Supporting Information

Oxidative cleavage of α-substituted styrenes using excited dibenzothiophene *S*-oxide and DMSO

Yuto Tamba,[1] Saki Maejima,*[1] and Hideki Yorimitsu*[1]

[1]Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

maejima.saki.4j@kyoto-u.ac.jp

yori@kuchem.kyoto-u.ac.jp

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General Information

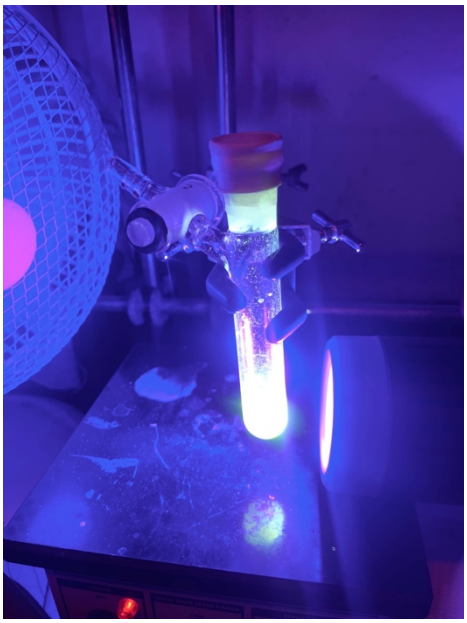
^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{19}F NMR (564 MHz) were recorded on a JEOL ECZ-600 spectrometer. Chemical shifts in ^{1}H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to residual $CHCl_3$ (δ = 7.26 ppm). Chemical shifts in ^{13}C NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to $CDCl_3$ (δ = 77.16 ppm). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts in ^{19}F NMR spectra were reference to C_6H_5F (δ = –113.5 ppm), as an external standard. High-resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer or on a Shimadzu LCMS-9030 instrument. GC-MS analysis was carried out using a Shimadzu GCMS-QP2010 SE equipped with a capillary column (SH-Rtx-5MS, 0.25 mm i.d., 30 m) with nitrogen gas as a carrier (pressure: 100 kPa).

All reactions were performed under nitrogen atmosphere. Dehydrated DMSO was purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F_{254}. Visualization of the developed chromatogram was performed by UV lamp (254 nm) and dinitrophenylhydrazine stain. Preparative flash chromatography was performed on Merck precoated analytical plates, 0.5-mm thick, silica gel 60 F_{254} or monolithic silica column.[1]

DBTSO and DBTSO-^{18}O were prepared according to the literature.[2, 3, 4] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

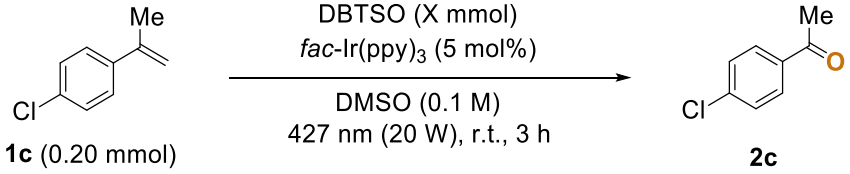
Photochemical reactions were performed by direct irradiation with a commercial LED from Kessil product PR160L-427 (20 W, λ_{max} = 427 nm, average intensity is 399 mW/cm^2). The reactions were conducted in a 10-mL Schlenk tube (φ = 2 cm) placed approximately 2 cm away from the light source. To suppress heating from the light source, the reaction vessel was externally air-cooled using two fans (Figure S1). Under these conditions, the reaction temperature was maintained at approximately 28 °C.

Figure S1. Set-up of the reaction.



Additional Information

Table S1. Condition screening

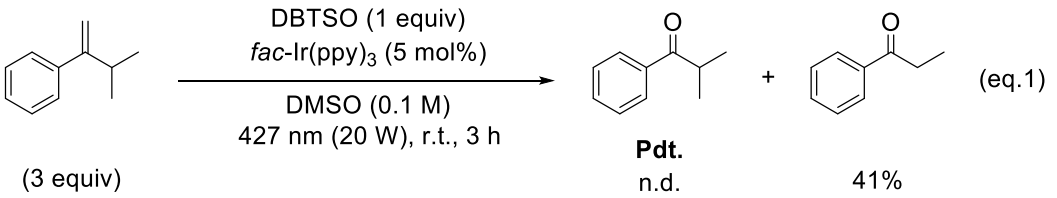


1c (0.20 mmol) **2c**

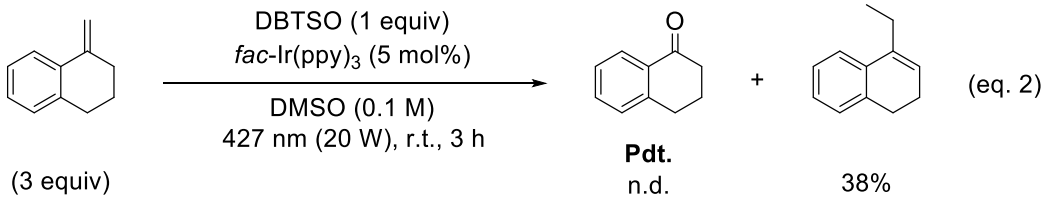
entry	DBTSO (X mmol)	**2c** (mmol)
1	DBTSO (0.10 mmol, 0.5 equiv)	0.096 (96%)[a]
2	DBTSO (0.20 mmol, 1.0 equiv)	0.088
3	DBTSO (0.30 mmol, 1.5 equiv)	0.098
4	DBTSO (0.20 mmol, 1.0 equiv) in DMSO (0.2 M)	0.092

[a] ^{1}H NMR yield based on DBTSO as the limiting reagent.

Scheme S1. Oxidative cleavage of α-isopropylstyrene and α-methylenetetralin.



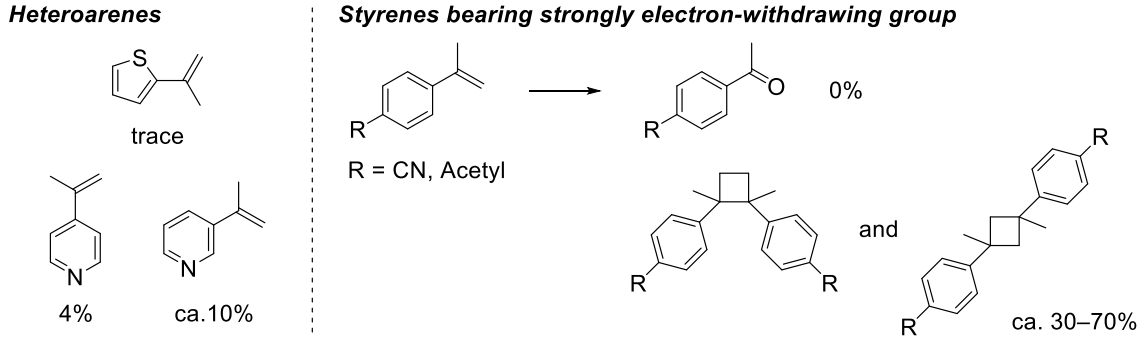
(3 equiv) **Pdt.** n.d. 41%



(3 equiv) **Pdt.** n.d. 38%

As described in eq. 1, Scheme 1, α-isopropylstyrene showed a tendency similar to α-butylstyrene (**1s**) in Figure 2D. In this case, the more stable isopropyl radical was exclusively released via β-scission, and propiophenone was obtained as the product. When α-methylenetetralin was used (eq. 2), methylative olefination was favored over the oxidative process to form 4-ethyl-1,2-dihydronaphthalene.

Figure S2. Unsuccessful substrates



The reactions of isopropenylpyridines and -thiophene afforded the desired products in disappointing yields, along with only small amounts of one-carbon homologation products.

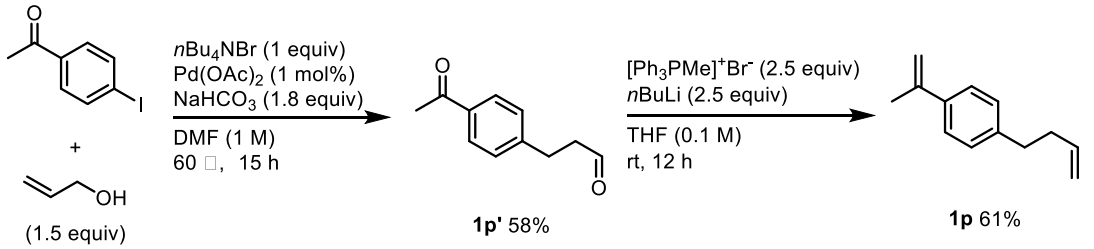
We examined the oxidative cleavage of α-methylstyrenes bearing strongly electron-withdrawing groups such as a nitrile or acetyl group at the para-position. However, no desired products were obtained. Instead, [2+2] photocyclization proceeded to give the corresponding dimeric cyclobutanes as the major products. This side reaction was likely induced by either triplet energy transfer or single-electron transfer from the excited photocatalyst to the styrenic substrates, which predominated over the triplet energy transfer to DBTSO and the subsequent process.

