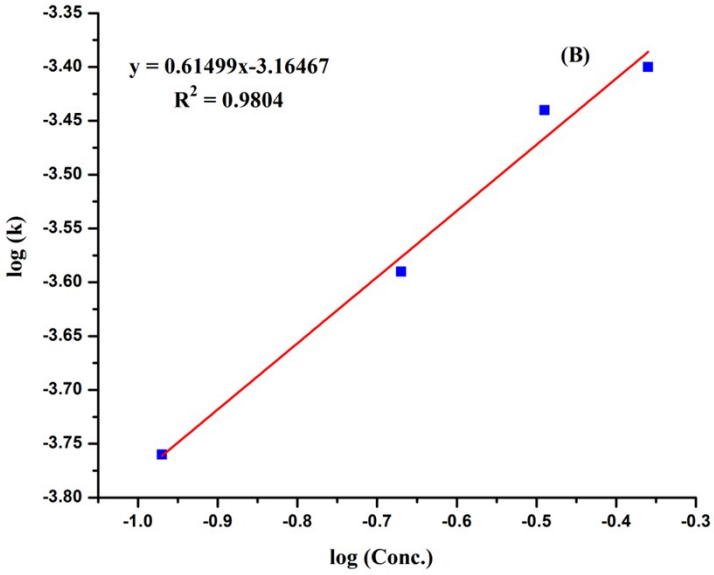


Figure S4. log(rate) *vs* log(conc.) graph of (**4a**).

3.8.3 Rate order determination with respect to catalyst

To an oven dried 15 mL screw cap pressure tube, benzyl alcohol (0.216 mmol, 1 eq.), benzyl phenyl sulfone (0.216 mmol, 1 eq.), KO^{t}Bu (0.216 mmol, 1 eq.), mesitylene (0.216 mmol, 1 eq.) as an internal standard, specific amount of catalyst and toluene (1.95 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2 mL. The reaction mixture was kept for stirring at 140°C (bath-temperature). At regular intervals (10 min, 20 min, 30 min, 40 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (mmol) vs time (min.) plot (**Figure S5**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of catalyst was given in (**Table 3**) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S6**) to determine the order of reaction with respect to catalyst.

Table S3. Rate of the olefination reaction at different initial concentration of catalyst.

Experiment	**Amount of catalyst (gm)**	**Initial concentration of catalyst (mmol)**	**Initial rate [mmol/min]× 10^{-4}**
1	0.0026	0.0065	1.52
2	0.0044	0.0108	2.55
3	0.0062	0.0151	3.75
4	0.0088	0.0216	4.67

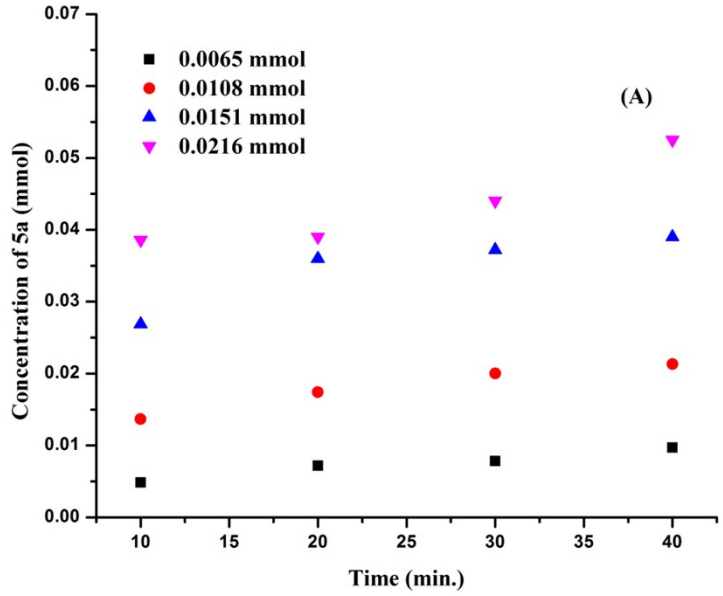


Figure S5. Concentration *vs* time plot at various concentrations of catalyst.

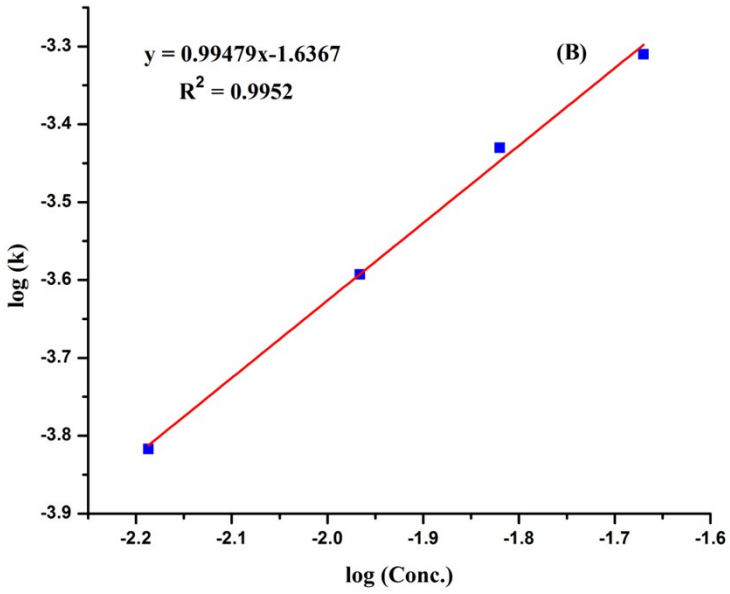


Figure S6. log(rate) *vs* log(conc.) graph at different concentration of catalyst.

3.8.4 Rate order determination with respect to KO^{t}Bu

To an oven dried 15 mL screw cap pressure tube, benzyl alcohol (0.216 mmol, 1 eq.), benzyl phenyl sulfone (0.216 mmol, 1 eq.), Ni catalyst (0.0108 mmol, 5 mol%), mesitylene (0.216 mmol, 1 eq.) as an internal standard, specific amount of KO^{t}Bu and toluene (1.95 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2 mL. The reaction mixture was kept for stirring at 140°C (bath-temperature). At regular intervals (10 min, 20 min, 30 min, 40 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with ethyl acetate and subjected to gas chromatographic analysis. The concentration of the product was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (mmol) vs time (min.) plot (**Figure S7**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of KO^{t}Bu was given in (**Table 4**) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S8**) to determine the order of reaction with respect to KO^{t}Bu.

Table S4. Rate of the olefination reaction at different initial concentration of KO^{t}Bu.

Experiment	**Amount of KO^{t}Bu (gm)**	**Initial concentration of KO^{t}Bu (mmol)**	**Initial rate [mmol/min]× 10^{-4}**
1	0.0073	0.065	1.52
2	0.0121	0.108	2.55
3	0.0242	0.216	3.75
4	0.0363	0.324	4.67

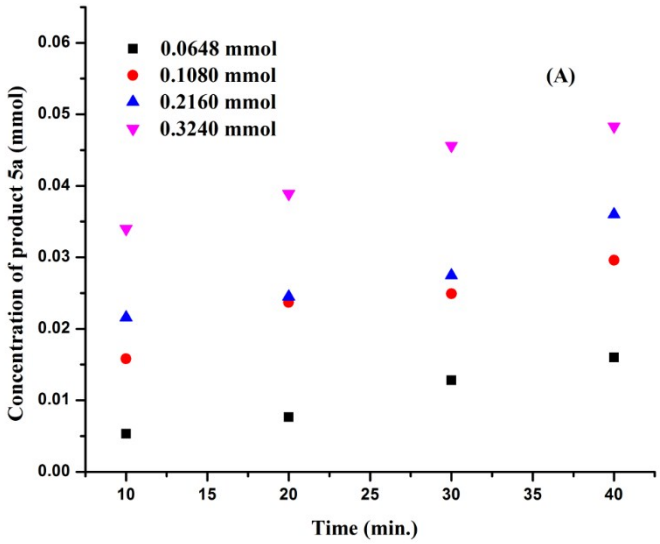


Figure S7. Concentration *vs* time plot at various concentrations of KO^{t}Bu.

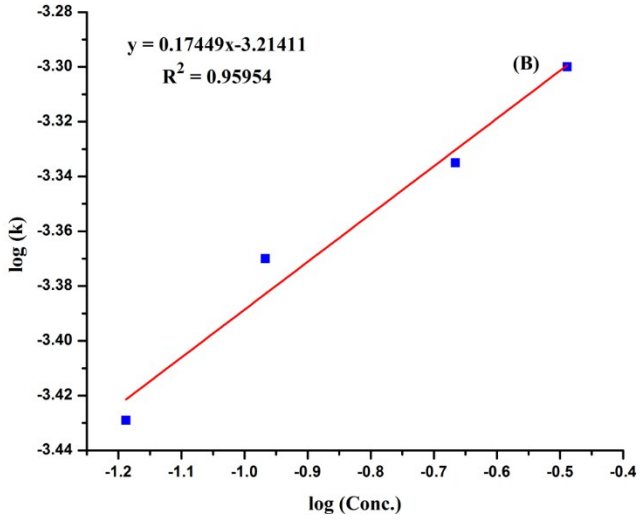
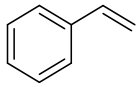


Figure S8. log(rate) *vs* log(conc.) graph at different concentration of KO^{t}Bu.

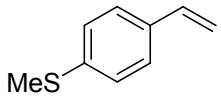
4. Characterization Data

Styrene(3a)[2]



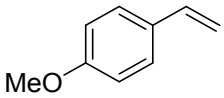
34 mg, 65% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.55 - 7.24 (m, 5 H), 6.79 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.82 (dd, *J* = 0.8, 17.6 Hz, 1 H), 5.31 (dd, *J* = 0.8, 10.9 Hz, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 137.5, 136.9, 128.5, 127.7, 126.2, 113.7.

methyl(4-vinylphenyl)sulfane (3b)[3]



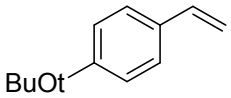
45 mg, 60% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.34 (d, *J* = 8.4 Hz, 2 H), 7.23 (dd, *J* = 4.6, 8.4 Hz, 3 H), 6.68 (dd, *J* = 11.1, 17.5 Hz, 1 H), 5.72 (d, *J* = 17.5 Hz, 1 H), 5.22 (d, *J* = 10.7 Hz, 1 H), 2.50 (s, 4 H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 138.0, 136.2, 134.6, 113.2, 15.8.

1-methoxy-4-vinylbenzene (3c)[2]



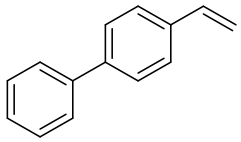
30 mg, 65% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.52 - 7.30 (m, 2 H), 7.01 - 6.84 (m, 2 H), 6.73 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.67 (dd, *J* = 0.9, 17.6 Hz, 1 H), 5.19 (dd, *J* = 0.9, 10.9 Hz, 1 H), 3.85 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 159.3, 136.2, 130.4, 127.3, 113.8, 111.5, 55.2.

1-tert-butoxy-4-vinylbenzene (3d)[4]



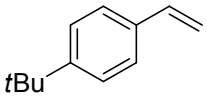
65 mg, 70% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.57 - 7.30 (m, 2 H), 7.18 - 6.96 (m, 2 H), 6.79 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.76 (dd, *J* = 0.9, 17.6 Hz, 1 H), 5.27 (dd, *J* = 0.9, 10.9 Hz, 1 H), 1.46 (s, 9 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 155.1, 136.1, 132.3, 126.4, 123.6, 111.9, 77.8, 28.5.

4-vinylbiphenyl (3e)[5]



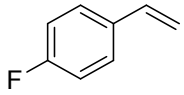
58 mg, 65% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.84 - 7.30 (m, 9 H), 6.78 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.81 (dd, *J* = 0.8, 17.6 Hz, 1 H), 5.29 (d, *J* = 10.9 Hz, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 126.9, 126.6, 113.9.

1-*tert*-butyl-4-vinylbenzene (3f)[5]



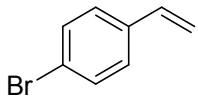
58 mg, 72% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.55 - 7.59 (m, 4 H), 6.86–7.01 (m, 1 H), 5.93 (dd, *J* = 1.0, 17.6 Hz, 1 H), 5.41 (dd, *J* = 1.0, 10.9 Hz, 1 H), 1.53 (s, 9 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 150.6, 136.7, 134.8, 126.0, 125.3, 112.7, 34.4, 31.2.

1-fluoro-4-vinylbenzene (3g)[2]



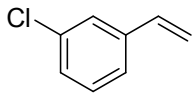
41 mg, 68% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.56 - 7.34 (m, 2 H), 7.19 - 6.93 (m, 2 H), 6.72 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.70 (d, *J* = 17.6 Hz, 1 H), 5.26 (d, *J* = 10.9 Hz, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 162.4 (d, J_{C-F} = 245.0 Hz), 135.6, 133.6 (d, J_{C-F} = 5.0 Hz), 127.7(d, J_{C-F} = 5.0 Hz), 115.3(d, J_{C-F} = 20.0 Hz), 113.3.

1-bromo-4-vinylbenzene (3h)[6]



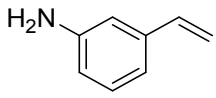
50 mg, 55% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.61 - 7.33 (m, 2 H), 7.32 - 7.13 (m, 2 H), 6.64 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.73 (dd, *J* = 0.7, 17.6 Hz, 1 H), 5.34 - 5.16 (m, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 136.4, 135.7, 131.6, 127.7, 121.5, 114.5.

1-chloro-3-vinylbenzene (3i)[7]



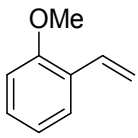
31 mg, 45% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.38 (s, 1 H), 7.33 - 7.13 (m, 3 H), 6.65 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.75 (d, *J* = 17.6 Hz, 1 H), 5.29 (d, *J* = 10.9 Hz, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 139.4, 135.6, 134.5, 129.7, 127.7, 126.1, 124.4, 115.3, 77.6, 76.4.

3-vinylaniline (3j)[8]



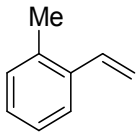
24 mg, 40% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.17 (t, *J* = 7.7 Hz, 1 H), 6.88 (d, *J* = 7.7 Hz, 1 H), 6.83 - 6.43 (m, 3 H), 5.76 (d, *J* = 17.6 Hz, 1 H), 5.27 (d, *J* = 10.9 Hz, 1 H), 3.61 (s, 2 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 146.4, 138.5, 136.9, 129.3, 116.7, 114.7, 113.5, 112.6, 77.6, 76.4.

1-methoxy-2-vinylbenzene(3k)[6]



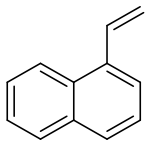
48 mg, 72% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.47 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.30 - 7.16 (m, 1 H), 7.14 - 6.71 (m, 3 H), 5.73 (dd, *J* = 1.6, 17.7 Hz, 1 H), 5.26 (dd, *J* = 1.6, 11.2 Hz, 1 H), 3.82 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 156.6, 131.6, 128.8, 126.6, 126.4, 120.5, 114.4, 110.7, 55.3.

1-methyl-2-vinylbenzene (3l)[7]



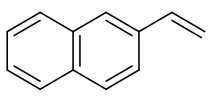
41 mg, 70% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.49 (br. s., 1 H), 7.24 - 7.10 (m, 3 H), 7.05 - 6.85 (m, 1 H), 5.65 (dd, *J* = 1.4, 17.4 Hz, 1 H), 5.30 (dd, *J* = 1.4, 11.0 Hz, 1 H), 2.37 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 134.8, 130.2, 127.6, 126.1, 125.3, 115.1, 19.7.

1-vinylnaphthalene (3m)[2]



50 mg, 65% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 8.36 - 8.08 (m, 1 H), 8.08 - 7.79 (m, 2 H), 7.79 - 7.36 (m, 5 H), 5.86 (dd, *J* = 1.5, 17.3 Hz, 1 H), 5.54 (dd, *J* = 1.5, 10.9 Hz, 1 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 135.6, 134.3, 133.5, 131.1, 128.5, 128.1, 126.0, 125.7, 125.6, 123.7, 123.6, 117.1.

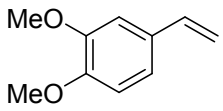
2-vinylnaphthalene (3n)[2]



54 mg, 70% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.97 - 7.74 (m, 4 H), 7.74 - 7.62 (m, 1 H), 7.56 - 7.40 (m, 2 H), 6.92 (dd, *J* = 10.9, 17.6 Hz, 1 H), 5.90 (dd, *J* = 0.8, 17.6 Hz, 1 H), 5.37 (dd, *J* = 0.6, 10.9 Hz, 1 H). ^{13}C NMR (50 MHz,

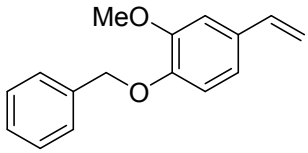
CHLOROFORM-d) δ = 136.9, 135.0, 133.1, 128.1, 128.0, 127.6, 126.3, 126.2, 125.9, 123.2, 114.1.

1,2-dimethoxy-4-vinylbenzene (3o)[2]



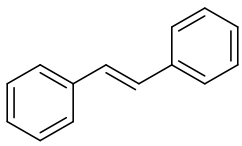
62 mg, 76% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.01 - 6.92 (m, 2 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.66 (dd, *J* = 10.7, 17.5 Hz, 1 H), 5.62 (d, *J* = 17.5 Hz, 1 H), 5.16 (d, *J* = 10.7 Hz, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 149.0, 149.0, 136.5, 130.7, 119.4, 111.8, 111.0, 108.5, 55.9, 55.8.

1-(benzyloxy)-2-methoxy-4-vinylbenzene (3p)



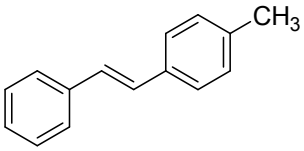
87 mg, 73% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.45 (d, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 7.4 Hz, 2 H), 7.32 (d, *J* = 7.2 Hz, 1 H), 7.00 (d, *J* = 1.9 Hz, 1 H), 6.89 (dd, *J* = 1.9, 8.0 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.65 (dd, *J* = 10.7, 17.5 Hz, 1 H), 5.62 (d, *J* = 17.5 Hz, 1 H), 5.21 - 5.10 (m, 3 H), 3.93 (s, 3 H). ^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 149.7, 148.1, 137.1, 136.5, 131.2, 128.5, 127.8, 127.2, 119.3, 113.9, 112.0, 109.2, 77.3, 76.7, 71.0, 56.0. HRMS (EI): *m/z* Calcd for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223; Found: 241.1221.

***(E)*-1,2-diphenylethene (5a)**[9]



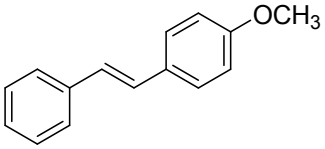
41 mg, 70% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ = 7.56-7.54 (m, 4H), 7.41-7.38 (m, 4H), 7.32-7.28 (m, 2H), 7.15 (s, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ = 137.3, 128.65 127.5, 126.5.

(*E*)-1-methyl-4-styrylbenzene (5b)[9]



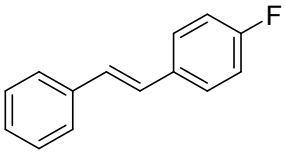
68 mg, 70% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.58 - 7.45 (m, 2 H), 7.45 - 7.25 (m, 4 H), 7.25 - 7.17 (m, 2 H), 7.17 - 6.99 (m, 3 H), 2.32 (s, 3 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 137.5, 134.5, 129.4, 128.7, 128.6, 127.7, 127.4, 126.4, 126.4, 21.2.

(*E*)-1-methoxy-4-styrylbenzene (5c)[9]



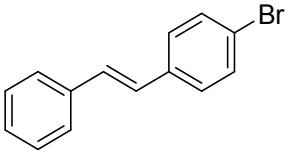
69 mg, 66% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ 7.52-7.23 (m, 7H), 7.12-7.00 (dd, *J = 7.4, 4.8* Hz, 2H), 6.90 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ = 159.3, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.3.

(*E*)-1-fluoro-4-styrylbenzene (5d)[9]



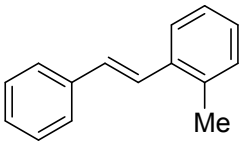
69 mg, 70% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ 7.52-7.44 (m, 4H), 7.39-7.35 (m, 1H), 7.33-7.29 (m, 2H), 7.09-7.00 (m, 4H). ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ = 162.3 (d, J_{C-F} = 245.5 Hz), 137.2, 133.5, 128.7, 128.0, 127.8, 127.6, 127.5, 126.4, 115.6 (d, J_{C-F} = 20.0 Hz).

(*E*)-1-bromo-4-styrylbenzene (5e)[10]



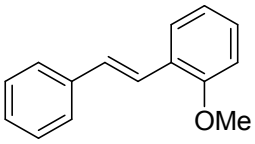
65 mg, 51% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.65 - 7.49 (m, 4 H), 7.49 - 7.30 (m, 6 H), 7.11 (d, *J* = 3.7 Hz, 2 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 136.9, 136.3, 131.8, 129.4, 128.7, 128.0, 127.9, 127.4, 126.5, 121.3.

(*E*)-1-methyl-2-styrylbenzene (5f)[9]



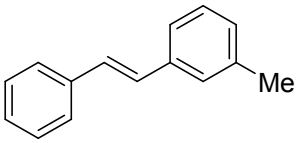
66 mg, 68% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ 7.64-7.52 (m, 3H), 7.43-7.28 (m, 4H), 7.24-7.19 (m, 3H), 7.01 (d, *J* =16.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ = 137.7, 136.3, 135.8, 130.4, 130.0, 128.7, 127.5, 126.5, 126.2, 125.4, 19.9.

(*E*)-1-methoxy-2-styrylbenzene (5g)[11]



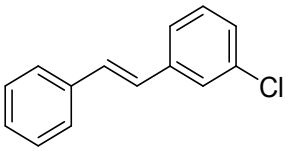
63 mg, 60% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.61 (dd, *J* = 1.5, 7.6 Hz, 1 H), 7.58 - 7.44 (m, 3 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.29 - 7.22 (m, 2 H), 7.12 (d, *J* = 16.8 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 3.90 (s, 3 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 156.9, 137.9, 129.1, 128.6, 128.6, 127.3, 126.5, 126.4, 126.4, 123.5, 120.7, 110.9, 55.5.

(*E*)-1-methyl-3-styrylbenzene (5h)[9]



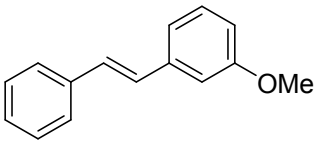
78 mg, 80% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.58 (d, *J* = 7.3 Hz, 2 H), 7.50 - 7.38 (m, 4 H), 7.38 - 7.28 (m, 2 H), 7.25 - 7.08 (m, 3 H), 2.45 (s, 3 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 138.2, 137.4, 137.2, 128.8, 128.6, 128.5, 128.4, 128.4, 127.5, 127.2, 126.5, 123.7, 77.3, 76.7, 21.4.

(*E*)-1-chloro-4-styrylbenzene (5i)[9]



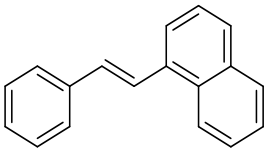
64 mg, 60% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ 7.53-7.49 (m, 3H), 7.40-7.20 (m, 6H), 7.12 (d, *J* =16.2 Hz, 1H), 7.01 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ = 139.2, 136.8, 134.6, 130.1, 129.8, 128.7, 128.0, 127.5, 127.2, 126.6, 126.3, 124.7.

(*E*)-1-methoxy-3-styrylbenzene (5j)[11]



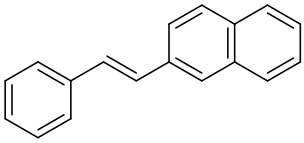
73 mg, 70% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.50 - 7.38 (m, 2 H), 7.35 - 7.13 (m, 5 H), 7.09 - 6.93 (m, 4 H), 6.81 - 6.70 (m, 1 H), 3.77 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 159.9, 138.8, 137.2, 129.6, 129.0, 128.6, 128.6, 127.6, 126.5, 119.2, 113.3, 111.7, 55.2.

(*E*)-1-styrylnaphthalene (5k)[2]



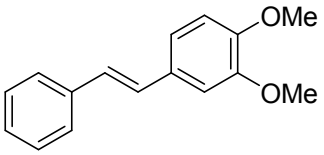
52 mg, 45% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.83-7.67 (m, 4H), 7.55-7.41 (m, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28-7.22 (m, 1H), 7.18-7.01 (m, 2H). ^{13}C NMR (126 MHz, CHLOROFORM-*d*) δ = 137.6, 135.0, 133.7, 131.8, 131.4, 129.0, 128.7, 128.6, 128.0, 127.8, 126.7, 126.1, 125.8, 125.7, 123.8, 123.6.

(*E*)-2-styrylnaphthalene (5l)[2]



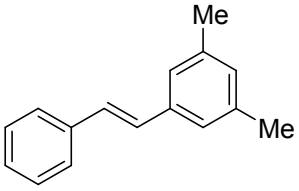
69 mg, 45% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.92 - 7.78 (m, 4 H), 7.77 - 7.70 (m, 1 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 7.46 (ddd, *J* = 1.5, 6.3, 8.2 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.33 - 7.24 (m, 3 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 137.3, 134.8, 133.7, 133.0, 129.0, 128.8, 128.7, 128.3, 128.0, 127.7, 126.6, 126.5, 126.3, 125.9, 123.5.

(*E*)-1,2-dimethoxy-4-styrylbenzene (5m)



102 mg, 85% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.52 (d, *J* = 7.6 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.31 - 7.21 (m, 1 H), 7.13 - 7.05 (m, 3 H), 7.04 - 6.95 (m, 1 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 3.97 (s, 3 H), 3.92 (s, 3 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 149.1, 148.9, 137.5, 130.4, 128.6, 128.4, 127.2, 126.8, 126.2, 119.8, 111.2, 108.7, 55.9, 55.8. HRMS (EI): *m/z* Calcd for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223; Found: 241.1222.

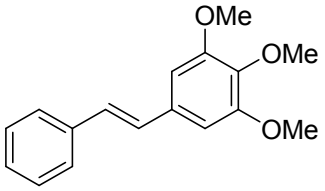
(*E*)-1,3-dimethyl-5-styrylbenzene (5n)[12]



93 mg, 90% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.54 (d, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.32 - 7.27 (m, 1 H), 7.19 (s, 2 H), 7.11 (d, *J* =

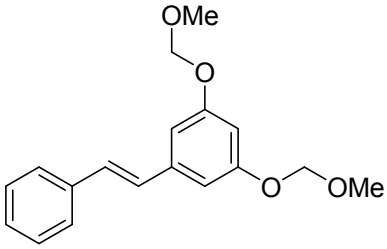
3.8 Hz, 2 H), 6.95 (s, 1 H), 2.38 (s, 7 H). ^{13}C NMR (101 MHz, CHLOROFORM-d) δ = 138.1, 137.5, 137.2, 129.4, 128.9, 128.6, 128.3, 127.4, 126.4, 124.4, 21.3.

(*E*)-1,2,3-trimethoxy-5-styrylbenzene (5o)



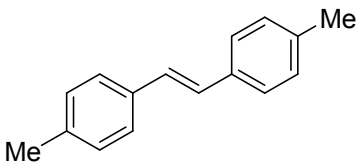
94 mg, 70% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ ppm 7.45 - 7.56 (m, 2 H), 7.24 - 7.42 (m, 3 H), 7.02 (s, 2 H), 6.74 (s, 2 H), 3.92 (s, 6 H), 3.87 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ ppm 153.4, 138.0, 137.2, 133.1, 128.7, 128.2, 127.6, 126.5, 103.6, 61.0, 56.2. HRMS (EI): *m/z* Calcd for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1329; Found: 271.1328.

(*E*)-1,3-bis(methoxymethoxy)-5-styrylbenzene (5p)



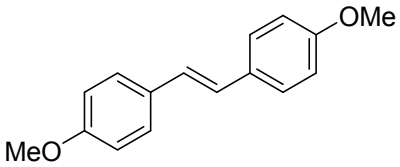
112 mg, 75% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ ppm 7.45 - 7.56 (m, 2 H), 7.24 - 7.40 (m, 3 H), 7.05 (d, *J* = 2.78 Hz, 2 H), 6.87 (d, *J* = 2.15 Hz, 2 H), 6.61 - 6.72 (m, 1 H), 5.19 (s, 4 H), 3.50 (s, 6 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ ppm 158.6, 139.6, 137.1, 129.4, 128.7, 128.4, 127.8, 126.6, 107.9, 104.4, 94.5, 56.1. HRMS (EI): *m/z* Calcd for $C_{18}H_{21}O_4$ $[M+H]^+$: 301.1434; Found: 301.1432.

(*E*)-1,2-dip-tolylethene (5q)[12]



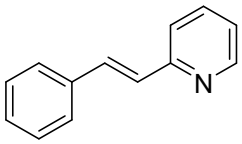
69 mg, 66% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.50 (d, *J* = 8.1 Hz, 4 H), 7.23 (s, 4 H), 7.13 (s, 2 H), 2.45 (s, 6 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 137.2, 134.7, 129.3, 127.6, 126.3, 21.2.

(*E*)-1,2-bis(4-methoxyphenyl)ethane (5r)[10]



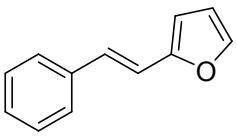
91 mg, 76% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.44 (d, *J* = 8.8 Hz, 4 H), 6.93 (d, *J* = 4.0 Hz, 4 H), 6.88 (s, 2 H), 3.84 (s, 6 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 159.0, 130.5, 127.4, 126.2, 114.1, 55.3.

(*E*)-2-styrylpyridine (5s)[13]



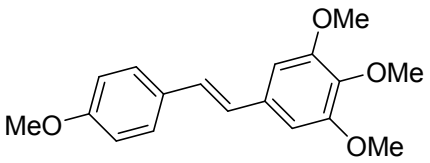
65 mg, 72% isolated yield. R_f = 0.4 (hexane/ethyl acetate = 10/1) ^{1}H NMR (400 MHz, CHLOROFORM-*d*): δ ppm 8.59 - 8.61 (m, 1 H), 7.61 - 7.68 (m, 2 H), 7.57 - 7.60 (m, 2 H), 7.36 - 7.39 (m, 3 H), 7.27 - 7.32 (m, 1 H), 7.13 - 7.19 (m, 2 H). ^{13}C NMR (101 MHz, CHLOROFORM-*d*): δ ppm 155.7, 149.8, 136.7, 136.7, 132.8, 128.8, 128.4, 128.0, 127.2, 122.2, 122.2.

(*E*)-2-styrylfuran (5t)[14]



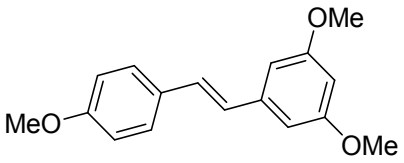
59 mg, 70% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (400MHz, CHLOROFORM-d) δ = 7.51 (d, *J* = 7.3 Hz, 2 H), 7.50 - 7.34 (m, 3 H), 7.30 (d, *J* = 7.3 Hz, 1 H), 7.09 (d, *J* = 15.9 Hz, 1 H), 6.95 (d, *J* = 16.5 Hz, 1 H), 6.59 - 6.43 (m, 1 H), 6.40 (d, *J* = 3.1 Hz, 1 H). ^{13}C NMR (101MHz, CHLOROFORM-d) δ = 153.3, 142.1, 137.0, 128.7, 127.6, 127.1, 126.3, 116.5, 111.6, 108.5.

(*E*)-1,2,3-trimethoxy-5-(4-methoxystyryl)benzene (8)[5]



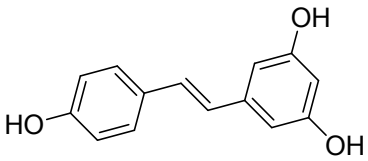
97 mg, 65% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.46 (d, *J* = 8.8 Hz, 2 H), 7.00 - 6.91 (m, 3 H), 6.73 (s, 2 H), 3.92 (s, 6 H), 3.88 (s, 3 H), 3.84 (s, 3 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 159.3, 153.4, 137.7, 133.4, 130.0, 127.7, 127.6, 126.6, 114.1, 103.4, 77.6, 76.4, 60.9, 56.1, 55.3.

(*E*)-1,3-dimethoxy-5-(4-methoxystyryl)benzene (9)[5]



74 mg, 55% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.55 - 7.41 (m, 2 H), 7.02 (s, 1 H), 6.98 - 6.91 (m, 2 H), 6.91 - 6.87 (m, 1 H), 6.67 (d, *J* = 2.1 Hz, 2 H), 6.39 (t, *J* = 2.2 Hz, 1 H), 3.84 (s, 10 H). ^{13}C NMR (50 MHz, CHLOROFORM-d) δ = 161.0, 159.4, 139.7, 129.9, 128.7, 127.8, 126.6, 114.1, 104.3, 99.6, 55.3.

(*E*)-5-(4-hydroxystyryl)benzene-1,3-diol (10)[5]



79 mg, 70% isolated yield. R_f = 0.25 (CH_2Cl_2/MeOH= 9/1). ^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.59 (s, 1 H), 8.25 (s, 2 H), 6.32 (d, *J* = 8.6 Hz, 2 H), 5.89 - 5.61 (m, 4 H), 5.33 (s, 2 H), 5.17 - 4.95 (m, 1 H). ^{13}C NMR (50 MHz, DMSO-d_6) δ = 158.6, 157.3, 139.5, 128.3, 128.0, 125.8, 115.7, 104.5, 102.0. HRMS (EI): *m/z* Calcd for $C_{14}H_{13}O_3[M+H]^+$: 229.0859; Found: 229.860.

5. References

1. S. P. Midya, J. Rana, J. Pitchaimani, A. Nandakumar, V. Madhu and E. Balaraman, *ChemSusChem*, 2018,**11**, 3911.

2. D. Srimani, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem. Int. Ed.,* **2014**, *53*, 11092.

3. D. S. Seferos, D. A. Banach, N. A. Alcantar, J. N. Israelachvili and G. C. Bazan, *J. Org. Chem.,* **2004**, *69*, 1110.

4. D. M. Knapp, E. P. Gillis, and M. D. Burke, *J. Am. Chem. Soc.*, **2009***, 131,* 6961.

5. C.-Z. Yao, Q.-Q.Li, M.-M. Wang, X.-S. Ning and Y.-B. Kang, *Chem. Commun.,* **2015**, *51*, 7729.

6. H. Lebel, M. Davi, S. Díez-González, and S. P. Nolan, *J. Org. Chem.,* **2007**, *72*, 144.

7. C. R. Smith and T.V. Rajan Babu, *Tetrahedron,* **2010**, *66,* 1102.

8. V. Udumula, J. H. Tyler, D. A. Davis, H. Wang, M. R. Linford, P. S. Minson, and D. J. Michaelis, *ACS Catal.,***2015**, *5*, 3457.

9. S. Fu, N. Y. Chen, X. Liu, Z. Shao, S. P. Luo, and Q. Liu, *J. Am. Chem. Soc.*, **2016**, *138*, 8588.

10. Q. Zhong, C. J. Liu, Q. Y. Wu, X. Meng, W. Gao, Z. J. Li, B. Chen, C. H. Tunga and L. Z. Wu, *Chem. Commun*., **2016**, *52*, 1800.

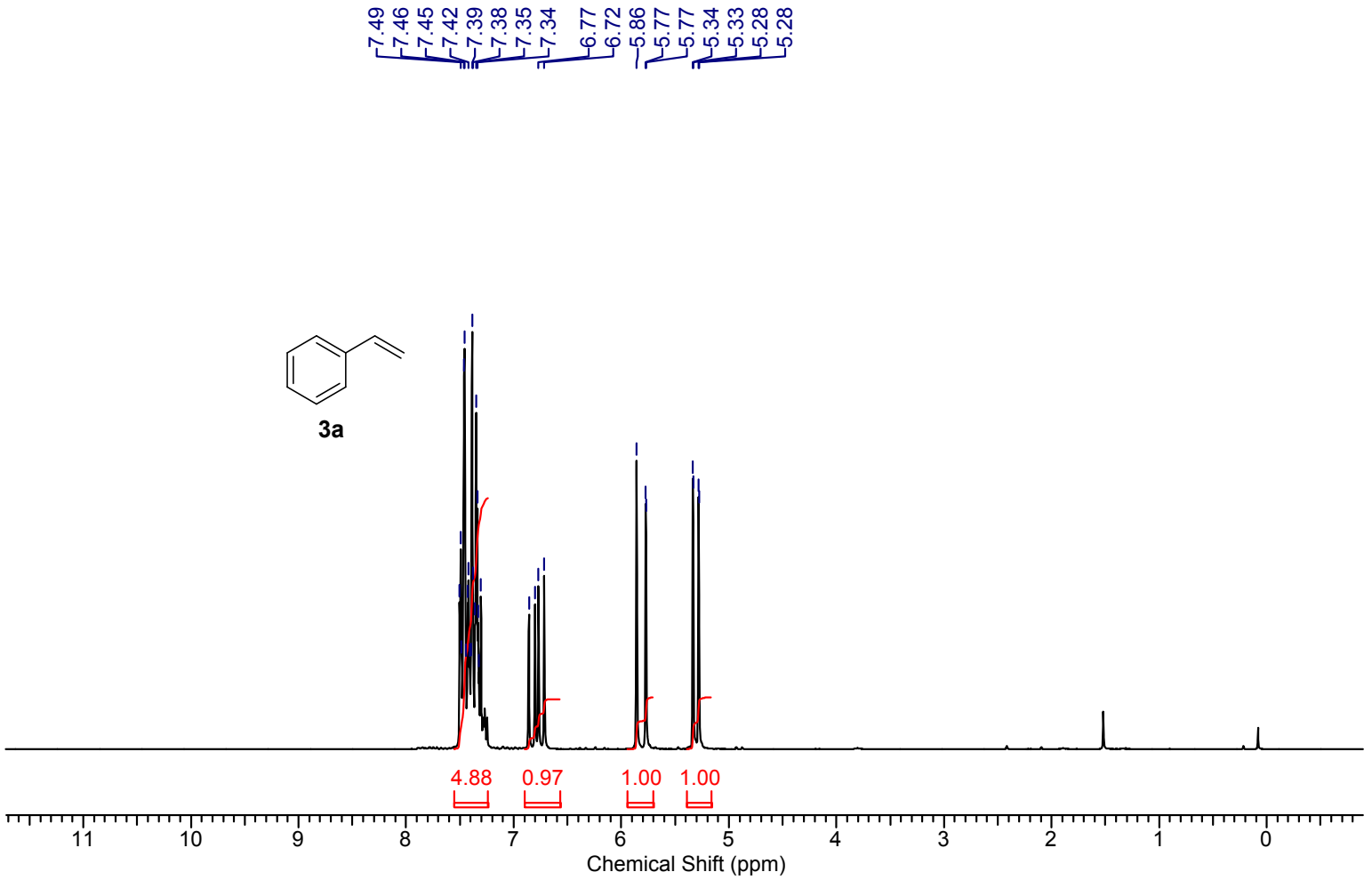
11. S. Keesara, S. Parvathaneni and M. R. Mandapati, *Tetrahedron,* **2014**, *55*, 6769.

12. R. Loska, C. M. R. Volla and P. Vogela, *Adv. Synth. Catal.,* **2008**, *350,* 2859.

13. L. Ilies, S. Asako, and E. Nakamura, *J. Am. Chem. Soc*., **2011**, *133*, 7672.

14. S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita and K. Kondo, *J. Org. Chem.,* **1979**, *44*, 2408.

6. Copy of NMR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5.77
5.34
5.33
5.28
5.28
3a
4.88
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1.00
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4
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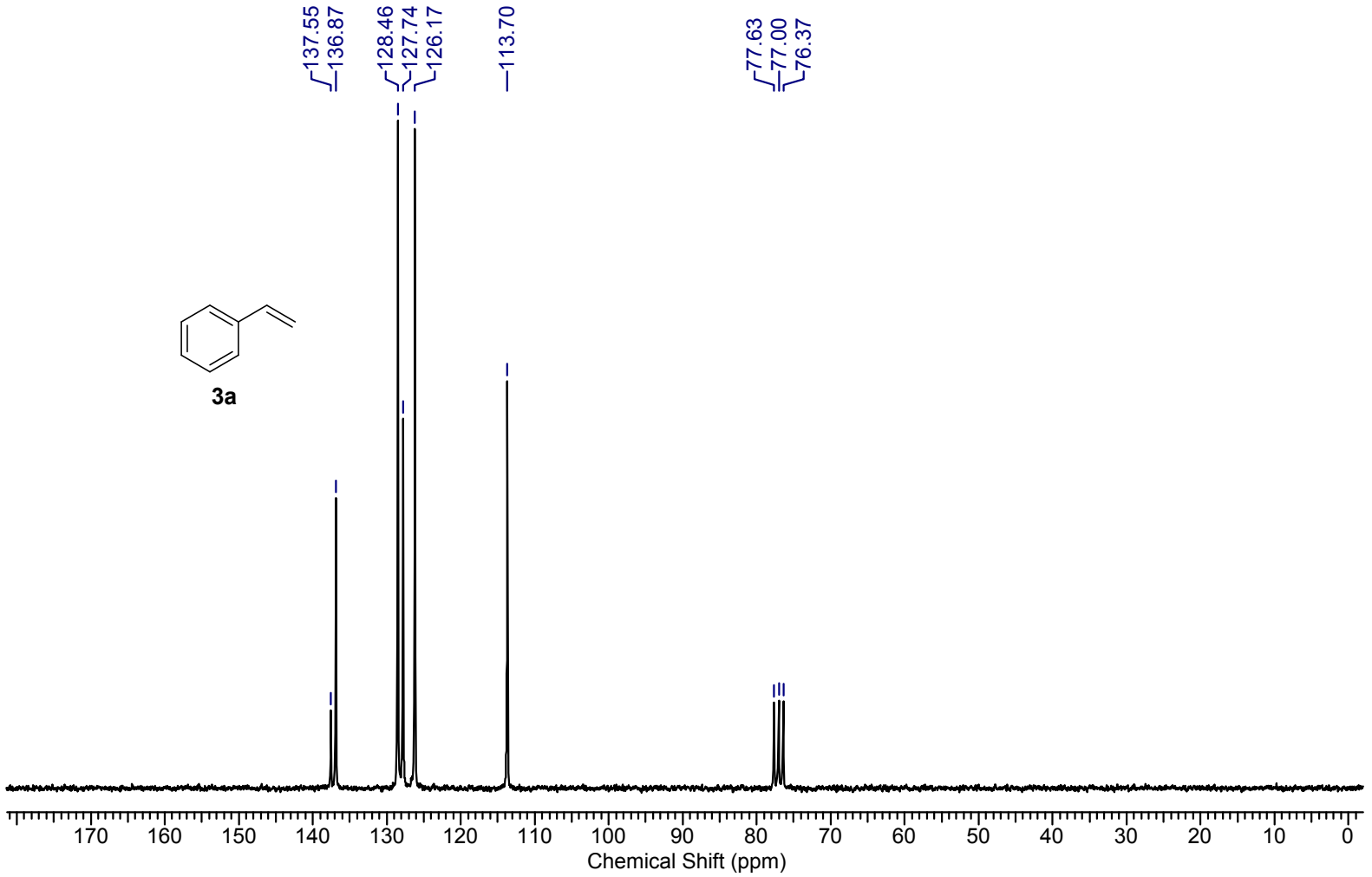
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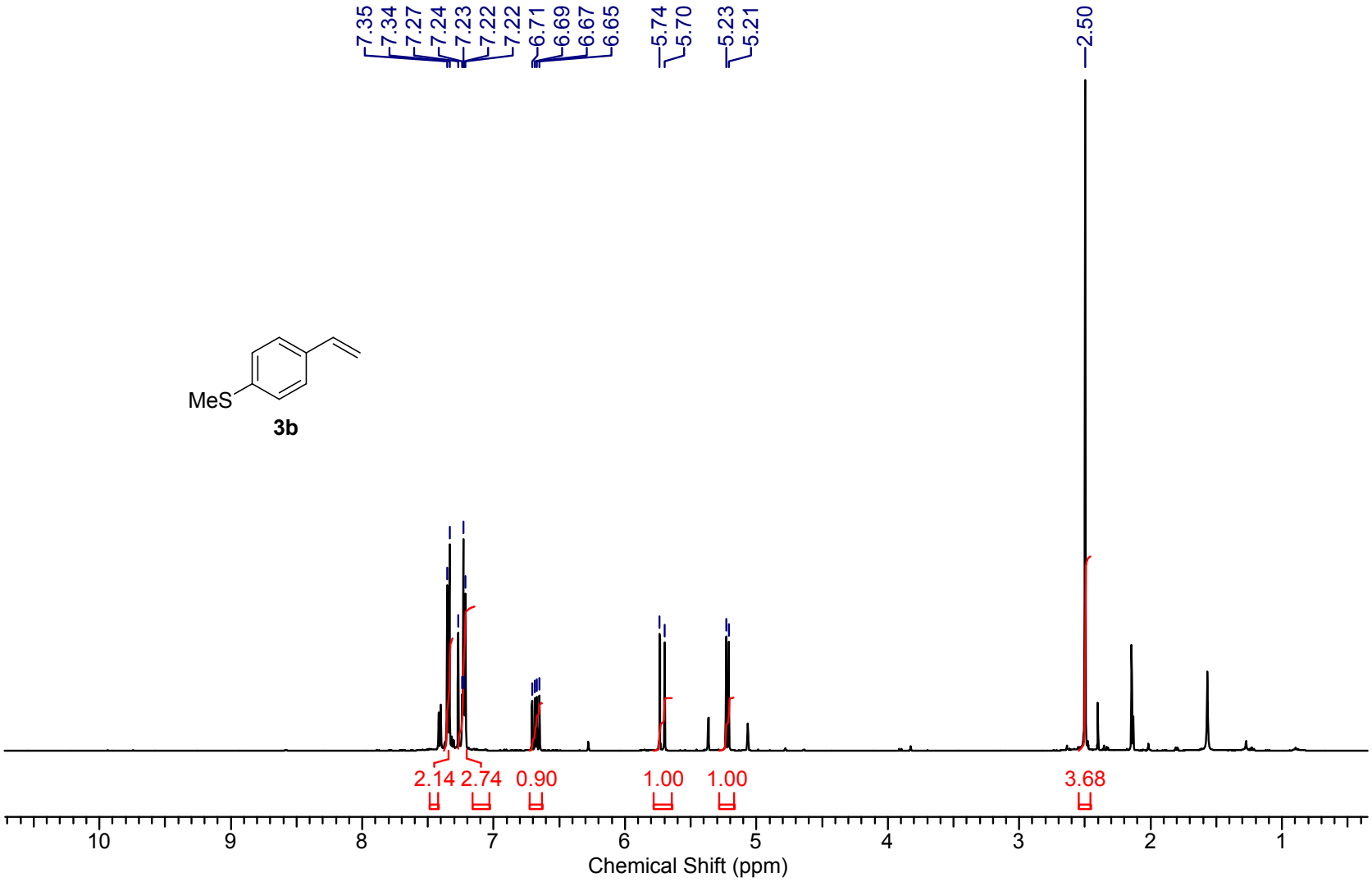
Chemical Shift (ppm)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5.70
5.23
5.21
2.50
MeS
3b
2.14
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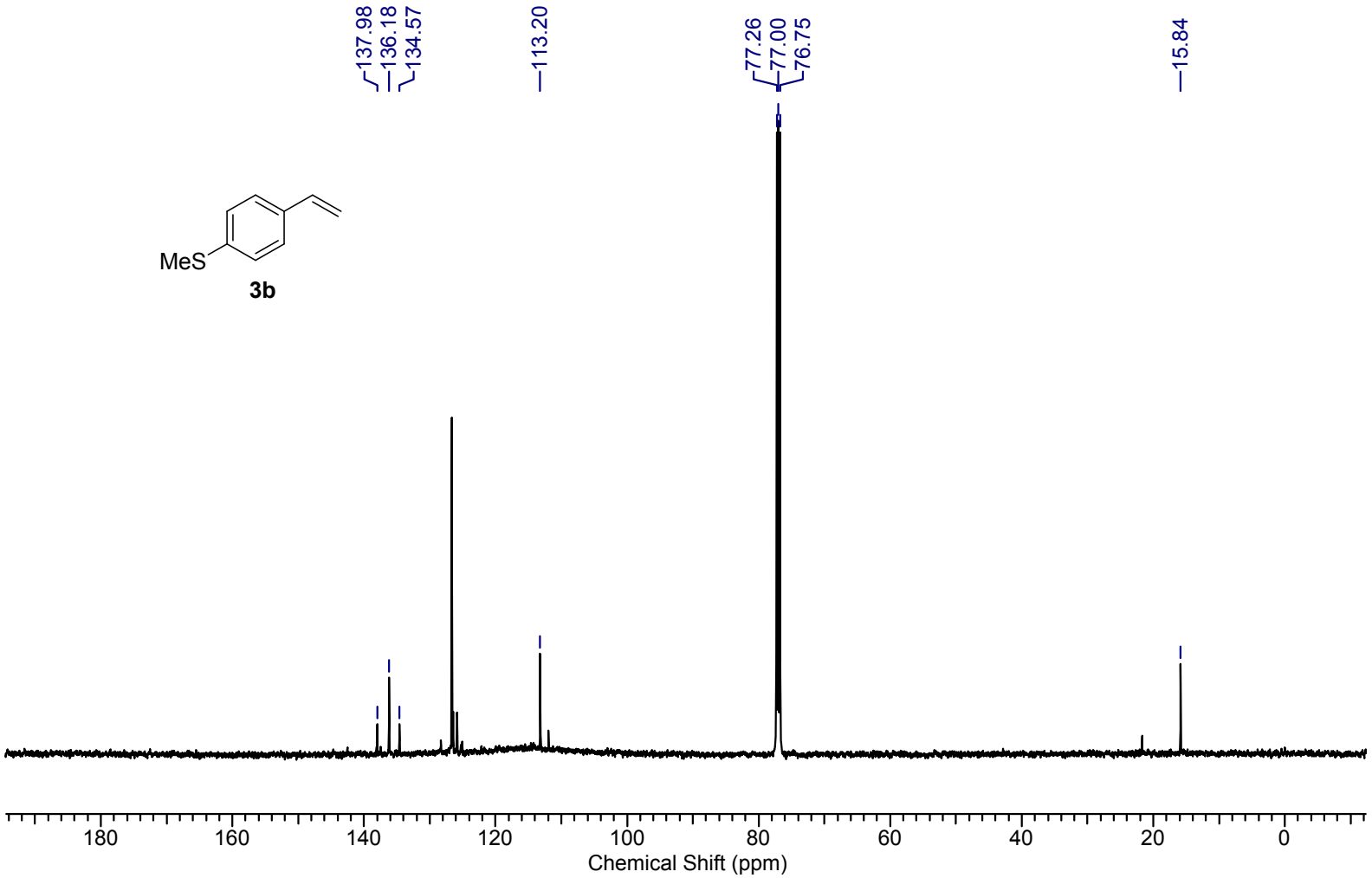
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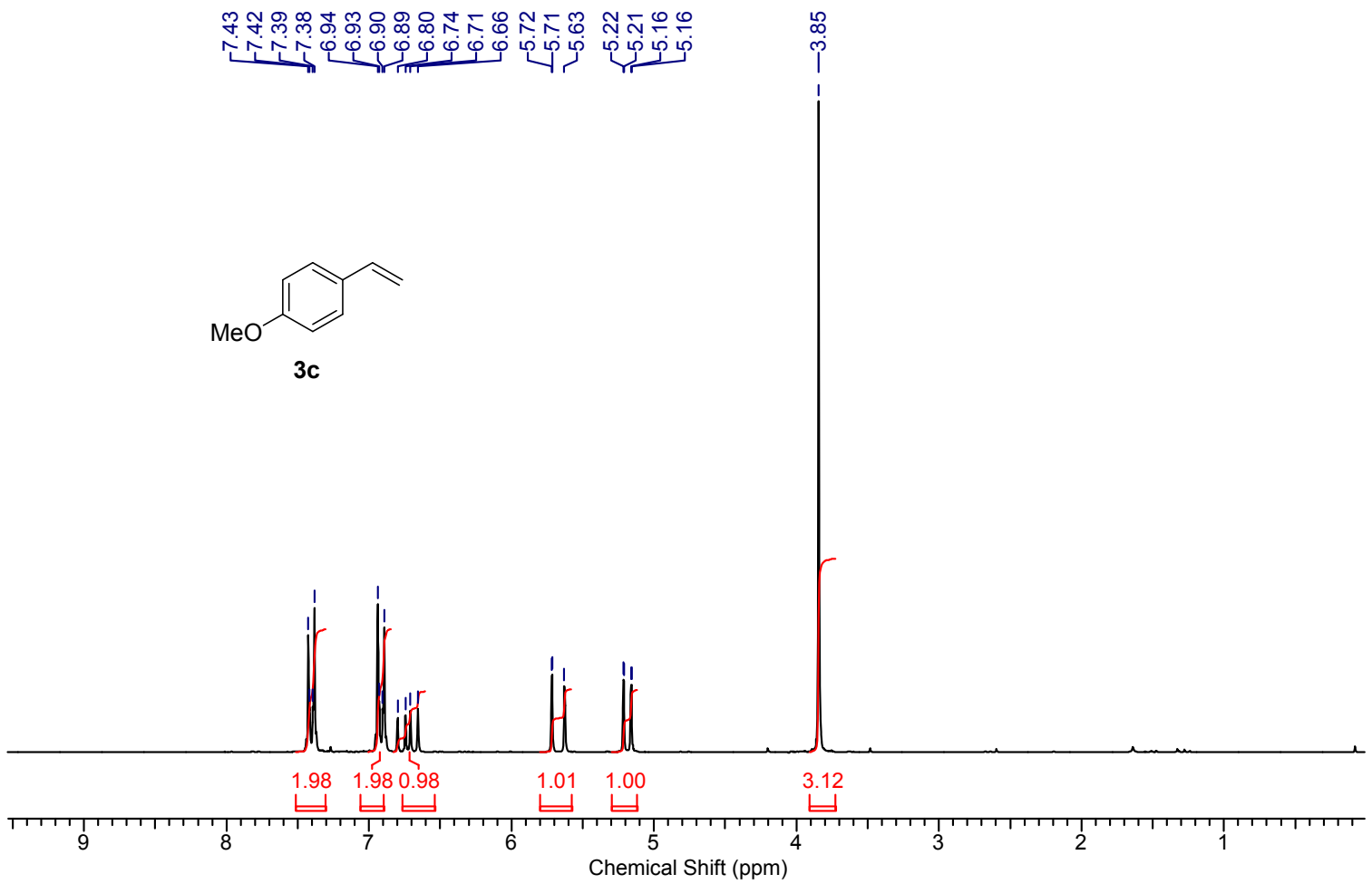
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5.72
5.71
5.63
5.22
5.21
5.16
5.16
3.85
MeO
3c
1.98
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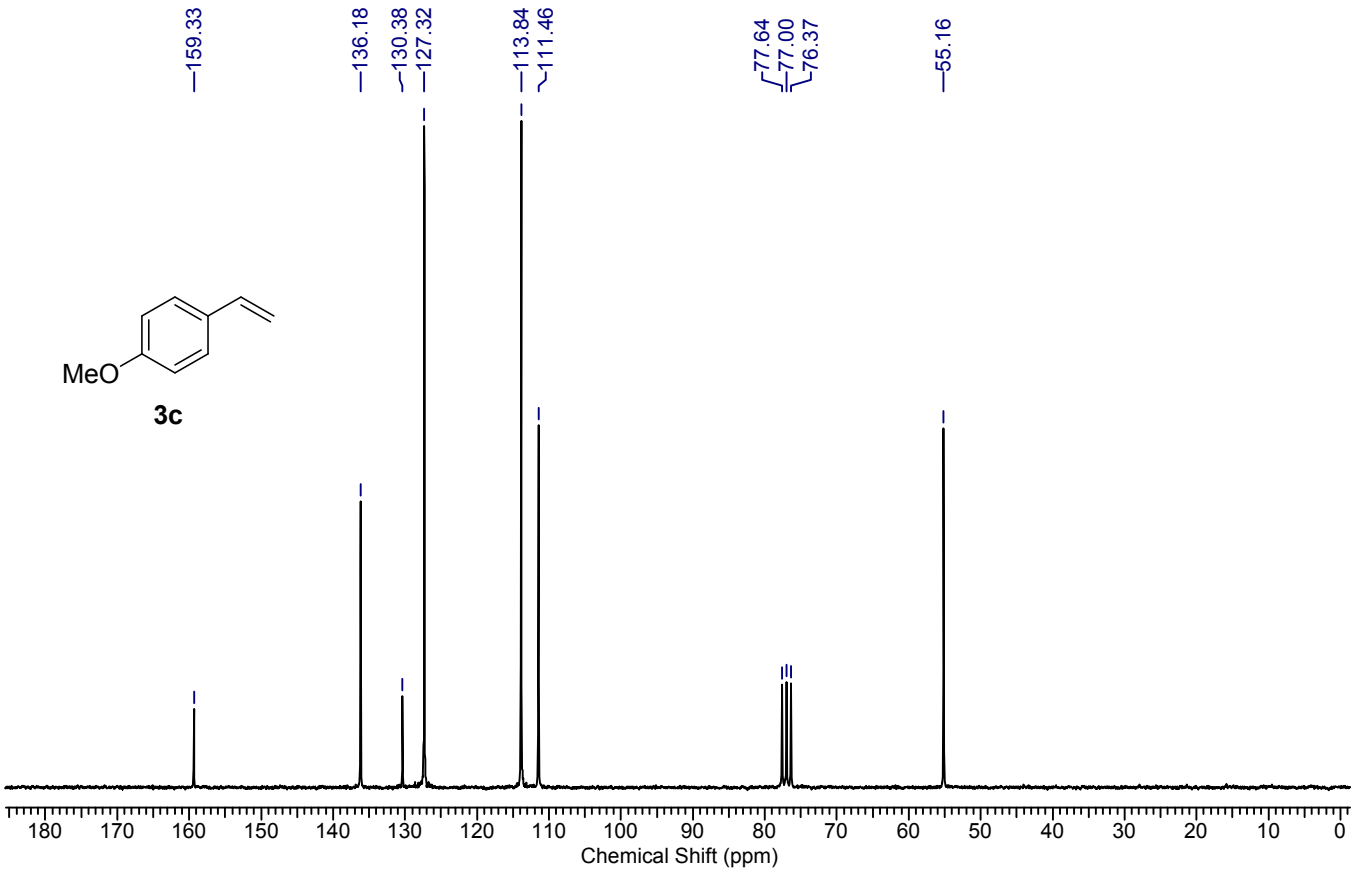
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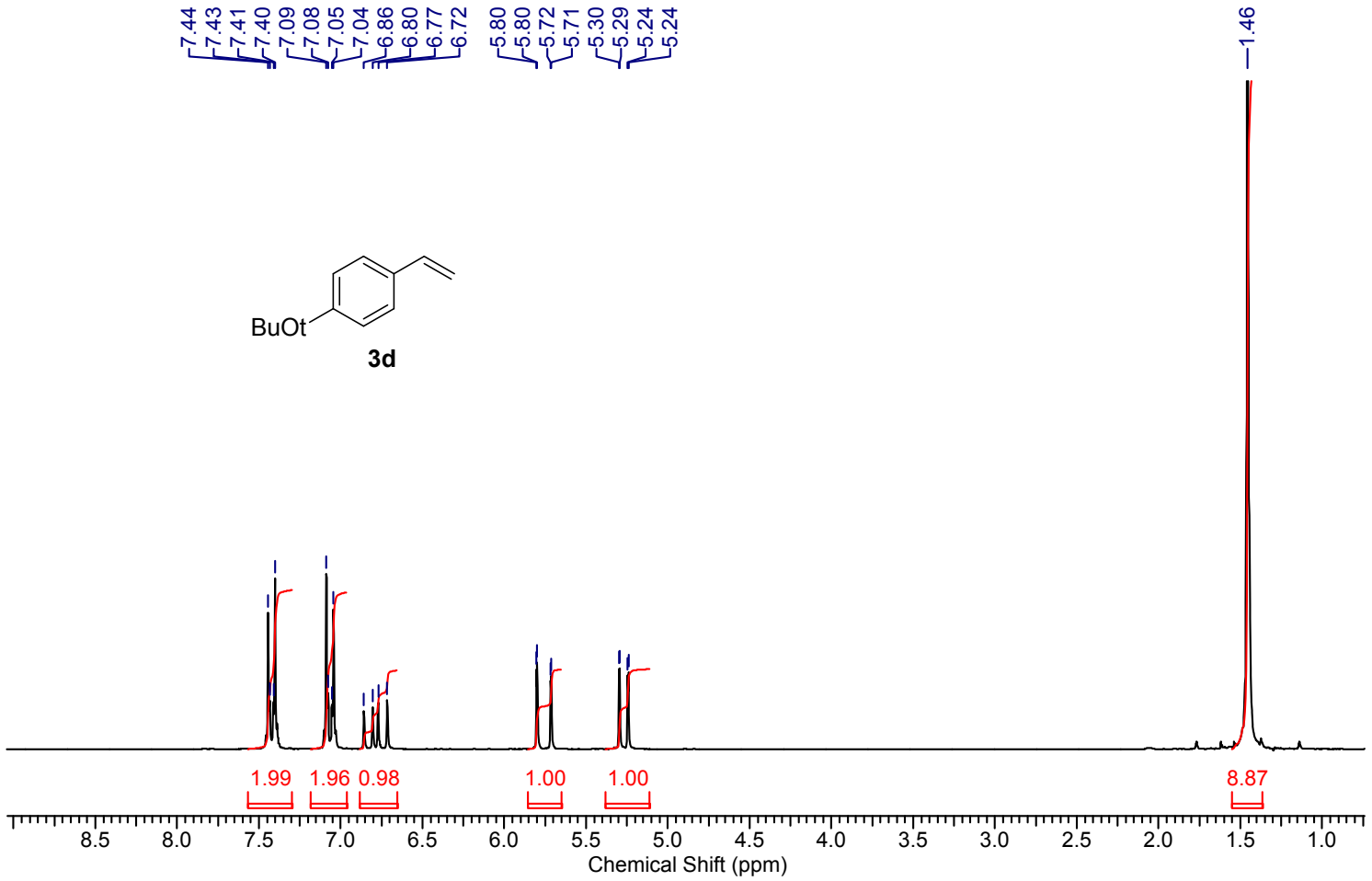
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7.04
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6.80
6.77
6.72
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5.80
5.72
5.71
5.30
5.29
5.24
5.24
1.46
BuOt
3d
1.99
1.96
0.98
1.00
1.00
8.87
8.5
8.0
7.5
7.0
6.5
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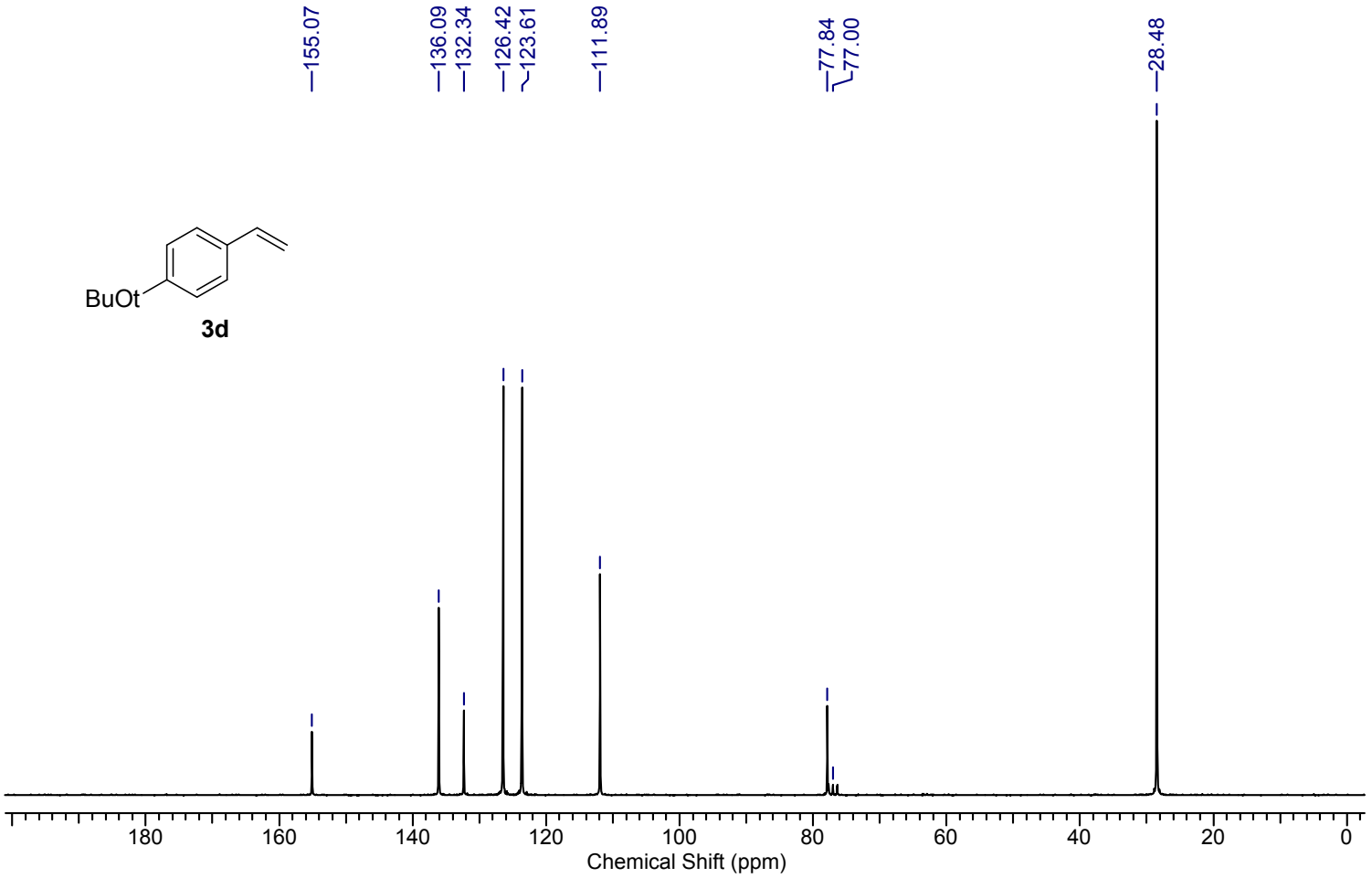
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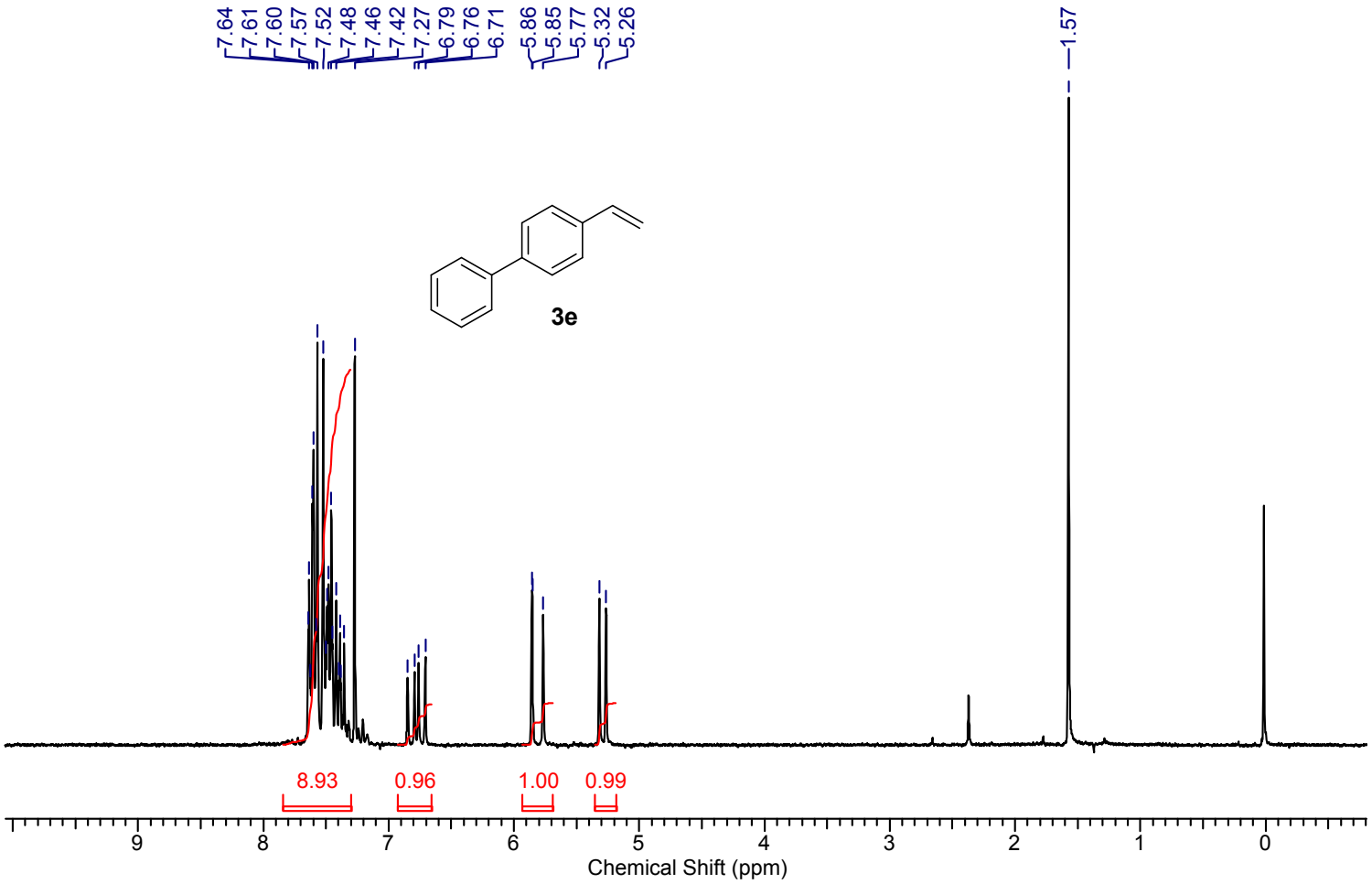
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7.42
7.27
6.79
6.76
6.71
5.86
5.85
5.77
5.32
5.26
1.57
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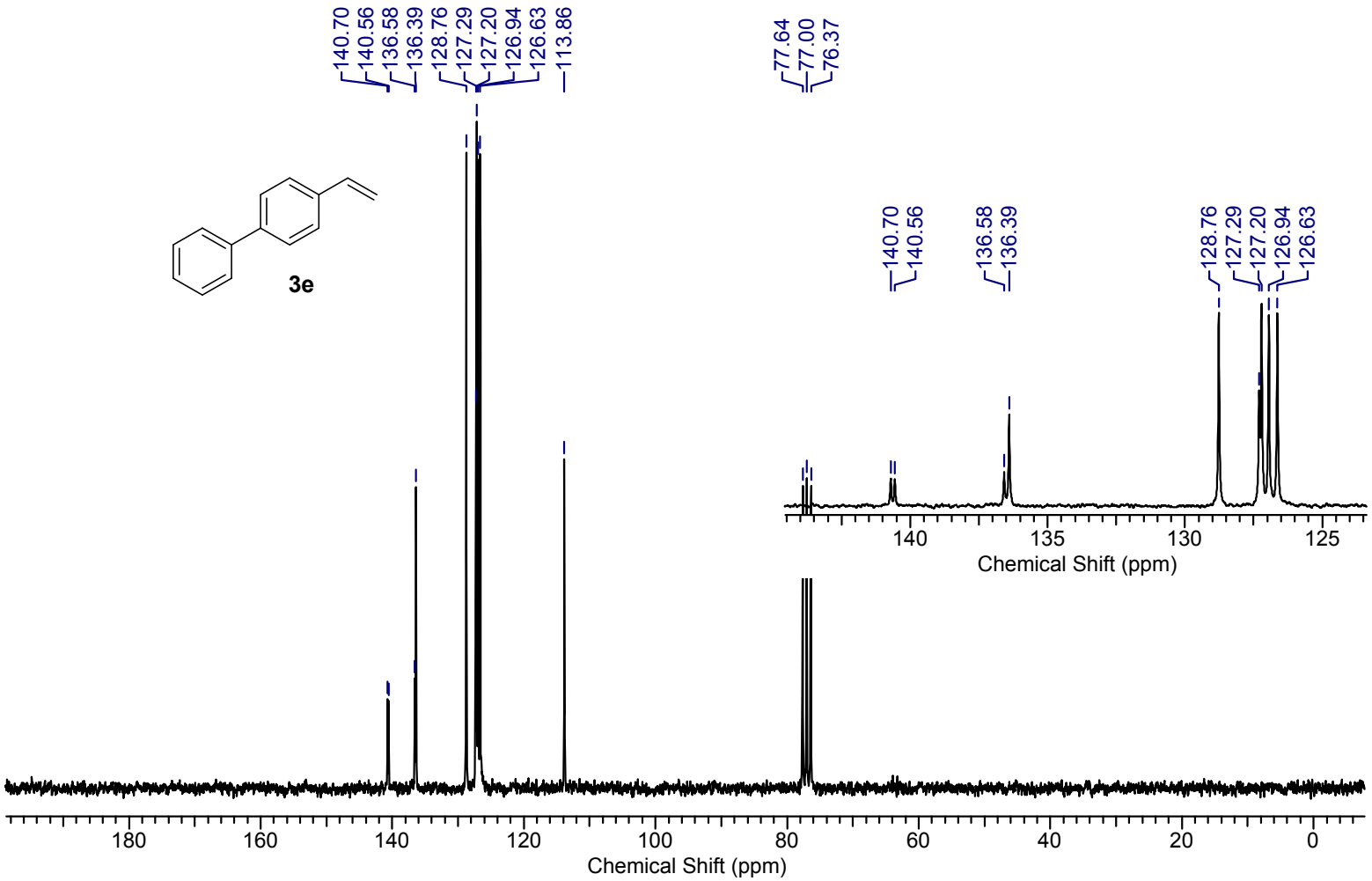
Chemical Shift (ppm)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127.29
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126.94
126.63
113.86
77.64
77.00
76.37
3e
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
140.70
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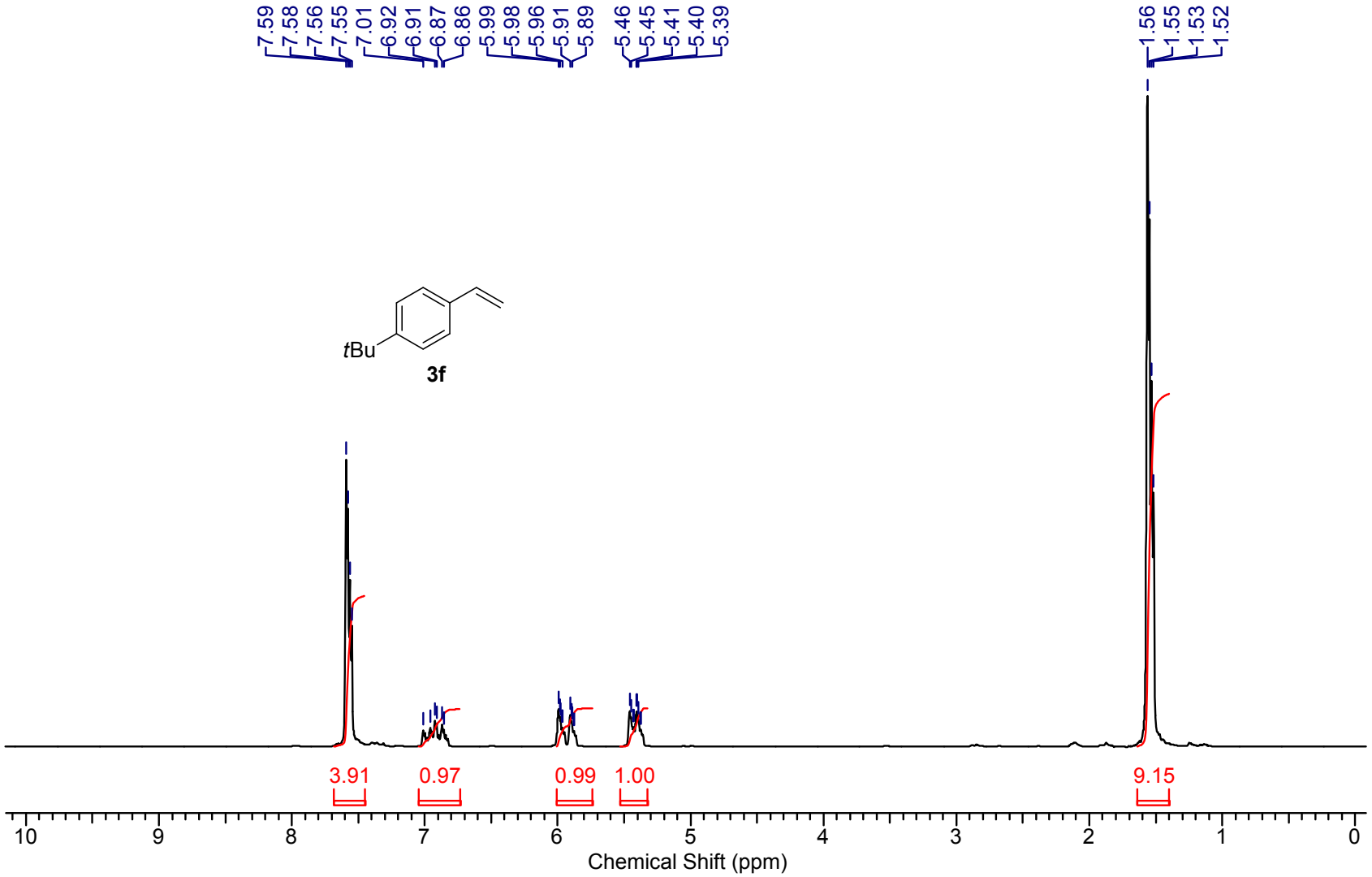
128.76
127.29
127.20
126.94
126.63
140
135
130
125
Chemical Shift (ppm)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5.99
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5.96
5.91
5.89
5.46
5.45
5.41
5.40
5.39
1.56
1.55
1.53
1.52
tBu
3f
3.91
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0.99
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9.15
10
9
8
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4
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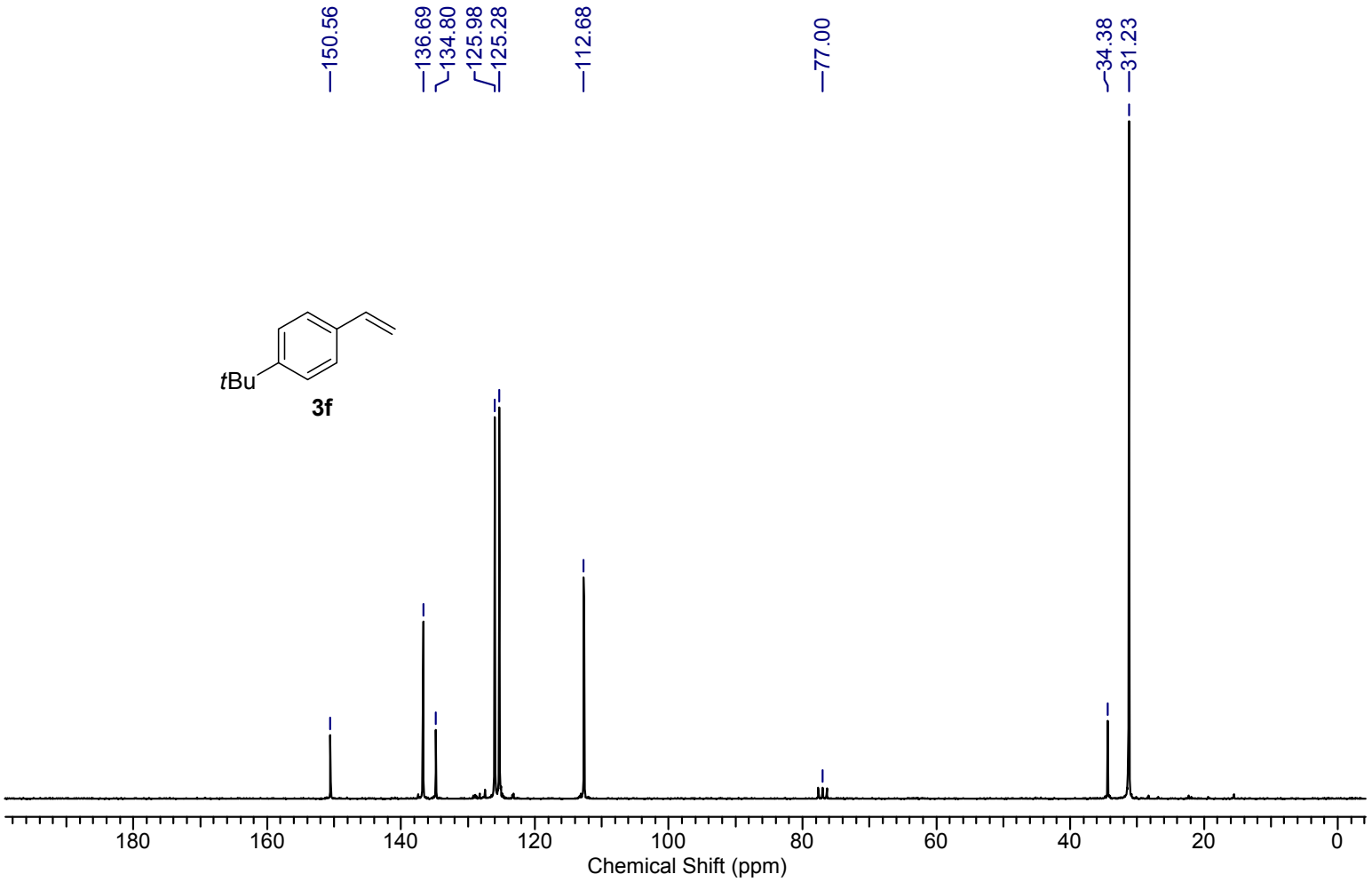
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tBu
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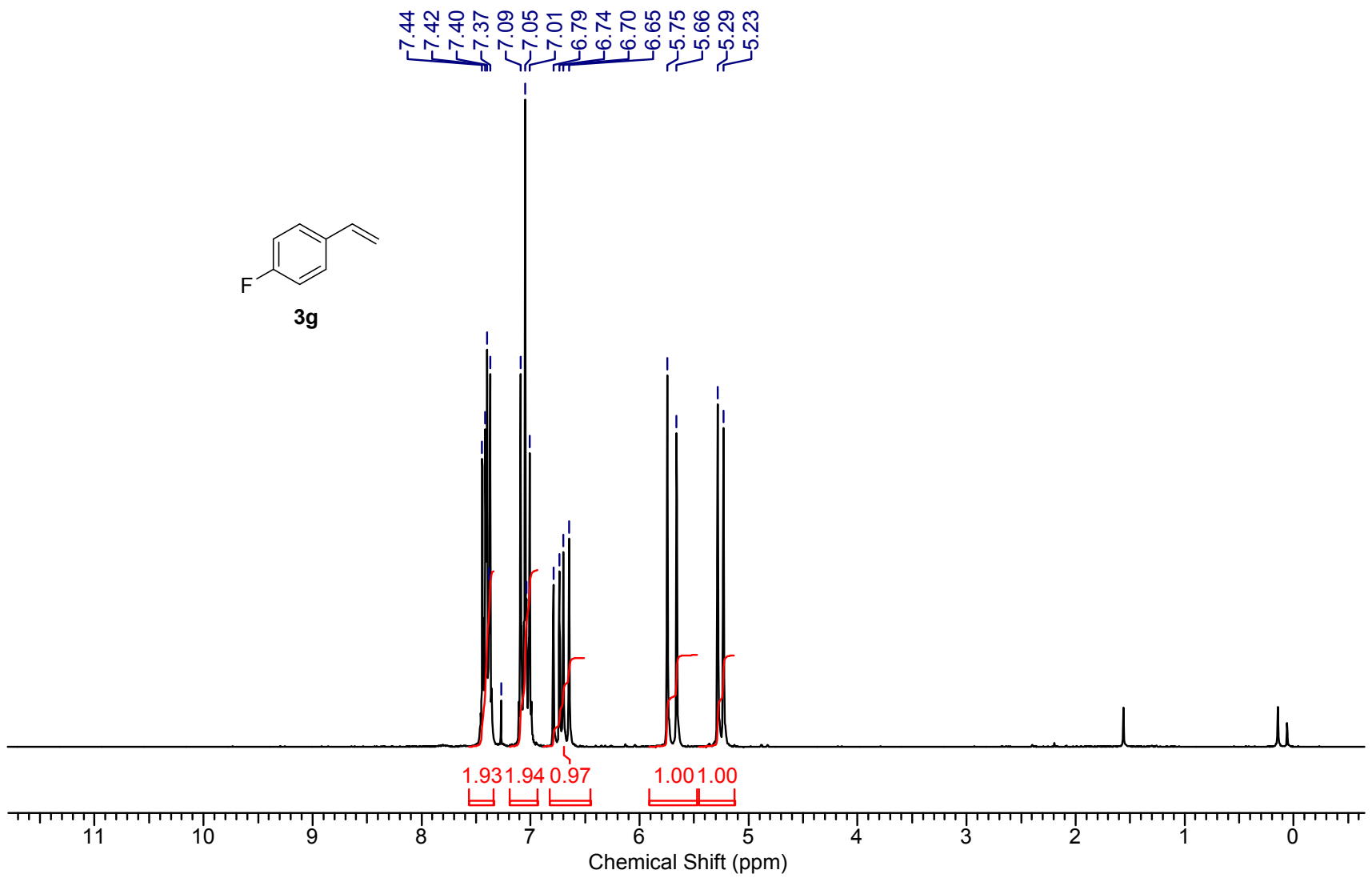
Chemical Shift (ppm)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5.29
5.23
F
3g
1.93
1.94
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1.00
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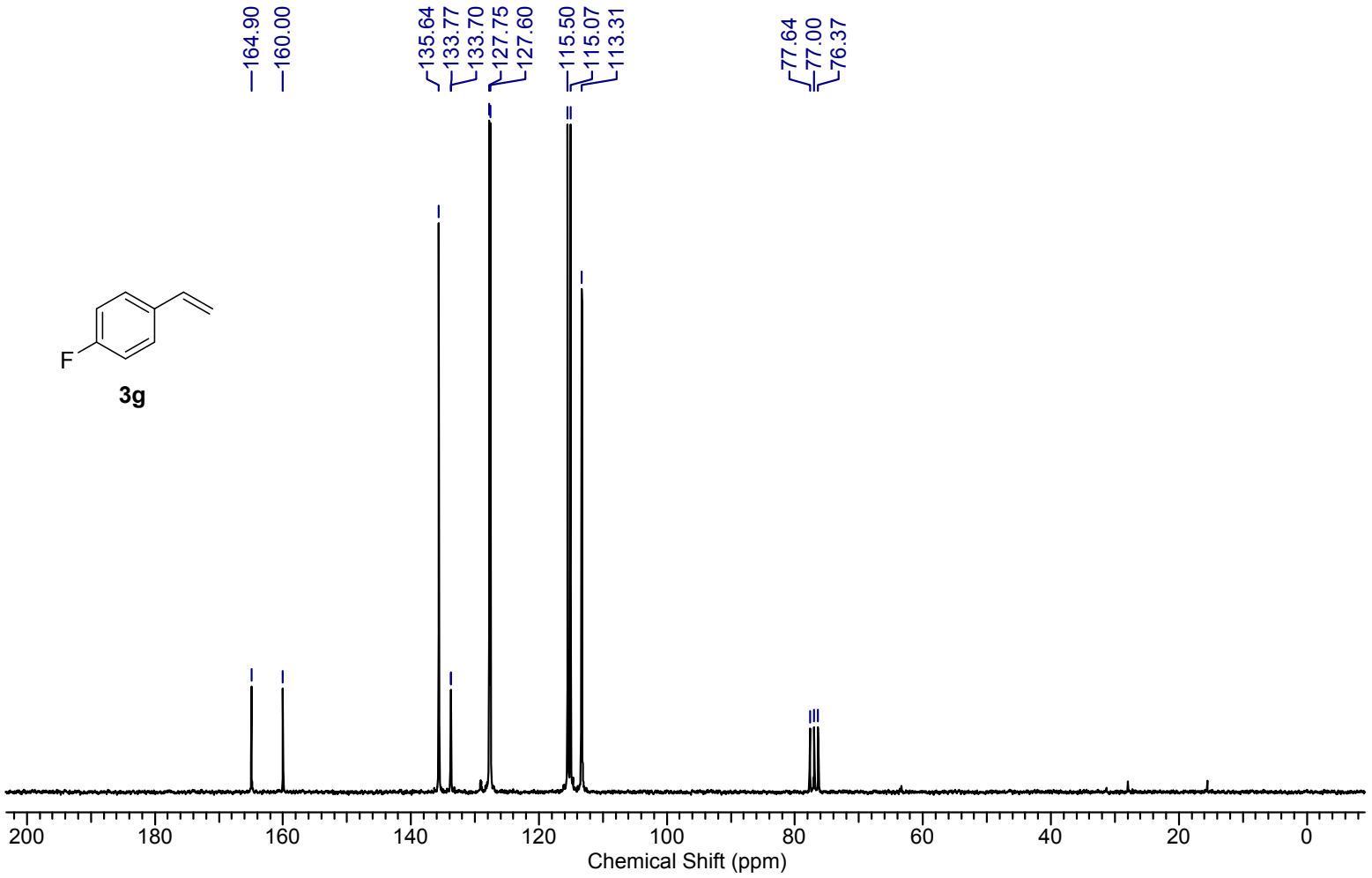
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F
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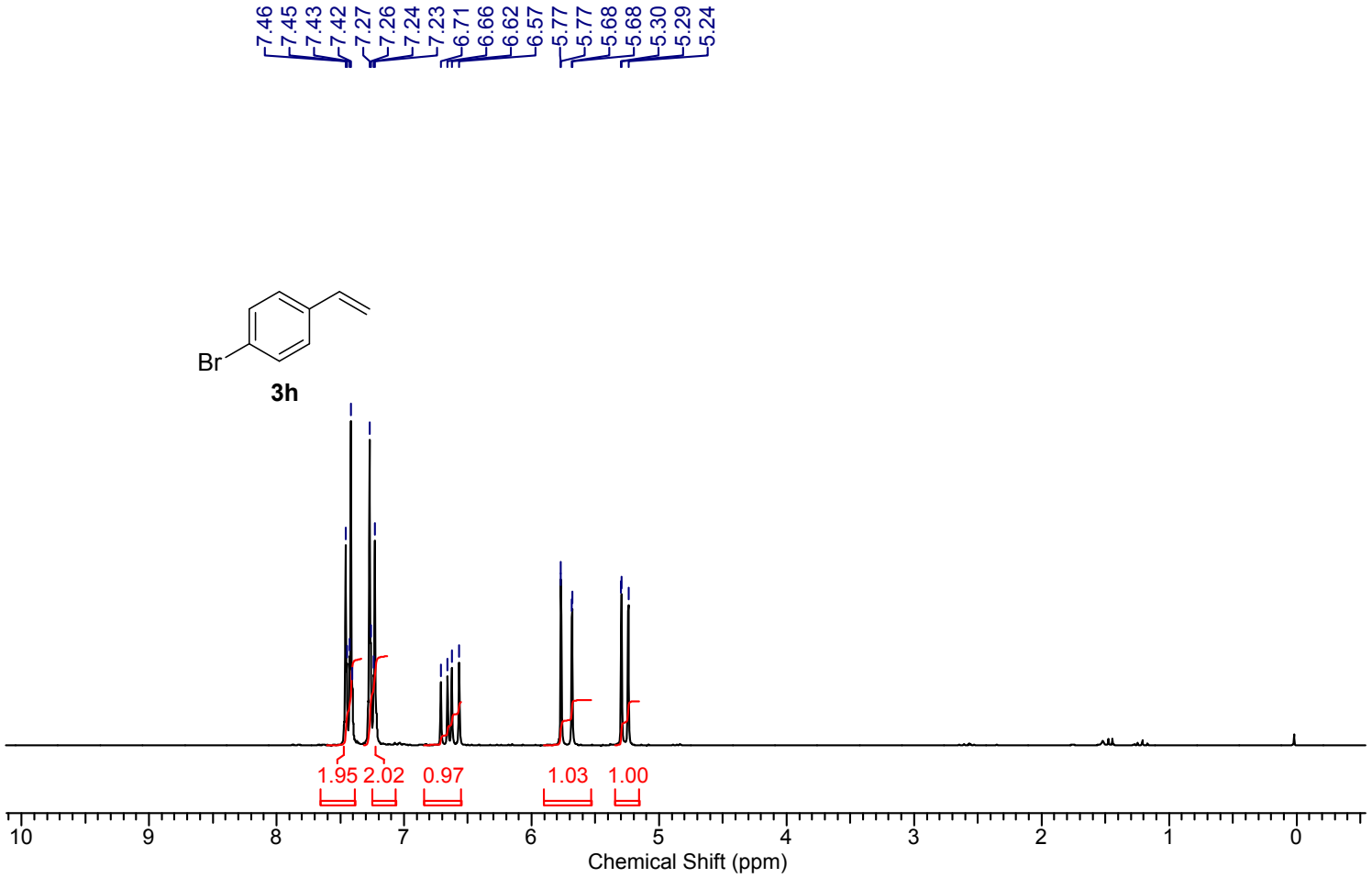
Chemical Shift (ppm)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5.77
5.68
5.68
5.30
5.29
5.24
Br
3h
1.95
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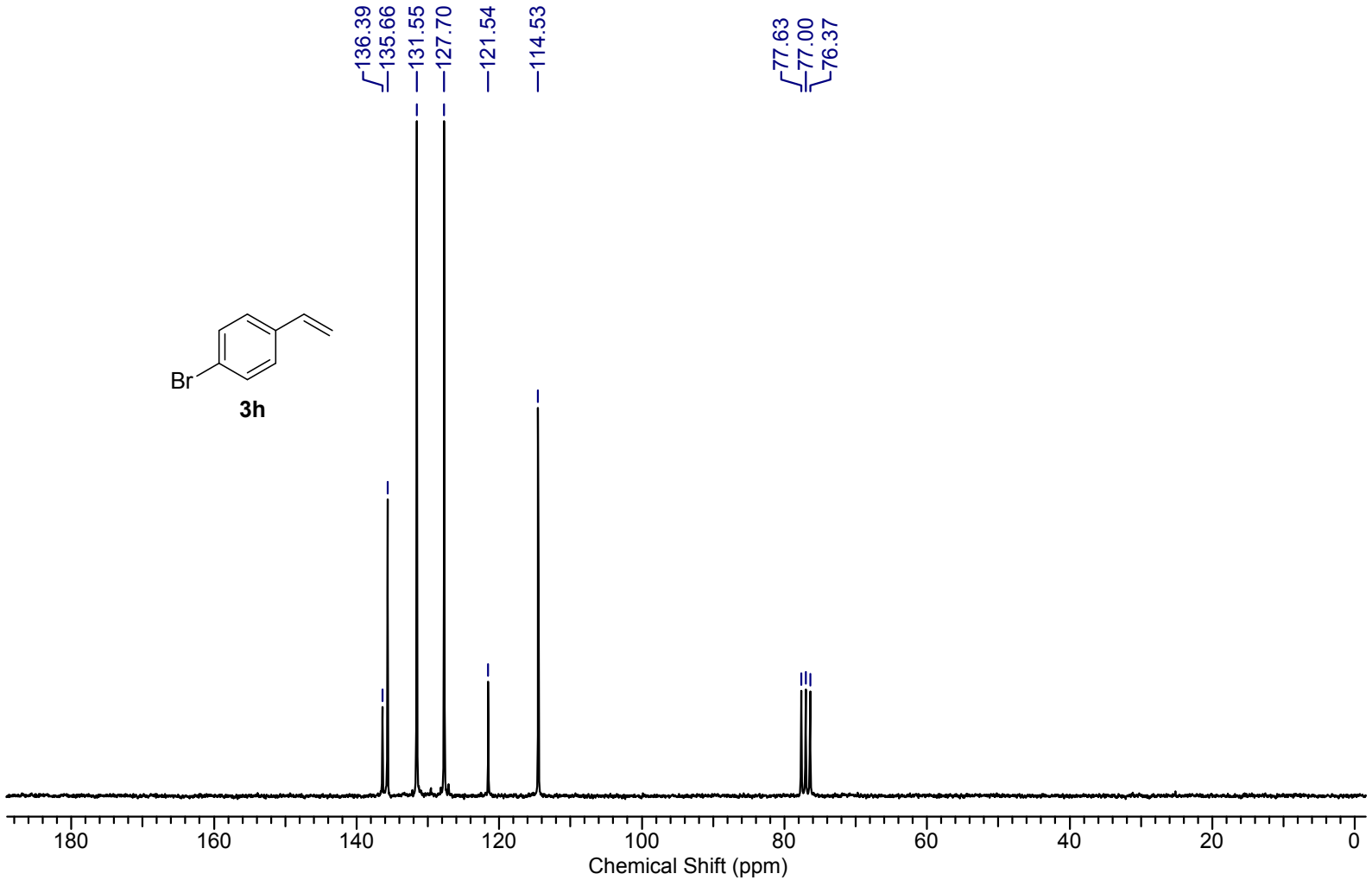
Chemical Shift (ppm)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Br
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20
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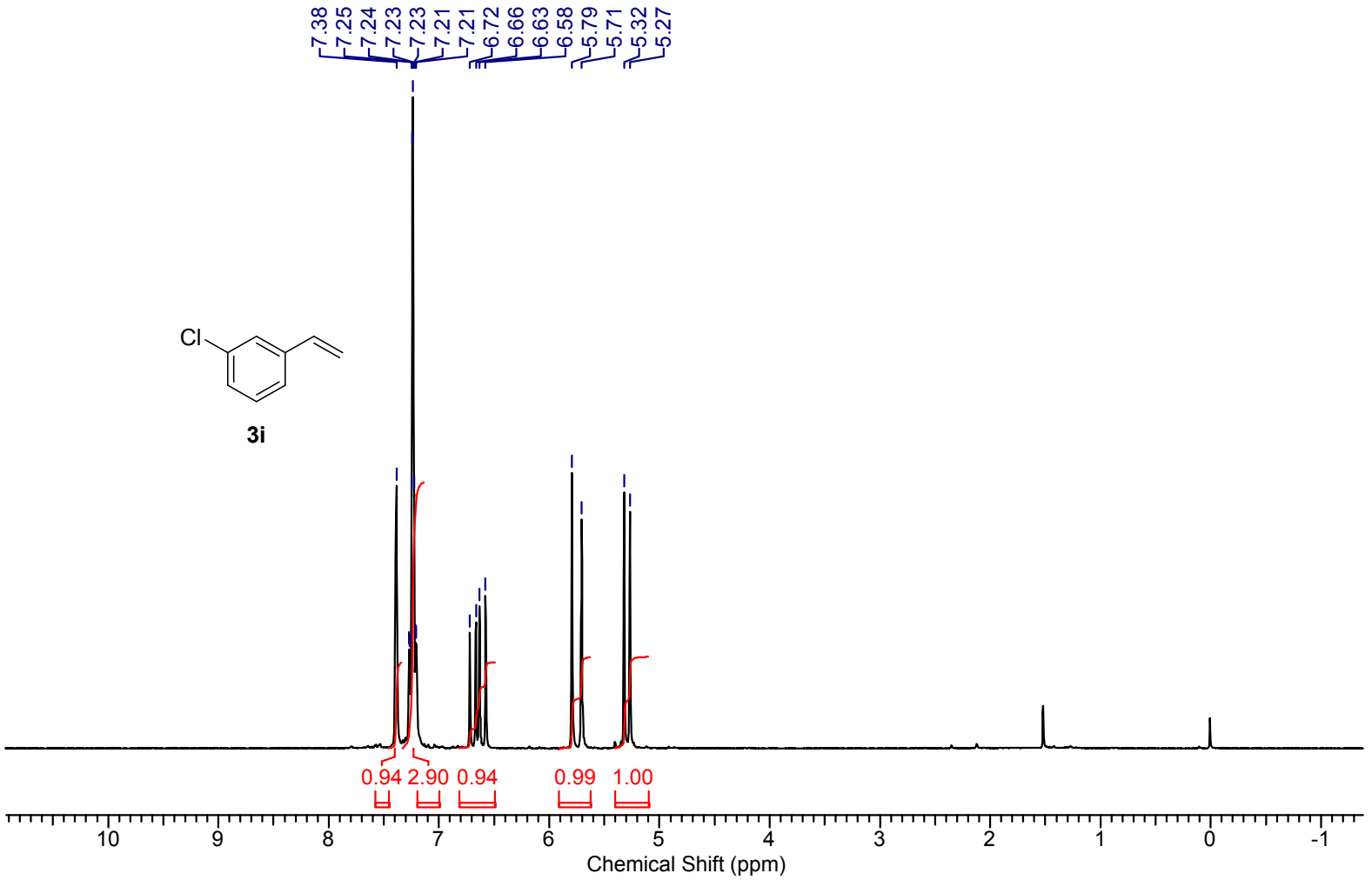
Chemical Shift (ppm)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6.63
6.58
5.79
5.71
5.32
5.27
Cl
3i
0.94
2.90
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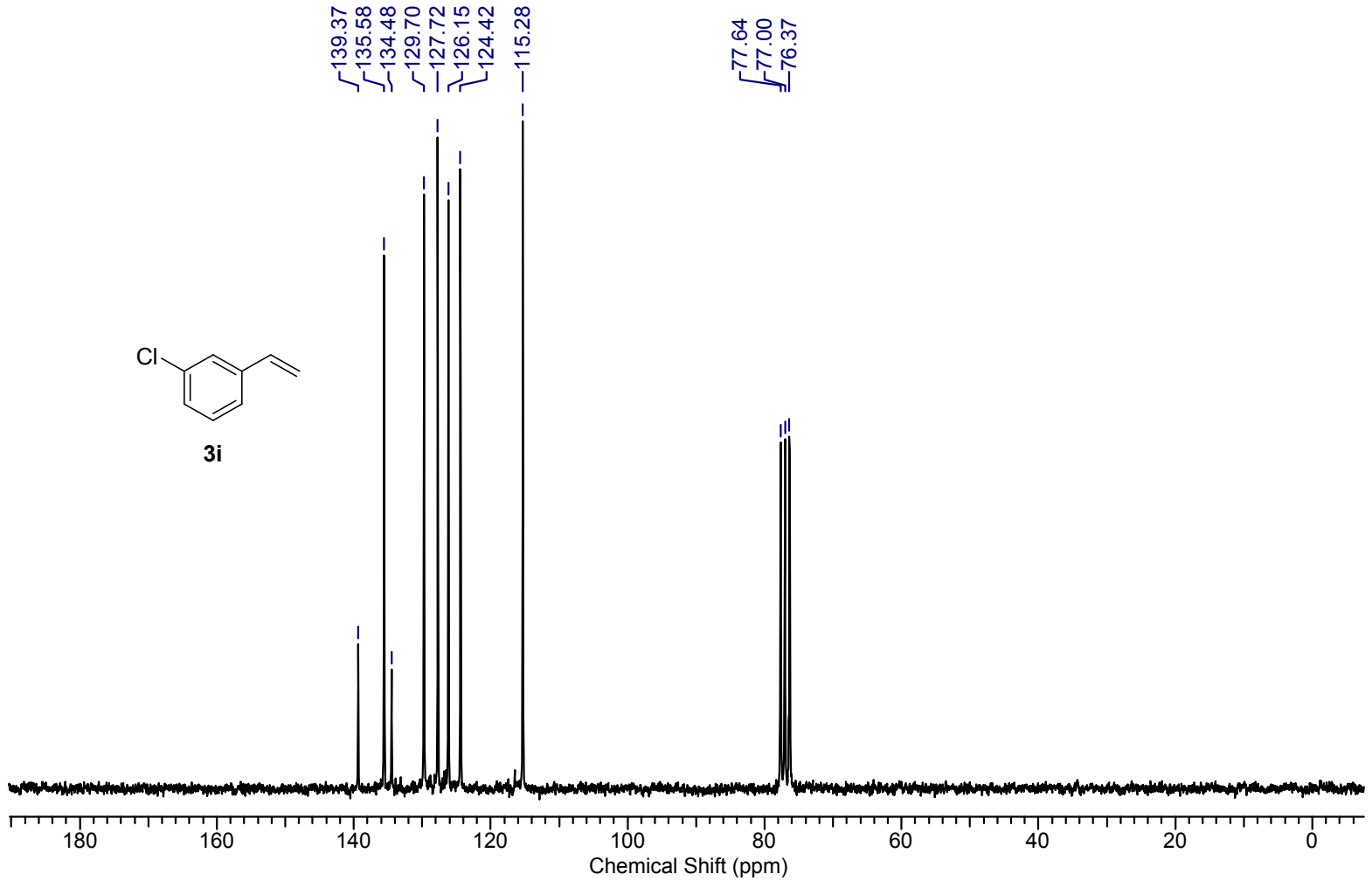
Chemical Shift (ppm)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Cl
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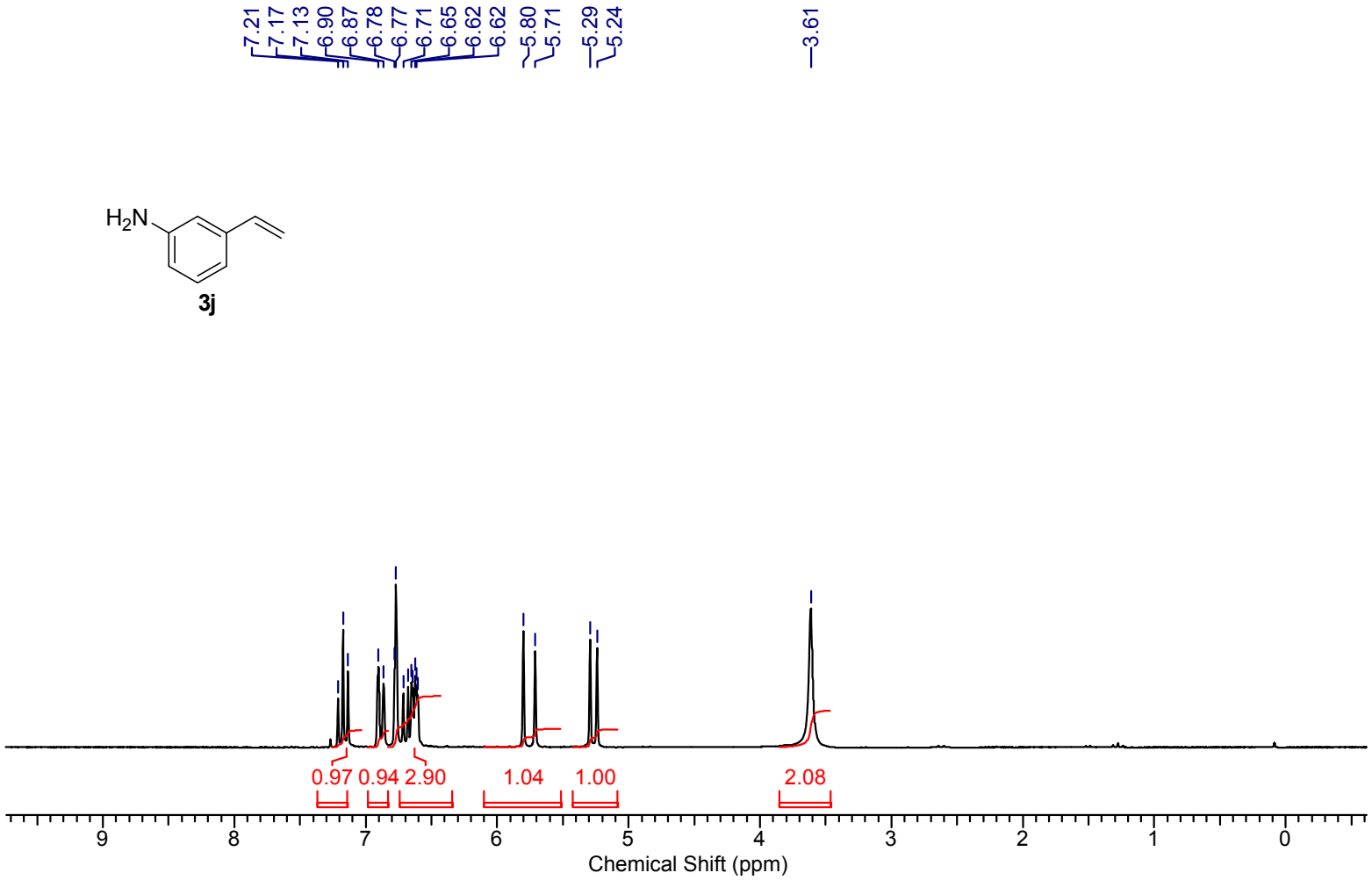
Chemical Shift (ppm)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5.29
5.24
3.61
H2N
3j
0.97
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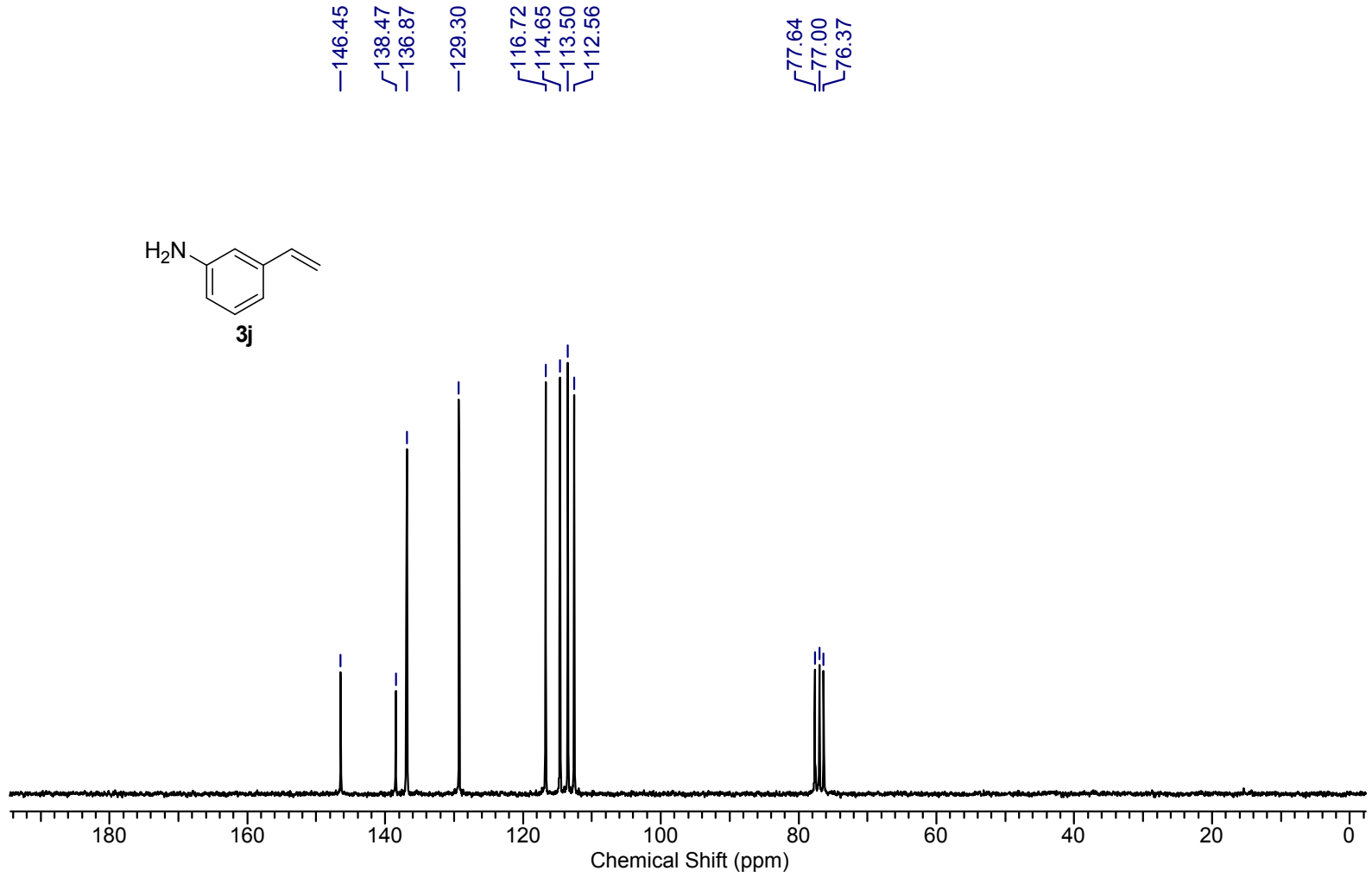
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112.56
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H2N
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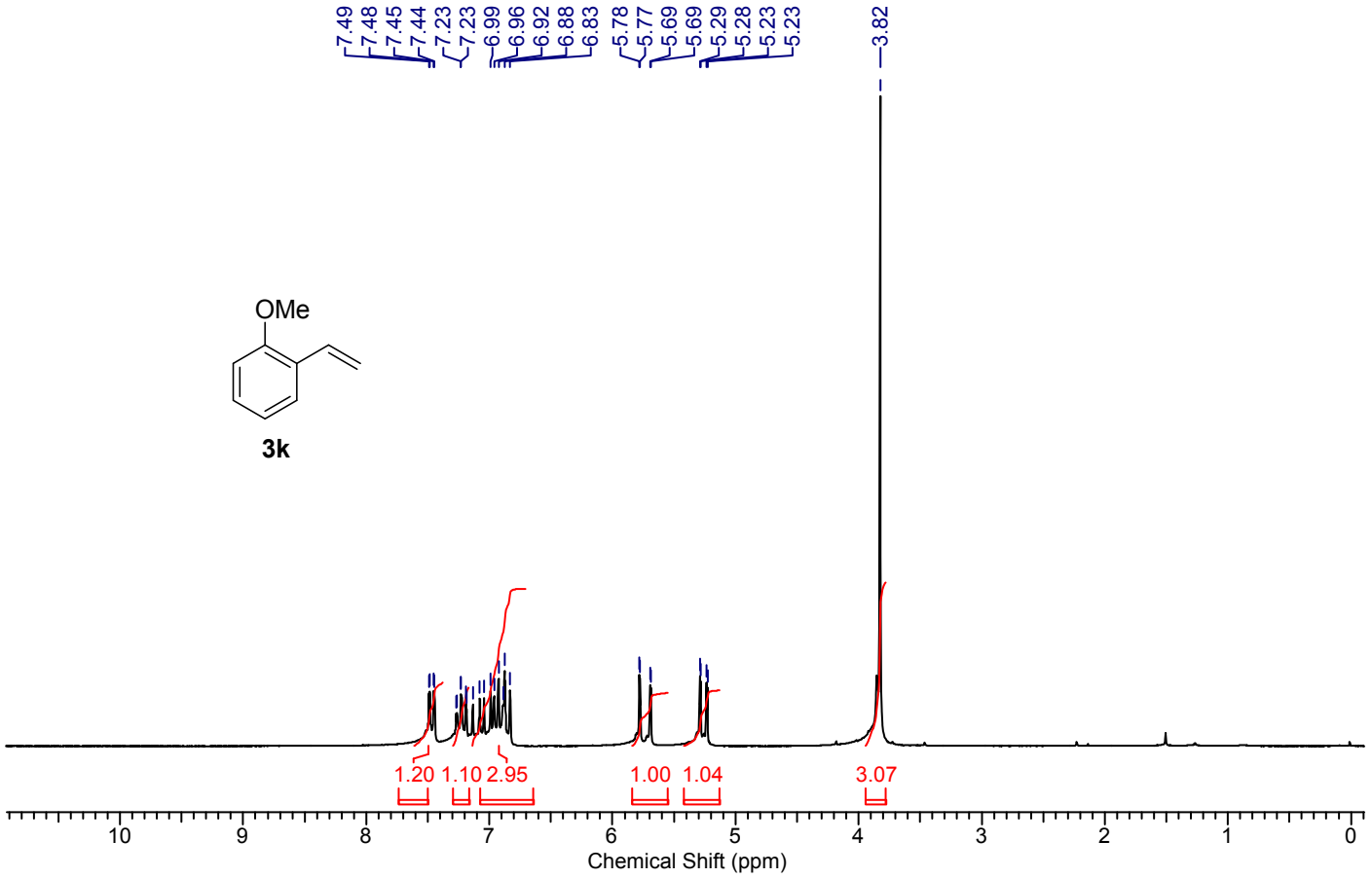
0
Chemical Shift (ppm)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6.88
6.83
5.78
5.77
5.69
5.69
5.29
5.28
5.23
5.23
3.82
OMe
3k
1.20
1.10
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4
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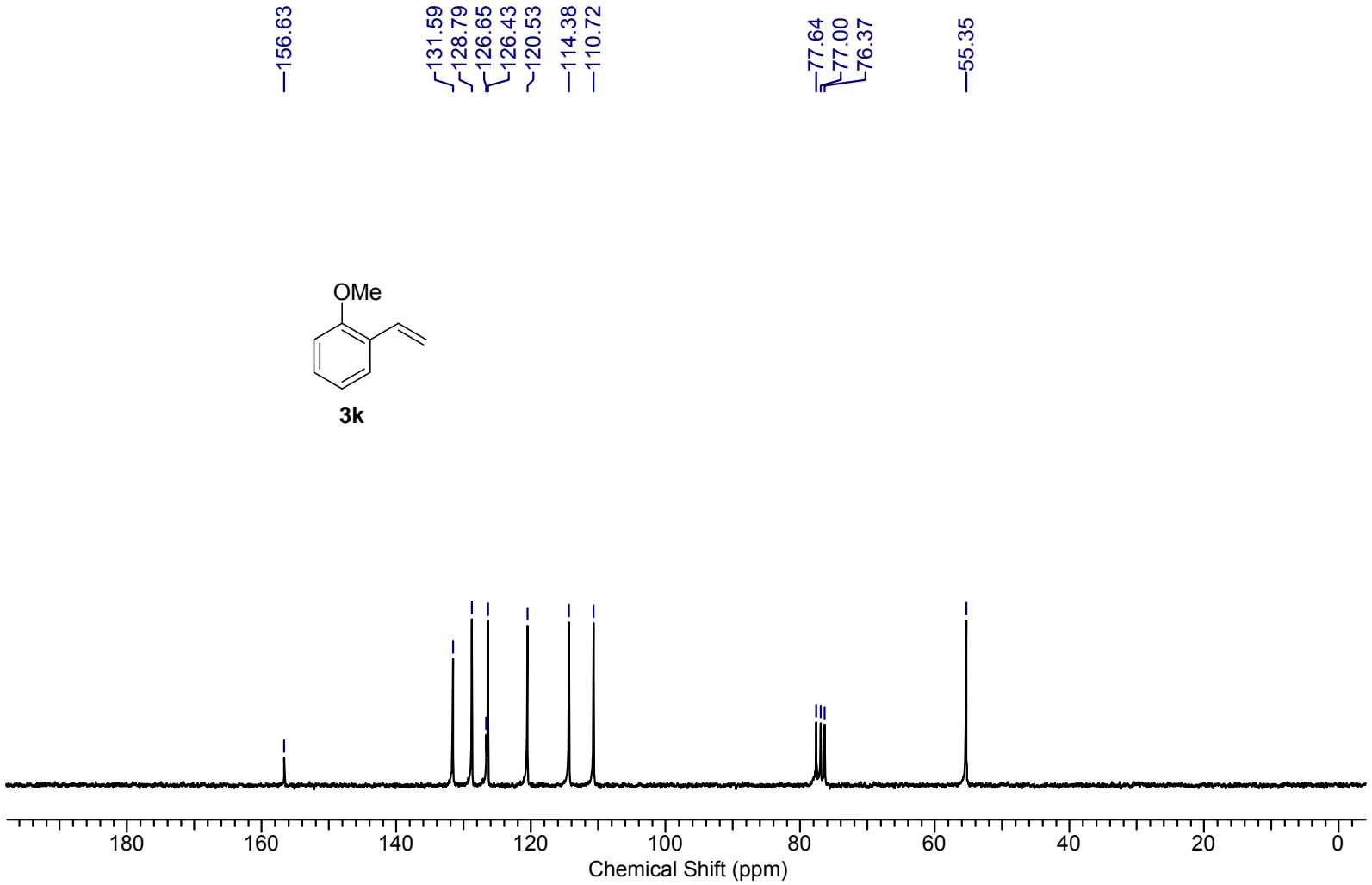
0
Chemical Shift (ppm)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110.72
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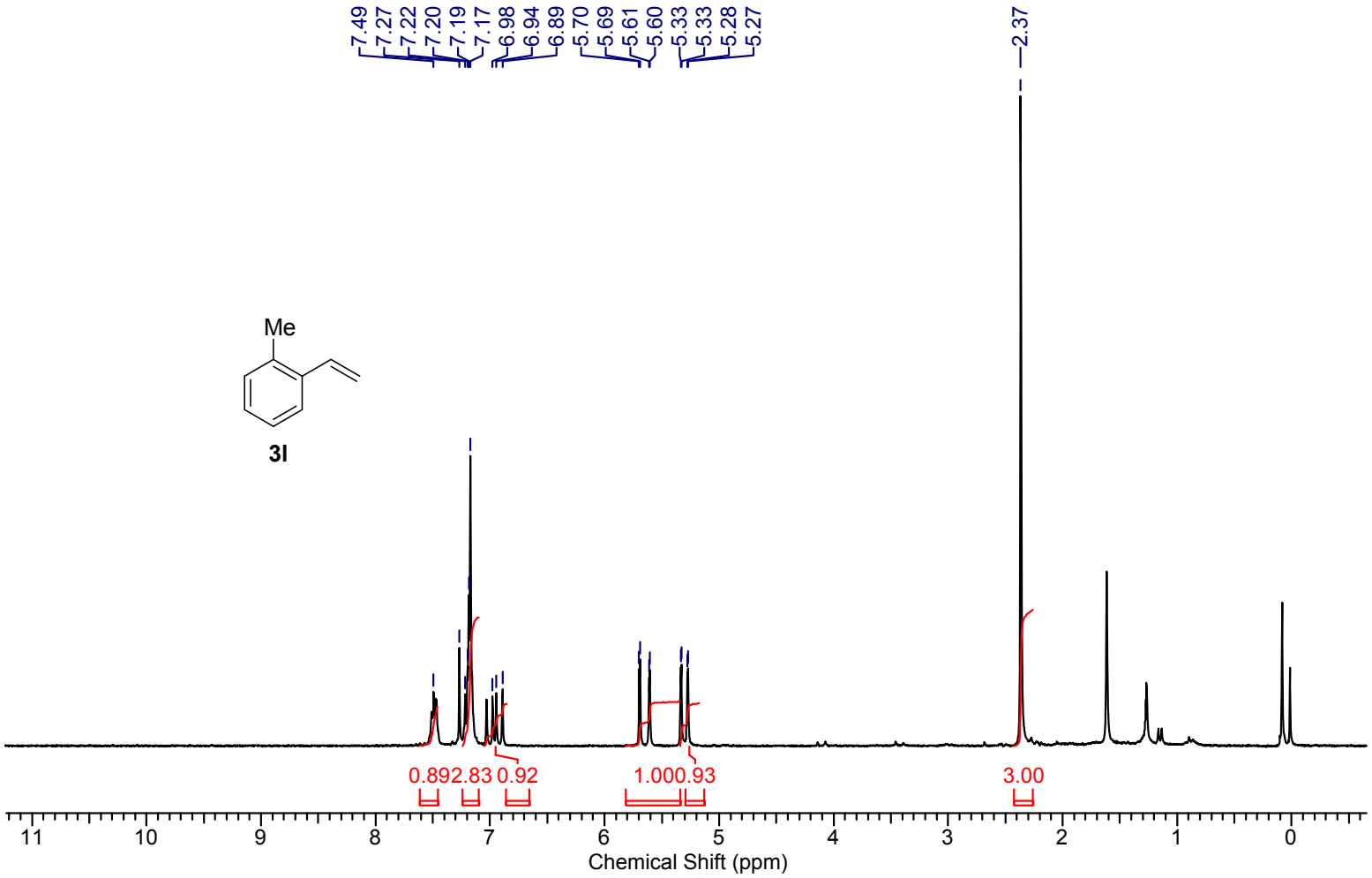
0
Chemical Shift (ppm)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5.69
5.61
5.60
5.33
5.33
5.28
5.27
2.37
Me
3l
0.89
2.83
0.92
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9
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7
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4
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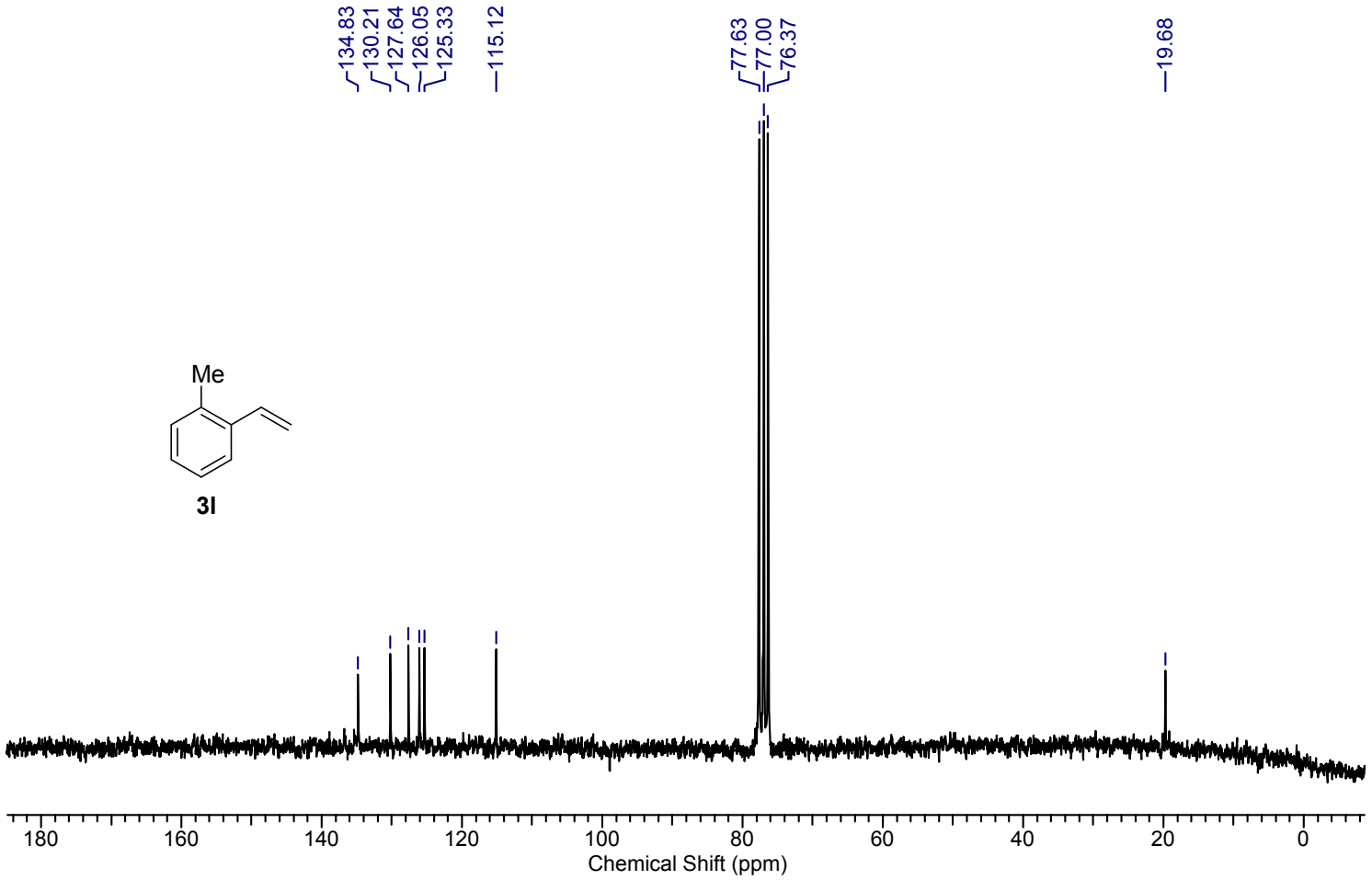
Chemical Shift (ppm)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20
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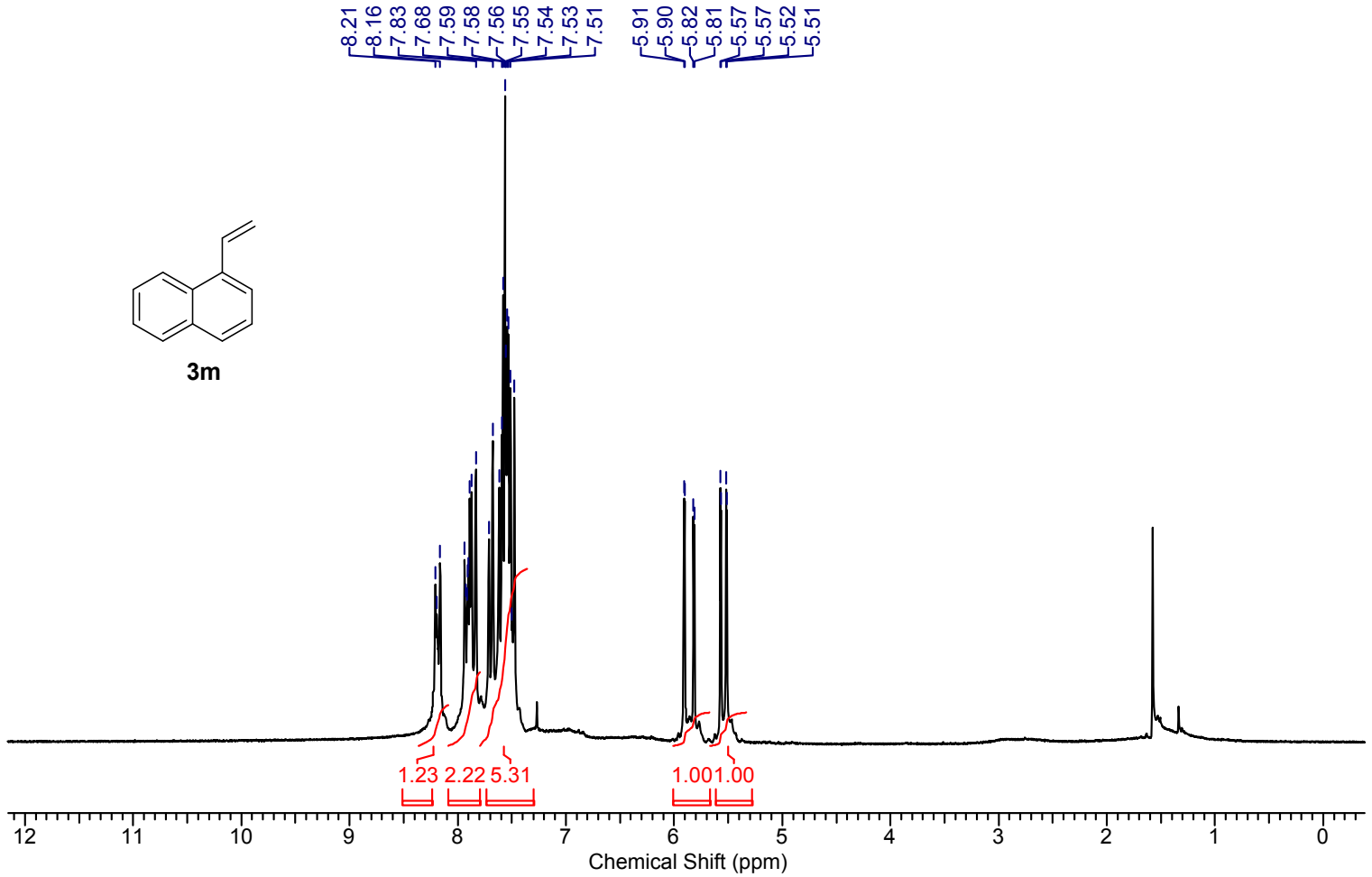
Chemical Shift (ppm)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5.90
5.82
5.81
5.57
5.57
5.52
5.51
3m
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2.22
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4
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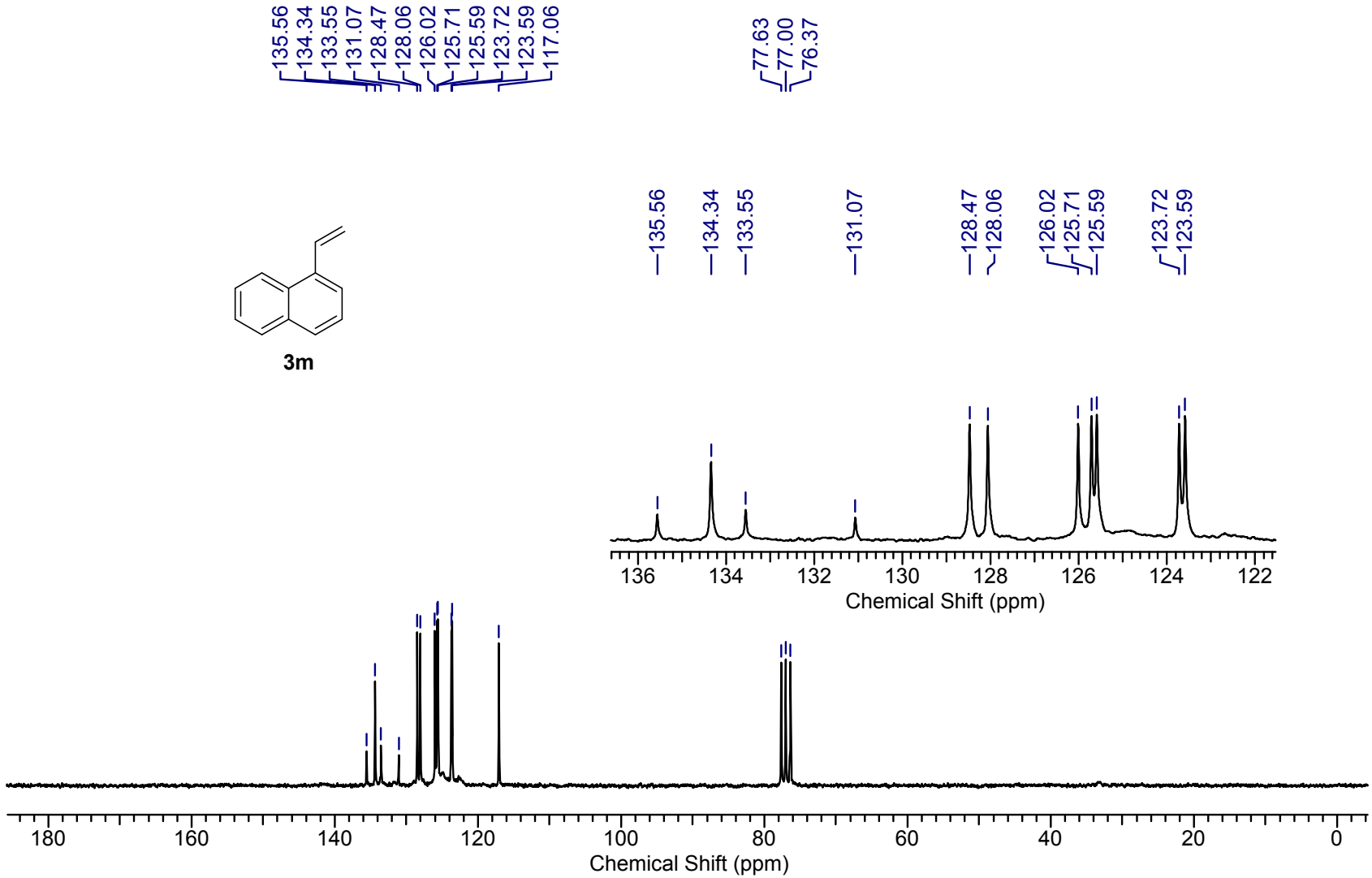
0
Chemical Shift (ppm)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128.06
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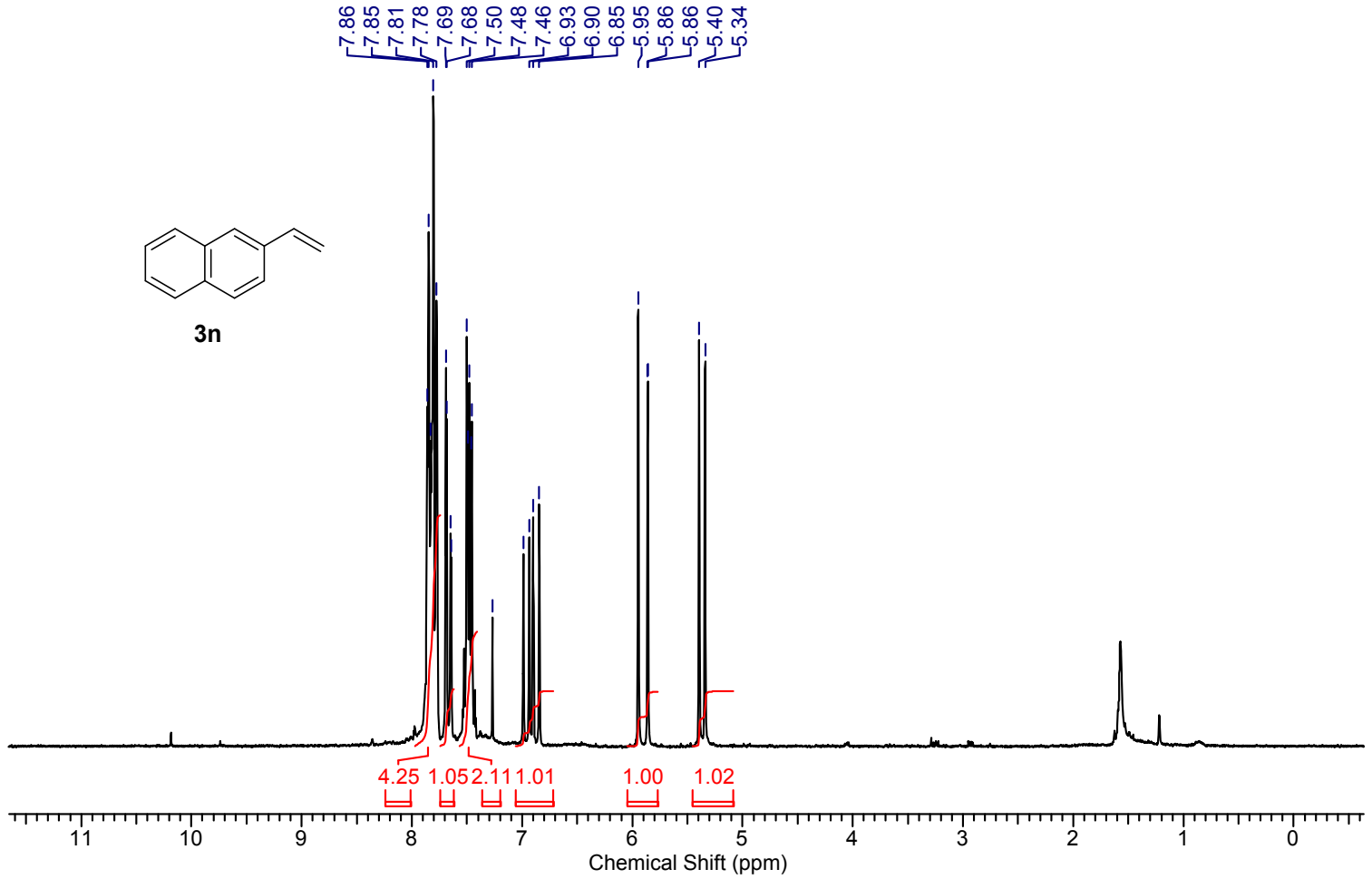
123.59
117.06
77.63
77.00
76.37
3m
Chemical Shift (ppm)
Chemical Shift (ppm)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6.85
5.95
5.86
5.86
5.40
5.34
3n
4.25
1.05
2.11
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1.00
1.02
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4
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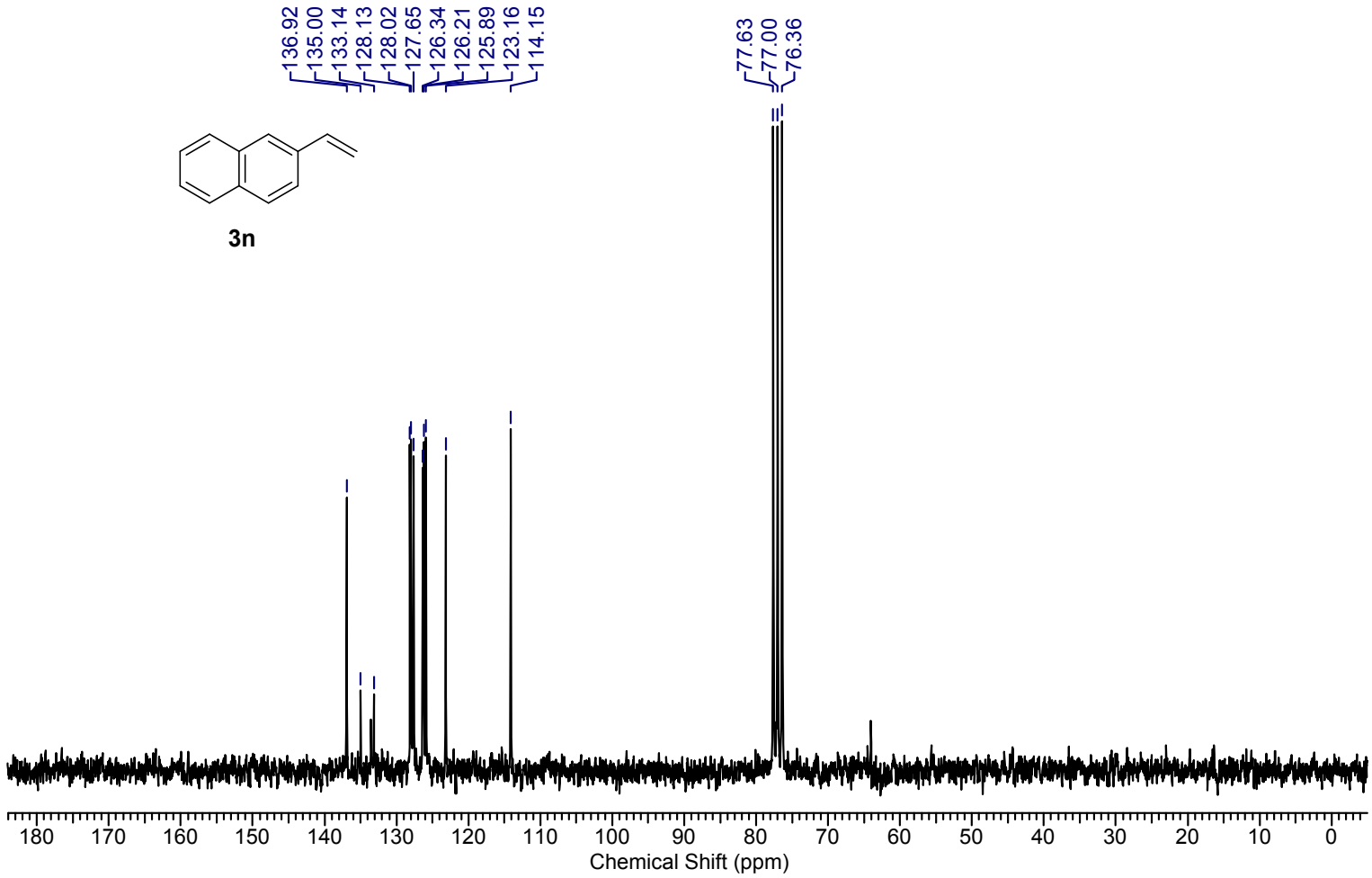
Chemical Shift (ppm)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133.14
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123.16
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76.36
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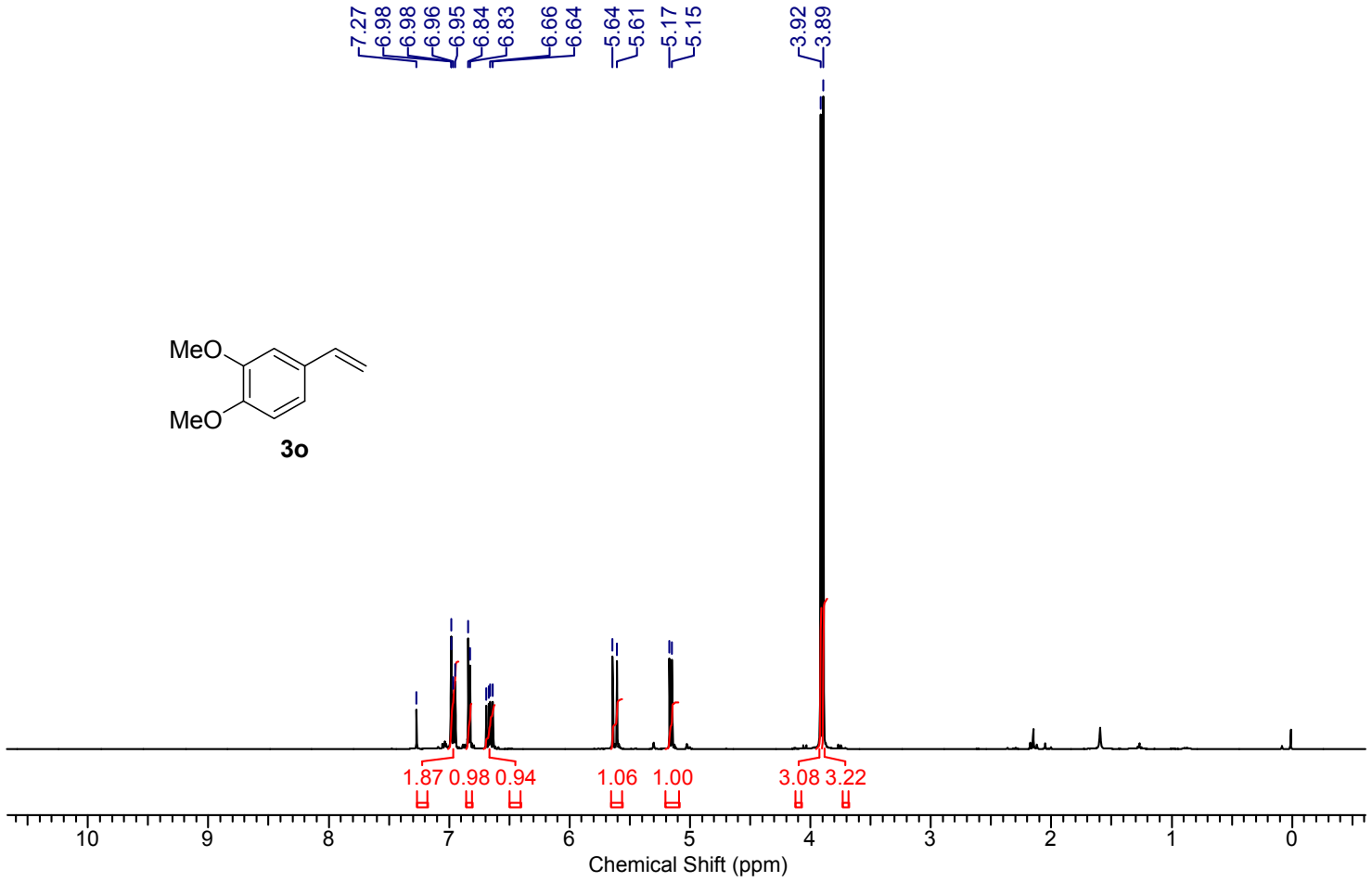
Chemical Shift (ppm)