Experimental Procedure

Preparation of 1i, 1k, and 1l

An oven-dried 50-mL two-necked round-bottomed flask was charged with methyltriphenylphosphonium bromide (2.1 g, 6.0 mmol, 1.2 equiv) in dry THF (20 mL) under N_2 atmosphere and cooled at 0 ℃. *n*BuLi (1.6 M in *n*-hexane, 3.8 mL, 6.0 mmol, 1.2 equiv) was added dropwise, and the resulting mixture was stirred at 0 ℃ for 1 h, after which acetophenone (5.0 mmol, 1 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with *n*-hexane (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 50/1) afforded the corresponding α-methylstyrene as a colorless oil.

Preparation of 1p



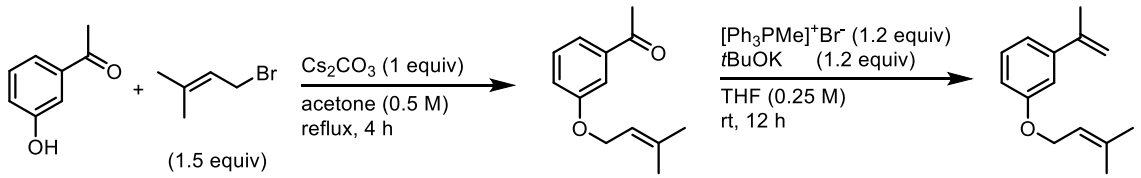
Synthesis of 1p':[5] An oven-dried 50-mL round-bottomed flask was charged with 4-iodoacetophenone (2.5 g, 10 mmol, 1 equiv), tetrabutylammonium bromide (3.2 g, 10 mmol, 1.0 equiv), sodium hydrogen carbonate (1.5 g, 18 mmol, 1.8 equiv), and palladium diacetate (22 mg, 0.10 mmol, 1.0 mol%) in DMF (10 mL). Allyl alcohol (1.0 mL, 15 mmol, 1.5 equiv) was then added. The resulting mixture was stirred at 60 ℃ for 15 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite, and water was then added to the filtrate. The aqueous layer was extracted with ethyl acetate (2 × 5 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane/EtOAc = 10/1 to 3/1) afforded dicarbonyl compound **1p'** (1.02 g, 5.8 mmol) as a colorless oil in 58% yield.
R_f = 0.3 (hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = 7.8 Hz, 2H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 201.0, 197.9, 146.2, 135.5, 128.8, 128.7,

44.9, 28.1, 26.7. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[6]

Synthesis of 1p: An oven-dried 50-mL two-necked round-bottomed flask was charged with methyltriphenylphosphonium bromide (4.5 g, 12.5 mmol, 2.5 equiv) in dry THF (35 mL) at 0 ℃ under a N_2 atmosphere. *n*BuLi (1.6 M in *n*-hexane, 7.8 mL, 12.5 mmol, 2.5 equiv) was added dropwise, and the resulting mixture was stirred at 0 ℃ for 2 h. A solution of **1p'** (0.88 g, 5.0 mmol, 1 equiv) in THF (15 mL) was added portionwise, and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with *n*-hexane (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane) afforded **1p** (527 mg, 3.1 mmol) as a colorless oil in 61% yield.

R_f = 0.6 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.86 (ddt, *J* = 17.4, 10.2, 6.6 Hz, 1H), 5.35 (s, 1H), 5.07–5.03 (m, 2H), 4.99–4.97 (m, 1H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.40–2.35 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.1, 141.3, 138.8, 138.2, 128.4, 125.5, 115.1, 111.9, 35.6, 35.1, 22.0; HRMS (ESI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{17}$: 173.1325; Found 173.1323.

Preparation of 1q



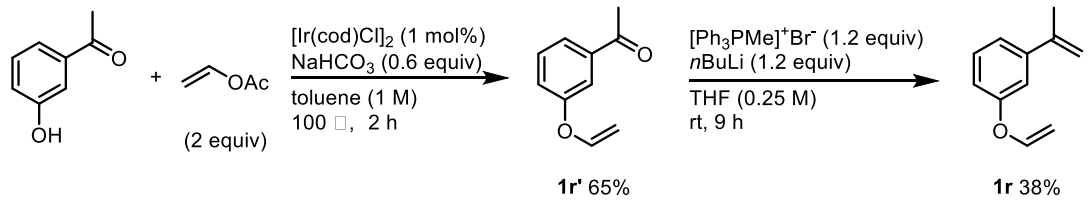
Synthesis of 1q':[7]An oven-dried 50-mL round-bottomed flask was charged with prenyl bromide (3.4 mL, 30 mmol, 1.5 equiv), 3-hydroxyacetophenone (2.8 g, 20 mmol, 1 equiv), and cesium carbonate (6.5 g, 20 mmol, 1.0 equiv) in acetone (40 mL). The reaction mixture was refluxed in an oil bath for 4 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite, and concentrated under reduced pressure. The resulting crude product was used directly in the next step without further purification.

Synthesis of 1q: An oven-dried 200-mL two-necked round-bottomed flask was charged with methyltriphenylphosphonium bromide (8.6 g, 24 mmol, 1.2 equiv) in dry THF (80 mL) at 0 ℃ under a N_2 atmosphere. *t*BuOK (2.7 g, 24 mmol, 1.2 equiv) was added portionwise, and the resulting mixture was stirred at 0 ℃ for 2 h. The crude **1q'** obtained

above was added to the reaction mixture, and the residue in the vial was diluted with THF (5 mL), and the resulting solution was added to the reaction mixture. The mixture was then stirred for 12 h at room temperature. It was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with *n*-hexane (3 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane) afforded **1q** (1.58 g, 7.8 mmol) as a yellow oil in 39% yield.

R_f = 0.5 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.83 (dd, *J* = 7.8, 2.4 Hz, 1H), 5.52–5.49 (m, 1H), 5.37 (s, 1H), 5.08 (s, 1H), 4.52 (d, *J* = 6.6 Hz, 2H), 2.14 (s, 3H), 1.80 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 158.9, 143.3, 142.8, 138.5, 129.2, 119.7, 118.1, 113.3, 112.8, 112.4, 64.8, 26.0, 22.0, 18.4; HRMS (ESI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{14}H_{19}O$: 203.1430; Found 203.1427.

Preparation of 1r



Synthesis of 1r':[8] An oven-dried 20-mL two-necked round-bottomed flask was charged with 3-hydroxyacetophenone (0.68 g, 5.0 mmol, 1 equiv), sodium hydrogen carbonate (0.25 g, 3.0 mmol, 0.60 equiv), and $[Ir(cod)Cl]_2$ (34 mg, 0.050 mmol, 1.0 mol%) in toluene (5 mL). Vinyl acetate (0.93 mL, 10 mmol, 2.0 equiv) was then added. The resulting mixture was heated at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 30/1) provided **1r'** (530 mg, 3.3 mmol) as a yellow oil in 65% yield.

R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (s, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 8.1, 2.7 Hz, 1H), 6.67 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.82 (dd, *J* = 13.8, 1.8 Hz, 1H), 4.51 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ; 197.6, 157.1, 147.7, 138.8, 130.0, 123.3, 122.1, 116.2, 96.4, 26.9; HRMS (ESI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{10}O_2$: 163.0754; Found 163.0751.

Synthesis of 1r: An oven-dried 30-mL two-necked round-bottomed flask was charged with methyltriphenylphosphonium bromide (1.4 g, 4.0 mmol, 1.2 equiv) in dry THF (13

mL) at 0 ℃ under N_2 atmosphere. *n*BuLi (1.6 M in *n*-hexane, 2.5 mL, 4.0 mmol, 1.2 equiv) was added dropwise, and the resulting mixture was stirred at 0 ℃ for 1 h. *O*-vinylated compound **1r'** obtained above (0.53 g, 3.3 mmol, 1 equiv) was added, and the reaction mixture was stirred for 9 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with *n*-hexane (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on monolithic silica column (hexane) afforded **1r** (203 mg, 1.3 mmol) as a yellow oil in 38% yield.

R_f = 0.6 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.10 (s, 1H), 6.92 (dd, *J* = 7.8, 2.9 Hz, 1H), 6.66 (dd, *J* = 13.4, 6.1 Hz, 1H), 5.38 (s, 1H), 5.11 (s, 1H), 4.77 (dd, *J* = 13.4, 1.6 Hz, 1H), 4.44 (dd, *J* = 6.1, 1.6 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 156.9, 148.4, 143.2, 142.8, 129.5, 120.6, 116.1, 114.6, 113.3, 95.2, 21.9; HRMS (APCI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{13}O$: 161.0961; Found 161.0960.

Standard procedure for oxidative cleavage of styrenes (SP)

A 10-mL Schlenk tube was charged with dibenzothiophene *S*-oxide (40 mg, 0.20 mmol, 1 equiv), *fac*-Ir(ppy)$_3$ (6.5 mg, 0.010 mmol, 5.0 mol%), an α-substituted styrene derivative **1** (0.60 mmol, 3.0 equiv), and DMSO (2.0 mL). The freeze-pump-thaw cycle was repeated three times. The reaction tube was then irradiated with a Kessil LED lamp (20 W) at room temperature for 3 h. After irradiation, the reaction mixture was diluted with distilled water (10 mL) and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 40/1) to obtain the corresponding acetophenone **2**.

Scale-up reaction

The reaction was performed on a 5-time scale according to **SP** using dibenzothiophene *S*-oxide (200 mg, 1.0 mmol, 1 equiv), 1-chloro-4-(1-methylethenyl)benzene (**1c**, 0.43 mL, 3.0 mmol, 3.0 equiv), *fac*-Ir(ppy)$_3$ (32.7 mg, 0.050 mmol, 5.0 mol%), and DMSO (10 mL). The reaction mixture was irradiated with Kessil LED lamps (20 W × 2) for 5 h. Purification was done by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 40/1) to give **2c** (101 mg, 0.66 mmol, 66%) as a colorless oil.

Competition experiments (Scheme 3)

Oxidative cleavage using excited DBTSO

The reaction was carried out according to **SP** using **1c** (57 μL, 0.40 mmol, 2.0 equiv) and **1h** (64 μL, 0.40 mmol, 2.0 equiv). After the irradiation, the reaction mixture was diluted with distilled water (10 mL) and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 40/1) to obtain **2c** (10.1 mg, 0.065 mmol) as a colorless oil in 33% yield. The yield of the acetophenone **2h** was analyzed to be 4% using the ^{1}H NMR spectrum of the crude mixture.

Oxidative cleavage using ruthenium tetroxide[9]

A 30-mL two-necked round-bottomed flask was charged with $RuCl_3$ (10 mg, 0.050 mmol, 0.10 equiv), **1c** (71 μL, 0.50 mmol, 1 equiv), and **1h** (80 μL, 0.50 mmol, 1.0 equiv) in H_2O (1.4 mL) and MeCN (8.6 mL). $NaIO_4$ (210 mg, 1.0 mmol, 2.0 equiv) was added slowly over 10 min, and the resulting mixture was stirred for 4 h at room temperature. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography on amino-modification of monolithic silica column[10] (hexane/EtOAc = 1/0 to 20/1) afforded 4'-methoxyacetophenone (**2h**, 32.2 mg, 0.21 mmol) as a white solid in 43% yield. The yield of the acetophenone **2c** was analyzed using the ^{1}H NMR spectrum of the crude mixture. The ^{1}H NMR yield of **2c** was determined to be 12%, based on its signals at δ 7.90 (d, J = 9.0 Hz, 2H) and δ 2.60 (s, 3H) that are consistent with the reported data[11] and the signal at δ 4.93 (s, 2H) for dibromomethane (35 μL, 0.50 mmol) as an internal standard (Figure S56).

Trapping of a methyl radical (Scheme 4A)

The reaction was carried out on a half scale according to **SP** using **1a** (39 μL, 0.30 mmol, 3.0 equiv), dibenzothiophene *S*-oxide (20 mg, 0.10 mmol, 1 equiv), and TEMPO (16 mg, 0.10 mmol, 1.0 equiv). After the irradiation, the reaction mixture was diluted with distilled water (10 mL) and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude mixture was analyzed using ^{1}H NMR. The ^{1}H NMR yield of **3** was determined to be 18%, based on its signals at δ 2.61 (s, 3H) and δ 1.08 (s, 6H) that are consistent with the reported data[12] and the signal at δ 4.93 (s, 2H) for dibromomethane (0.1 mmol, 7 μL) as an internal standard (Figure S57).

^{18}O-Labeling experiment using DBTSO-^{18}*O* (Scheme 4B)

The reaction was performed on a half scale according to **SP** using **1a** (39 μL, 0.30 mmol, 3.0 equiv) and ^{18}O-labelled dibenzothiophene *S*-oxide (20 mg, 0.10 mmol, 1 equiv, ^{18}O:^{16}O = 96:4). After the irradiation, the reaction mixture was subjected to short-path filtration through silica gel (hexane/EtOAc = 3/1) to remove DMSO, and the resulting material was further purified by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 40/1) to obtain **2a** (9.8 mg, 0.082 mmol, 94% ^{16}O) as a colorless oil in 82% yield.

Light on/off experiment (Scheme 4C)

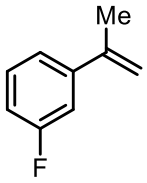
The reaction was performed according to **SP** using **1a** (78 μL, 0.60 mmol, 3.0 equiv), mesitylene (27.6 μL, 0.20 mmol) as an internal standard, and DMSO-d_6 (2.0 mL) as a solvent.

The reaction vial was set to a vial holder and irradiated with a Kessil lamp (20 W) for 10 min to analyze the ^{1}H NMR yield, then stirred for 10 min in the dark to analyze the ^{1}H NMR yield. The on/off cycle was repeated two more times.

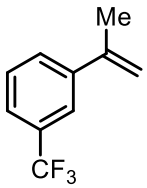
Investigation of the selectivity of β-scission (Scheme 4D)

The reaction was carried out according to **SP** using 2-phenyl-1-hexene (**1s**, 107 μL, 0.60 mmol, 3.0 equiv) and dibenzothiophene *S*-oxide (40 mg, 0.20 mmol, 1 equiv). After irradiation, the reaction mixture was diluted with distilled water (10 mL) and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on monolithic silica column (hexane/EtOAc = 1/0 to 40/1) to obtain the mixture of valerophenone (**2s**, 9.6 mg, 0.059 mmol, 30%) and propiophenone (**2s'**, 3.1 mg, 0.023 mmol, 12%).[13, 14] See Figure S58 for the determination of the yields.

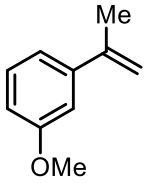
Characterization Data



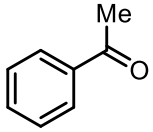
1-fluoro-3-(prop-1-en-2-yl)benzene (1i):
Purification was done by silica gel chromatography with an eluent (hexane) as a colorless oil (405 mg, 3.0 mmol, 60%); R_f = 0.6 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31–7.24 (m, 2H), 7.15 (dt, *J* = 10.8, 2.1 Hz, 1H), 6.98–6.95 (m, 1H), 5.39 (s, 1H), 5.13 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.0 (d, *J* = 244.5 Hz), 143.7 (d, *J* = 7.2 Hz), 142.3, 129.7 (d, *J* = 8.6 Hz), 121.3, 114.3 (d, *J* = 21.7 Hz), 113.6, 112.6 (d, *J* = 23.3 Hz), 21.8; ^{19}F NMR (564 MHz, $CDCl_3$): δ –114.1. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[15]



1-(prop-1-en-2-yl)-3-(trifluoromethyl)benzene (1k):
Purification was done by silica gel chromatography with an eluent (hexane/EtOAc = 1/0 to 100/1) as a colorless oil (456 mg, 2.4 mmol, 49%); R_f = 0.6 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 5.43 (s, 1H), 5.19 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.2, 142.1, 130.7 (q, *J* = 31.9 Hz), 128.9, 128.8, 124.4 (q, *J* = 273 Hz), 124.2 (q, *J* = 3.8 Hz), 122.4 (q, *J* = 4.4 Hz), 114.2, 21.8; ^{19}F NMR (564 MHz, $CDCl_3$): δ –63.0. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[16]

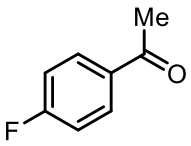


1-methoxy-3-(prop-1-en-2-yl)benzene (1l):
Purification was done by silica gel chromatography with an eluent (hexane/EtOAc = 1/0 to 100/1) as a colorless oil (760 mg, 5.0 mmol, 99%); R_f = 0.4 (hexane/EtOAc = 100/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 7.01 (s, 1H), 6.83 (dd, *J* = 7.8, 2.1 Hz, 1H), 5.37 (s, 1H), 5.09 (s, 1H), 3.83 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.6, 143.3, 142.9, 129.3, 118.2, 112.9, 112.7, 111.6, 55.4, 22.0. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[17]