7.27
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6.83
6.66
6.64
5.64
5.61
5.17
5.15
3.92
3.89
MeO
MeO
3o
1.87 0.98 0.94
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4
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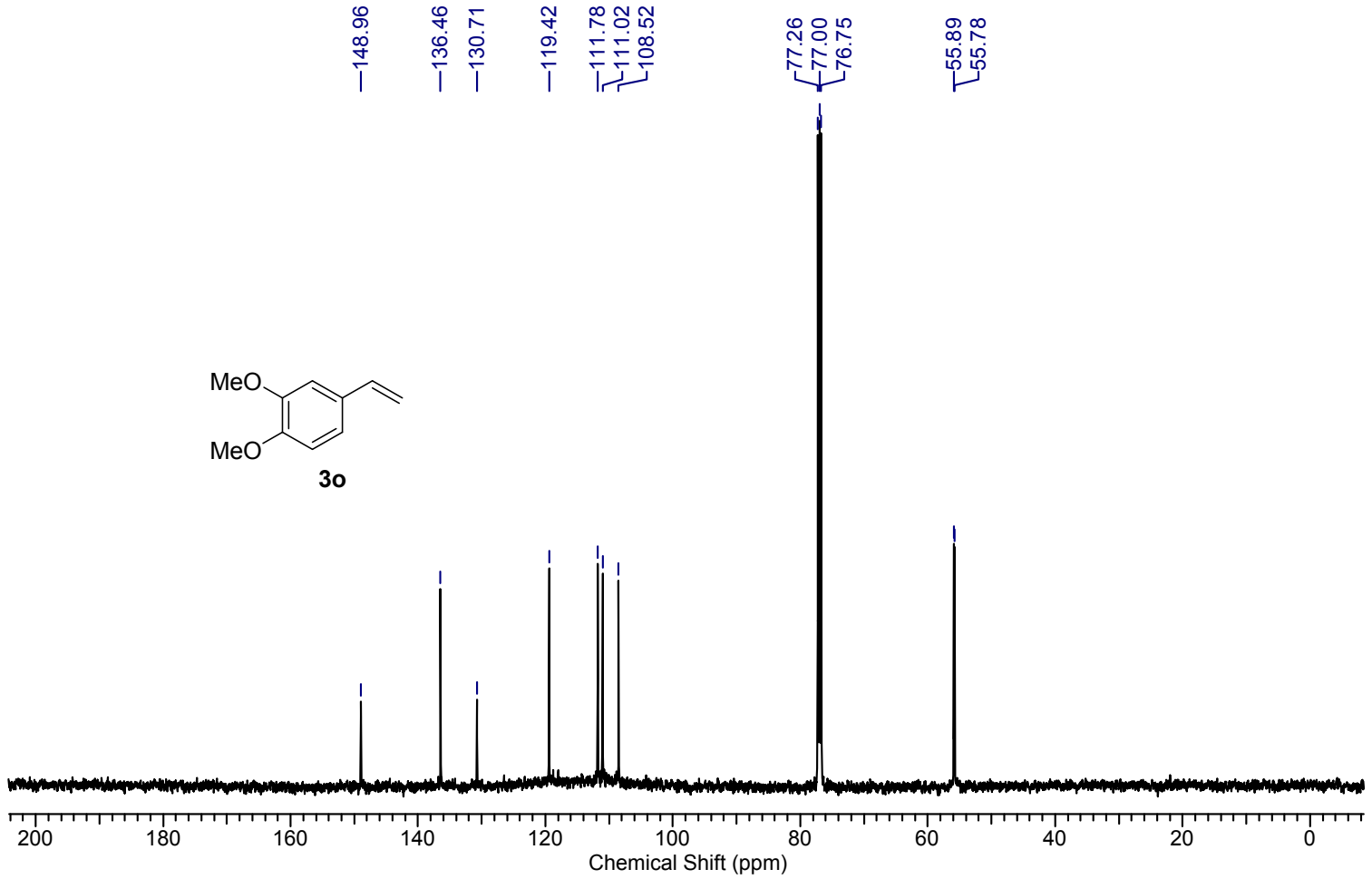
Chemical Shift (ppm)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119.42
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111.02
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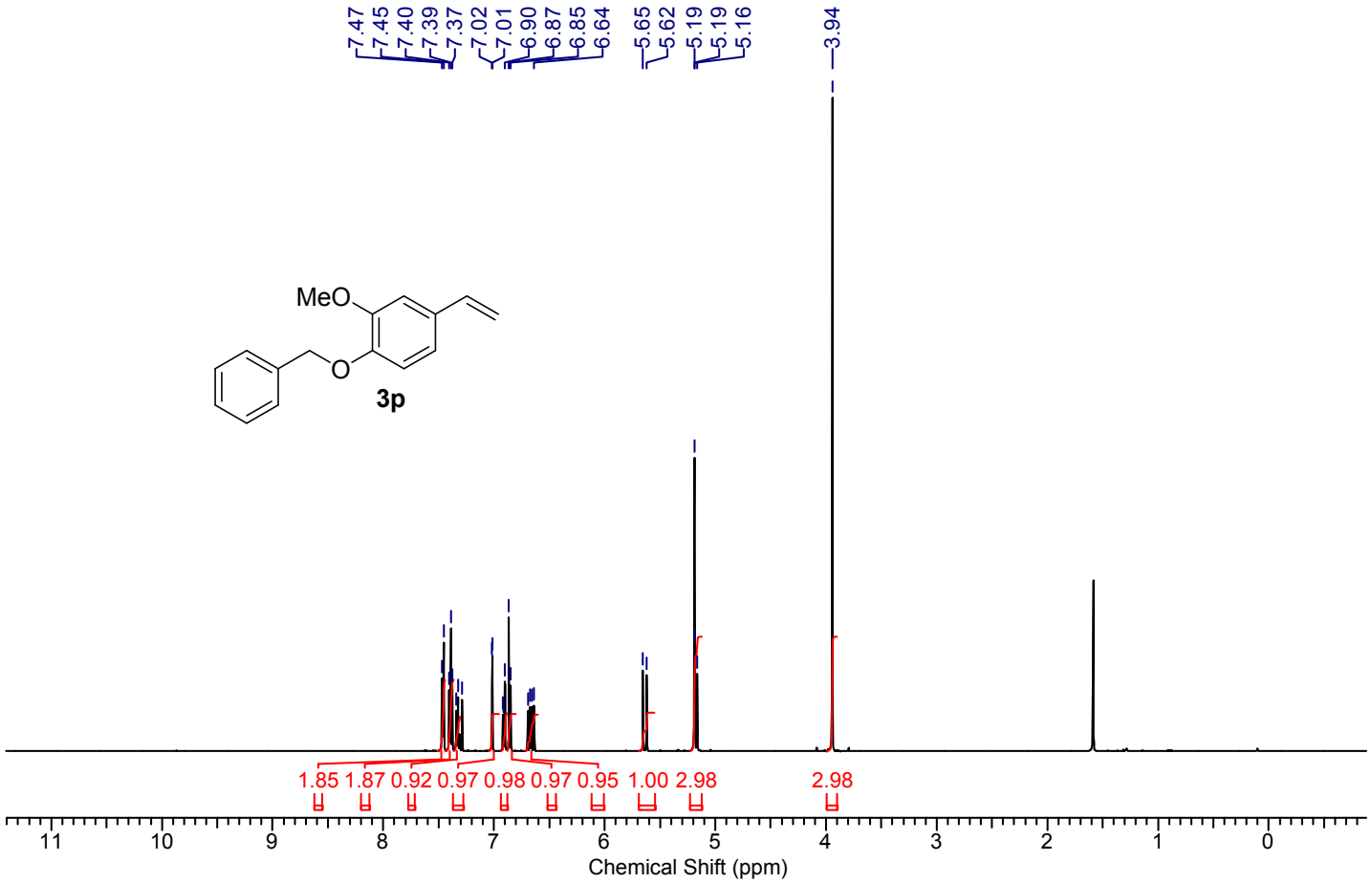
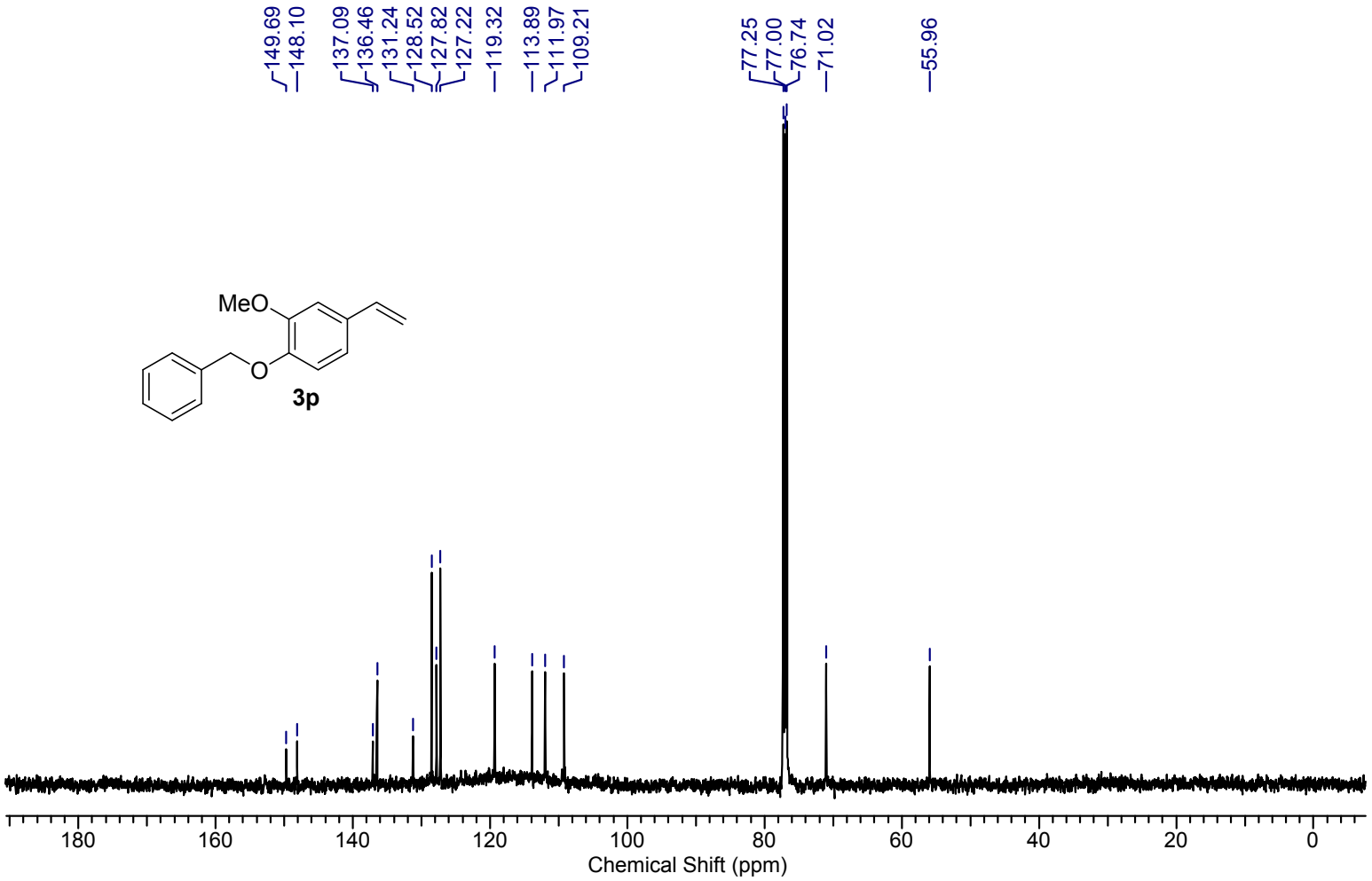
77.26
77.00
76.75
55.89
55.78
MeO
MeO
3o
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.47
7.45
7.40
7.39
7.37
7.02
7.01
6.90
6.87
6.85
6.64
5.65
5.62
5.19
5.19
5.16
3.94
MeO
O
3p
1.85 1.87 0.92 0.97 0.98 0.97 0.95 1.00 2.98
2.98
11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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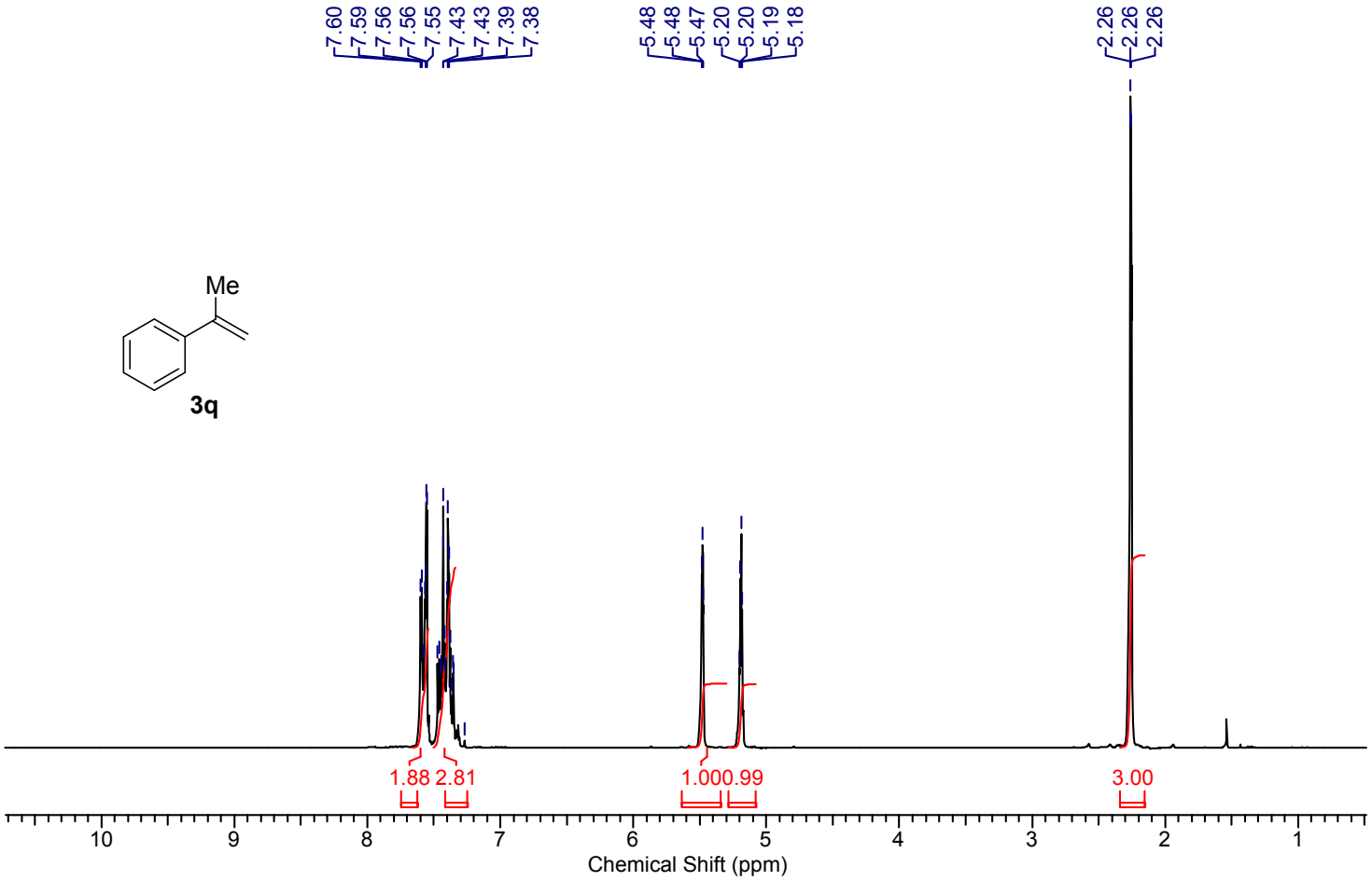
148.10
137.09
136.46
131.24
128.52
127.82
127.22
119.32
113.89
111.97
109.21
77.25
77.00
76.74
71.02
55.96
MeO
O
3p
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)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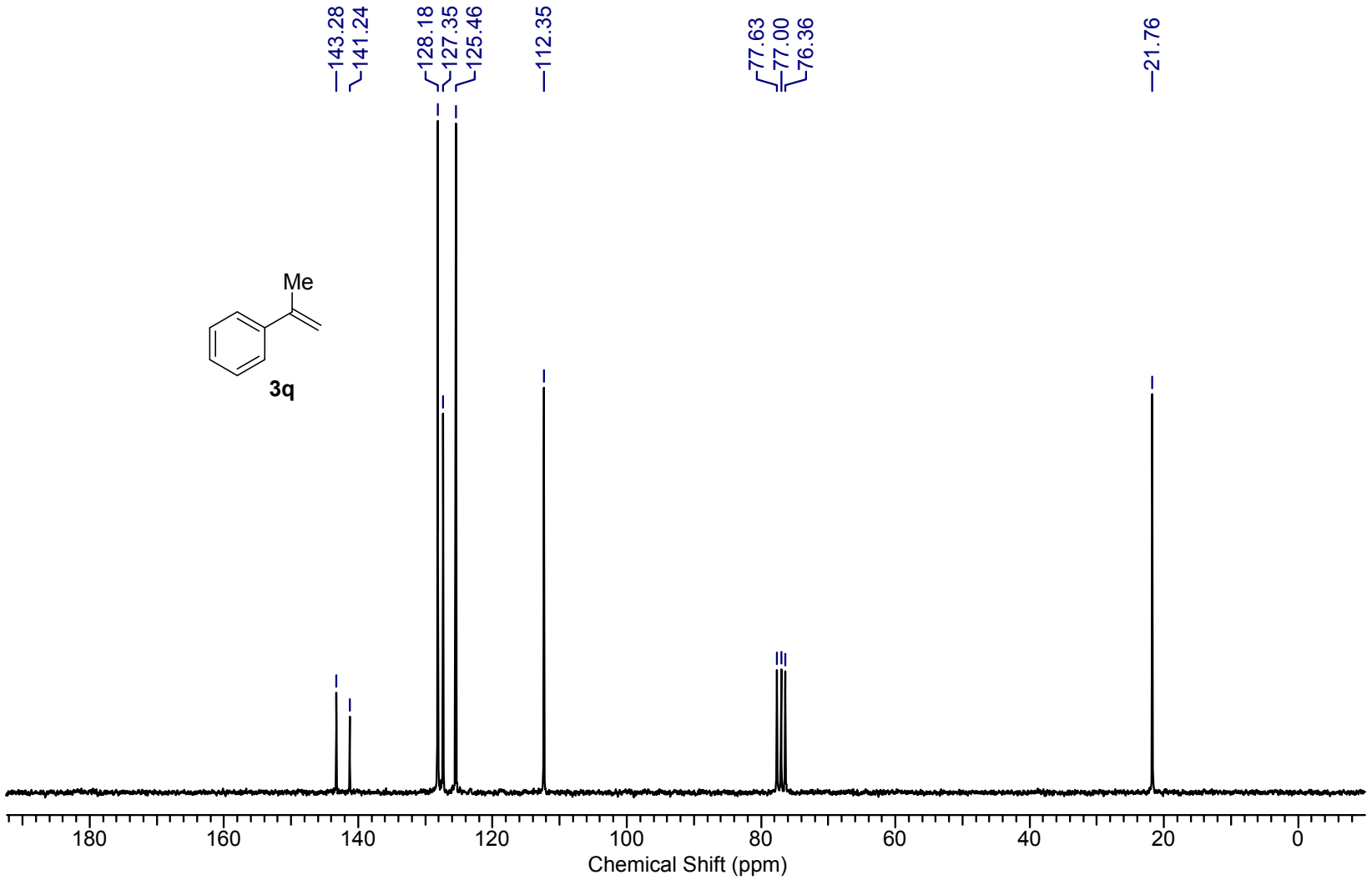
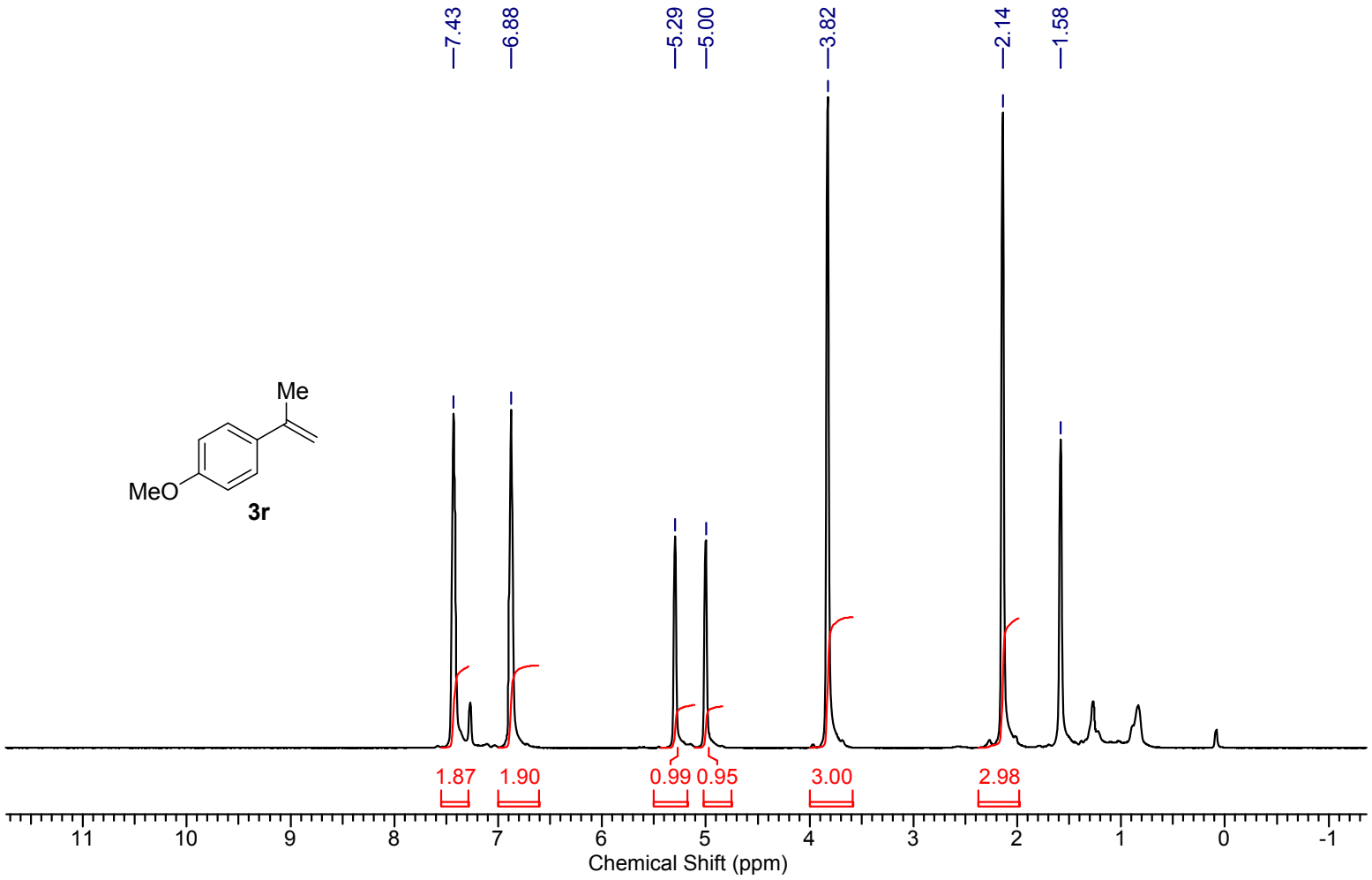
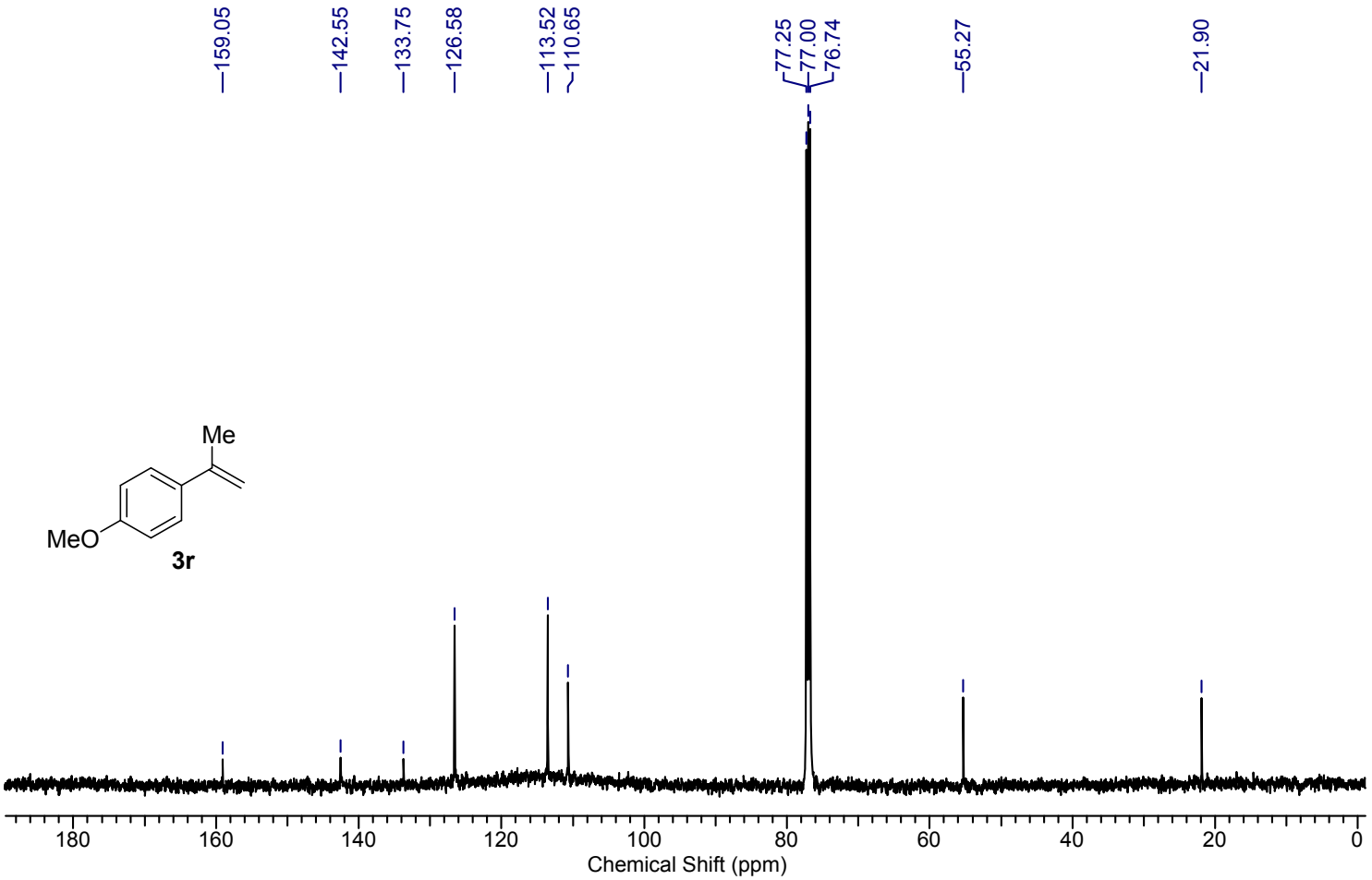
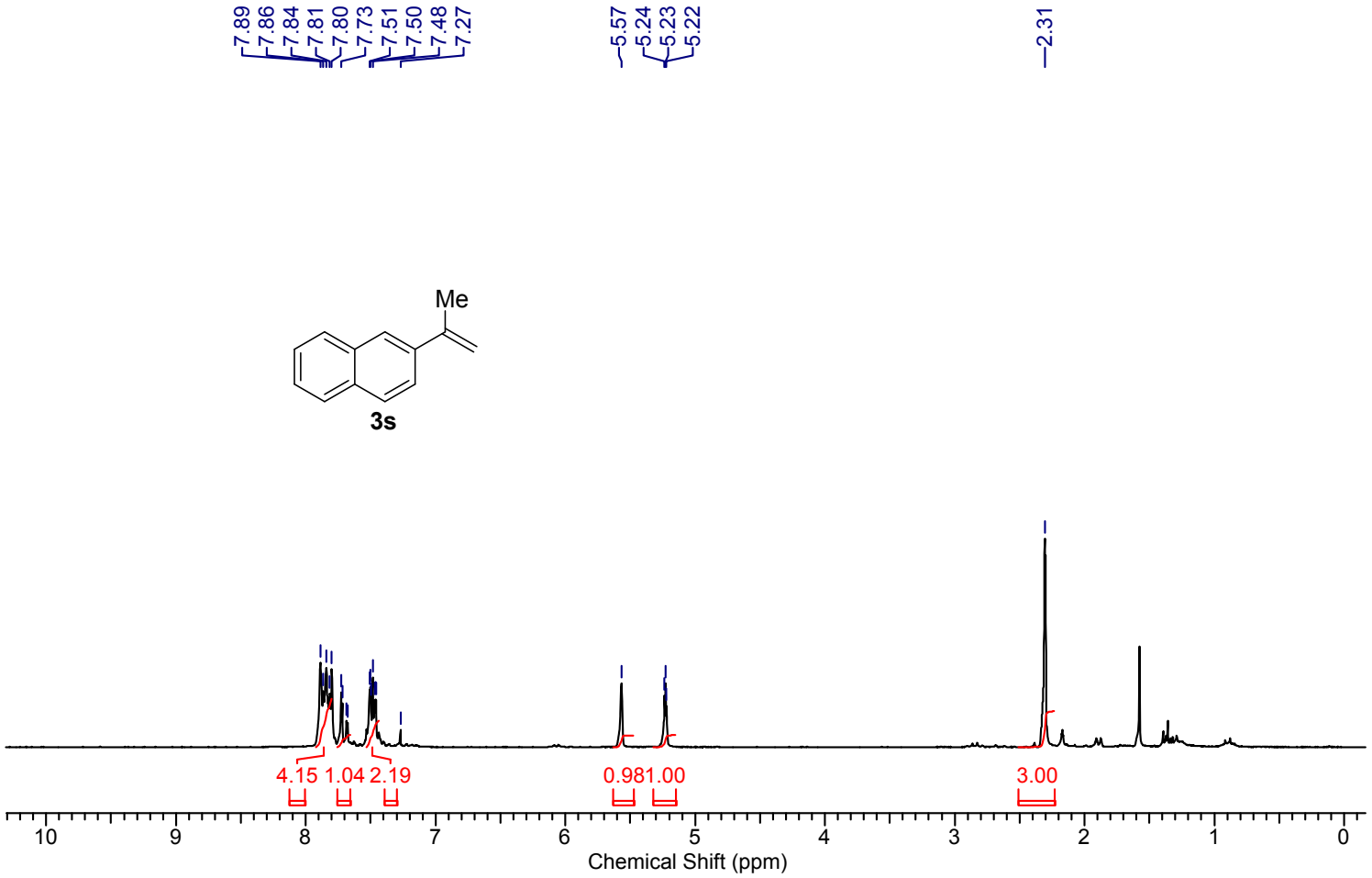
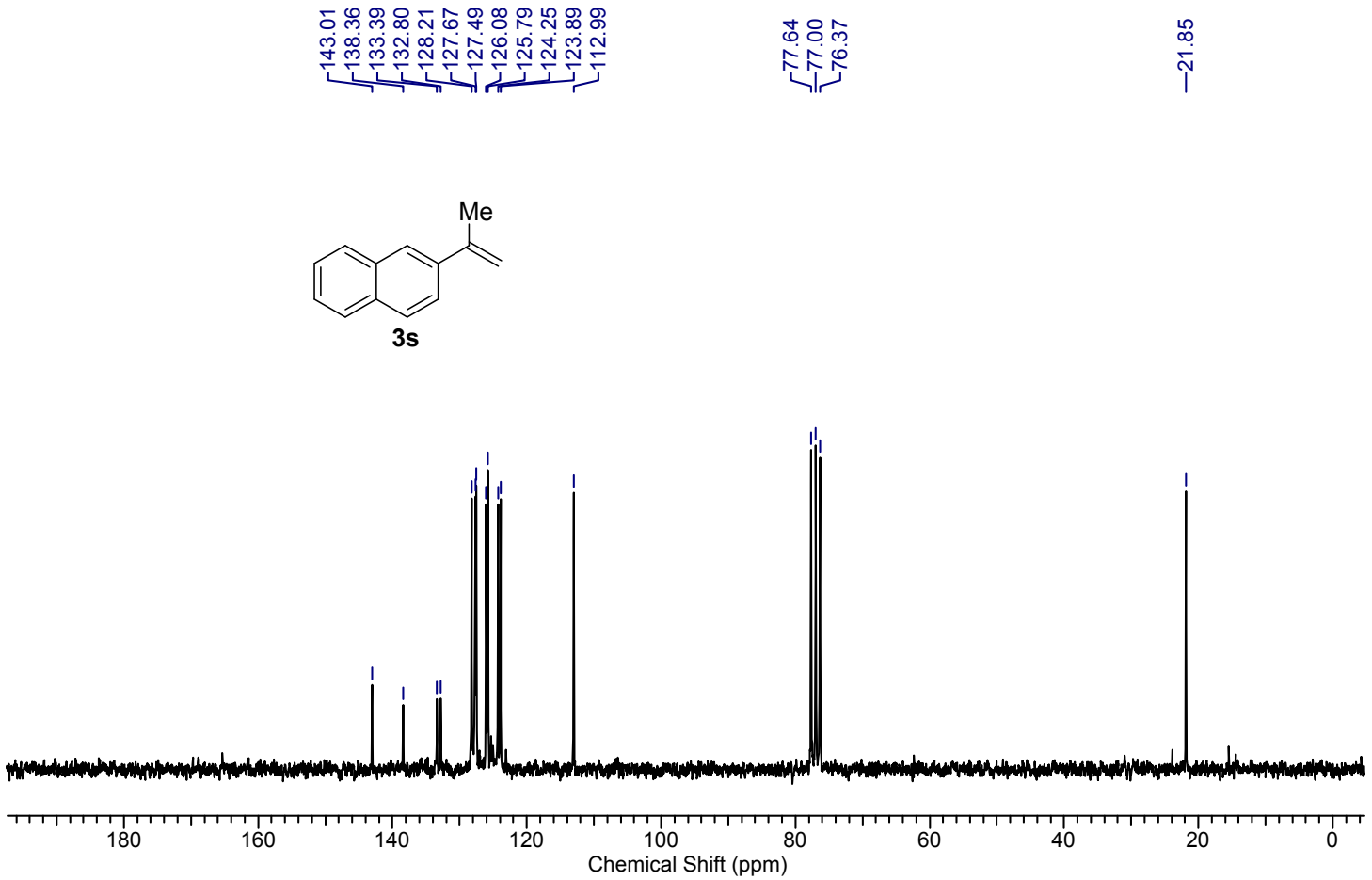
7.59
7.56
7.56
7.55
7.43
7.43
7.39
7.38
5.48
5.48
5.47
5.20
5.20
5.19
5.18
2.26
2.26
2.26
Me
3q
1.88
2.81
1.00
0.99
3.00
10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