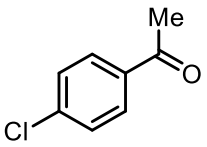
acetophenone (2a):
The reaction was performed on half the scale of **SP** with the same reaction time of 3 h. A colorless oil (9.6 mg, 80%) was obtained from **1a**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 2.62

(s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.4, 137.2, 133.3, 128.7, 128.5, 26.8. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[18]



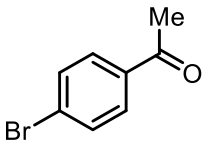
4'-fluoroacetophenone (2b):

The reaction was performed on half the scale of **SP** with the same reaction time of 3 h. A colorless oil (6.9 mg, 50%) was obtained from **1b**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00–7.97 (m, 2H), 7.15−7.11 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.7, 165.9 (d, J = 254.7 Hz), 133.7, 131.1 (d, J = 10.1 Hz), 115.8 (d, J = 21.6 Hz), 26.7; ^{19}F NMR (564 MHz, $CDCl_3$): δ –105.7. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[12]



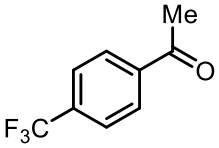
4'-chloroacetophenone (2c):

A colorless oil (22.0 mg, 0.14 mmol, 71%) was obtained from **1c** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (151 MHz,): δ 197.0, 139.7, 135.5, 129.9, 129.0, 26.7. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[12]



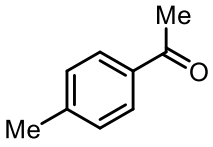
4'-bromoacetophenone (2d):

The ^{1}H NMR yield of **2d** was determined to be 18%, based on its signals at δ 7.80 (m, 2H) that is consistent with the reported data[19] and the signal at δ 6.08 (s, 3H) for 1,3,5-trimethoxybenzene (34 mg, 0.20 mmol) as an internal standard (Figure S28).



4'-trifluoromethylacetophenone (2e):

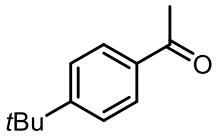
The ^{1}H NMR yield of **2e** was determined to be 16%, based on its signals at δ 8.06 (d, J = 8.4 Hz) and δ 7.73 (d, J = 8.4 Hz) that are consistent with the reported data[20] and the signal at δ 4.93 (s, 2H) for dibromomethane (14 μL, 0.20 mmol) as an internal standard (Figure S29).



4'-methylacetophenone (2f):

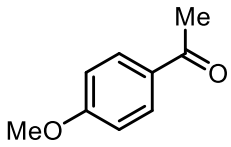
The reaction was performed on half the scale of **SP** with the same reaction time of 3 h. A colorless oil (4.1 mg, 31%) was obtained from **1f**. Purification was done by monolithic silica column with an eluent

(hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.1, 144.0, 134.8, 129.4, 128.6, 26.7, 21.8. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[21]



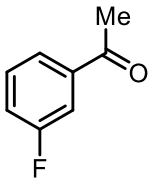
4'-*tert*-butylacetophenone (2g):

A colorless oil (12.4 mg, 35%) was obtained from **1g** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 2.59 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.0, 157.0, 134.7, 128.4, 125.7, 35.3, 31.2, 26.7. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[22]



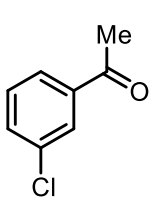
4'-methoxyacetophenone (2h):

The ^{1}H NMR yield of **2h** was determined to be 7%, based on its signal at δ 7.94 (d, *J* = 8.4 Hz) that are consistent with the reported data[23] and the signal at δ 4.93 (s, 2H) for dibromomethane (14 μL, 0.20 mmol) as an internal standard (Figure S34).



3'-fluoroacetophenone (2i):

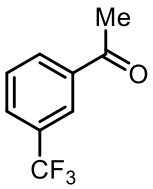
A colorless oil (21.5 mg, 78%) was obtained from **1i** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 9.3 Hz, 1H), 7.45 (dt, *J* = 5.6, 7.2 Hz, 1H), 7.27 (dt, *J* = 3.4, 7.2 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.0, 163.0 (d, *J* = 247.5 Hz), 139.3 (d, *J* = 5.7 Hz), 130.4 (d, *J* = 7.2 Hz), 124.3, 120.3 (d, *J* = 21.7 Hz), 115.1 (d, *J* = 21.6 Hz), 26.9; ^{19}F NMR (564 MHz, $CDCl_3$): δ −112.3. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[24]



3'-chloroacetophenone (2j):

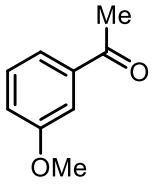
A colorless oil (25.4 mg, 82%) was obtained from **1j** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.9,

138.7, 135.1, 133.2, 130.1, 128.6, 126.6, 26.8. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[25]



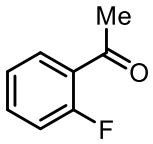
3'-trifluoromethylacetophenone (2k):

A colorless oil (19.0 mg, 50%) was obtained from **1k** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.8, 137.6, 131.6, 131.4 (q, *J* = 32.8 Hz), 129.7 (q, *J* = 4.2 Hz), 129.5, 125.3 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 273.0 Hz), 26.8; ^{19}F NMR (564 MHz, $CDCl_3$): δ −63.2. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[26]



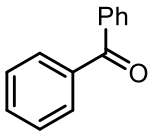
3'-methoxyacetophenone (2l):

A white powder (21 mg, 68%) was obtained from **1l** according to **SP**. Purification was done by silica gel chromatography with an eluent (hexane/EtOAc = 1/0 to 30/1); R_f = 0.3 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.11 (dd, *J* = 7.8, 2.7 Hz, 1H), 3.86 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.1, 160.0, 138.6, 129.7, 121.3, 119.8, 112.5, 55.6, 26.9. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[27]



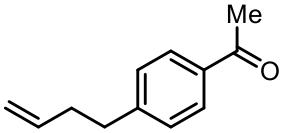
2'-fluoroacetophenone (2n):

A colorless oil (15.1 mg, 55%) was obtained from **1n** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (td, *J* = 7.8, 1.6 Hz, 1H), 7.54–7.51 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 11.1, 8.4 Hz, 1H), 2.65 (d, *J* = 4.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.2 (d, *J* = 2.9 Hz), 162.4 (d, *J* = 254.7 Hz), 134.9 (d, *J* = 8.6 Hz), 130.7, 125.8 (d, *J* = 11.6 Hz), 124.5 (d, *J* = 4.4 Hz), 116.8 (d, *J* = 23.1 Hz), 31.7 (d, *J* = 7.2 Hz); ^{19}F NMR (564 MHz, $CDCl_3$): δ −109.7. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[28]



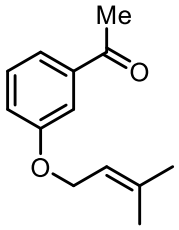
benzophenone (2o):

A white powder (14.0 mg, 0.768 mmol, 38%) was obtained from **1o** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.7 Hz, 4H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.9, 137.7, 132.6, 130.2, 128.4. All the resonances in the ^{1}H and ^{13}C NMR spectra were consistent with the reported value.[12]



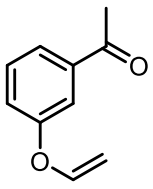
4'-(3-butenyl)acetophenone (2p):

A colorless oil (8.7 mg, 25%) was obtained from **1p** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.83 (ddt, *J* = 17.4, 10.2, 6.4 Hz, 1H), 5.01–4.98 (m, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 3H), 2.41–2.37 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.1, 147.9, 137.6, 135.2, 128.8, 128.6, 115.6, 35.5, 35.2, 26.7; HRMS (APCI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{12}H_{15}O$: 175.1117; Found 175.1118.



3'-((3-methyl-2-butenyl)oxy)acetophenone (2q):

A colorless oil (24.4 mg, 60%) was obtained from **1q** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.1 Hz, 1H), 7.50 (s, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.12 (dd, *J* = 8.1, 2.7 Hz, 1H), 5.51–5.48 (m, 1H), 4.56 (d, *J* = 6.6 Hz, 2H), 2.59 (s, 3H), 1.81 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 198.2, 159.2, 138.9, 138.5, 129.7, 121.2, 120.4, 119.3, 113.3, 65.1, 26.9, 26.0, 18.4; HRMS (ESI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{17}O_2$: 205.1223; Found 205.1221.



3'-vinyloxyacetophenone (2r):

A yellow oil (19.4 mg, 60%) was obtained from **1r** according to **SP**. Purification was done by monolithic silica column with an eluent (hexane/EtOAc = 1/0 to 40/1); R_f = 0.4 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (s, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 8.1, 2.7 Hz, 1H), 6.67 (dd, *J* = 13.8, 6.0 Hz, 1H), 4.82 (dd, *J* = 13.8, 1.8 Hz, 1H), 4.51 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.6, 157.1, 147.7, 138.8, 130.0, 123.3, 122.1, 116.2, 96.4, 26.9; HRMS (ESI-MS, positive) *m/z*: $[M+H]^+$ Calcd. for $C_{10}H_{11}O_2$: 163.0754; Found 163.0751.

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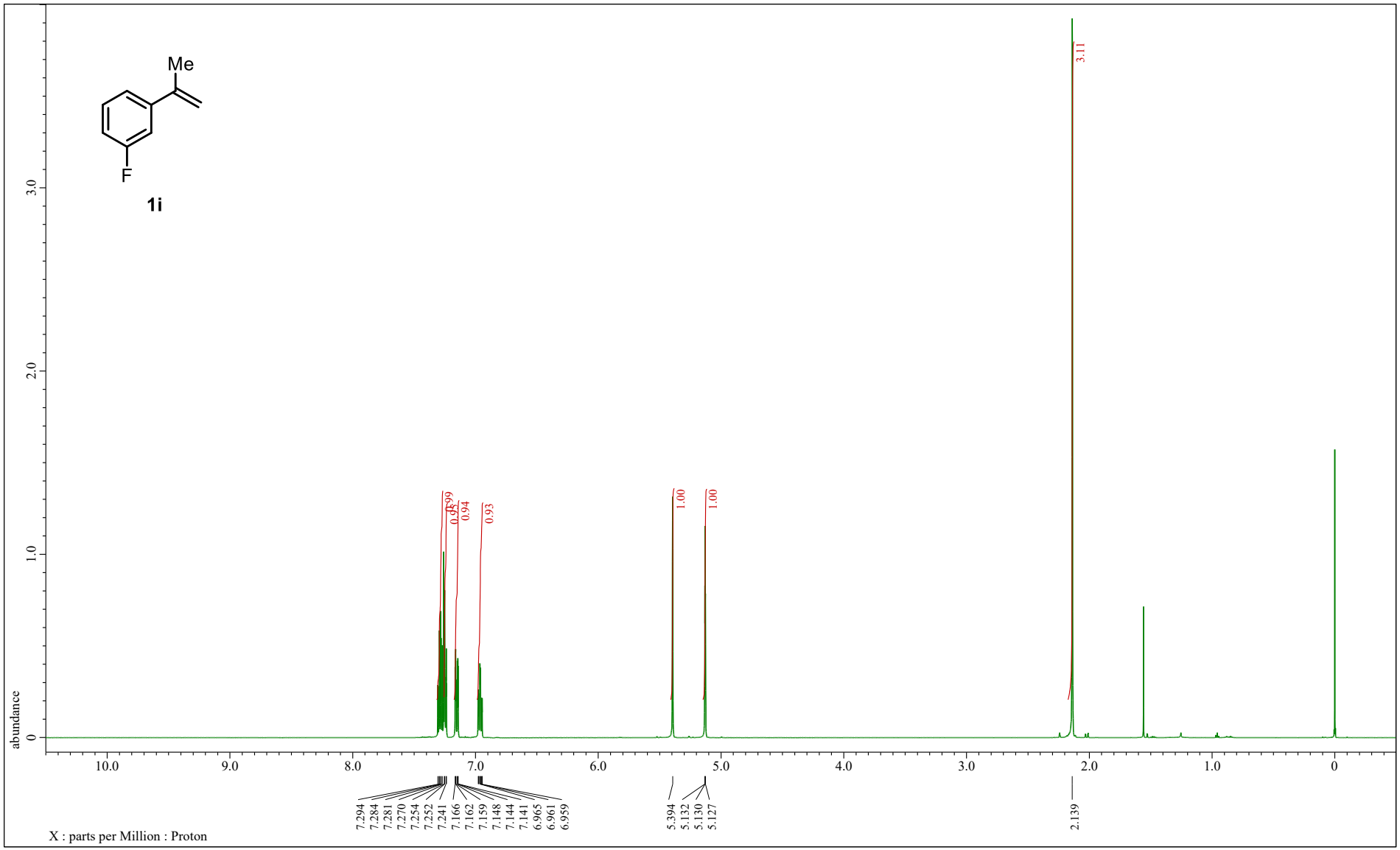

Figure S3. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1i**.

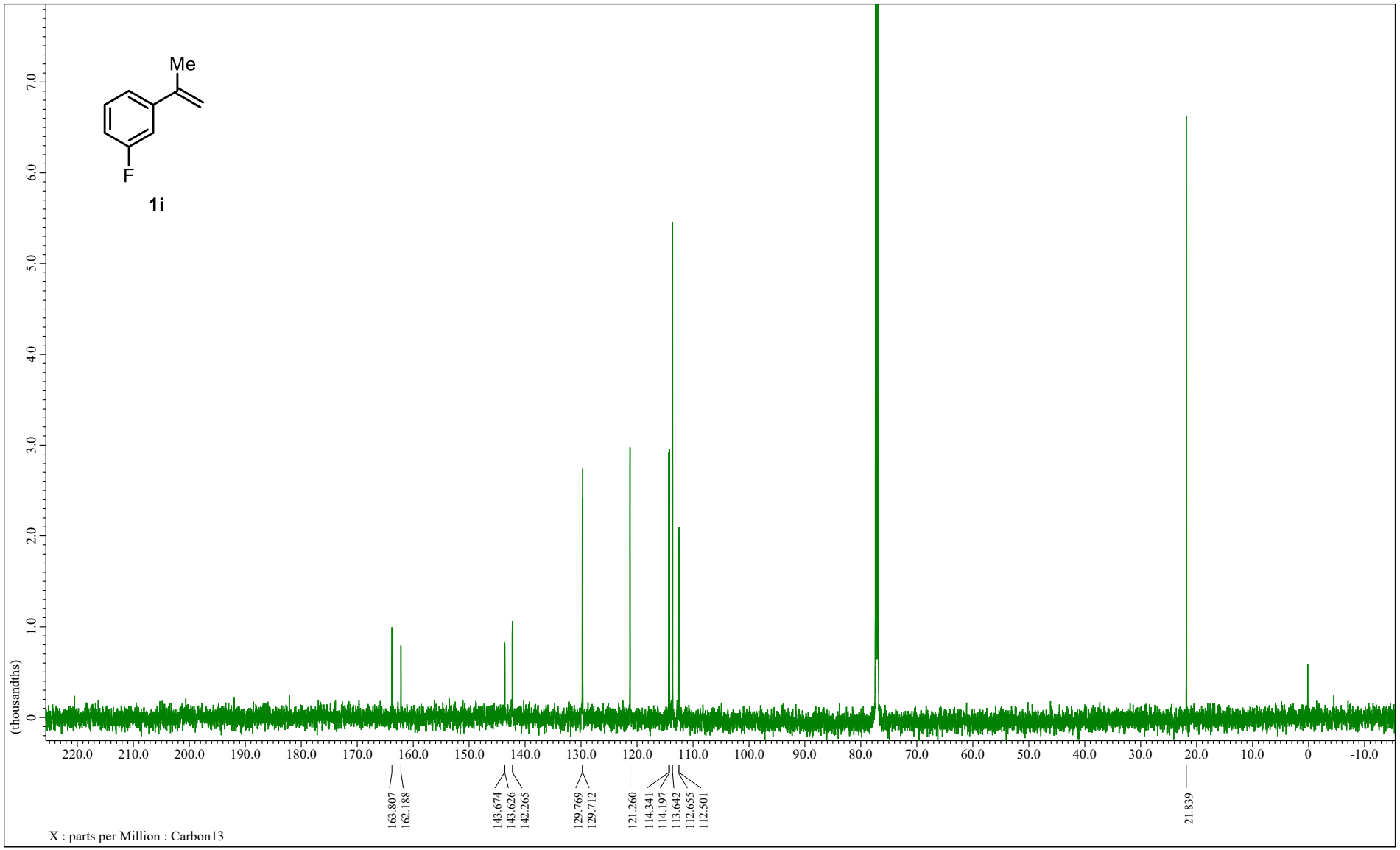

Figure S4. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1i**.