143.28
141.24
128.18
127.35
125.46
112.35
77.63
77.00
76.36
21.76
Me
3q
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.43
6.88
5.29
5.00
3.82
2.14
1.58
Me
MeO
3r
1.87
1.90
0.99
0.95
3.00
2.98
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


159.05
142.55
133.75
126.58
113.52
110.65
77.25
77.00
76.74
55.27
21.90
Me
MeO
3r
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.89
7.86
7.84
7.81
7.80
7.73
7.51
7.50
7.48
7.27
5.57
5.24
5.23
5.22
2.31
Me
3s
4.15
1.04
2.19
0.98
1.00
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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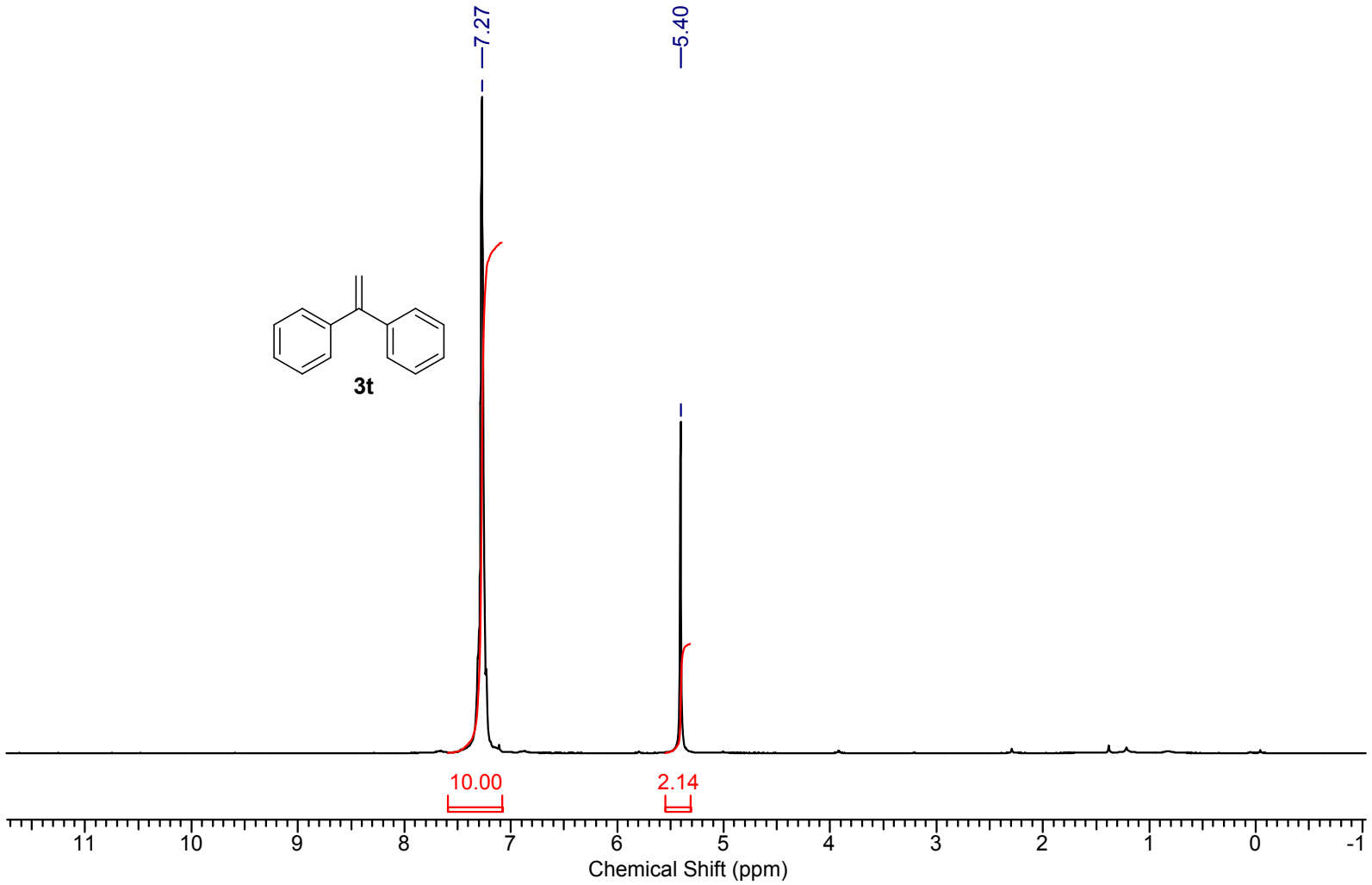
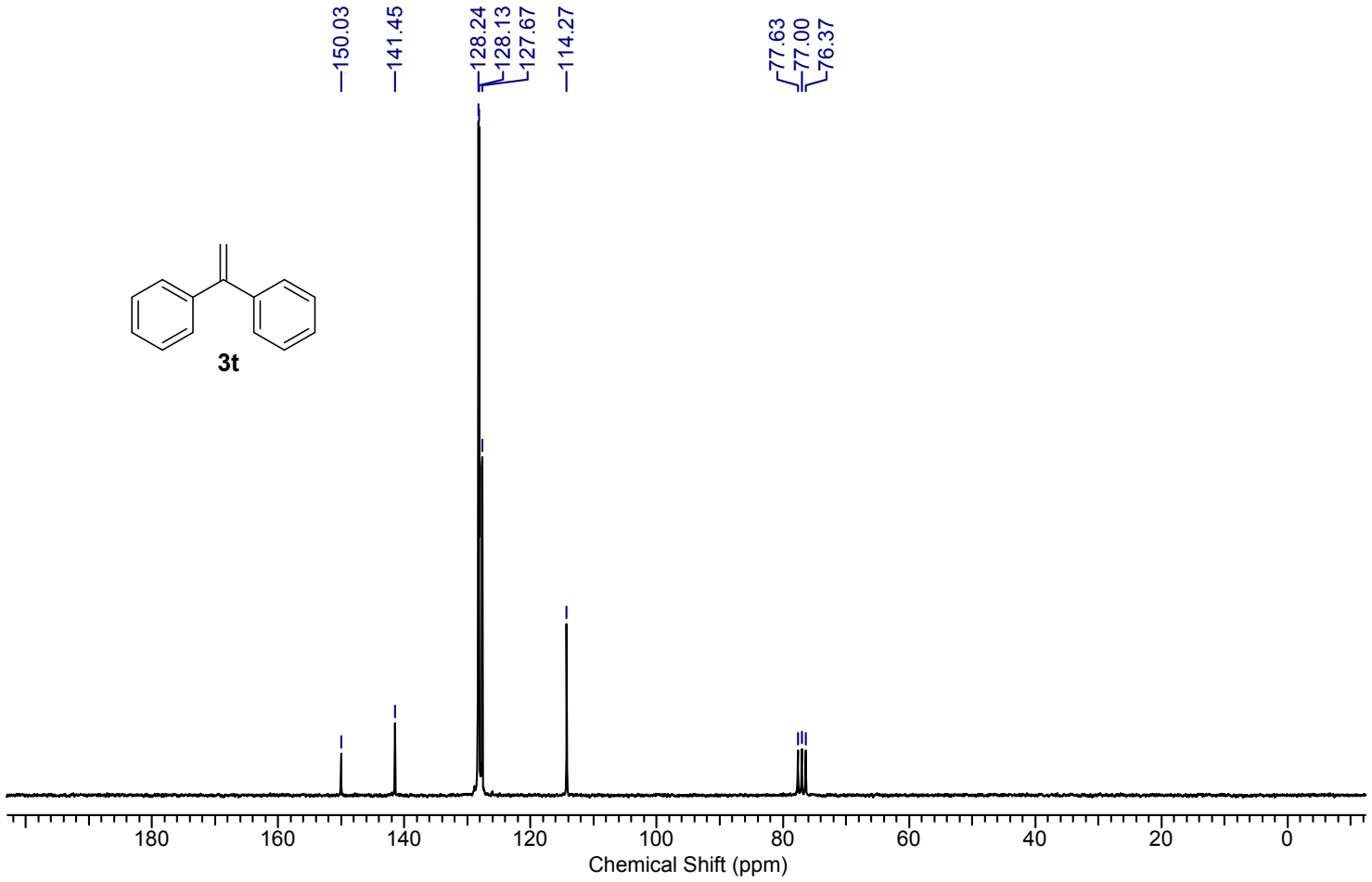
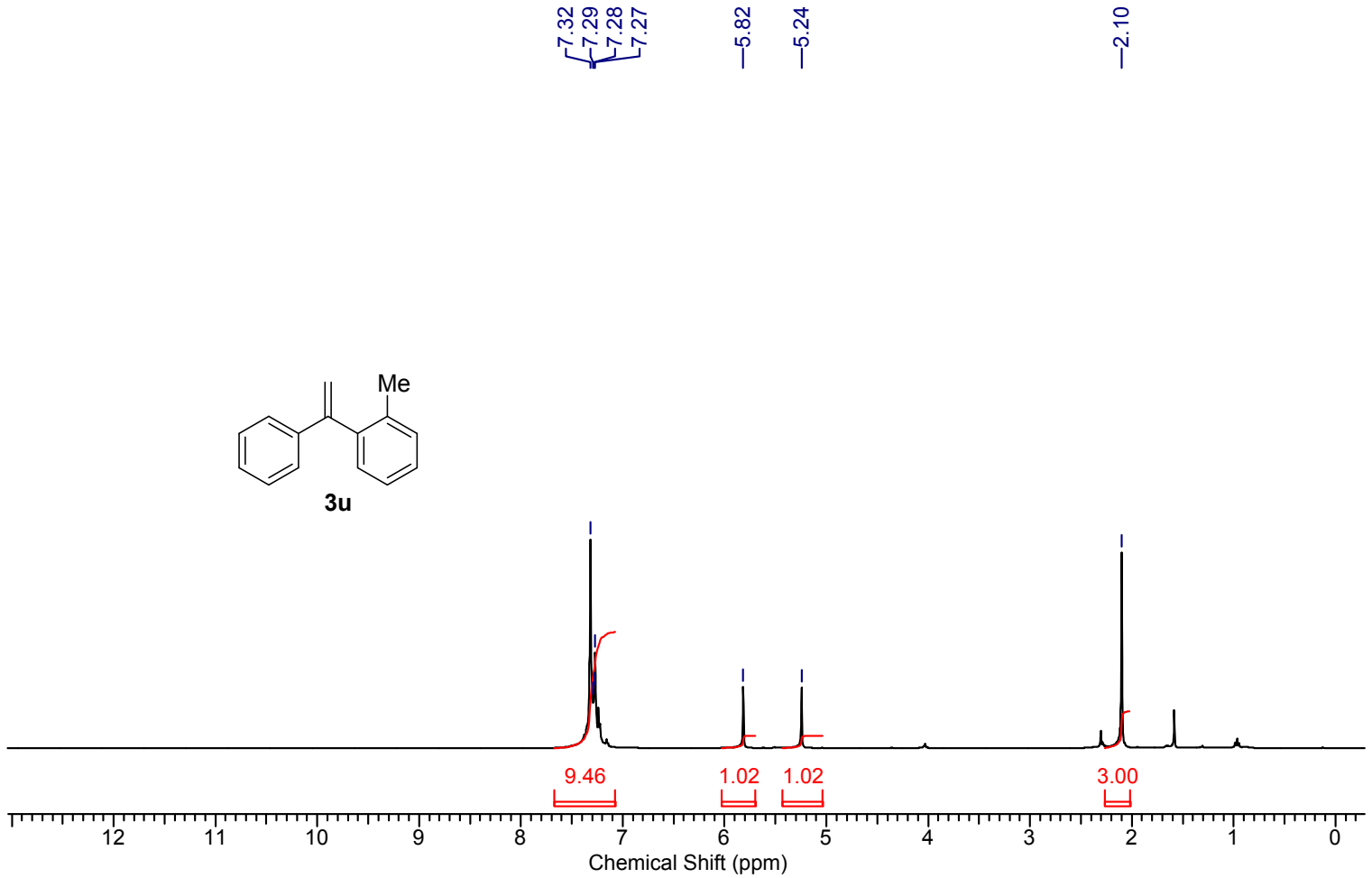
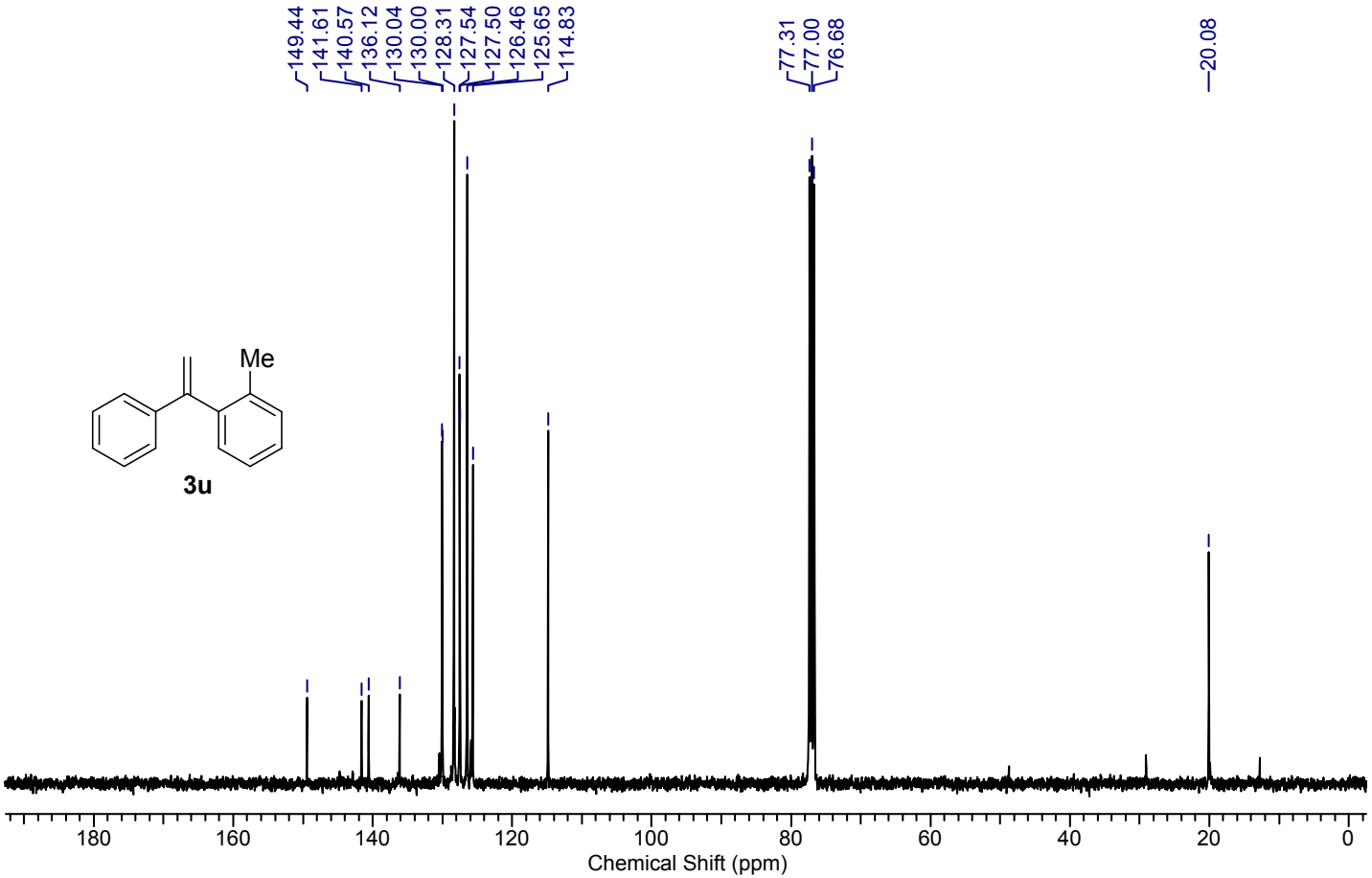
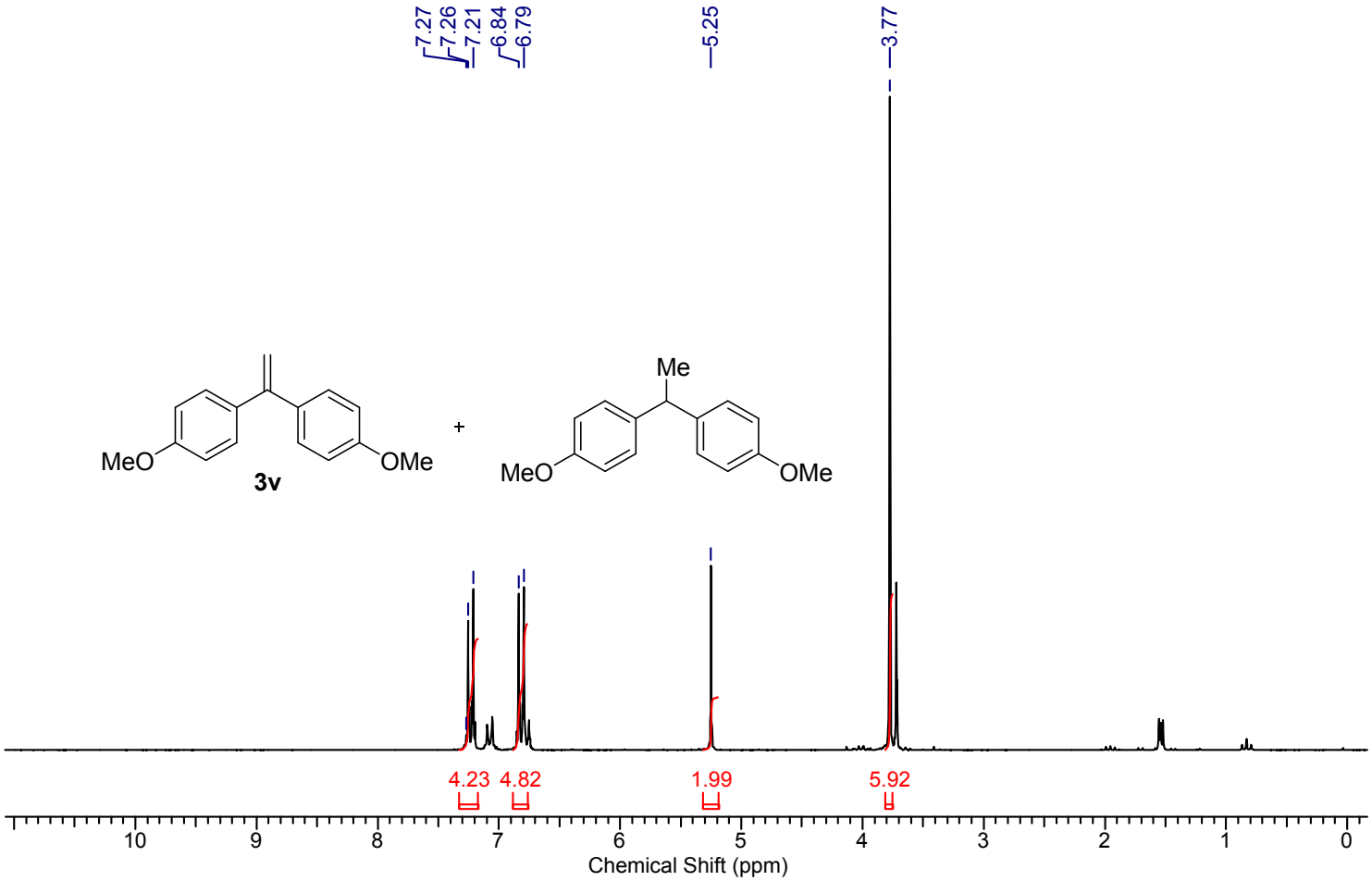
138.36
133.39
132.80
128.21
127.67
127.49
126.08
125.79
124.25
123.89
112.99
77.64
77.00
76.37
21.85
Me
3s
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