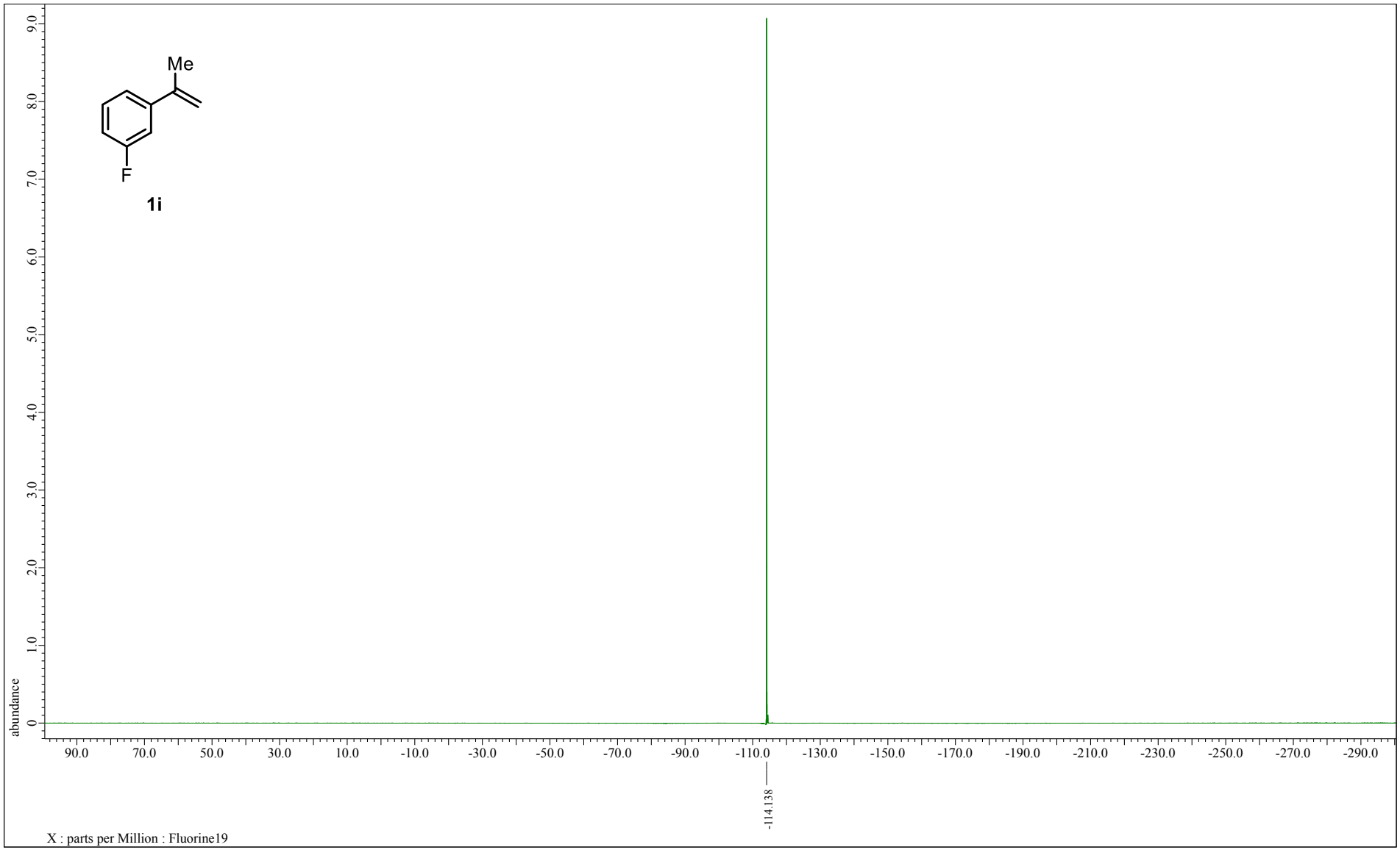

Figure S5. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **1i**.

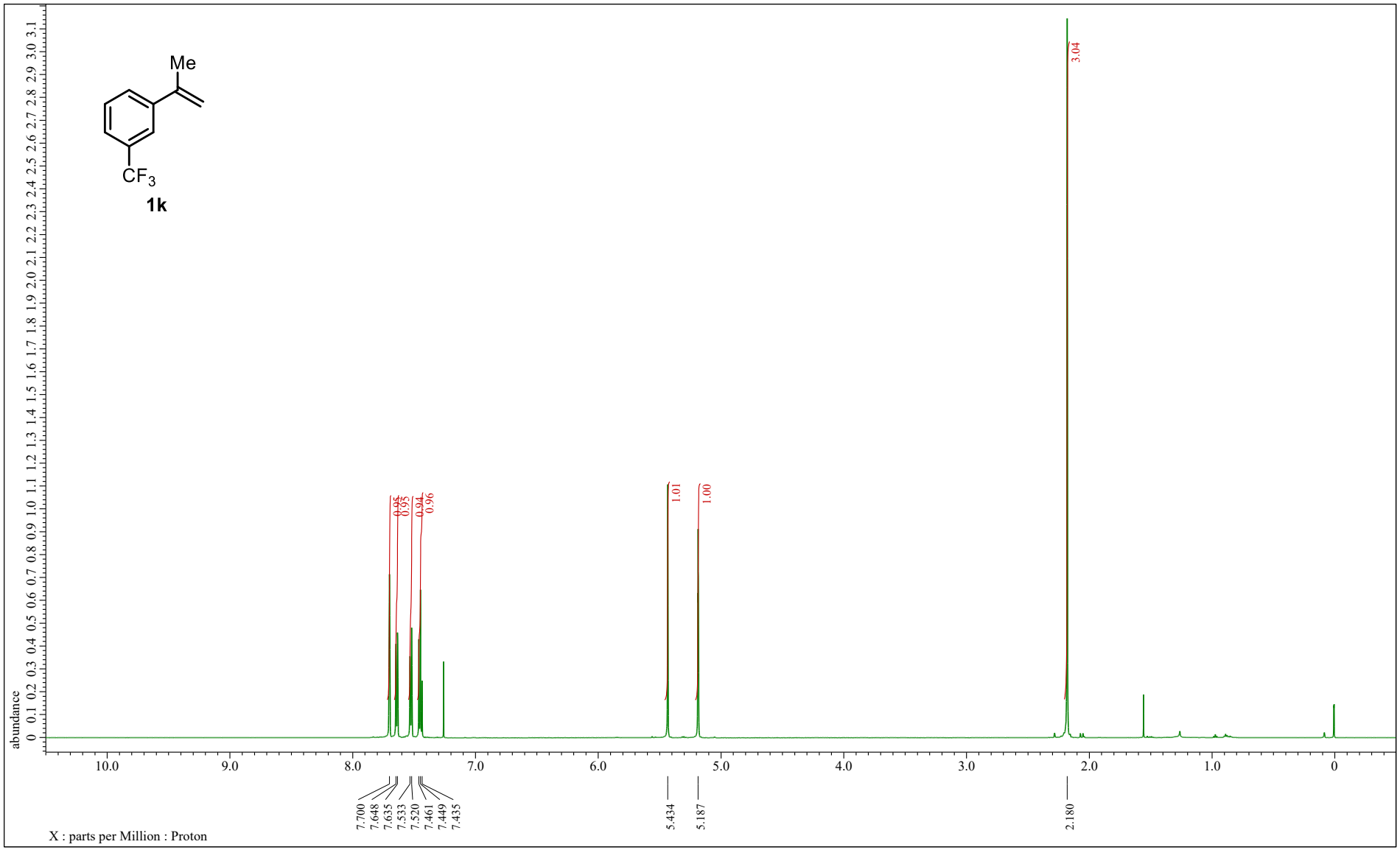

Figure S6. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1k**.