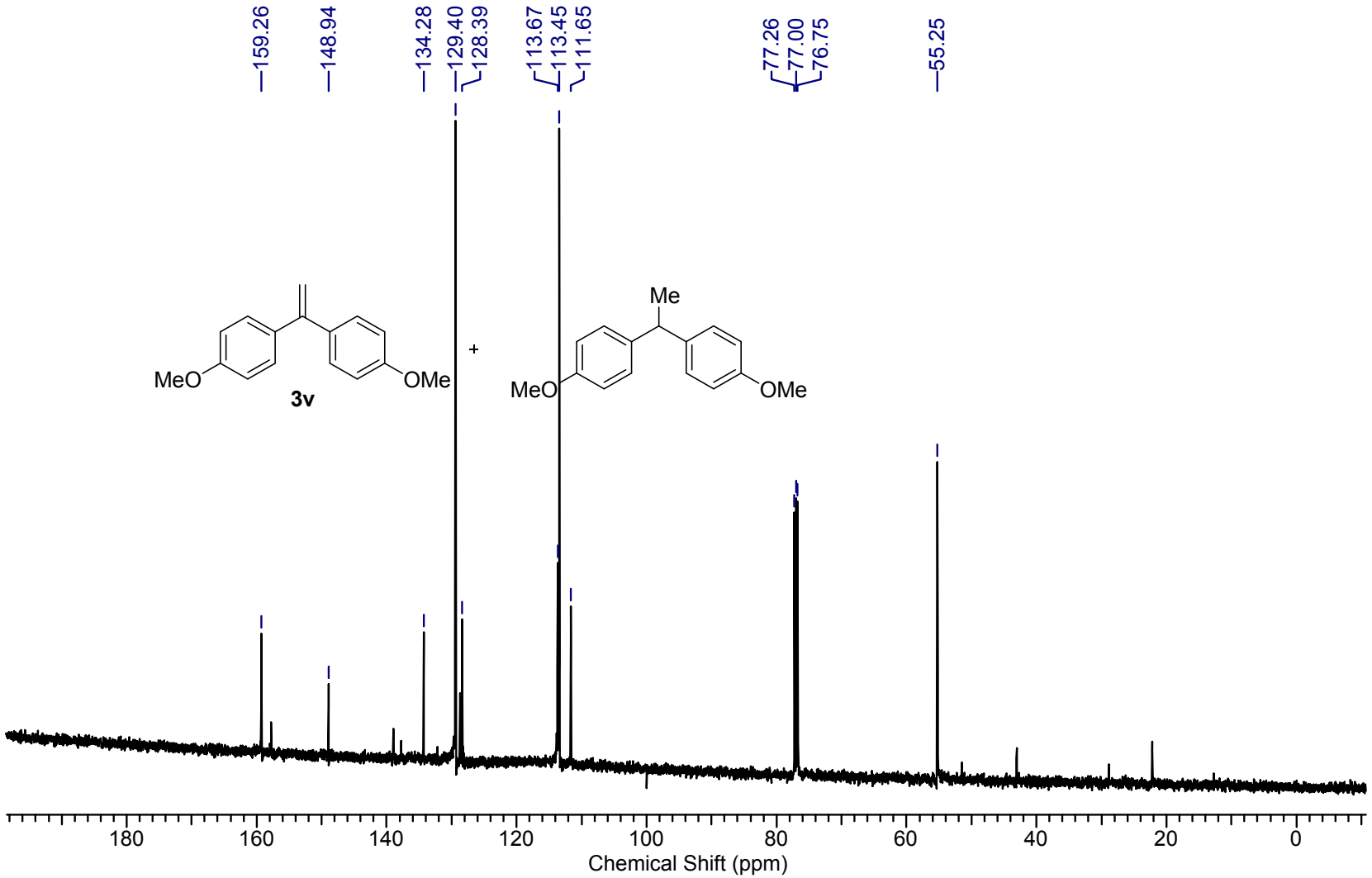

7.27
5.40
3t
10.00
2.14
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

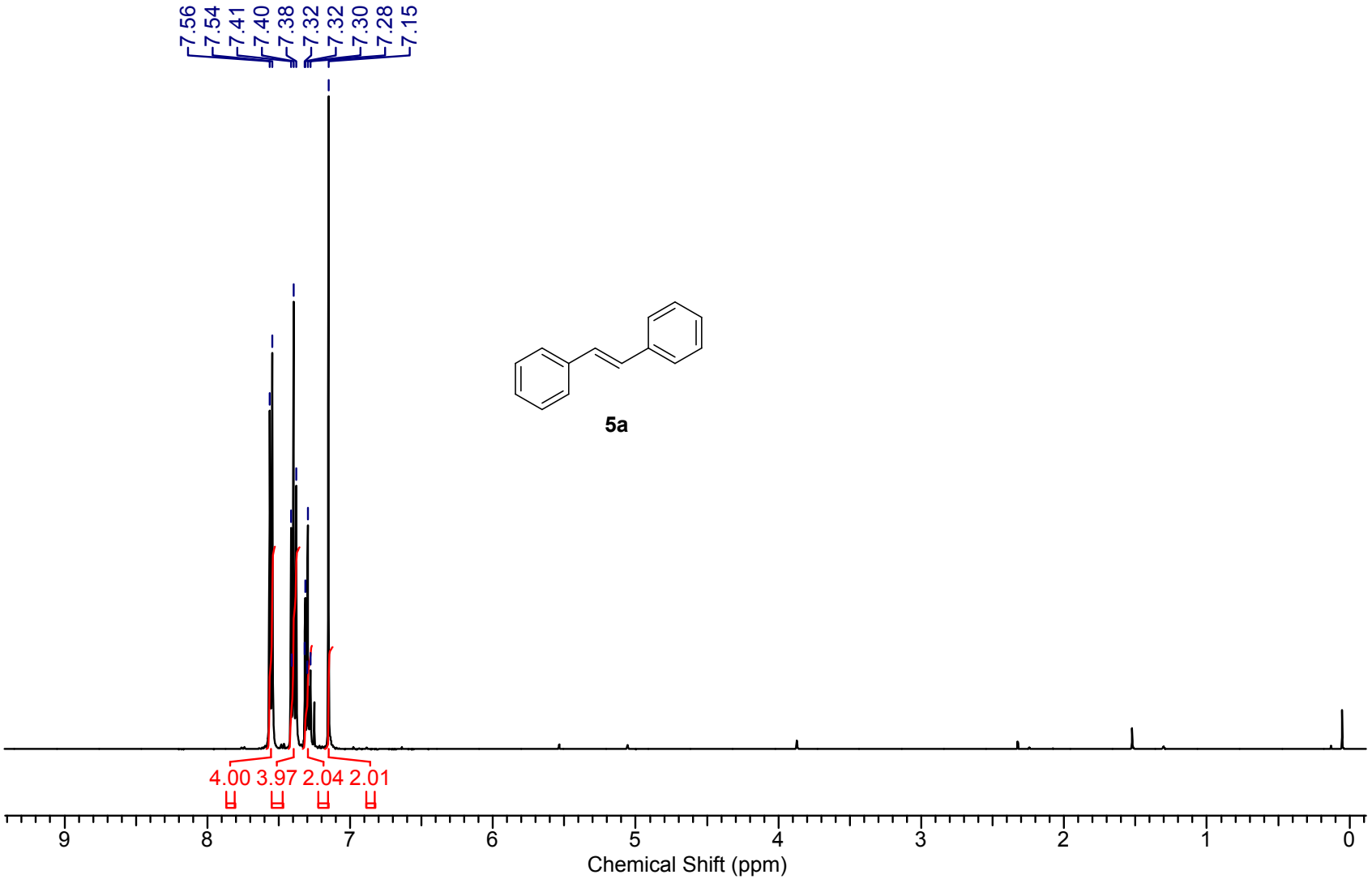

150.03
141.45
128.24
128.13
127.67
114.27
77.63
77.00
76.37
3t
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.32
7.29
7.28
7.27
5.82
5.24
2.10
Me
3u
9.46
1.02
1.02
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

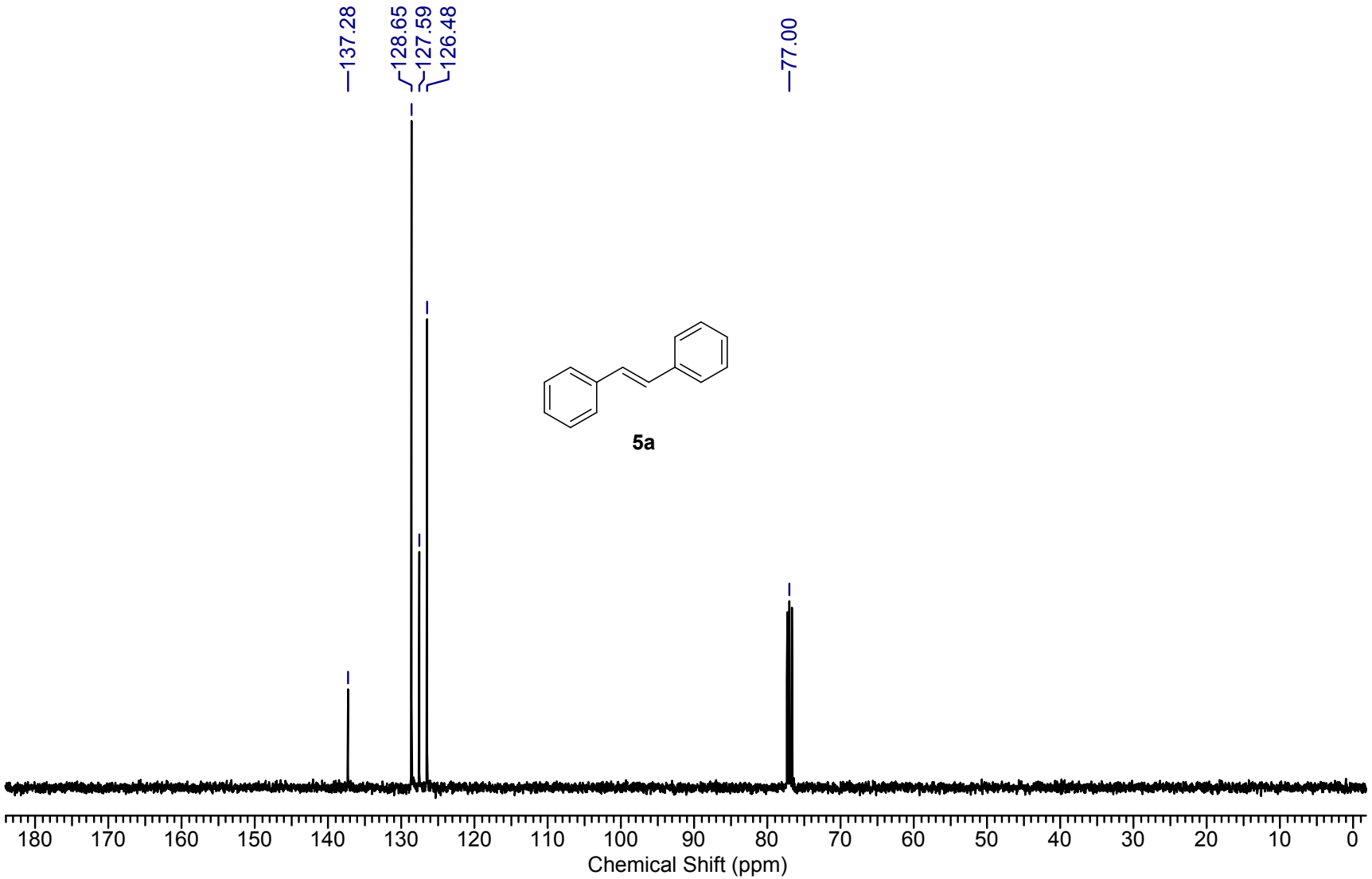

149.44
141.61
140.57
136.12
130.04
130.00
128.31
127.54
127.50
126.46
125.65
114.83
77.31
77.00
76.68
20.08
Me
3u
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

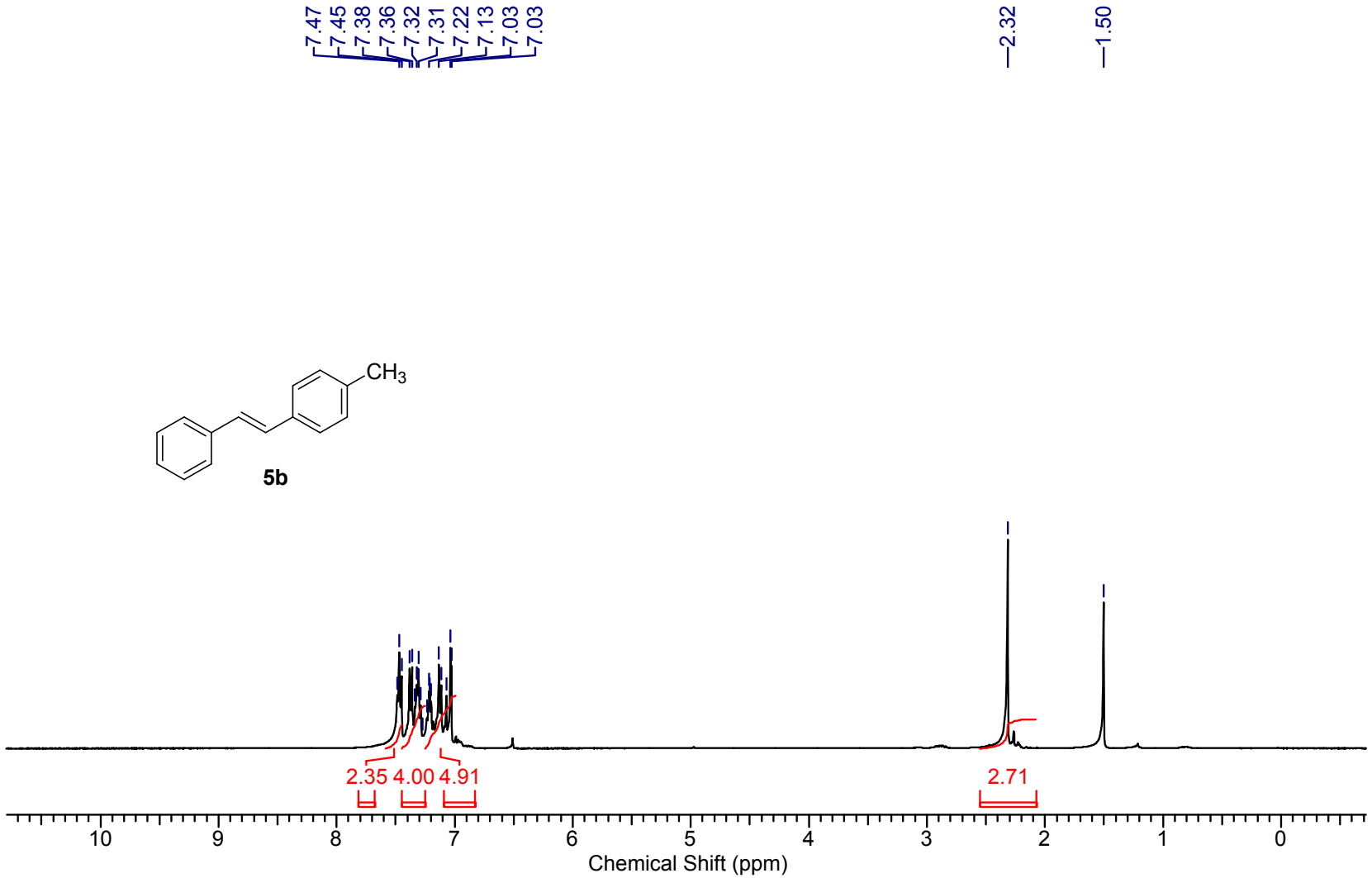

7.27
7.26
7.21
6.84
6.79
5.25
3.77
MeO
OMe
3v
+
Me
MeO
OMe
4.23
4.82
1.99
5.92
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

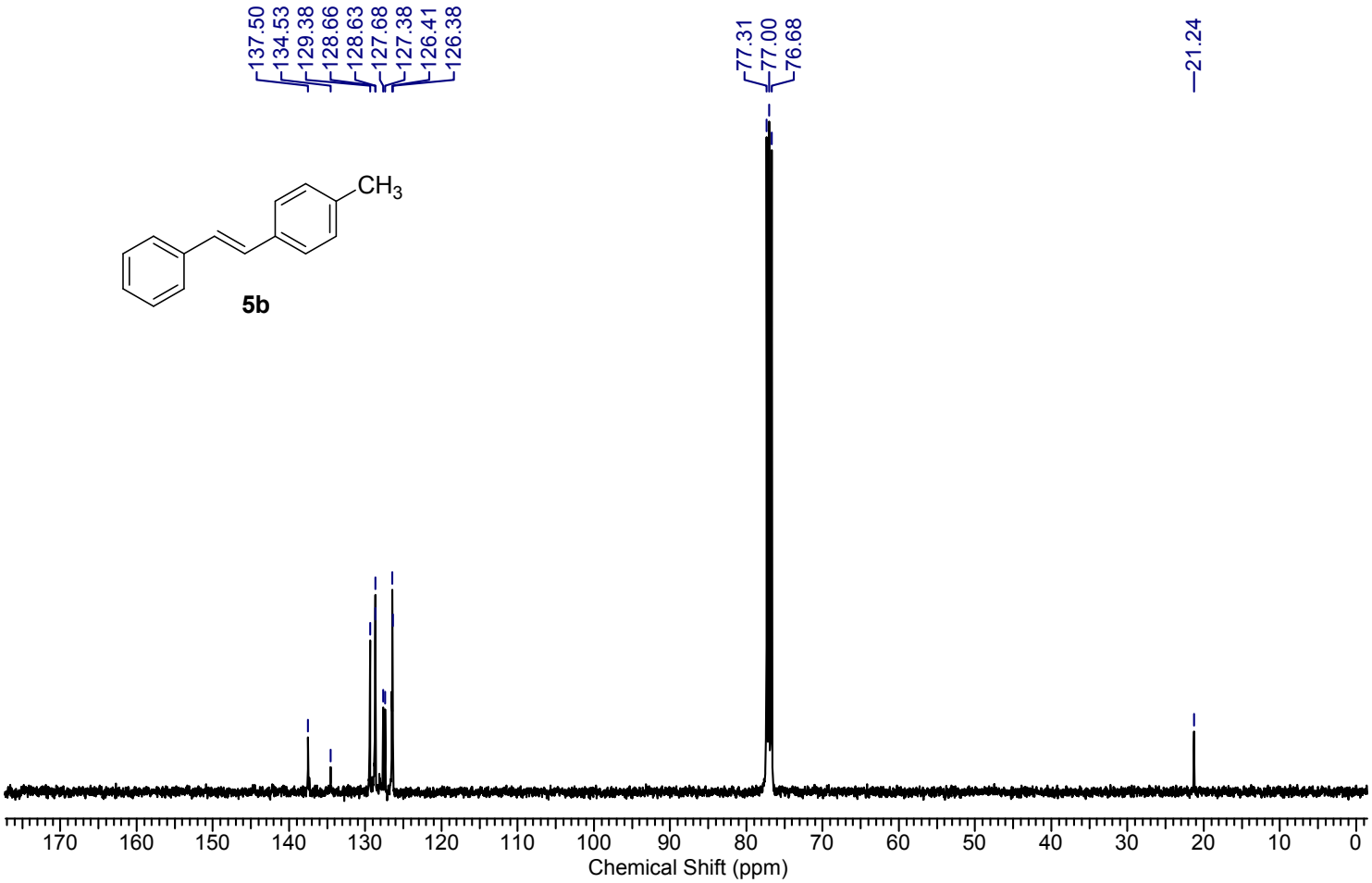

159.26
148.94
134.28
129.40
128.39
113.67
113.45
111.65
77.26
77.00
76.75
55.25
MeO
OMe
3v
+
Me
MeO
OMe
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.56
7.54
7.41
7.40
7.38
7.32
7.32
7.30
7.28
7.15
4.00 3.97 2.04 2.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

5a


137.28
128.65
127.59
126.48
77.00
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.47
7.45
7.38
7.36
7.32
7.31
7.22
7.13
7.03
7.03
2.32
1.50
CH3
5b
2.35 4.00 4.91
2.71
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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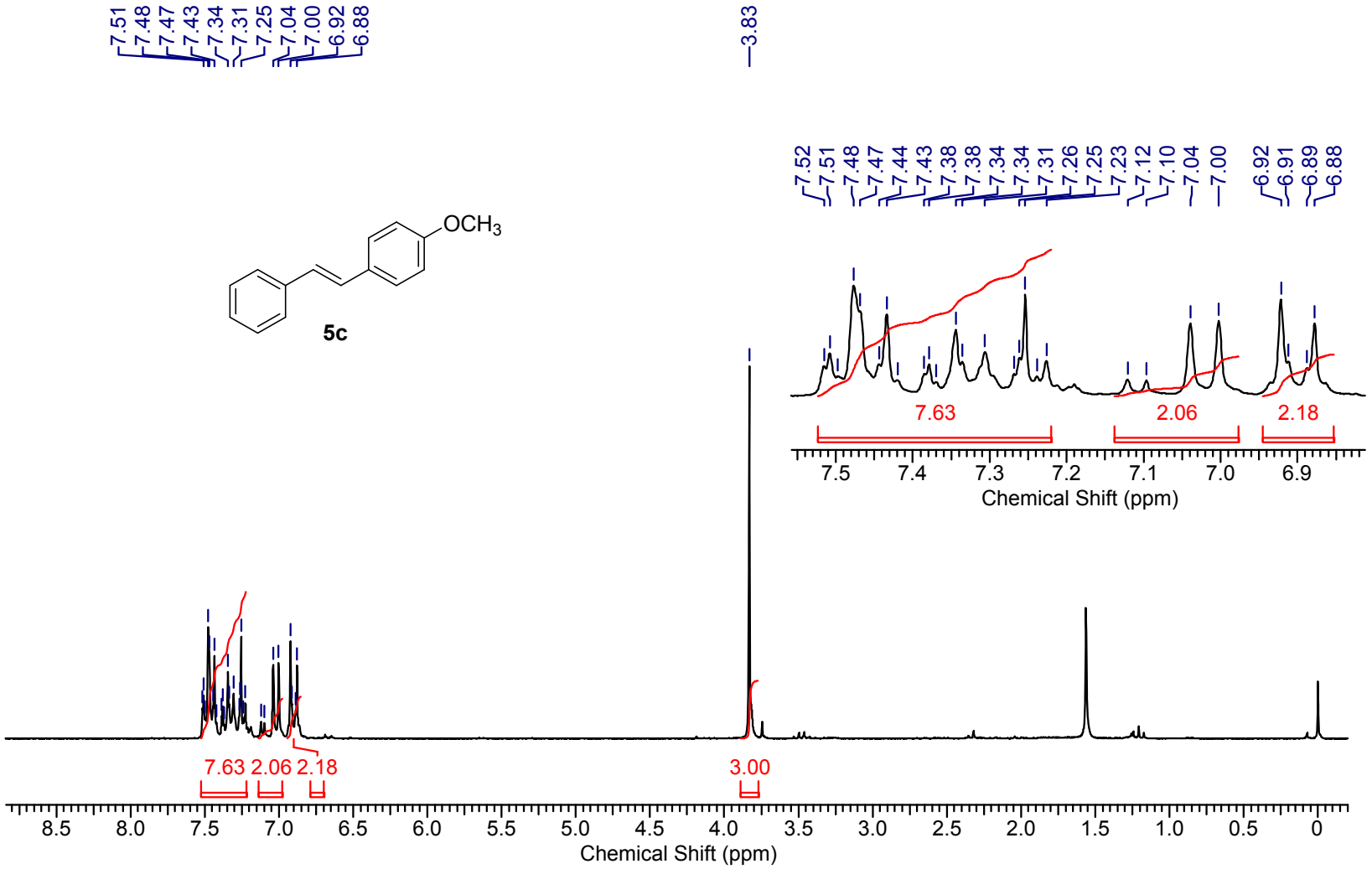
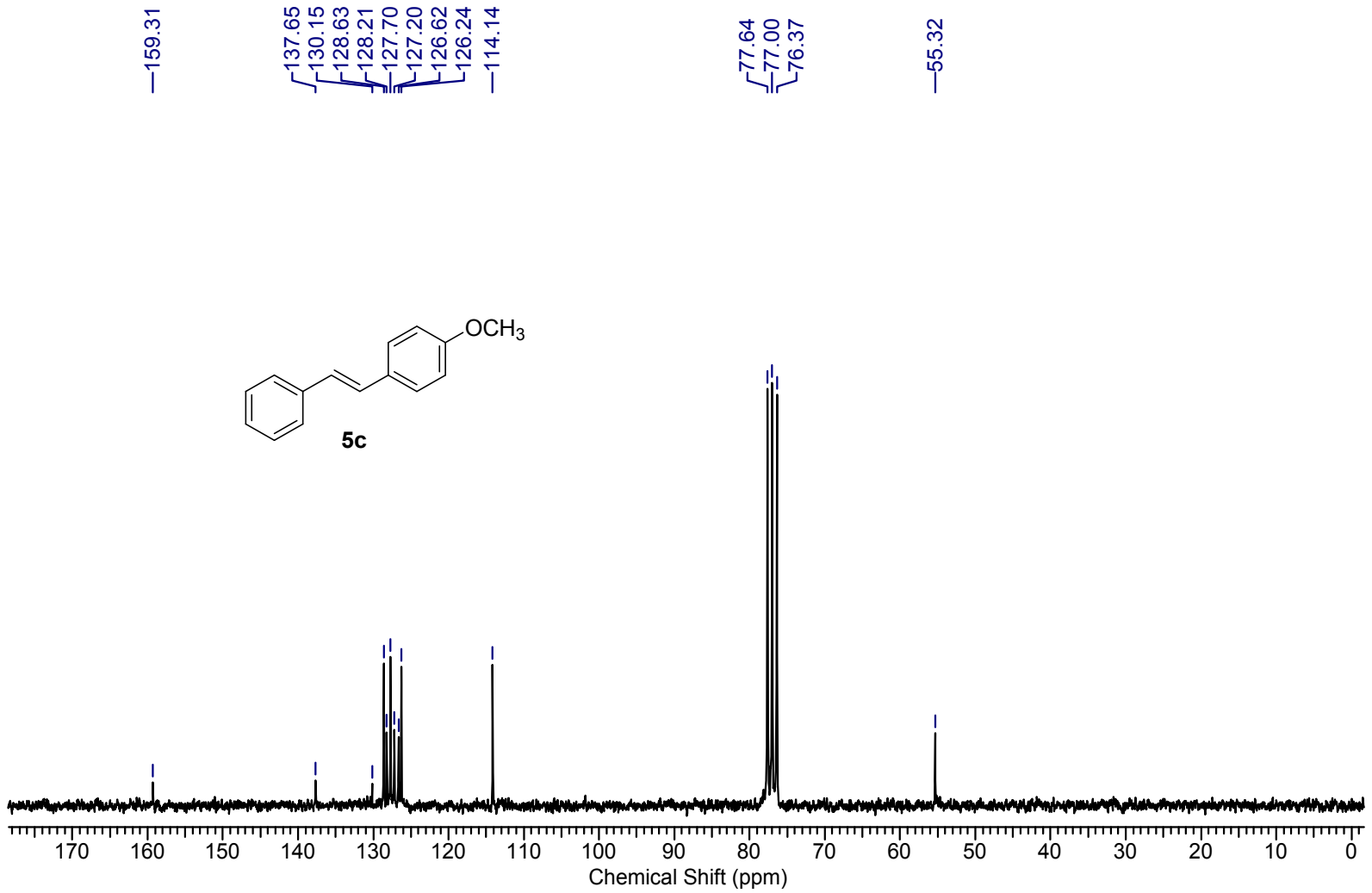
134.53
129.38
128.66
128.63
127.68
127.38
126.41
126.38
77.31
77.00
76.68
21.24
CH3
5b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.51
7.48
7.47
7.43
7.34
7.31
7.25
7.04
7.00
6.92
6.88
3.83
7.52
7.51
7.48
7.47
7.44
7.43
7.38
7.38
7.34
7.34
7.31
7.26
7.25
7.23
7.12
7.10
7.04
7.00
6.92
6.91
6.89
6.88
OCH3
5c
7.63
2.06
2.18
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)
7.63 2.06 2.18
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


159.31
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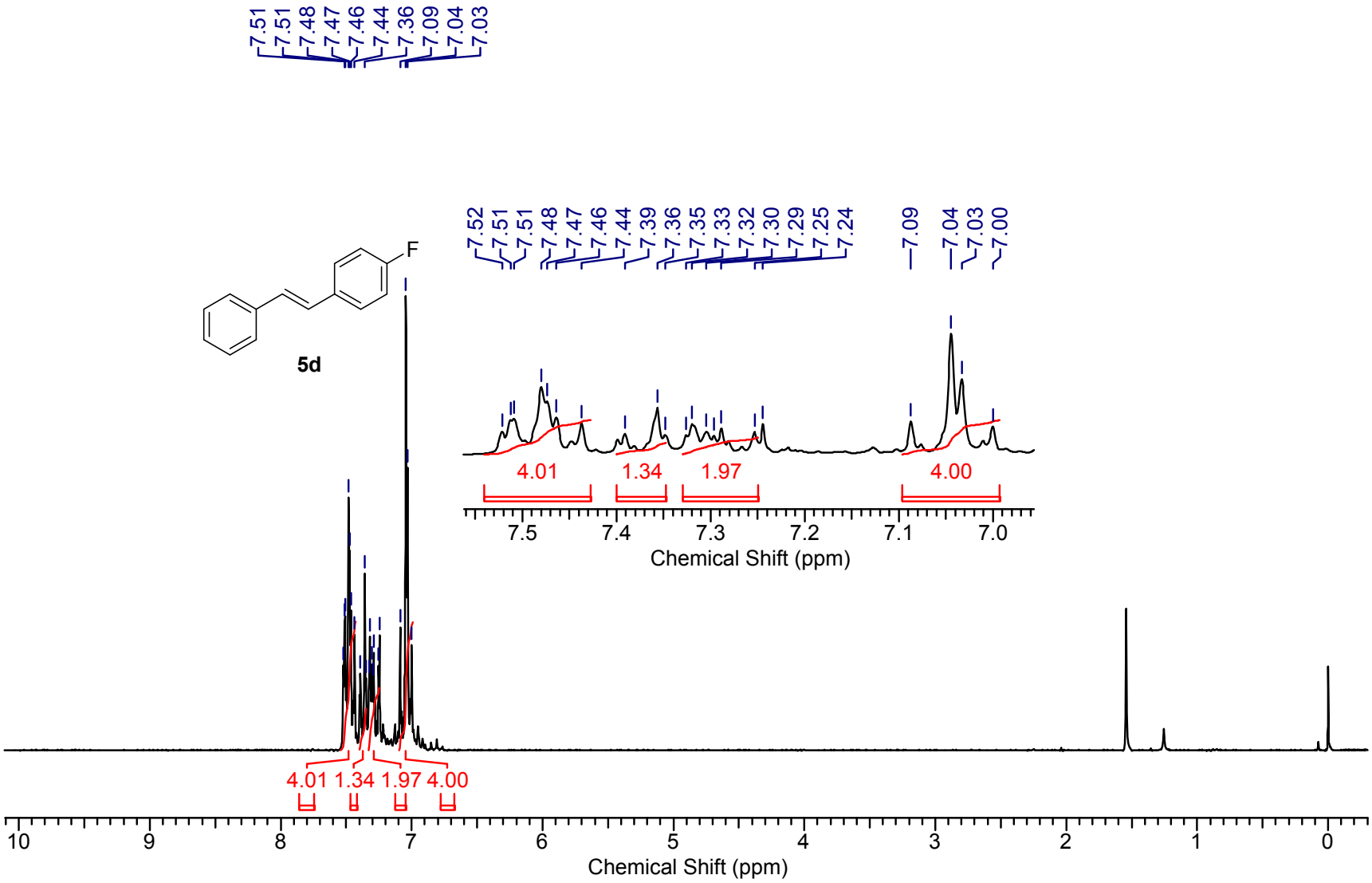
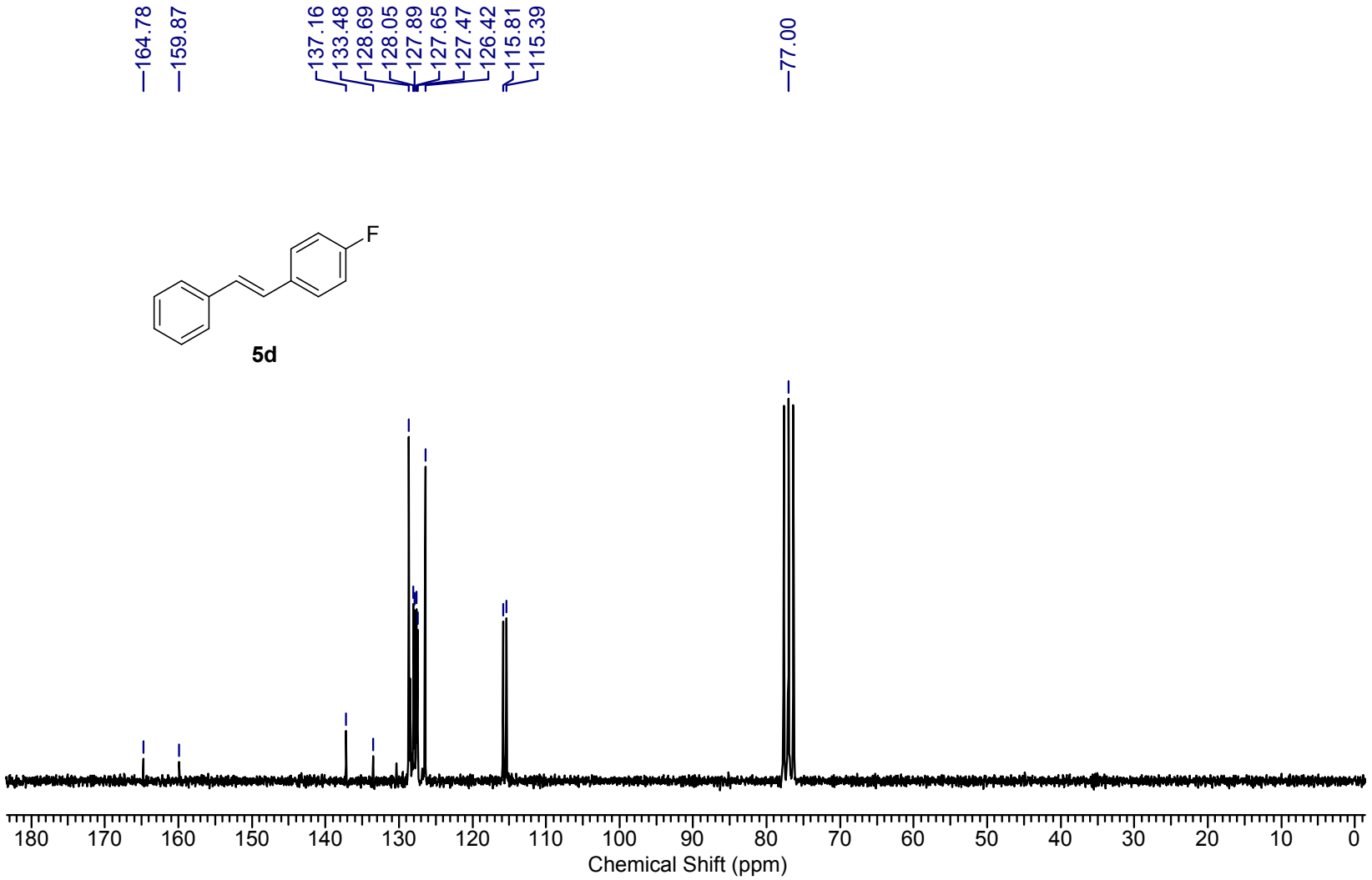
130.15
128.63
128.21
127.70
127.20
126.62
126.24
114.14
77.64
77.00
76.37
55.32
OCH3
5c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.51
7.51
7.48
7.47
7.46
7.44
7.36
7.09
7.04
7.03
F
5d
7.52
7.51
7.51
7.48
7.47
7.46
7.44
7.39
7.36
7.35
7.33
7.32
7.30
7.29
7.25
7.24
7.09
7.04
7.03
7.00
4.01
1.34
1.97
4.00
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
4.01 1.34 1.97 4.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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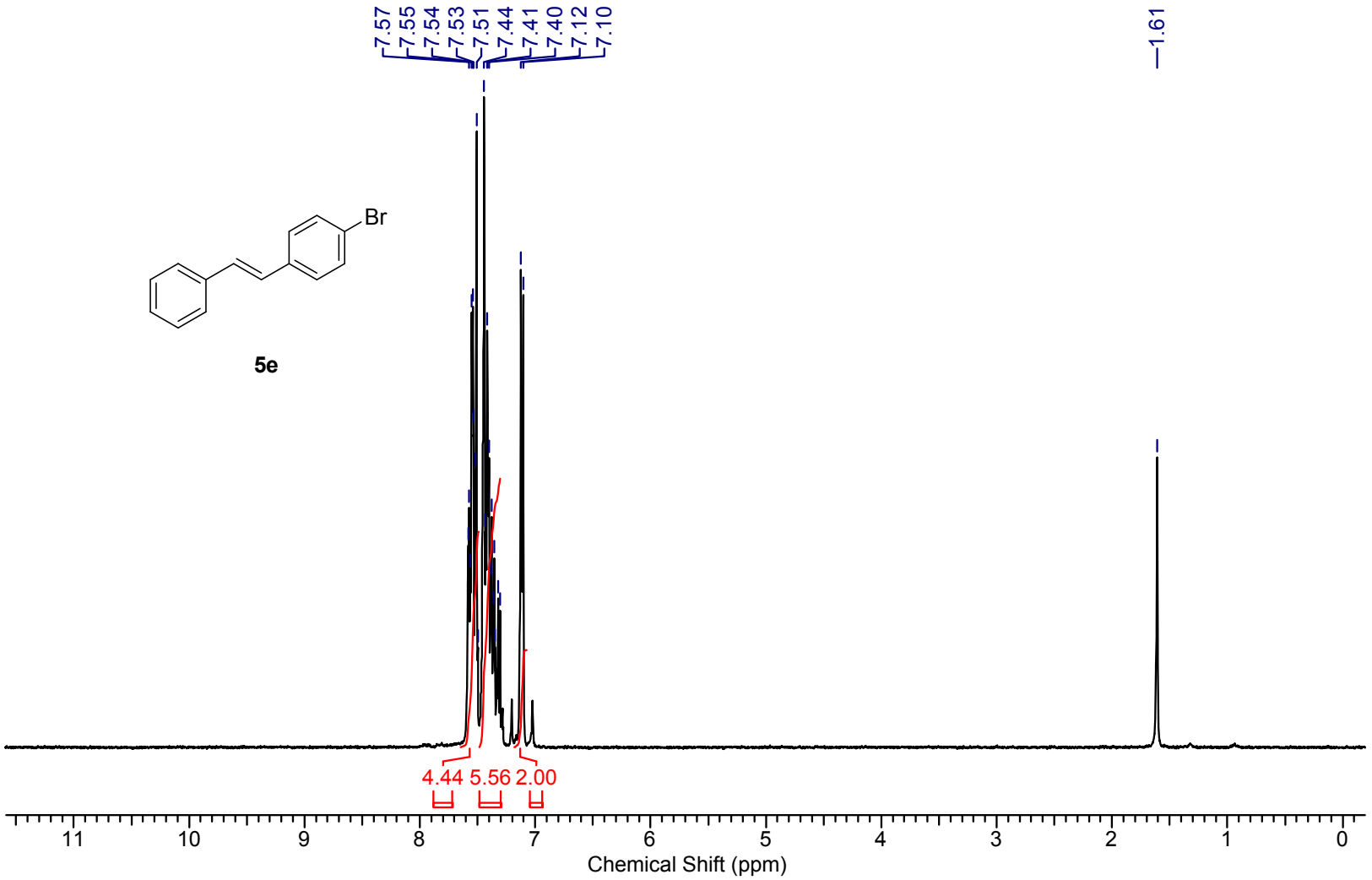
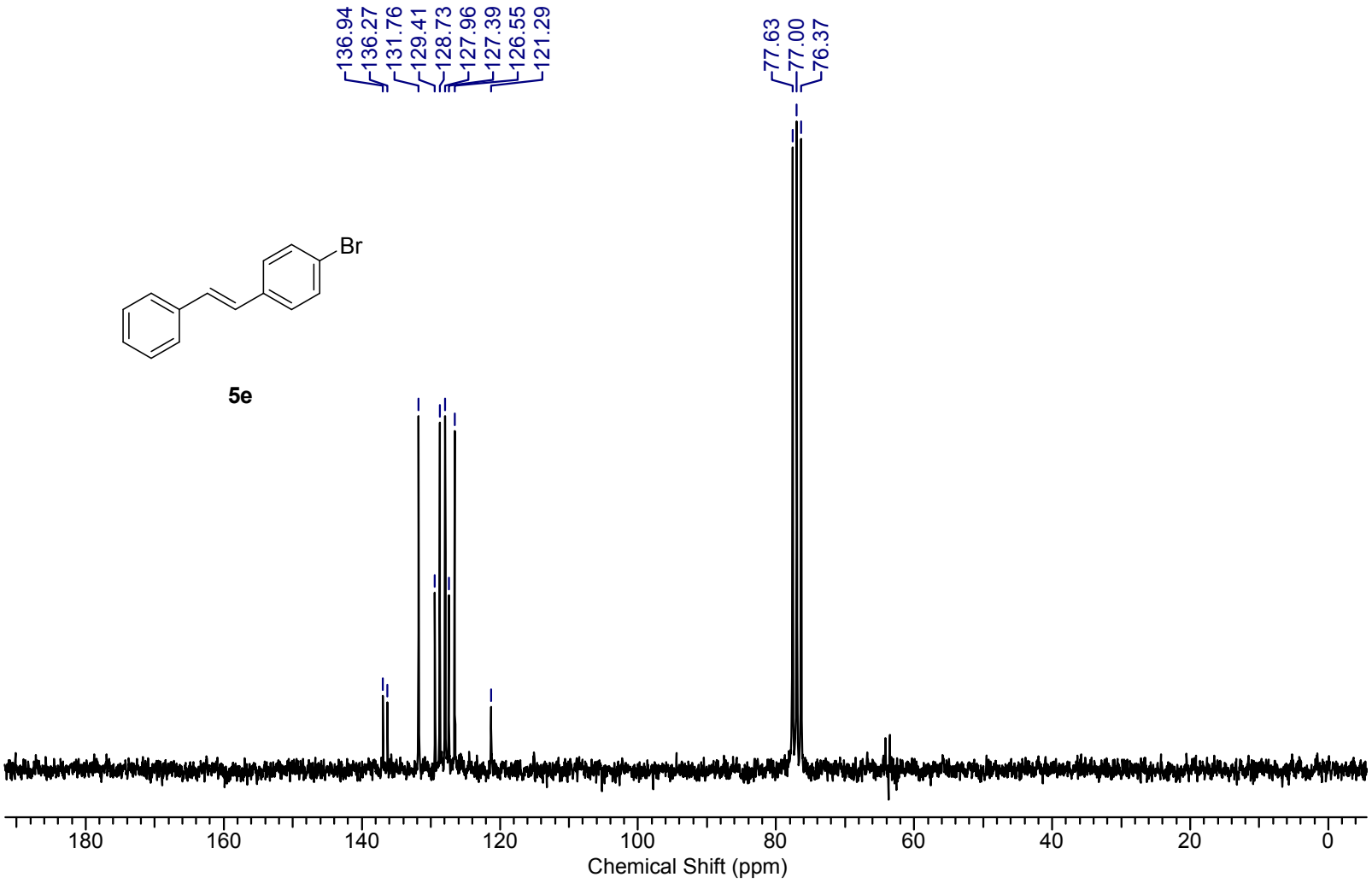
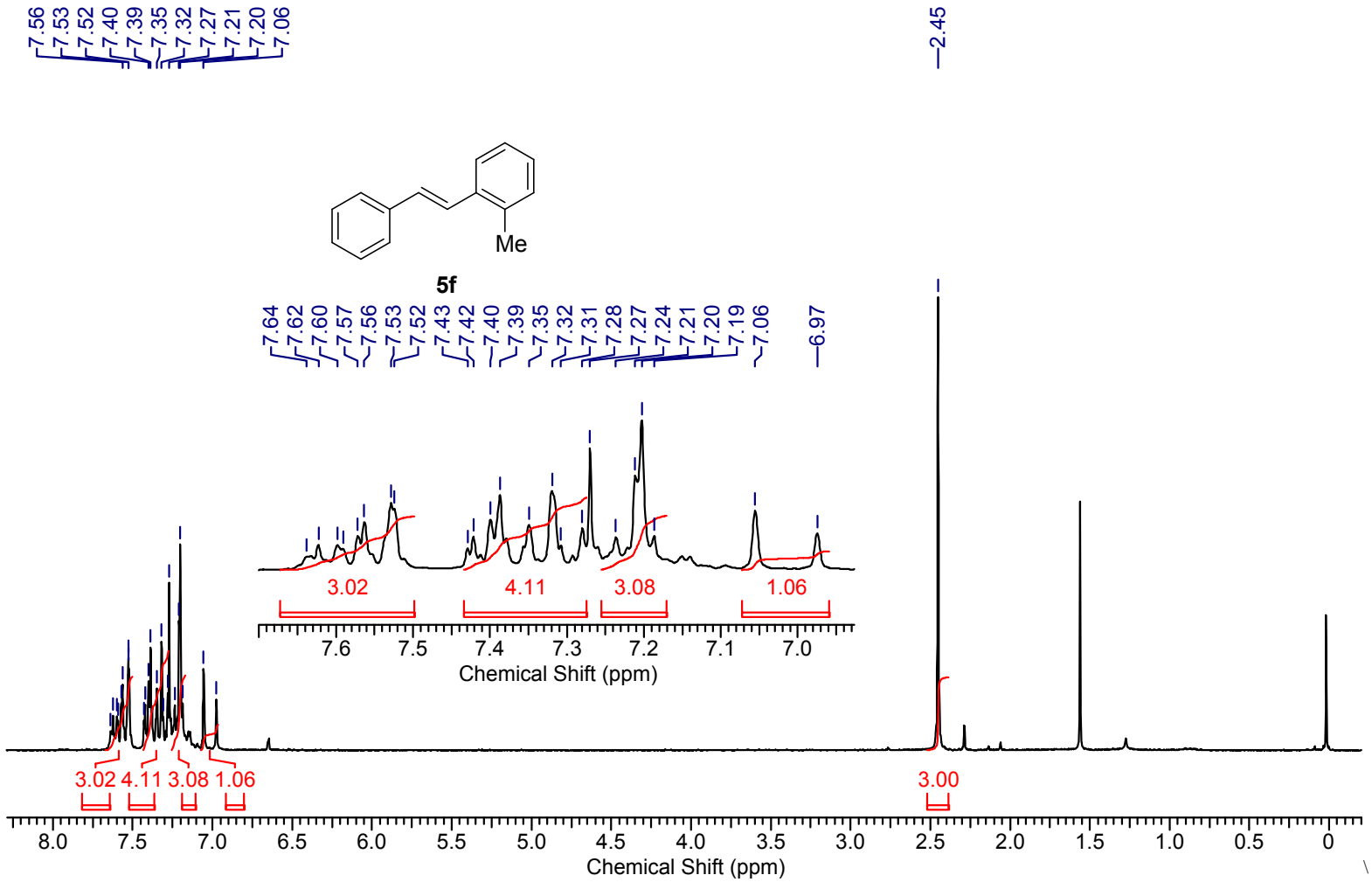
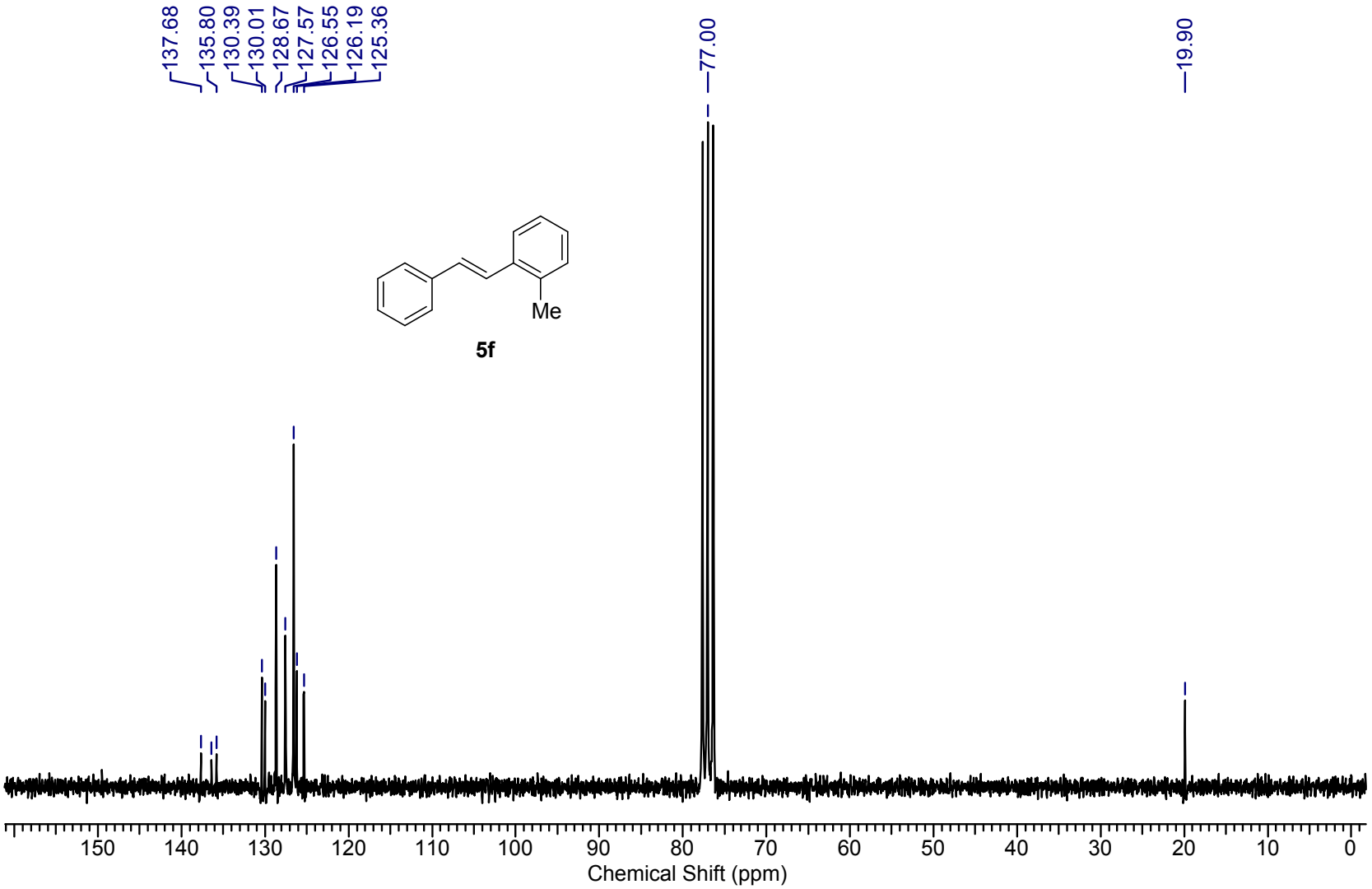
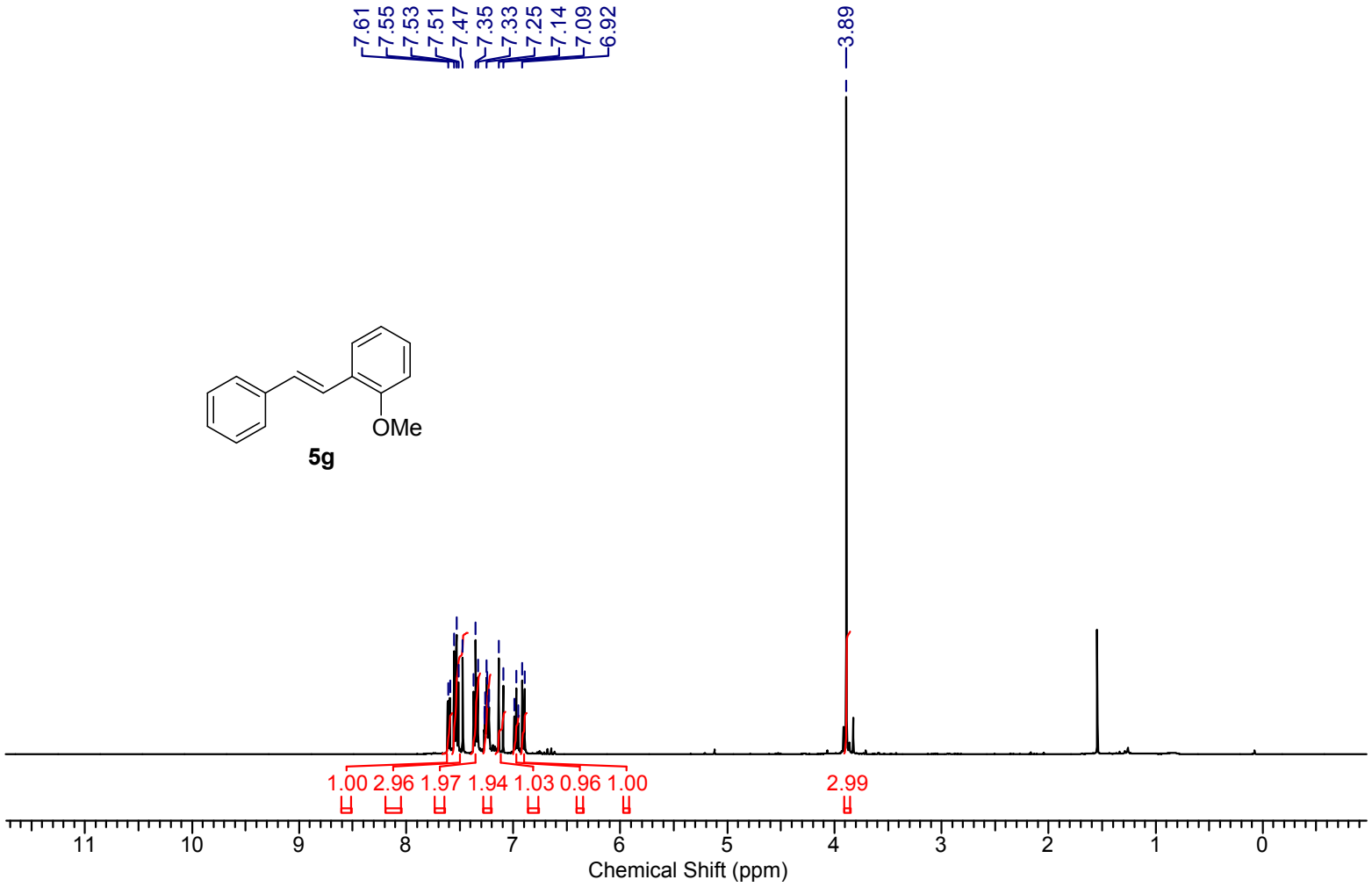
159.87
137.16
133.48
128.69
128.05
127.89
127.65
127.47
126.42
115.81
115.39
77.00
F
5d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