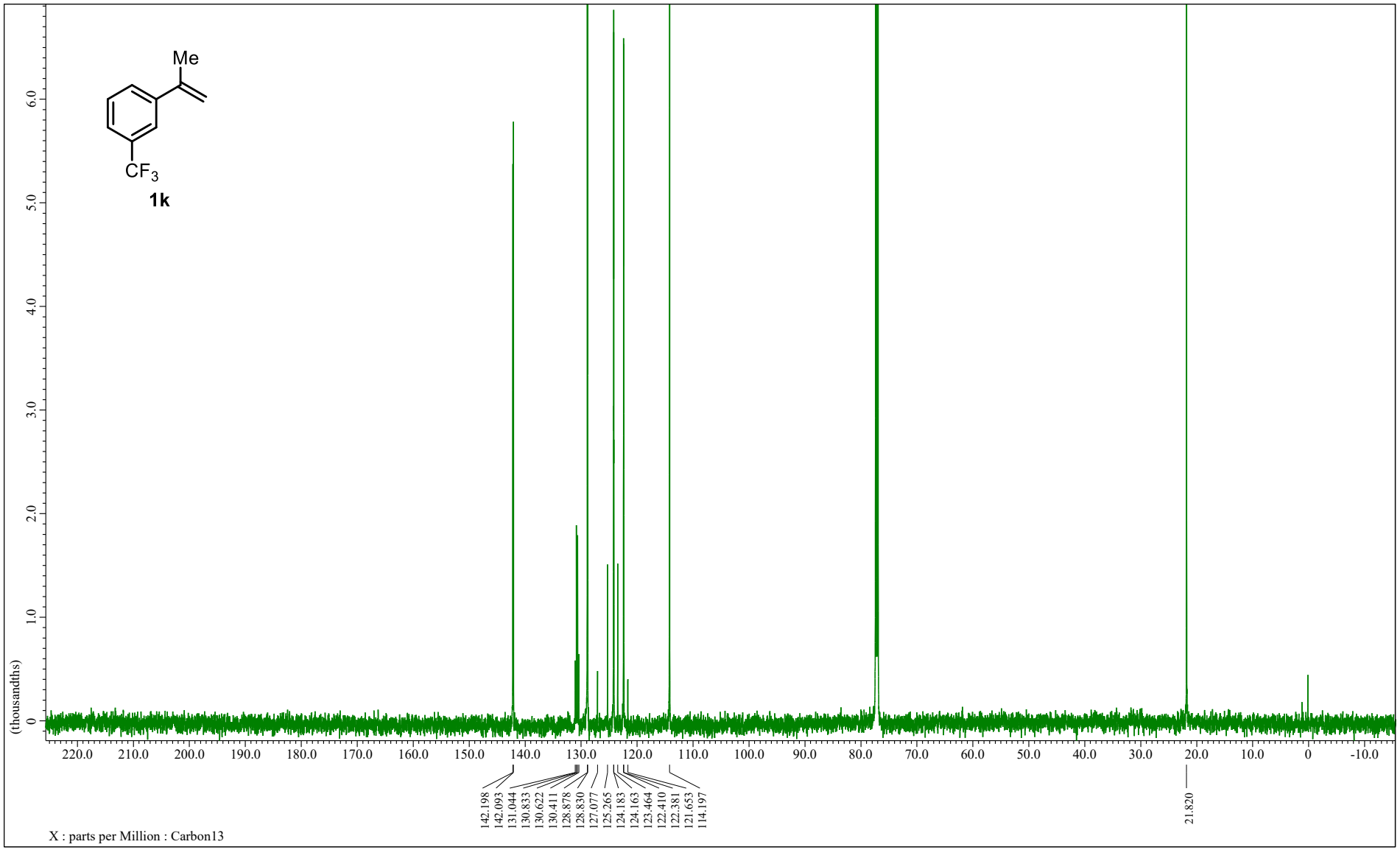

Figure S7. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1k**.

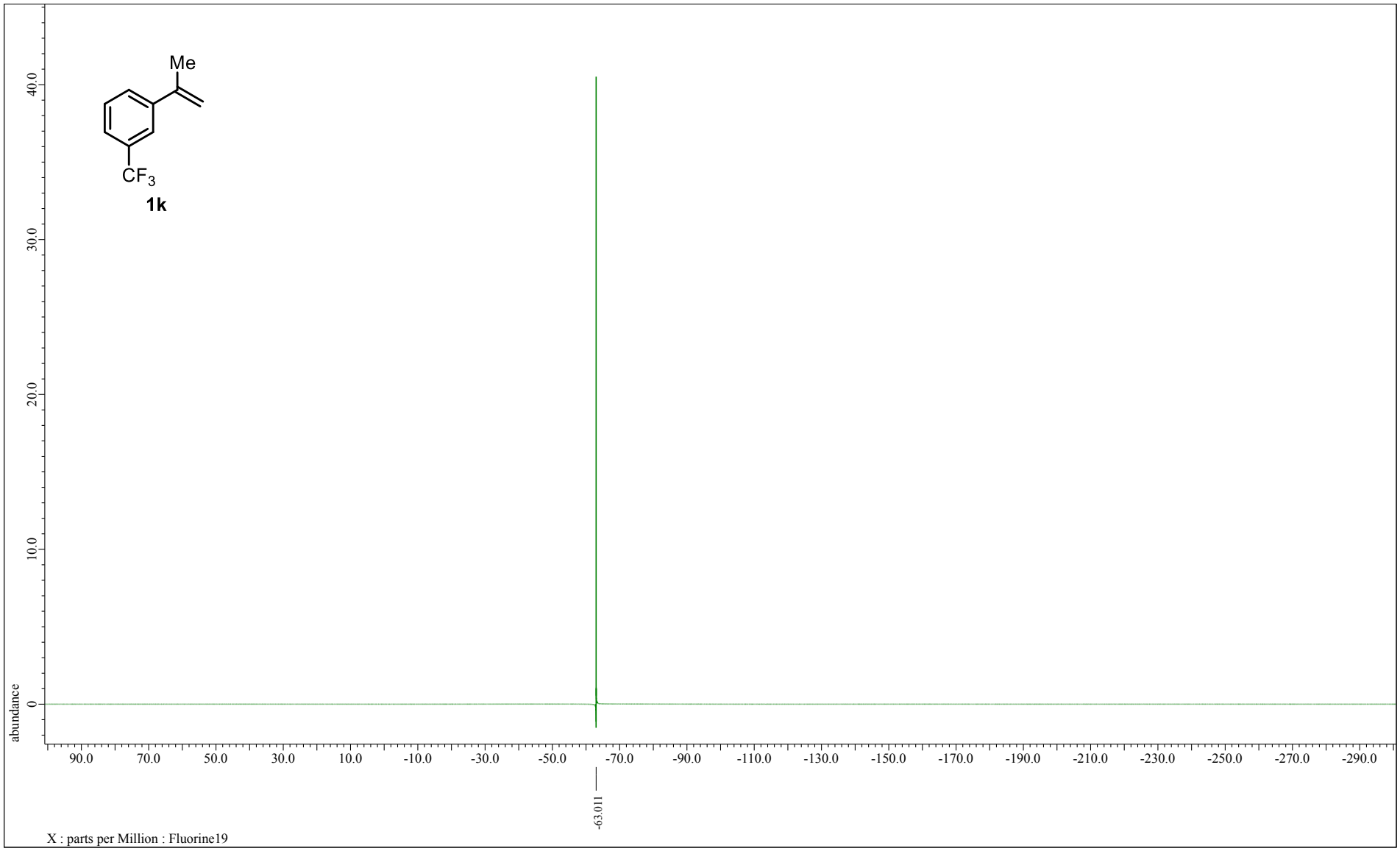

Figure S8. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **1k**.

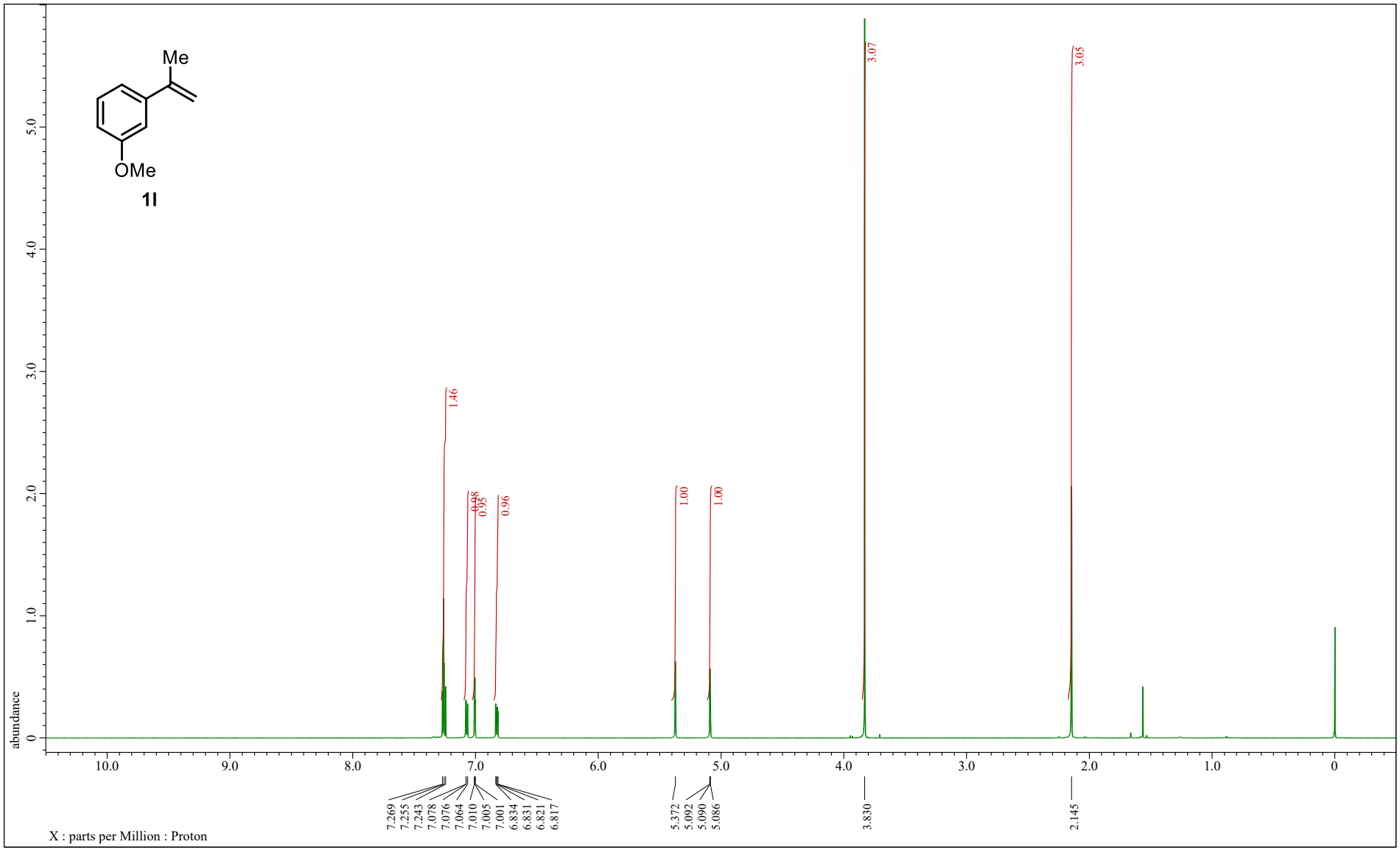

Figure S9. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1l**.