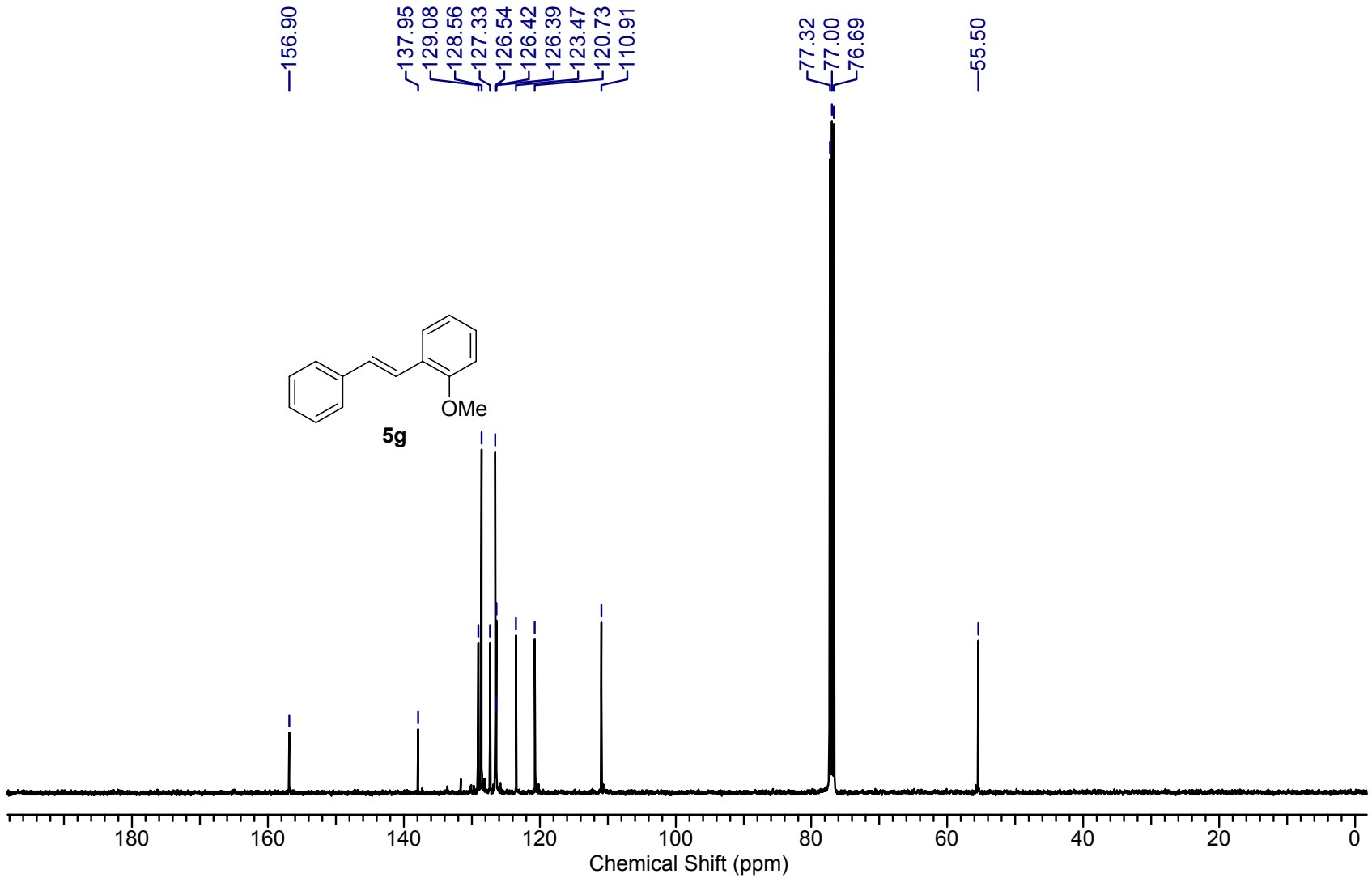

7.57
7.55
7.54
7.53
7.51
7.44
7.41
7.40
7.12
7.10
1.61
Br
5e
4.44 5.56 2.00
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

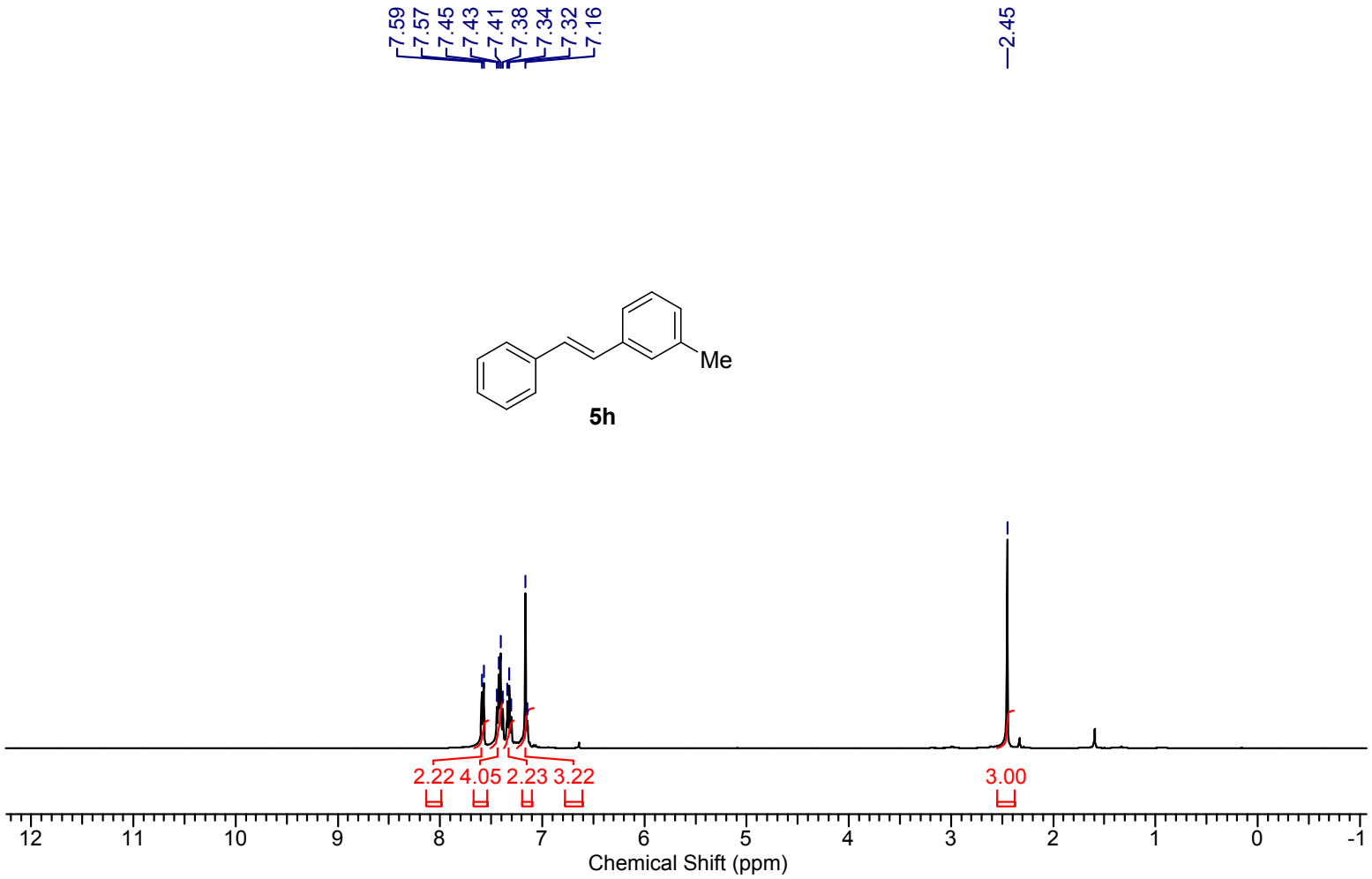

136.94
136.27
131.76
129.41
128.73
127.96
127.39
126.55
121.29
77.63
77.00
76.37
Br
5e
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

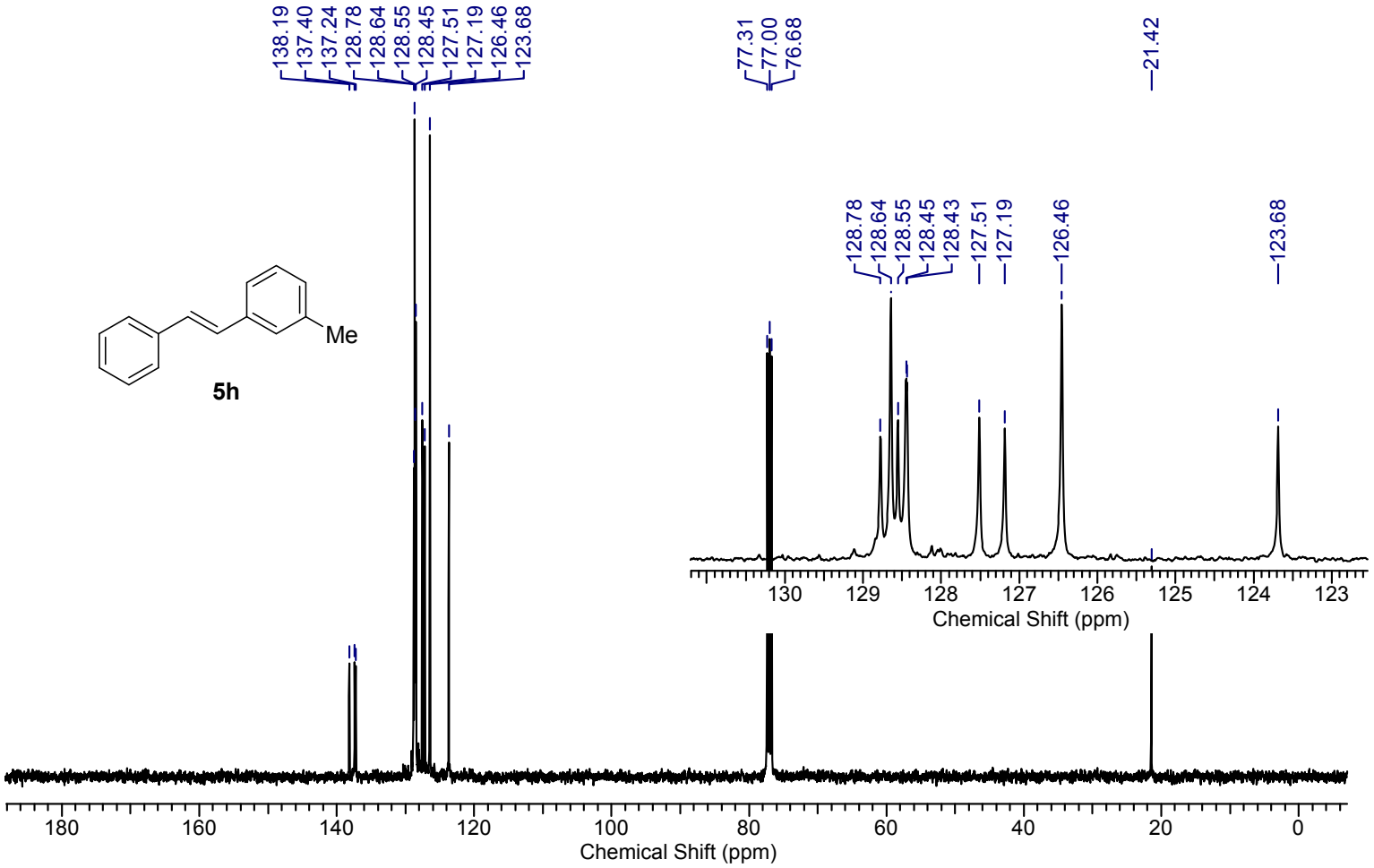

7.56
7.53
7.52
7.40
7.39
7.35
7.32
7.27
7.21
7.20
7.06
2.45
Me
5f
7.64
7.62
7.60
7.57
7.56
7.53
7.52
7.43
7.42
7.40
7.39
7.35
7.32
7.31
7.28
7.27
7.24
7.21
7.20
7.19
7.06
6.97
3.02
4.11
3.08
1.06
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
3.02 4.11 3.08 1.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

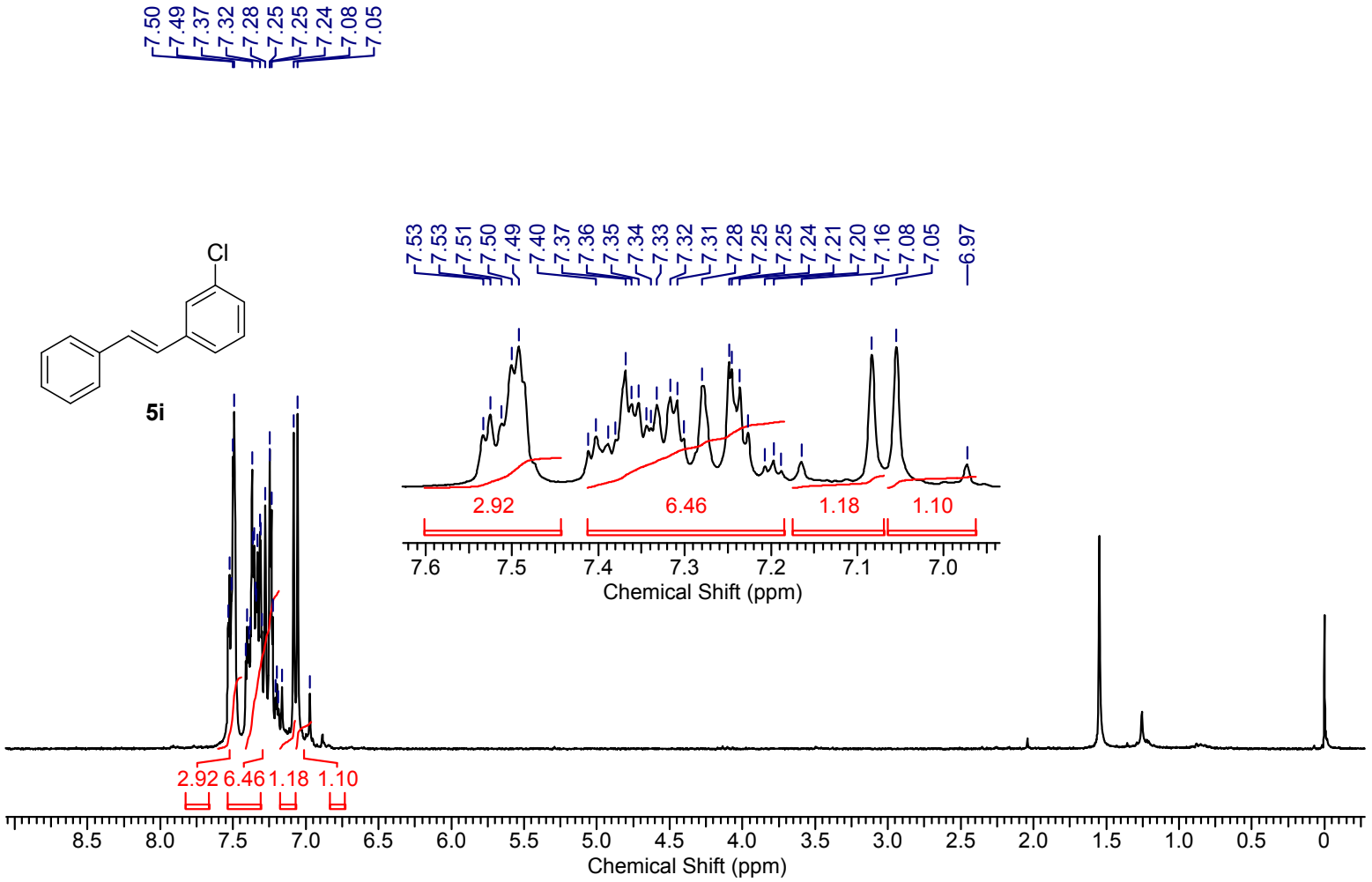

137.68
135.80
130.39
130.01
128.67
127.57
126.55
126.19
125.36
77.00
19.90
Me
5f
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

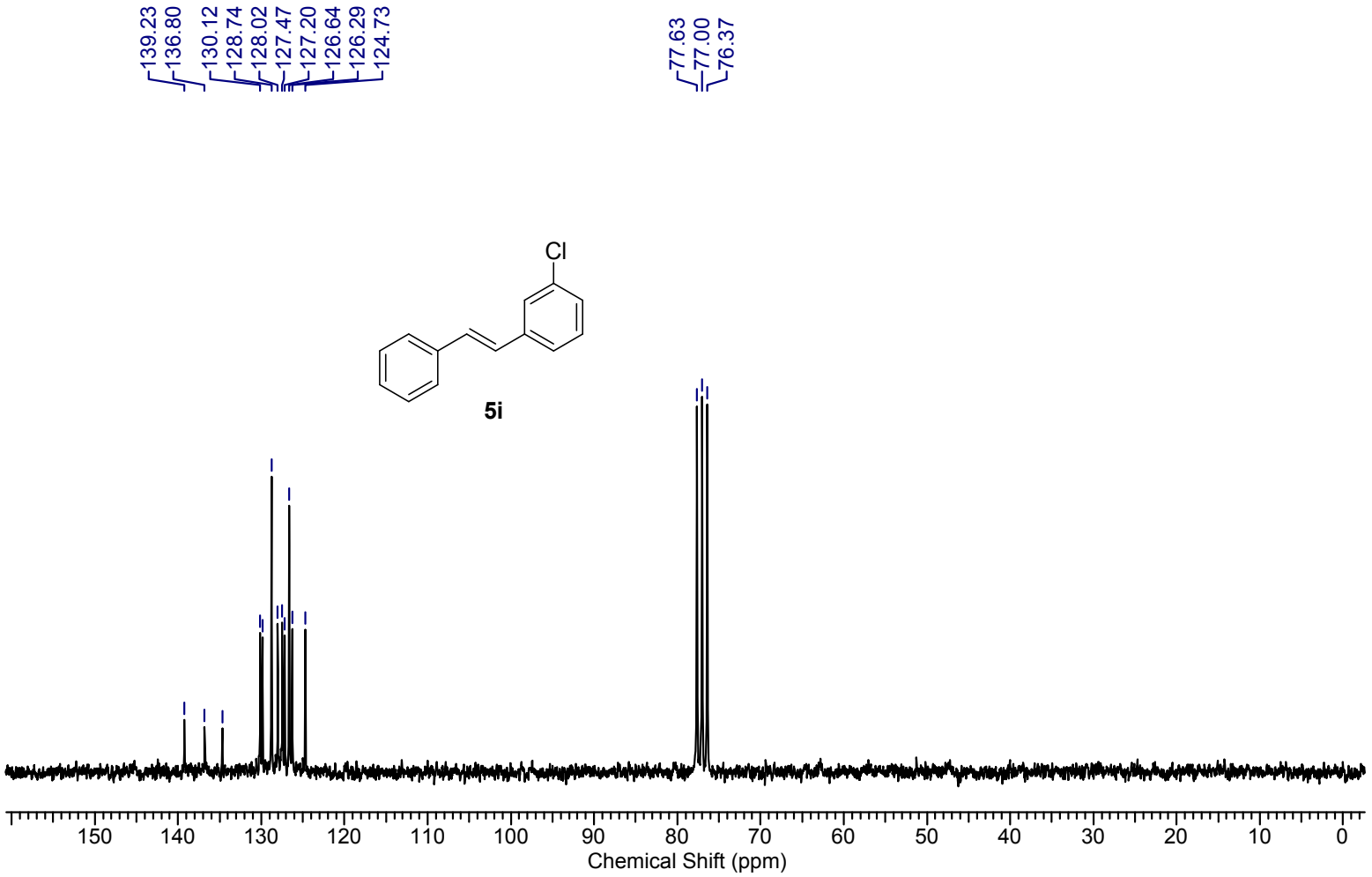

7.61
7.55
7.53
7.51
7.47
7.35
7.33
7.25
7.14
7.09
6.92
3.89
OMe
5g
1.00 2.96 1.97 1.94 1.03 0.96 1.00
2.99
11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

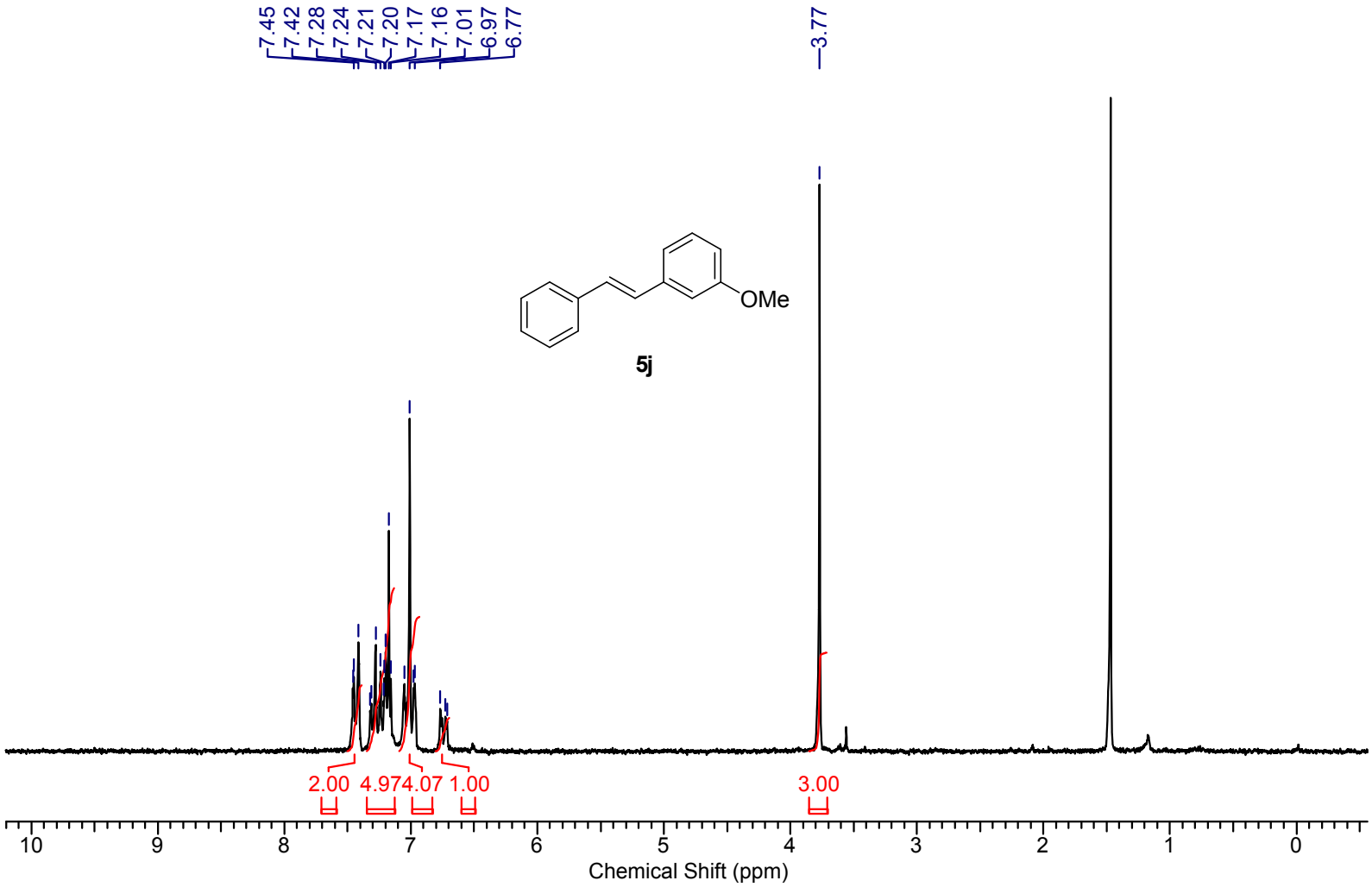

156.90
137.95
129.08
128.56
127.33
126.54
126.42
126.39
123.47
120.73
110.91
77.32
77.00
76.69
55.50
OMe
5g
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

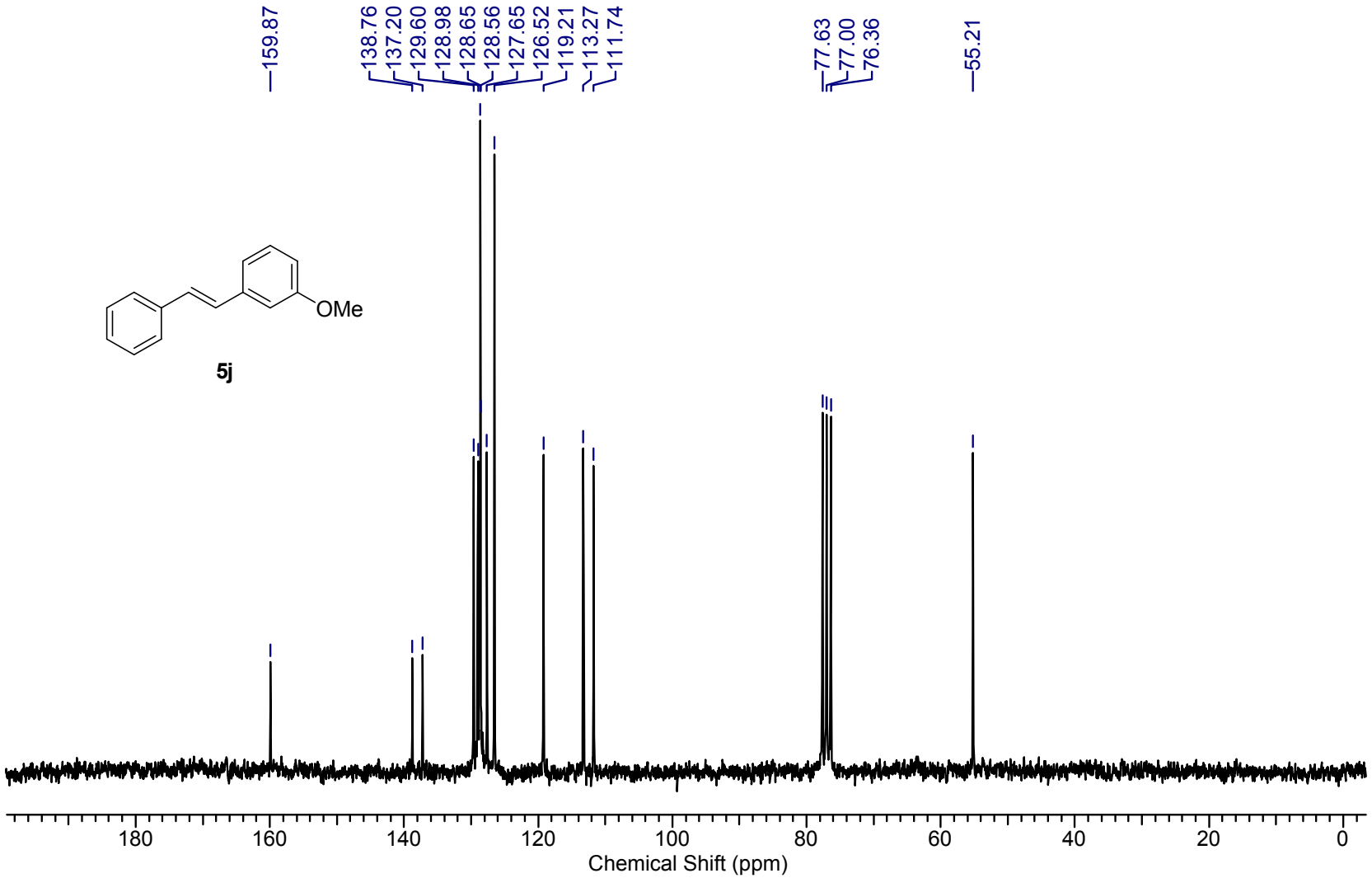

7.59
7.57
7.45
7.43
7.41
7.38
7.34
7.32
7.16
2.45
Me
5h
2.22
4.05
2.23
3.22
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


138.19
137.40
137.24
128.78
128.64
128.55
128.45
127.51
127.19
126.46
123.68
77.31
77.00
76.68
21.42
Me
5h
128.78
128.64
128.55
128.45
128.43
127.51
127.19
126.46
123.68
130
129
128
127
126
125
124
123
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.50
7.49
7.37
7.32
7.28
7.25
7.25
7.24
7.08
7.05
Cl
5i
7.53
7.53
7.51
7.50
7.49
7.40
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.28
7.25
7.25
7.24
7.21
7.20
7.16
7.08
7.05
6.97
2.92
6.46
1.18
1.10
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)
2.92
6.46
1.18
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


139.23
136.80
130.12
128.74
128.02
127.47
127.20
126.64
126.29
124.73
77.63
77.00
76.37
Cl
5i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.45
7.42
7.28
7.24
7.21
7.20
7.17
7.16
7.01
6.97
6.77
3.77
OMe
5j
2.00
4.97
4.07
1.00
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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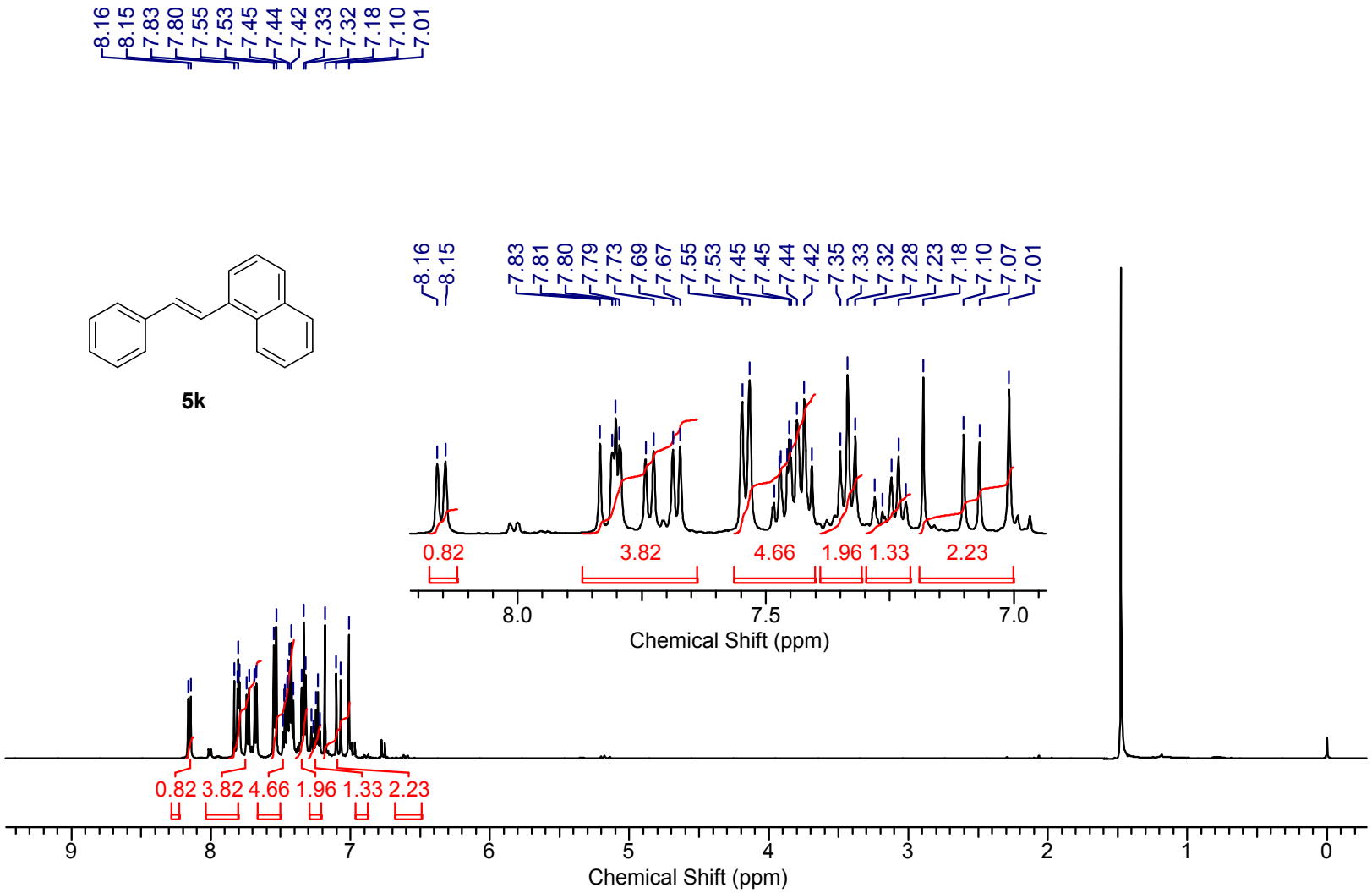
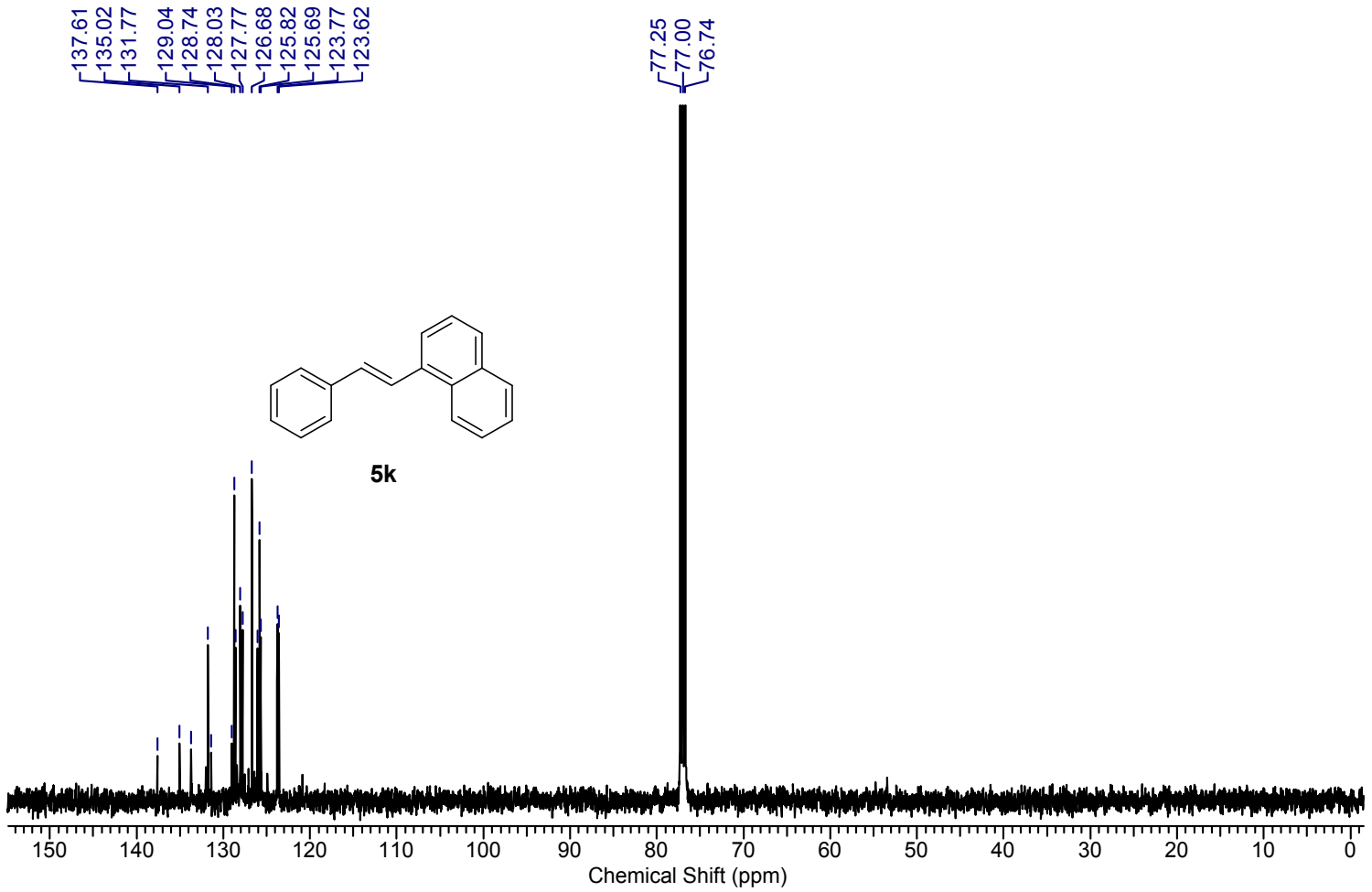
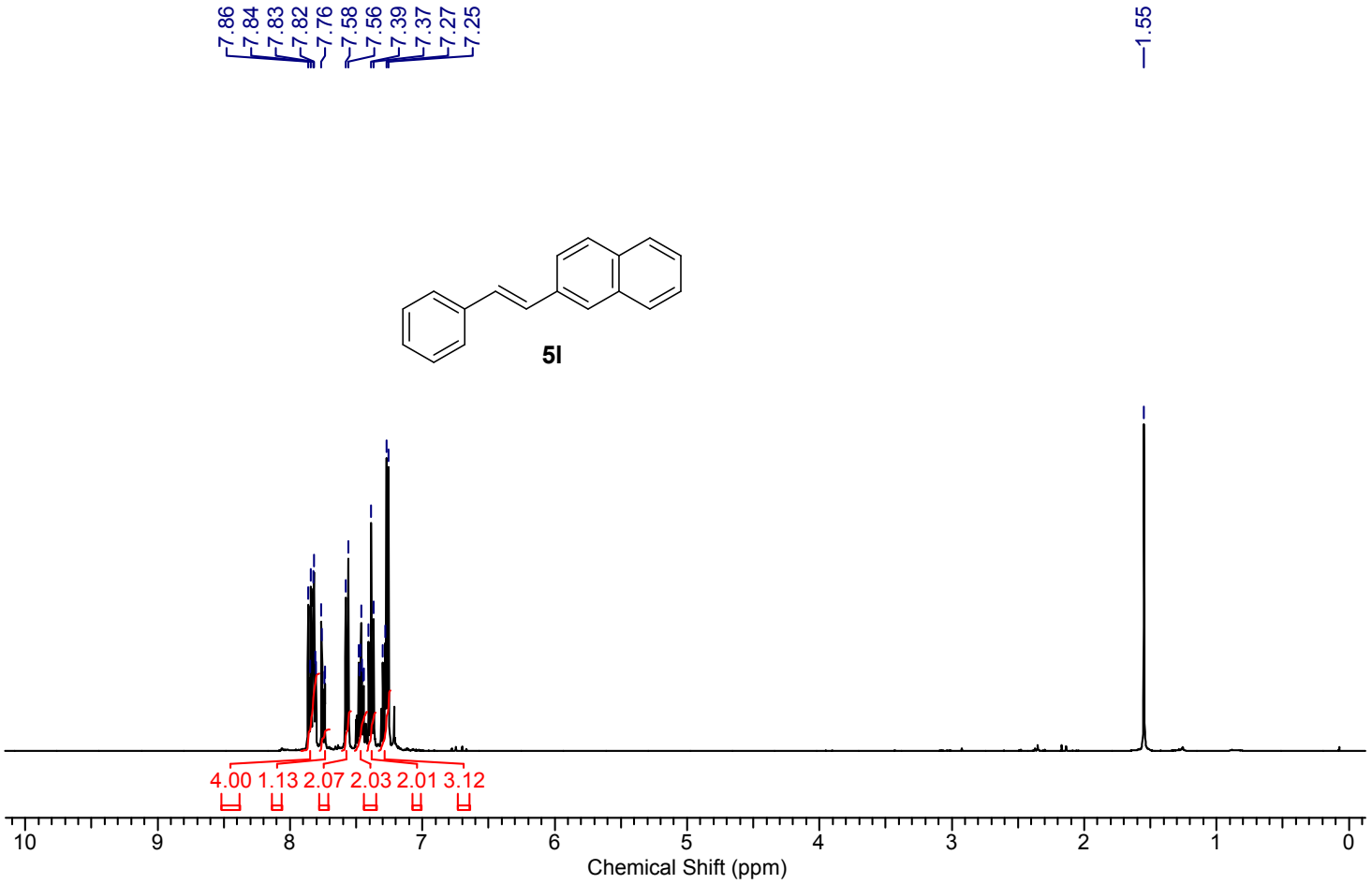
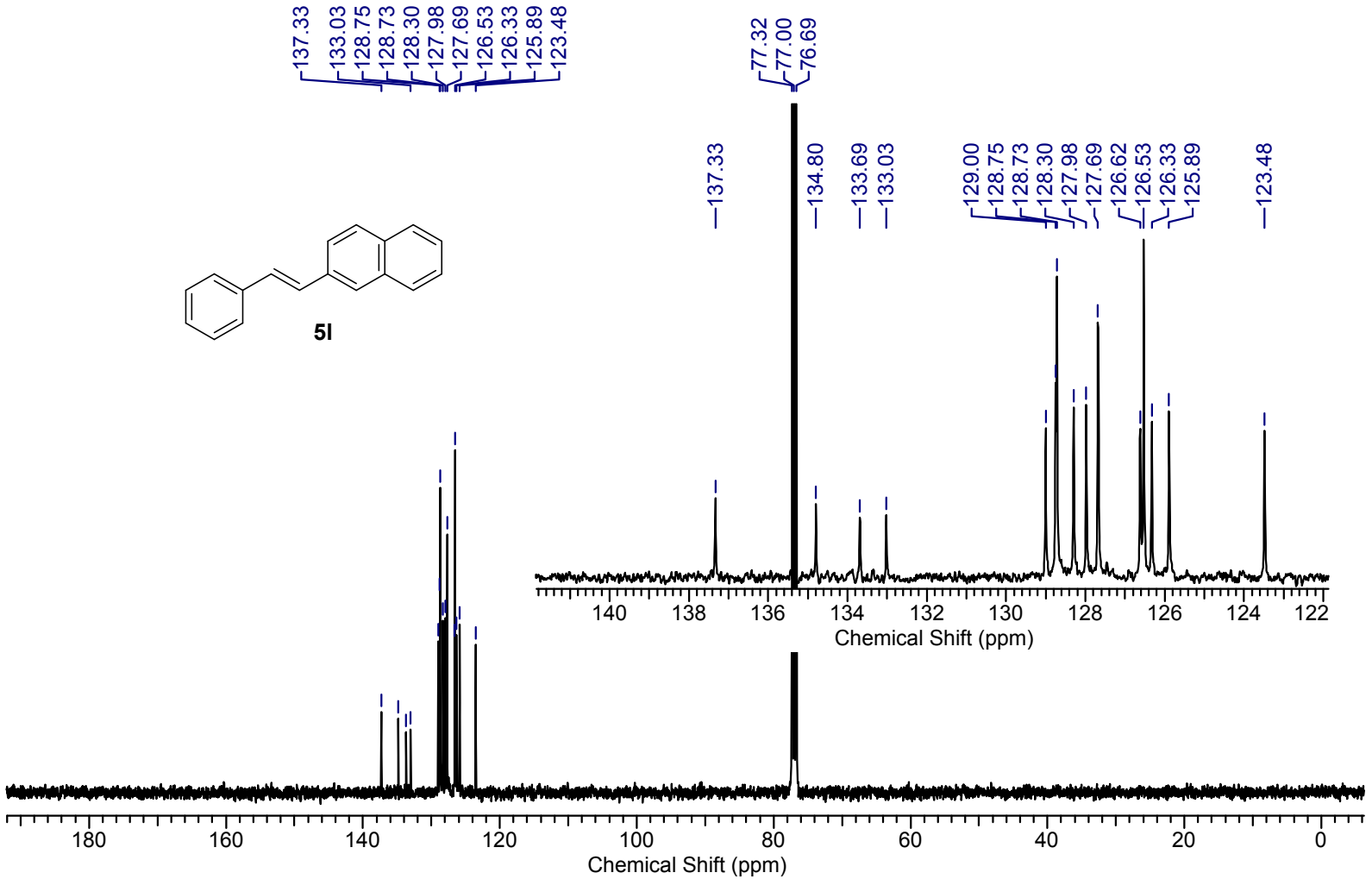
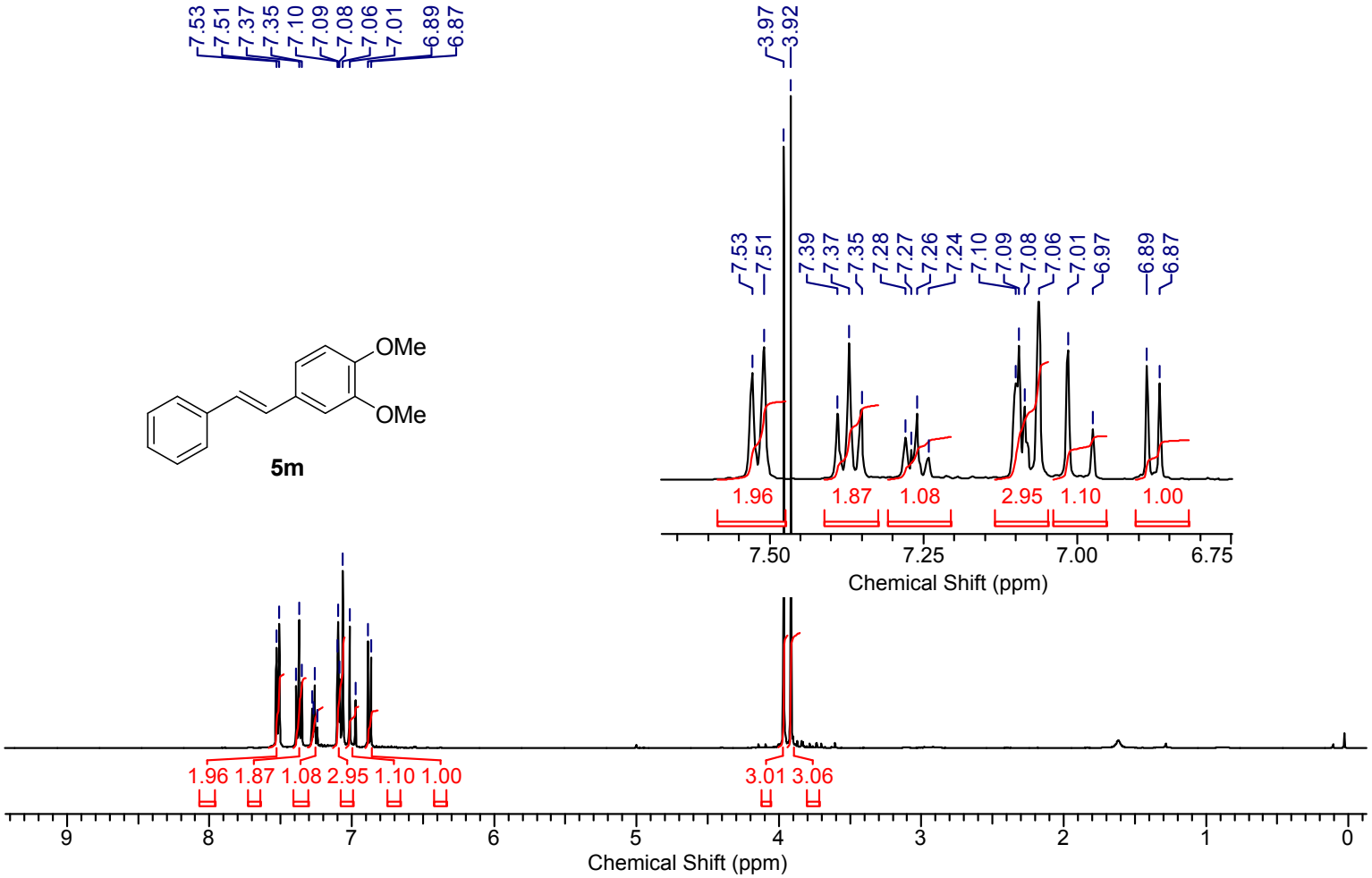
138.76
137.20
129.60
128.98
128.65
128.56
127.65
126.52
119.21
113.27
111.74
77.63
77.00
76.36
55.21
OMe
5j
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

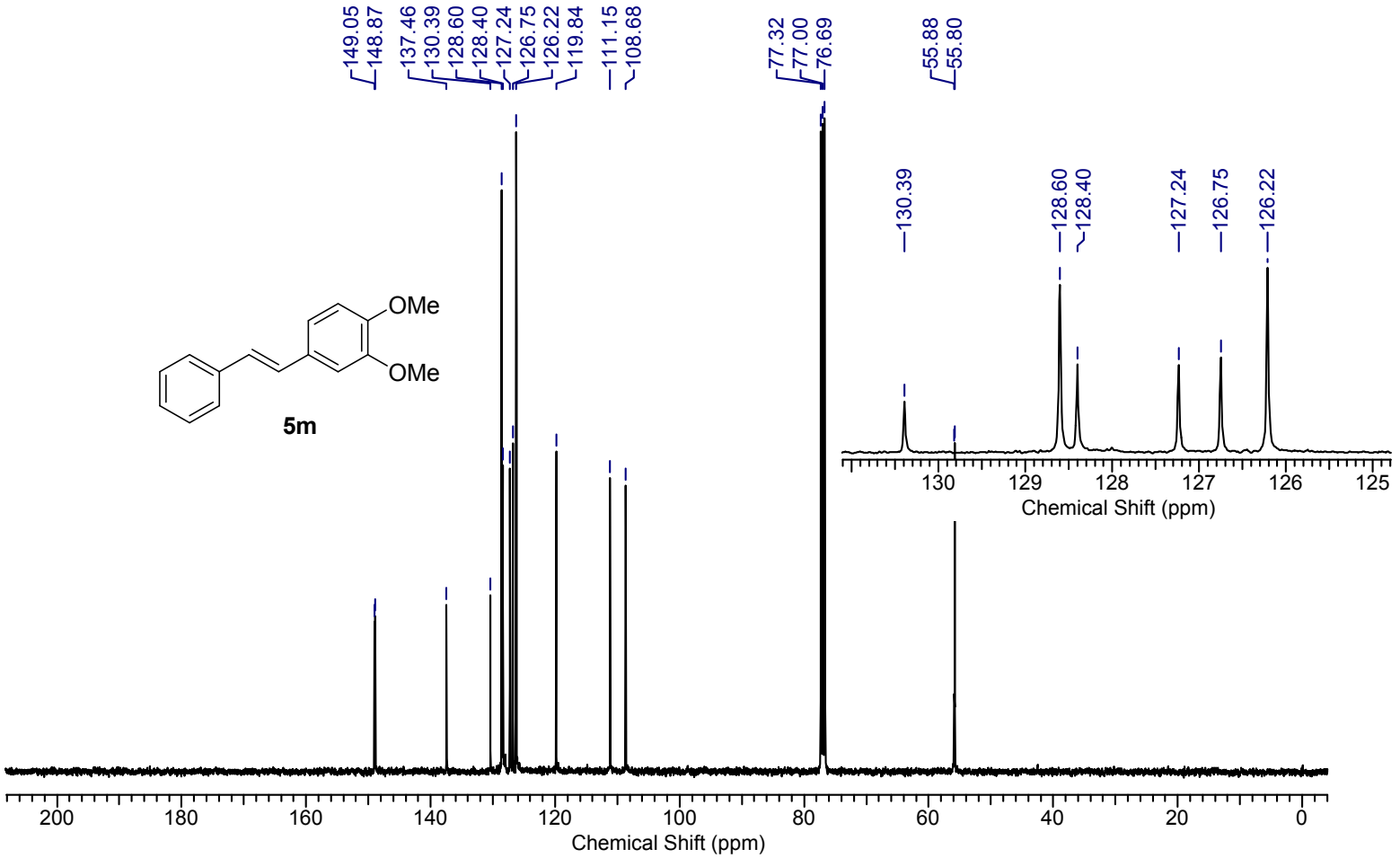

8.16
8.15
7.83
7.80
7.55
7.53
7.45
7.44
7.42
7.33
7.32
7.18
7.10
7.01
5k
8.16
8.15
7.83
7.81
7.80
7.79
7.73
7.69
7.67
7.55
7.53
7.45
7.45
7.44
7.42
7.35
7.33
7.32
7.28
7.23
7.18
7.10
7.07
7.01
0.82
3.82
4.66
1.96
1.33
2.23
8.0
7.5
7.0
Chemical Shift (ppm)
0.82
3.82
4.66
1.96
1.33
2.23
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

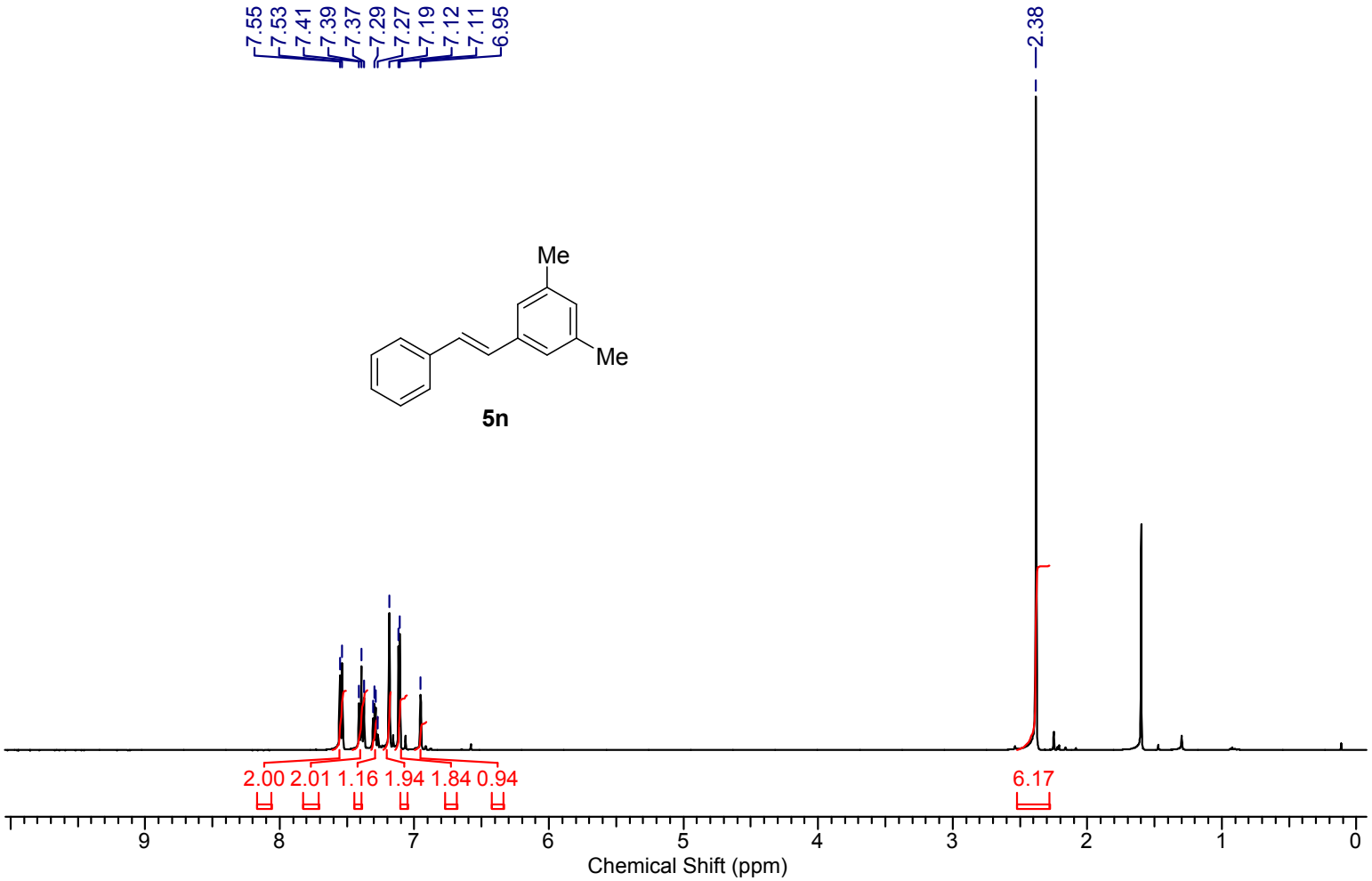

137.61
135.02
131.77
129.04
128.74
128.03
127.77
126.68
125.82
125.69
123.77
123.62
77.25
77.00
76.74
5k
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

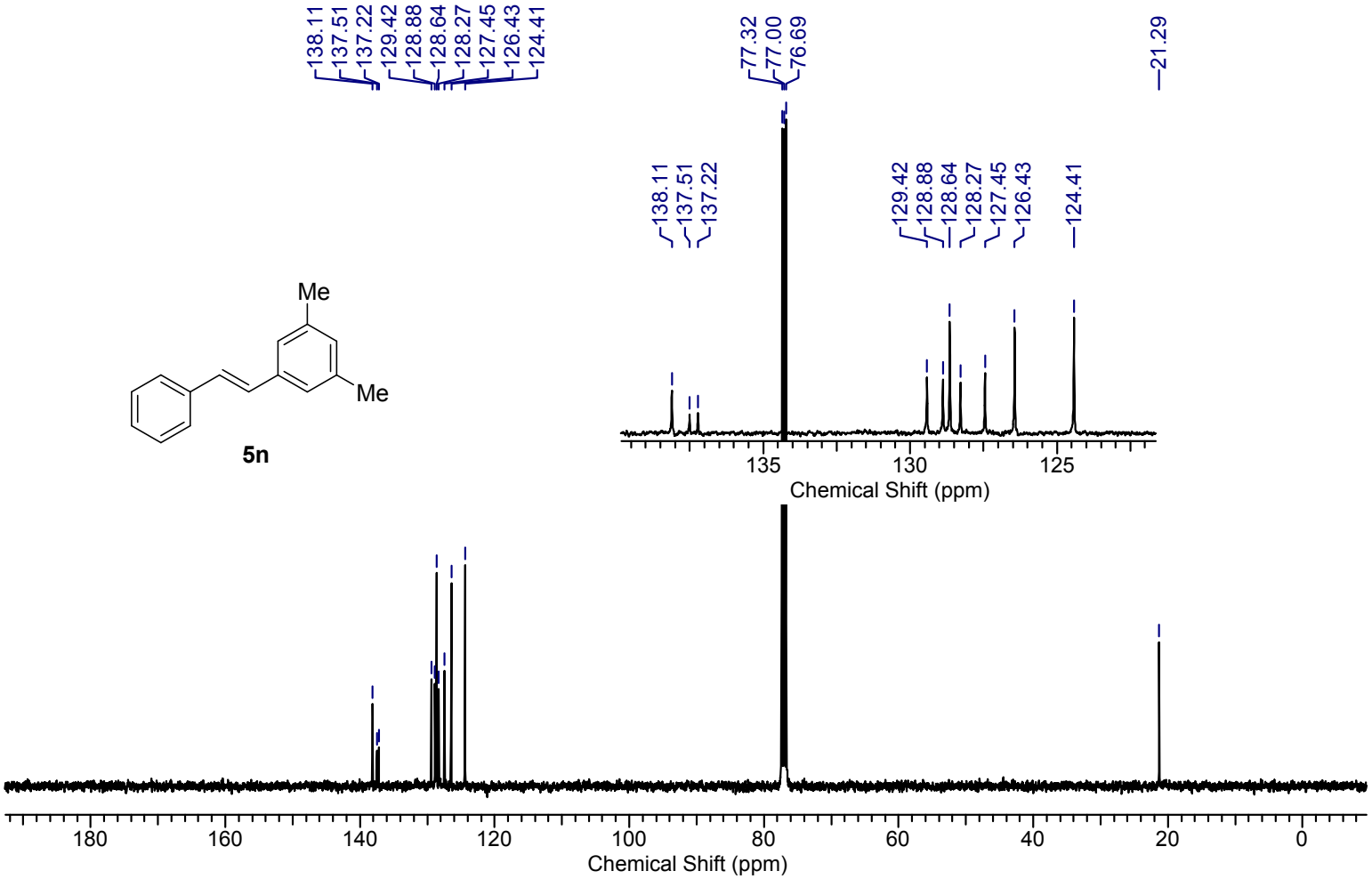

7.86
7.84
7.83
7.82
7.76
7.58
7.56
7.39
7.37
7.27
7.25
1.55
5l
4.00 1.13 2.07 2.03 2.01 3.12
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)


137.33
133.03
128.75
128.73
128.30
127.98
127.69
126.53
126.33
125.89
123.48
77.32
77.00
76.69
5l
137.33
134.80
133.69
133.03
129.00
128.75
128.73
128.30
127.98
127.69
126.62
126.53
126.33
125.89
123.48
140
138
136
134
132
130
128
126
124
122
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.53
7.51
7.37
7.35
7.10
7.09
7.08
7.06
7.01
6.89
6.87
3.97
3.92
OMe
OMe
5m
1.96 1.87 1.08 2.95 1.10 1.00
3.01 3.06
Chemical Shift (ppm)
7.53
7.51
7.39
7.37
7.35
7.28
7.27
7.26
7.24
7.10
7.09
7.08
7.06
7.01
6.97
6.89
6.87
1.96 1.87 1.08 2.95 1.10 1.00
Chemical Shift (ppm)


149.05
148.87
137.46
130.39
128.60
128.40
127.24
126.75
126.22
119.84
111.15
108.68
77.32
77.00
76.69
55.88
55.80
OMe
OMe
5m
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
130.39
128.60
128.40
127.24
126.75
126.22
130
129
128
127
126
125
Chemical Shift (ppm)


7.55
7.53
7.41
7.39
7.37
7.29
7.27
7.19
7.12
7.11
6.95
2.38
Me
Me
5n
2.00 2.01 1.16 1.94 1.84 0.94
6.17
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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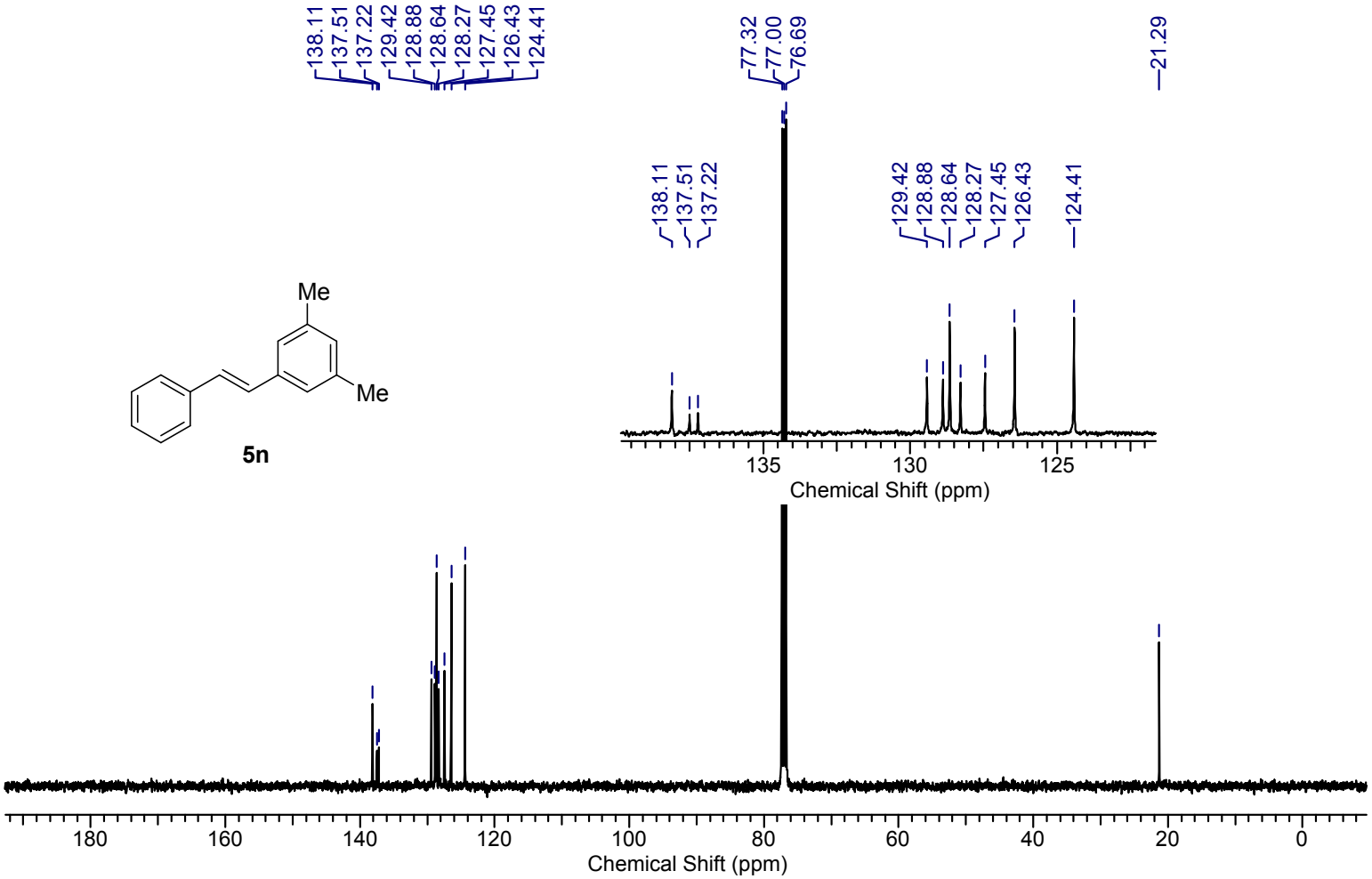
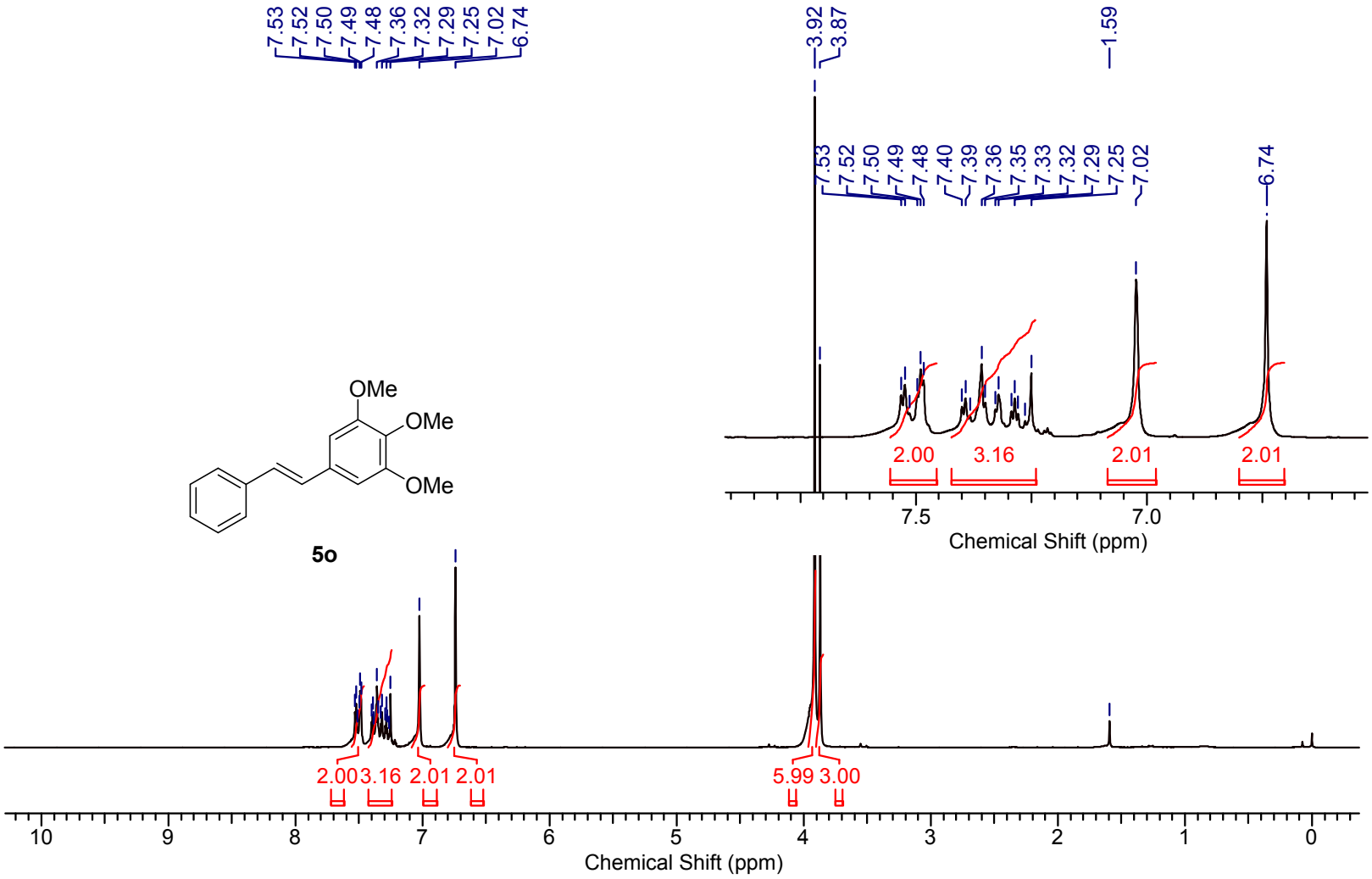
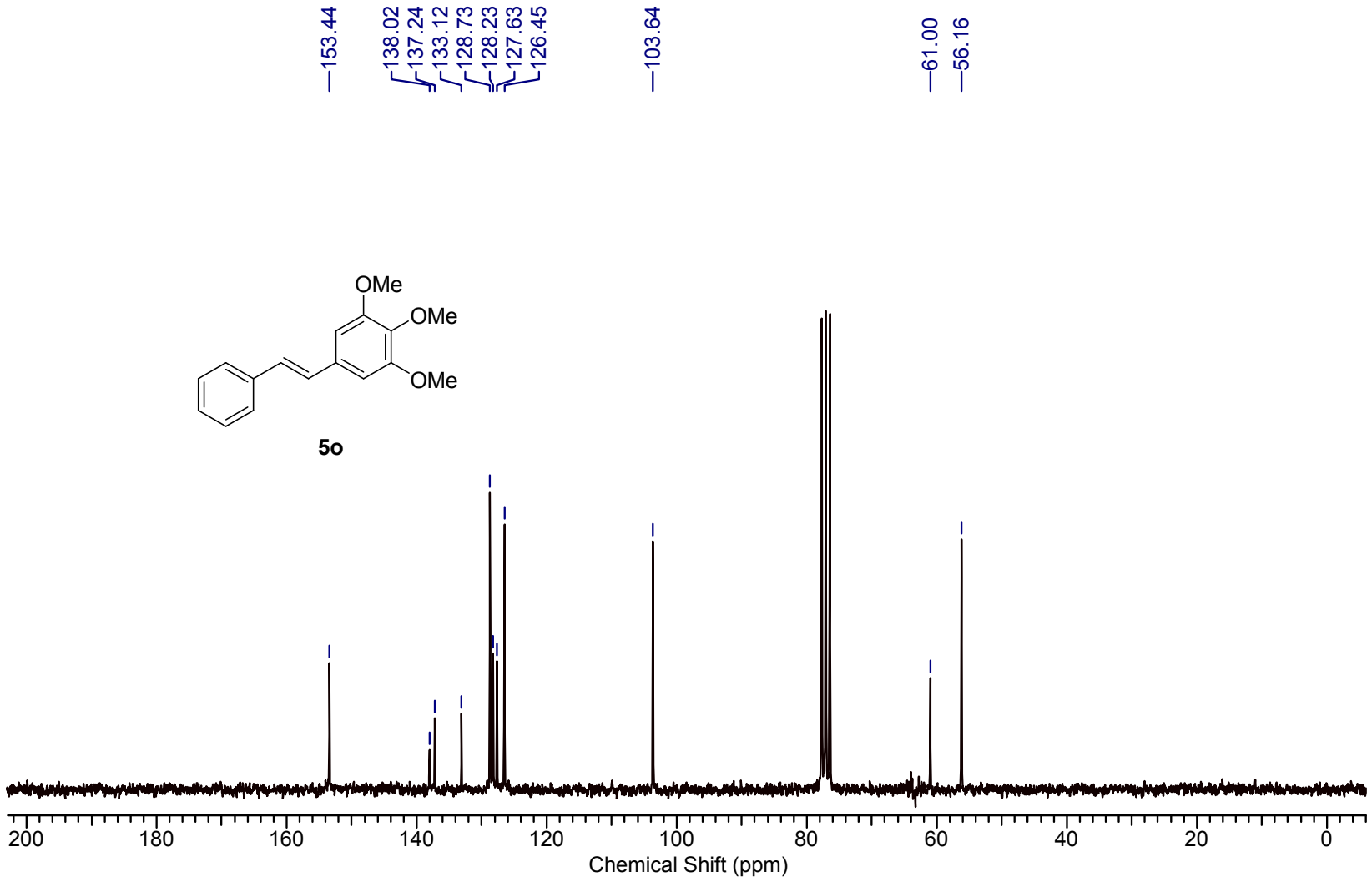
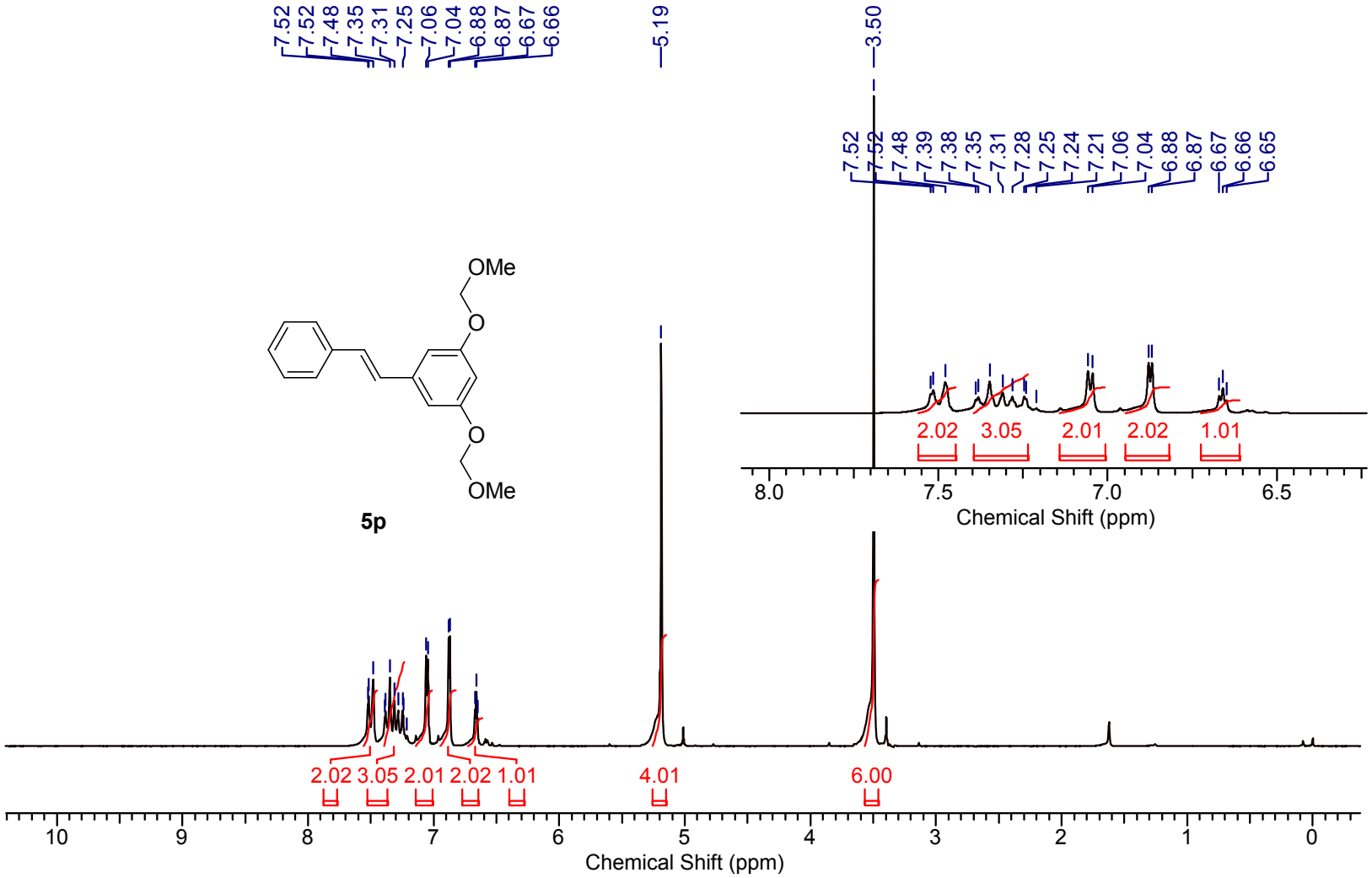
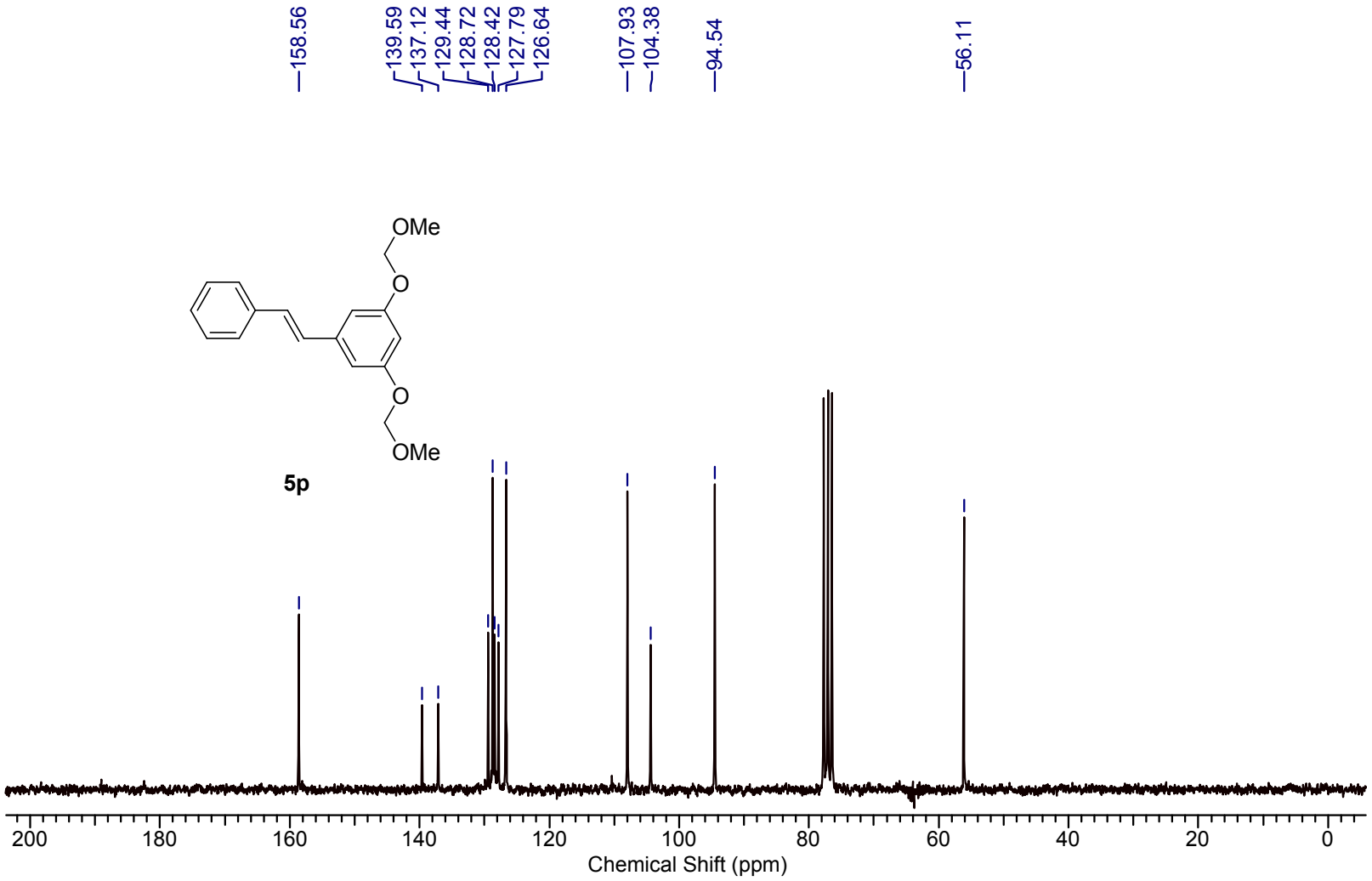
137.51
137.22
129.42
128.88
128.64
128.27
127.45
126.43
124.41
77.32
77.00
76.69
21.29
Me
Me
5n
135
130
125
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


138.11
137.51
137.22
129.42
128.88
128.64
128.27
127.45
126.43
124.41
77.32
77.00
76.69
21.29
Me
Me
5n
135
130
125
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.53
7.52
7.50
7.49
7.48
7.36
7.32
7.29
7.25
7.02
6.74
3.92
3.87
1.59
OMe
OMe
OMe
5o
2.00
3.16
2.01
2.01
5.99
3.00
Chemical Shift (ppm)


153.44
138.02
137.24
133.12
128.73
128.23
127.63
126.45
103.64
61.00
56.16
OMe
OMe
OMe
5o
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.52
7.52
7.48
7.35
7.31
7.25
7.06
7.04
6.88
6.87
6.67
6.66
5.19
3.50
OMe
O
O
OMe
5p
2.02
3.05
2.01
2.02
1.01
4.01
6.00
Chemical Shift (ppm)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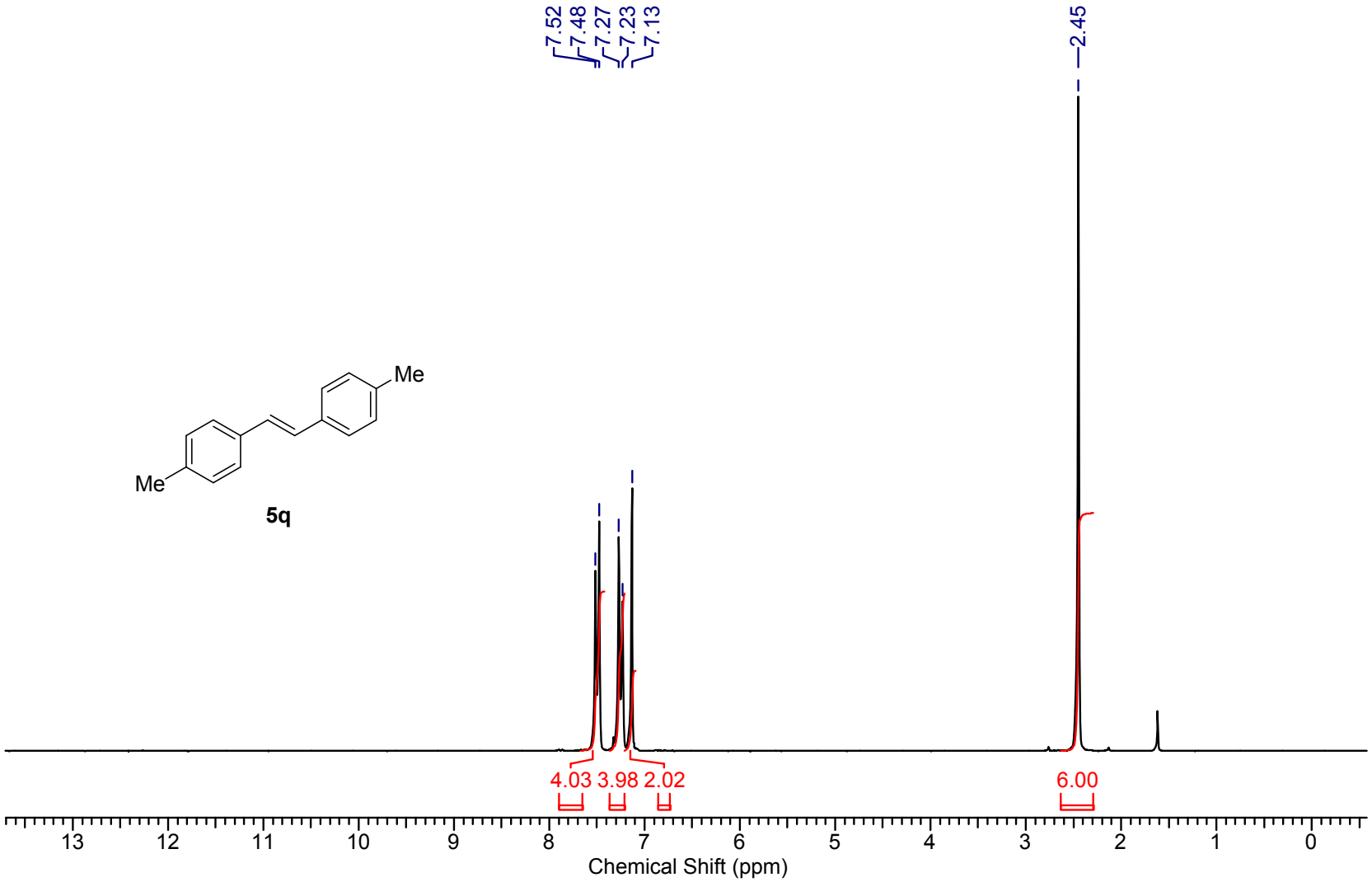
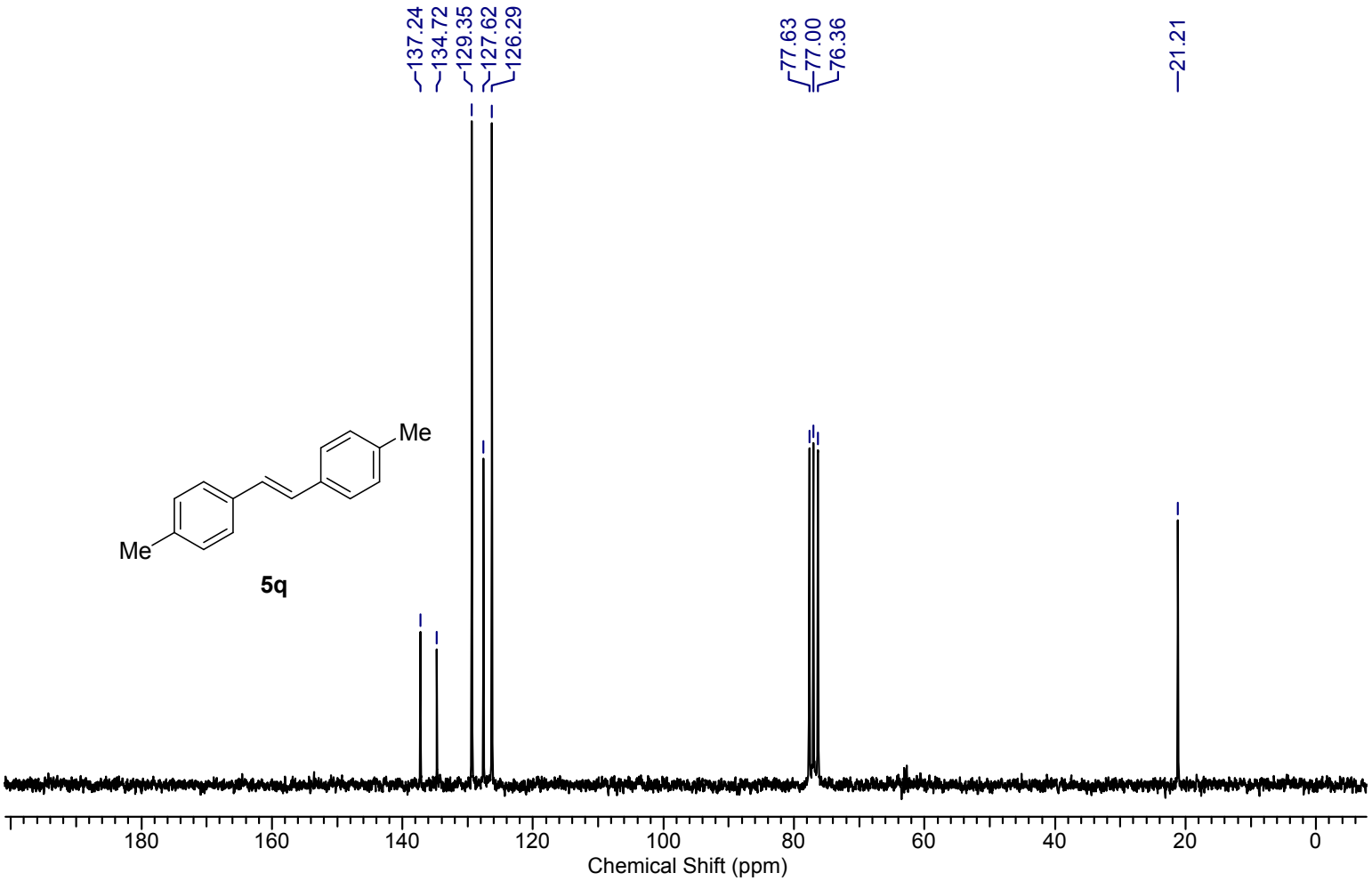
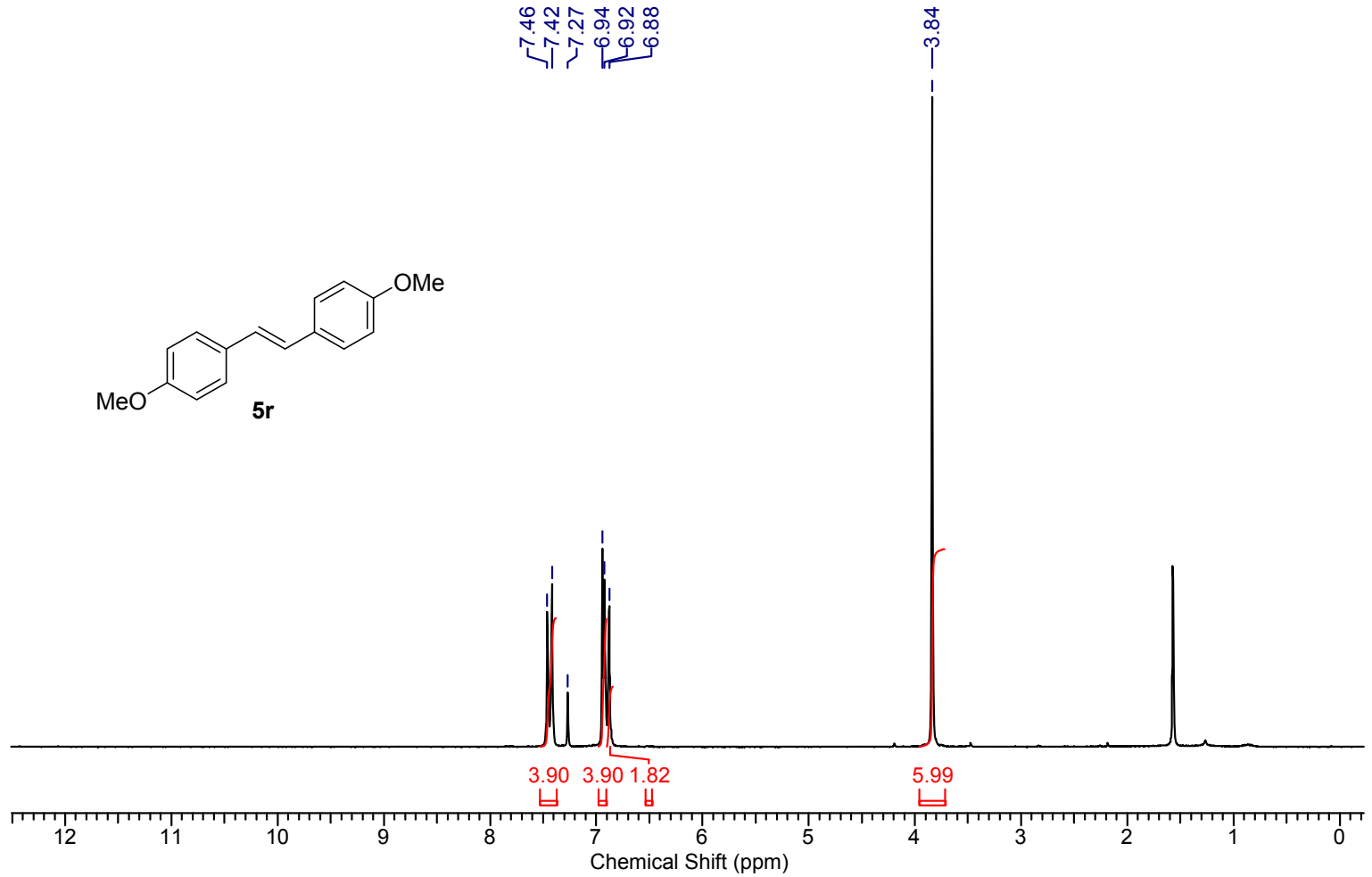
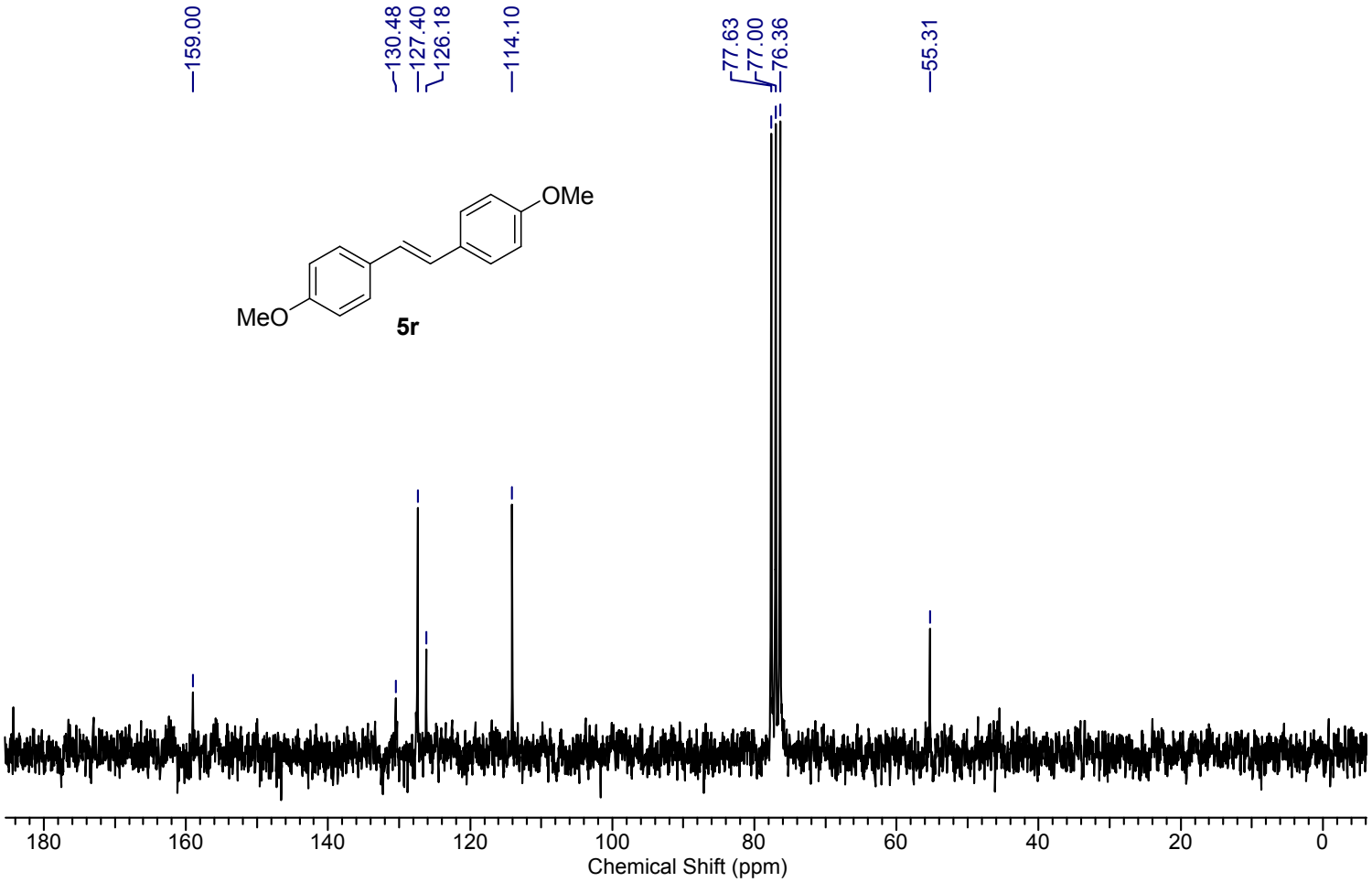
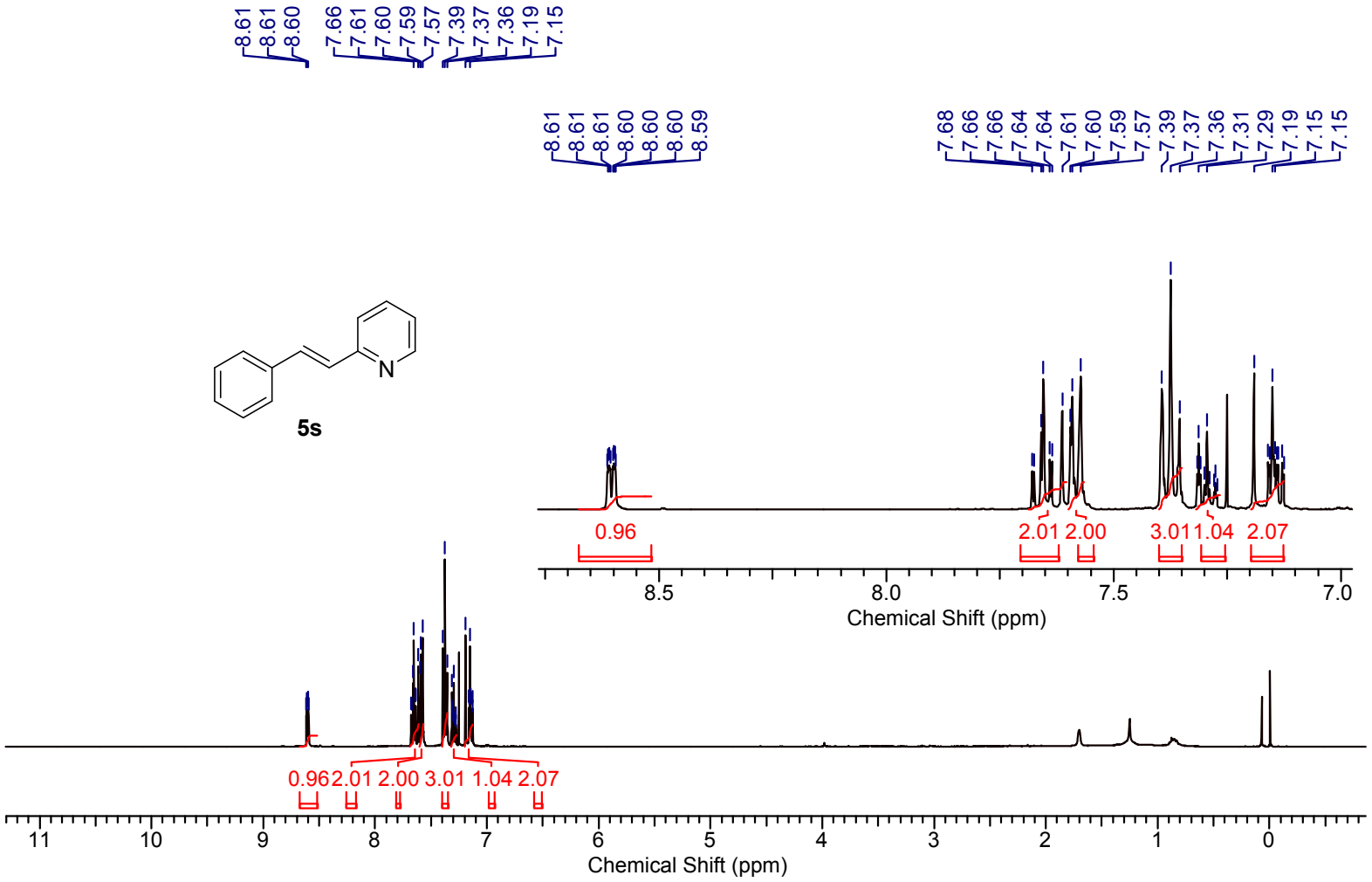
139.59
137.12
129.44
128.72
128.42
127.79
126.64
107.93
104.38
94.54
56.11
OMe
O
O
OMe
5p
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

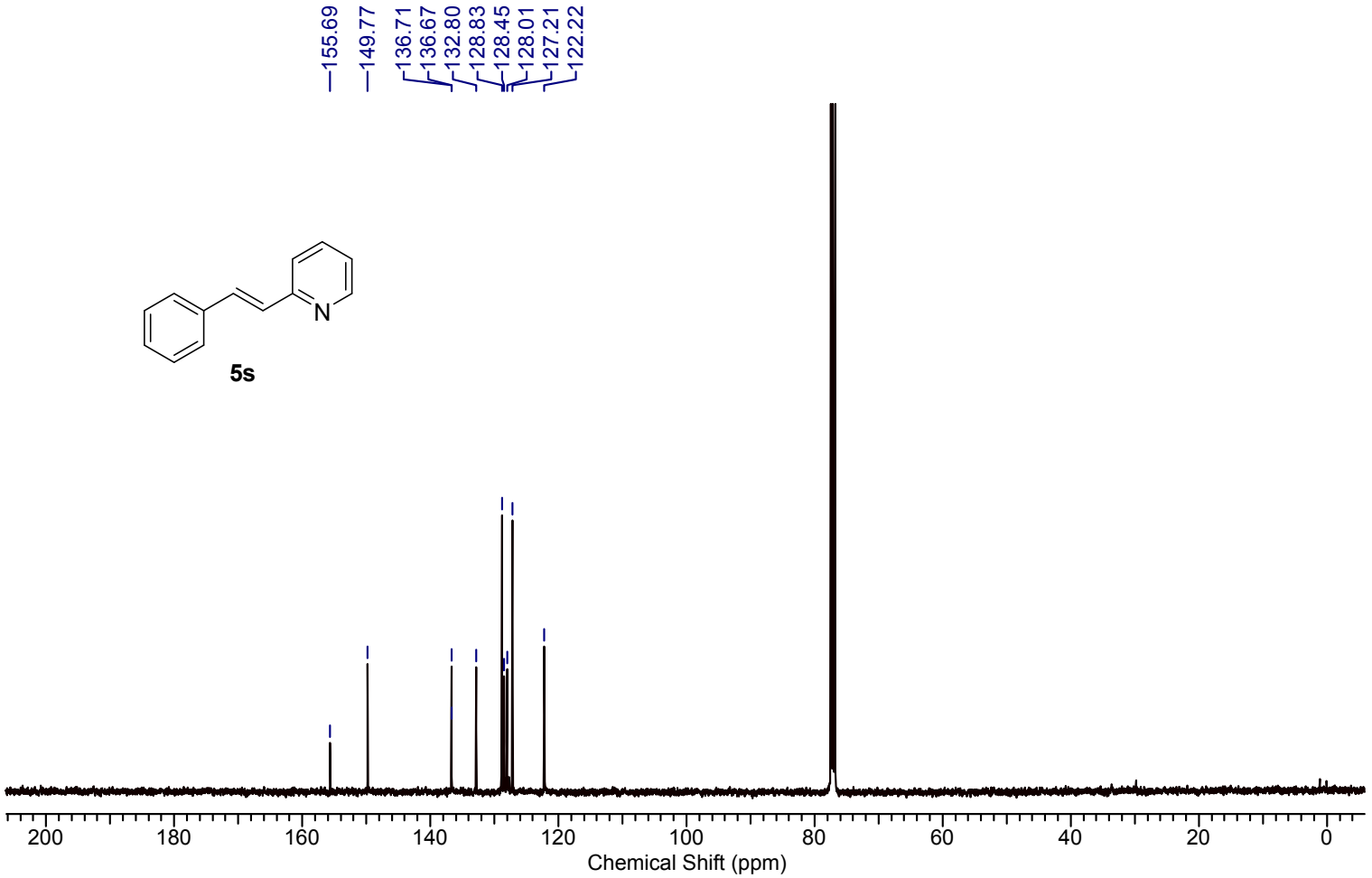

7.52
7.48
7.27
7.23
7.13
2.45
Me
Me
5q
4.03
3.98
2.02
6.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

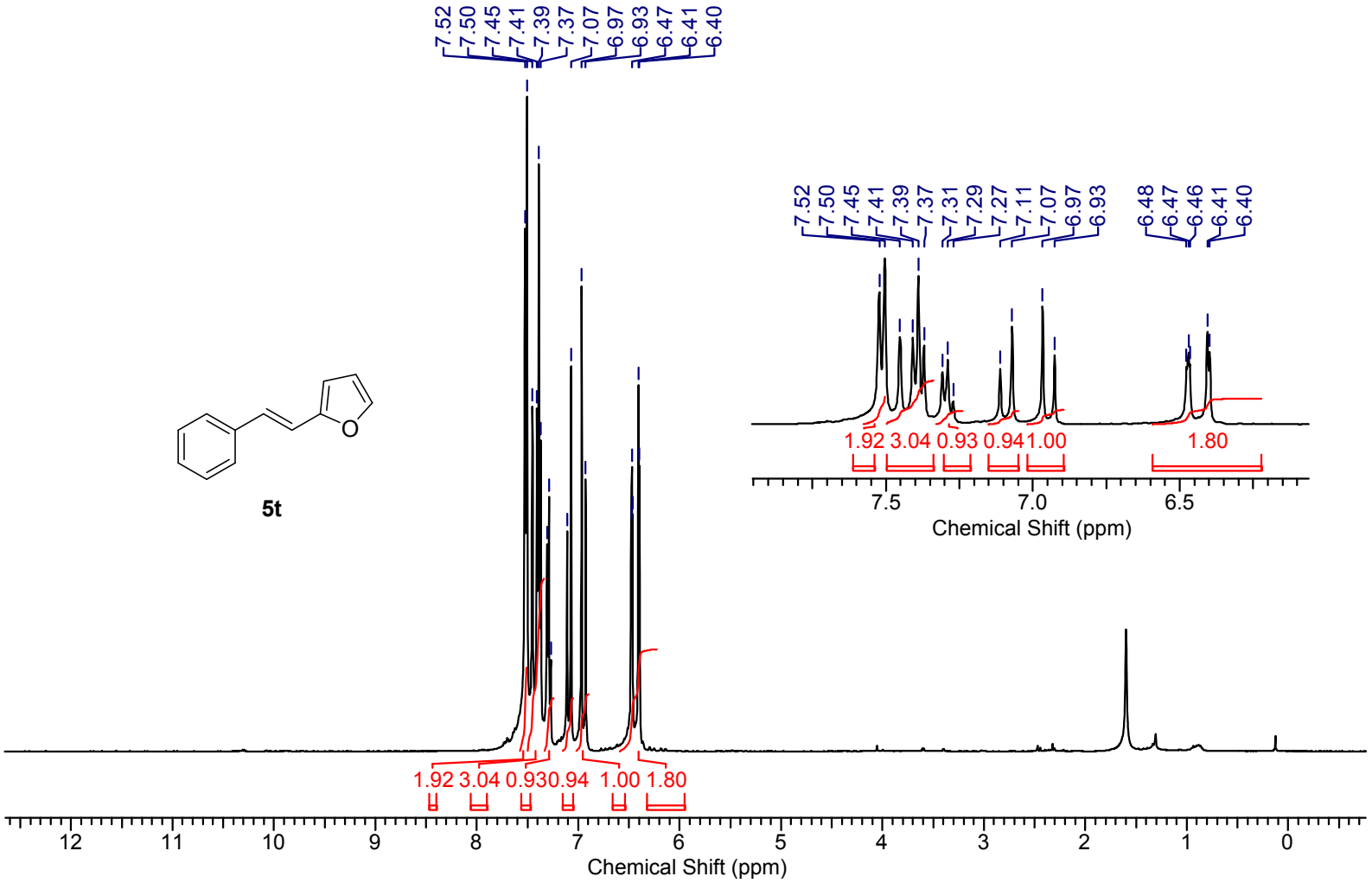

137.24
134.72
129.35
127.62
126.29
77.63
77.00
76.36
21.21
Me
Me
5q
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

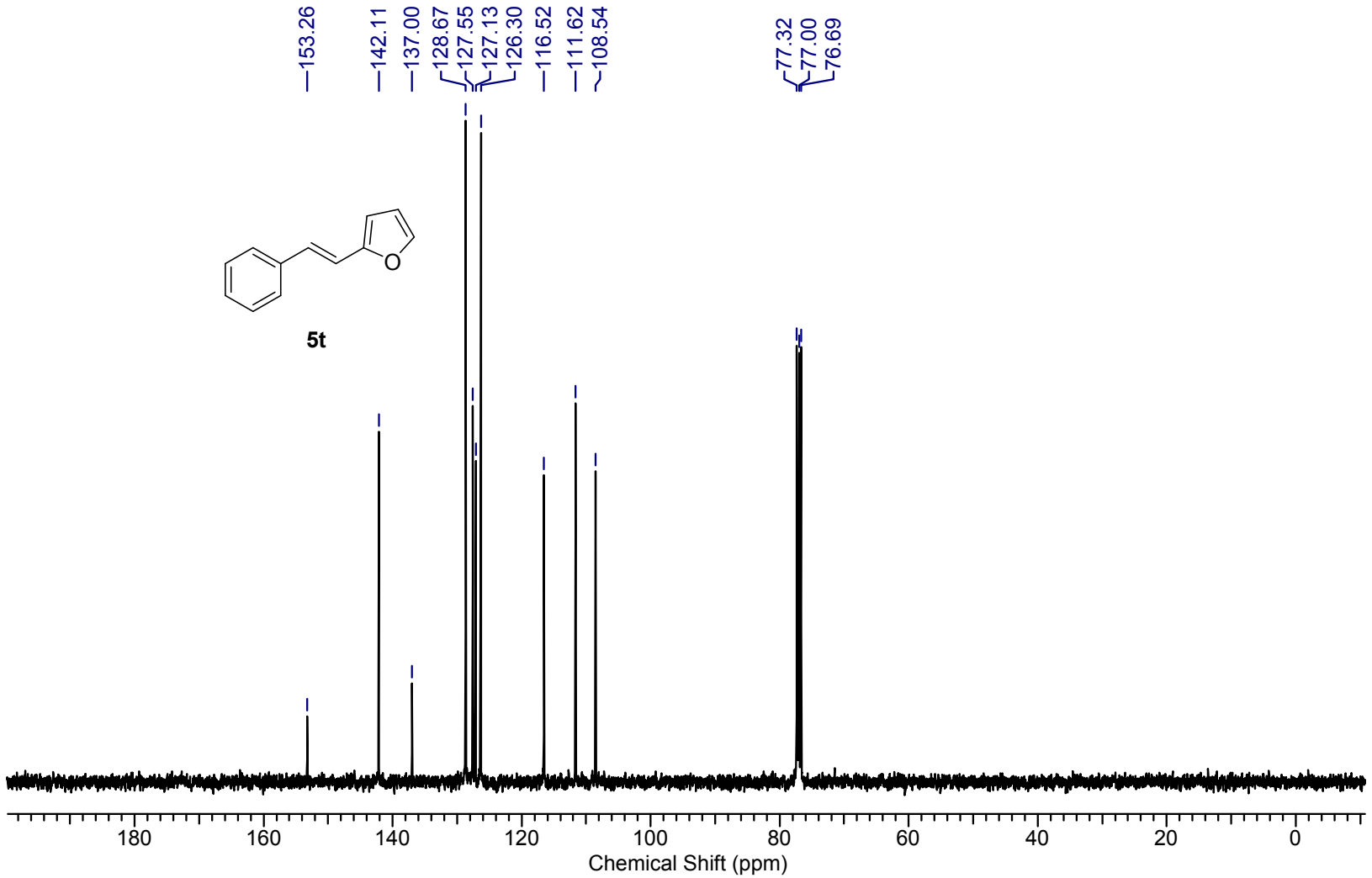

7.46
7.42
7.27
6.94
6.92
6.88
3.84
OMe
MeO
5r
3.90
3.90
1.82
5.99
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

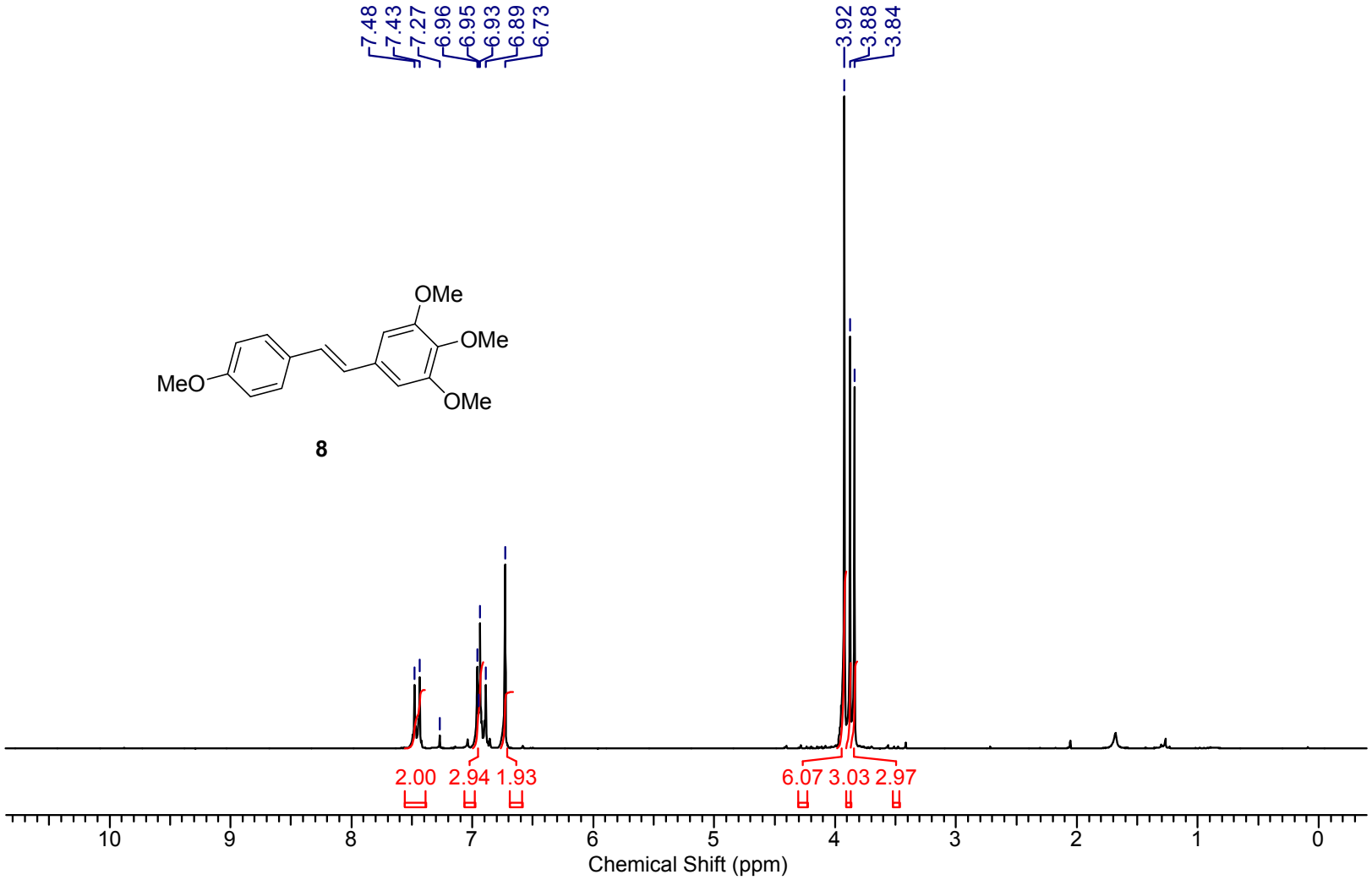

159.00
130.48
127.40
126.18
114.10
77.63
77.00
76.36
55.31
OMe
MeO
5r
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

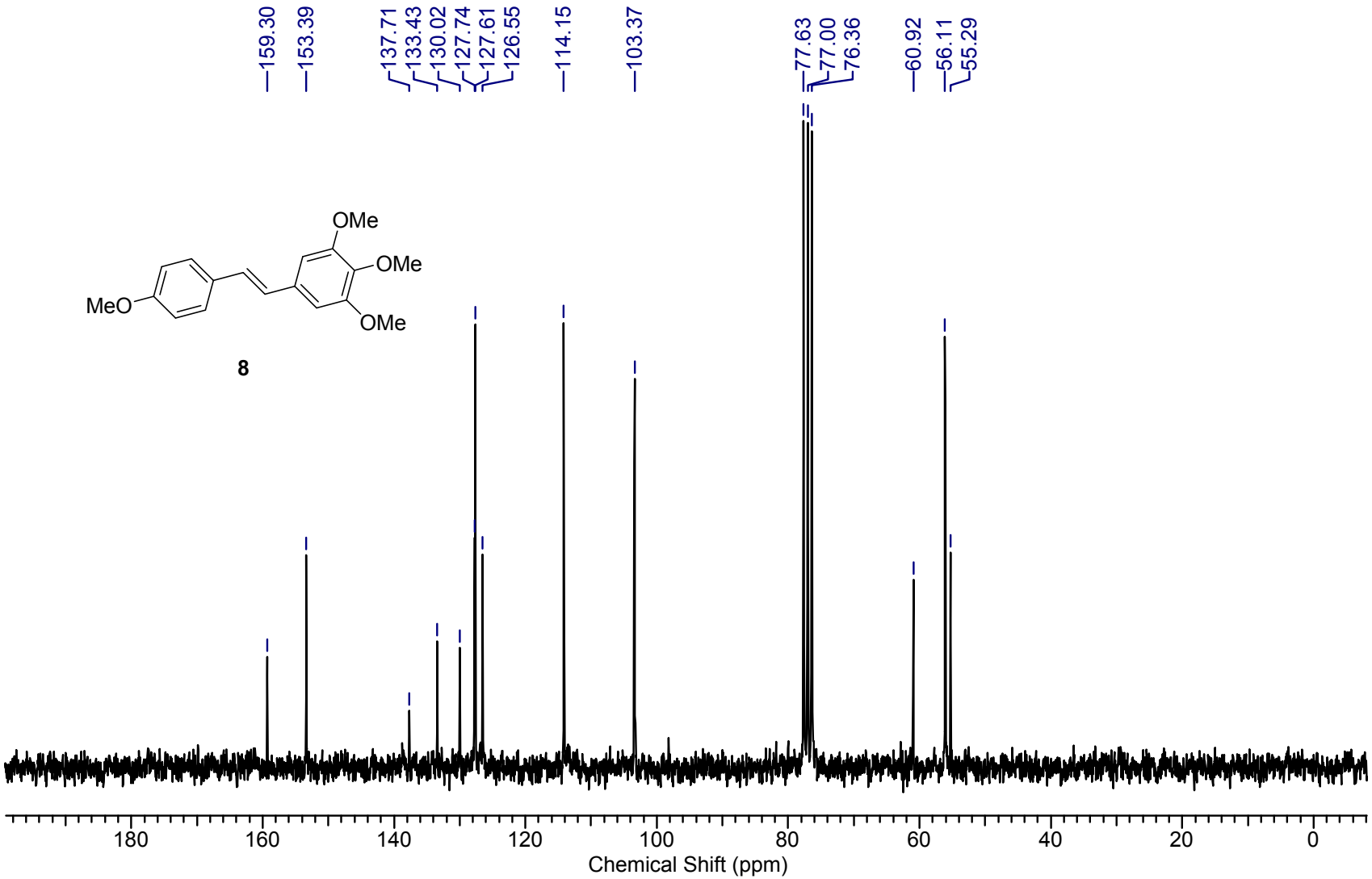

8.61
8.61
8.60
7.66
7.61
7.60
7.59
7.57
7.39
7.37
7.36
7.19
7.15
8.61
8.61
8.61
8.60
8.60
8.60
8.59
7.68
7.66
7.66
7.64
7.64
7.61
7.60
7.59
7.57
7.39
7.37
7.36
7.31
7.29
7.19
7.15
7.15
N
5s
0.96
2.01
2.00
3.01
1.04
2.07
8.5
8.0
7.5
7.0
Chemical Shift (ppm)
0.96
2.01
2.00
3.01
1.04
2.07
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

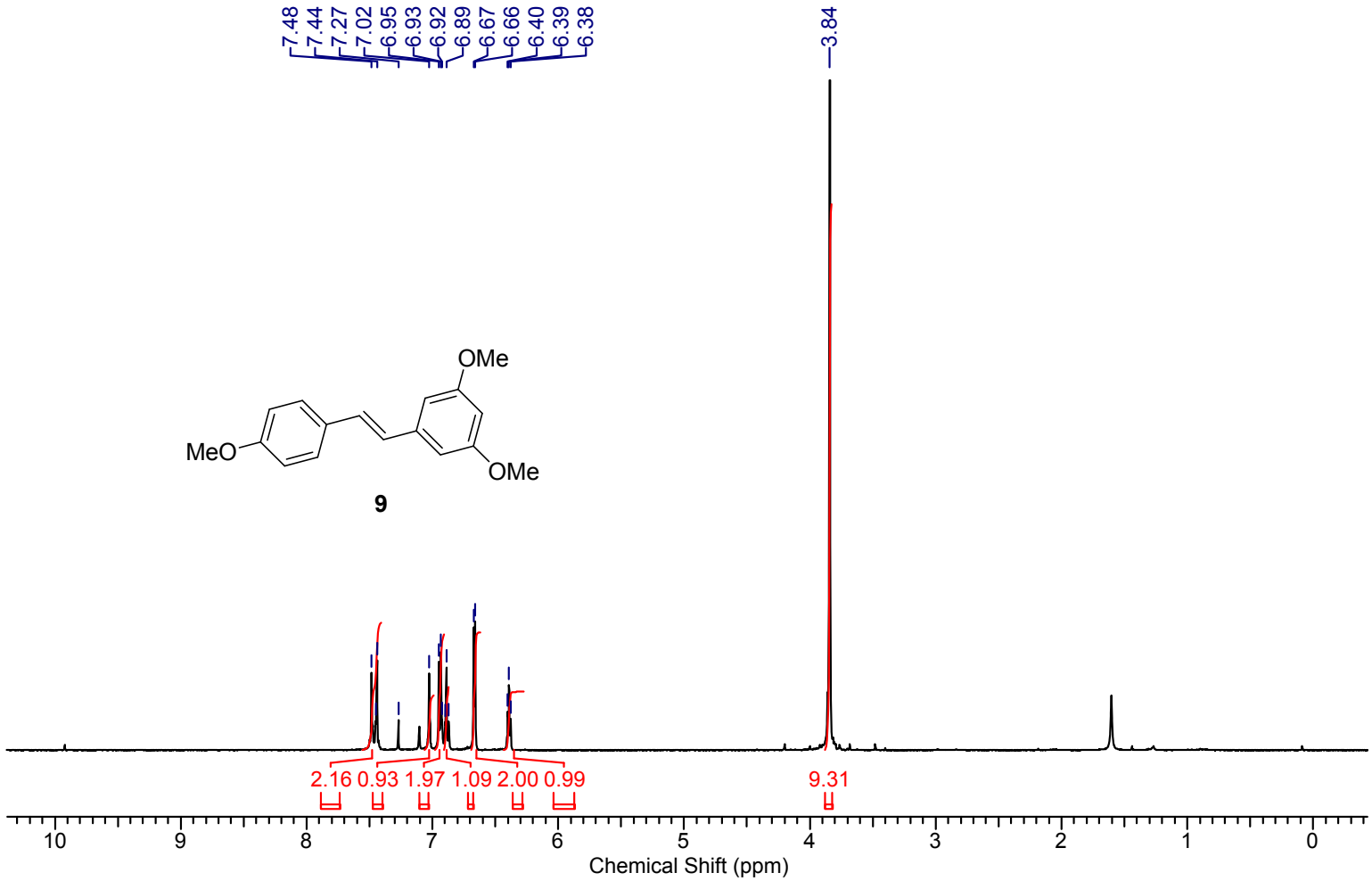

155.69
149.77
136.71
136.67
132.80
128.83
128.45
128.01
127.21
122.22
N
5s
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

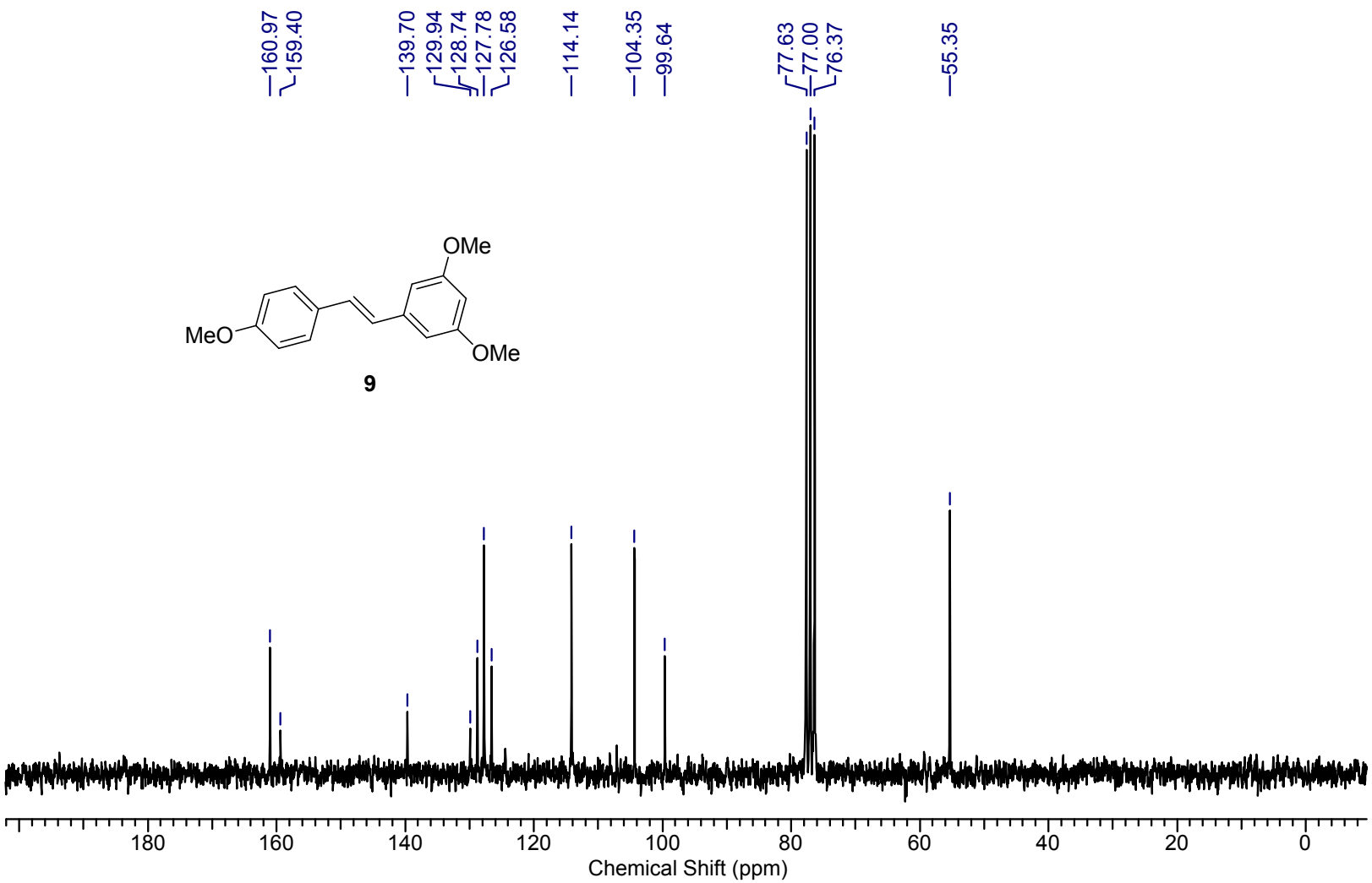

7.52
7.50
7.45
7.41
7.39
7.37
7.07
6.97
6.93
6.47
6.41
6.40
O
5t
1.92 3.04 0.93 0.94 1.00 1.80
12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
7.52
7.50
7.45
7.41
7.39
7.37
7.31
7.29
7.27
7.11
7.07
6.97
6.93
6.48
6.47
6.46
6.41
6.40
1.92 3.04 0.93 0.94 1.00 1.80
7.5 7.0 6.5
Chemical Shift (ppm)

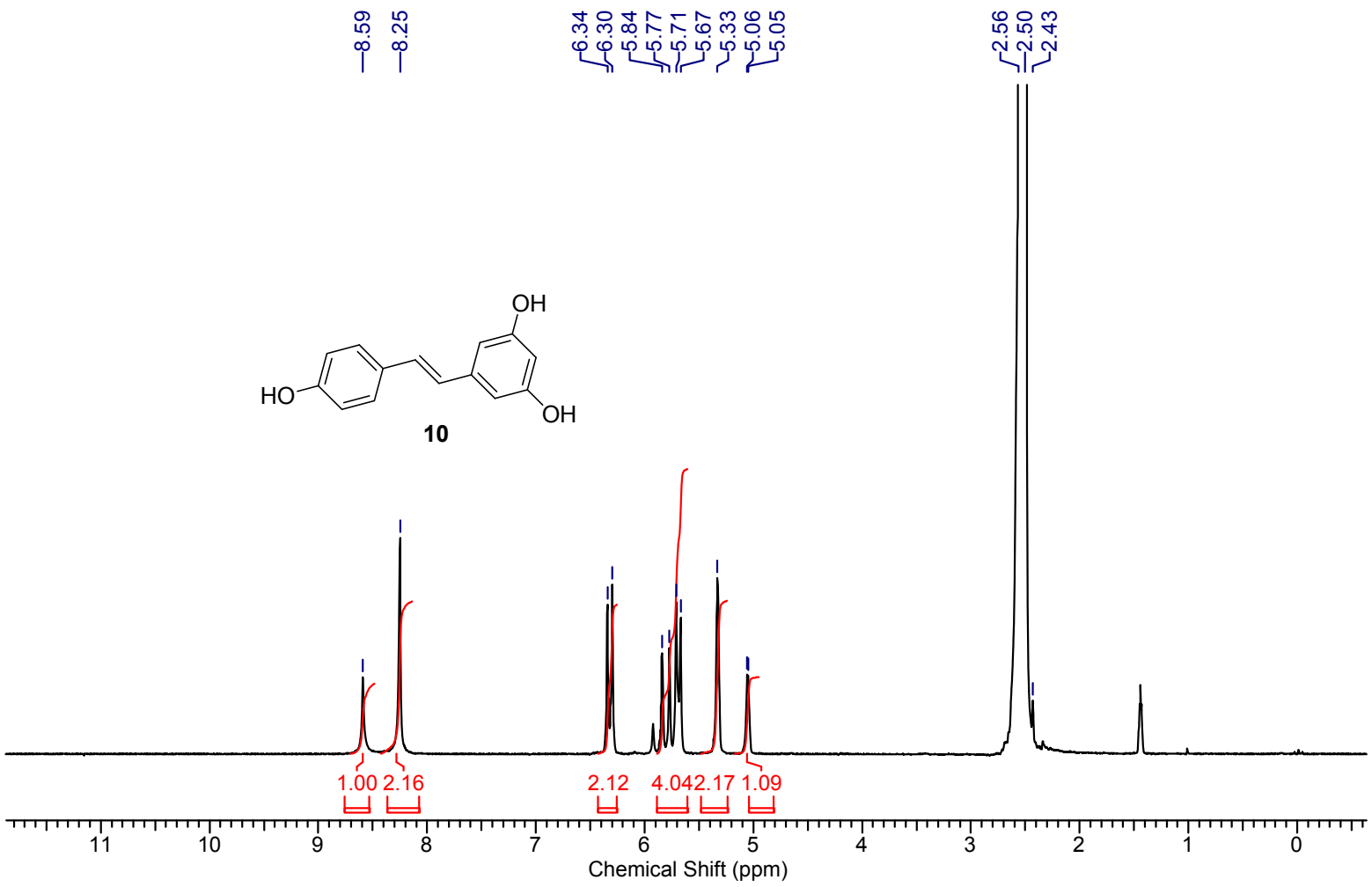

153.26
142.11
137.00
128.67
127.55
127.13
126.30
116.52
111.62
108.54
77.32
77.00
76.69
O
5t
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

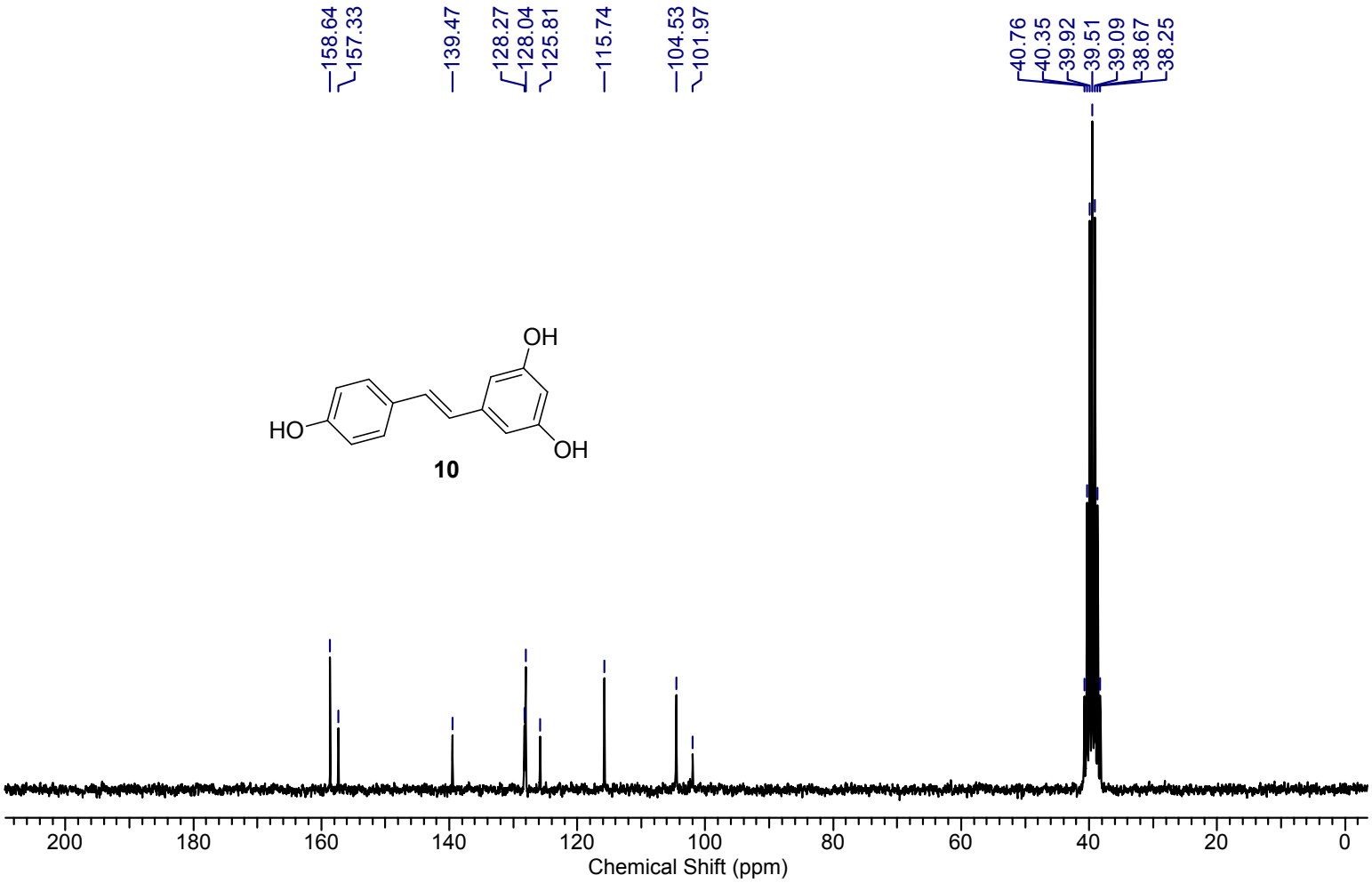

7.48
7.43
7.27
6.96
6.95
6.93
6.89
6.73
3.92
3.88
3.84
OMe
OMe
OMe
MeO
8
2.00
2.94
1.93
6.07
3.03
2.97
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


159.30
153.39
137.71
133.43
130.02
127.74
127.61
126.55
114.15
103.37
77.63
77.00
76.36
60.92
56.11
55.29
OMe
OMe
OMe
MeO
8
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.48
7.44
7.27
7.02
6.95
6.93
6.92
6.89
6.67
6.66
6.40
6.39
6.38
3.84
OMe
MeO
OMe
9
2.16 0.93 1.97 1.09 2.00 0.99
9.31
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


160.97
159.40
139.70
129.94
128.74
127.78
126.58
114.14
104.35
99.64
77.63
77.00
76.37
55.35
OMe
MeO
OMe
9
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


8.59
8.25
6.34
6.30
5.84
5.77
5.71
5.67
5.33
5.06
5.05
2.56
2.50
2.43
OH
HO
OH
10
1.00
2.16
2.12
4.04
2.17
1.09
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


158.64
157.33
139.47
128.27
128.04
125.81
115.74
104.53
101.97
40.76
40.35
39.92
39.51
39.09
38.67
38.25
OH
HO
OH
10
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)