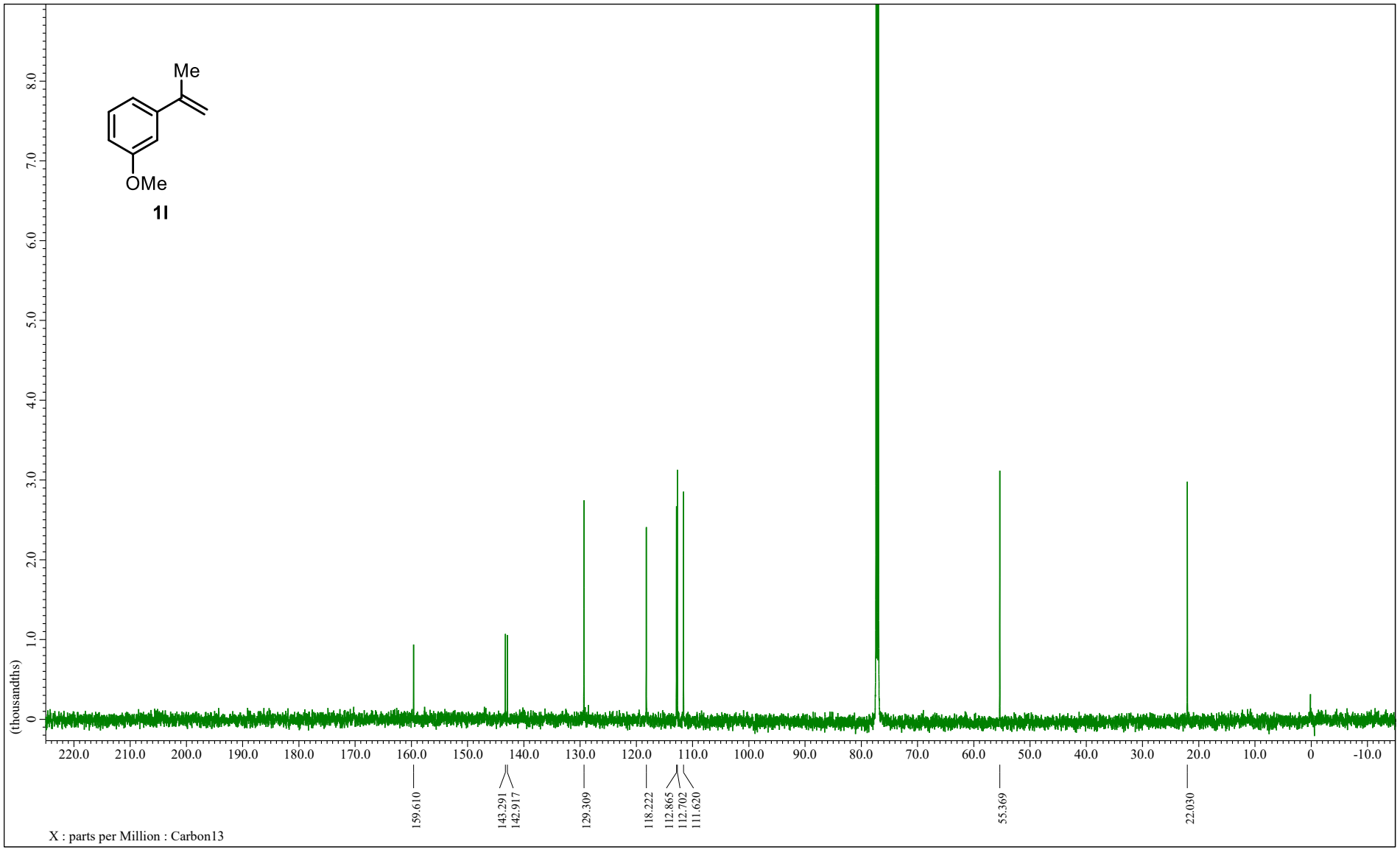

Figure S10. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1l**.

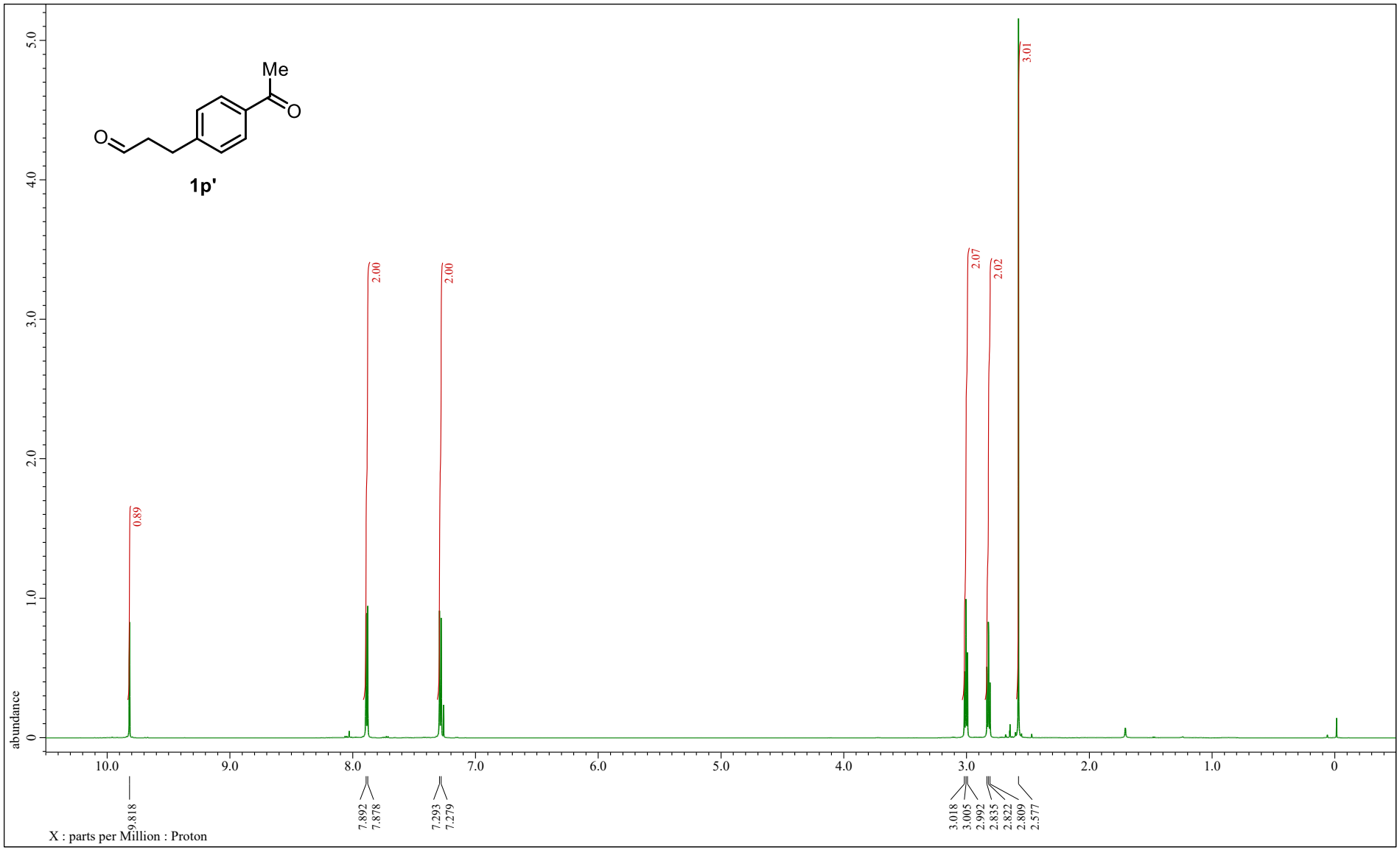

Figure S11. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1p'**.

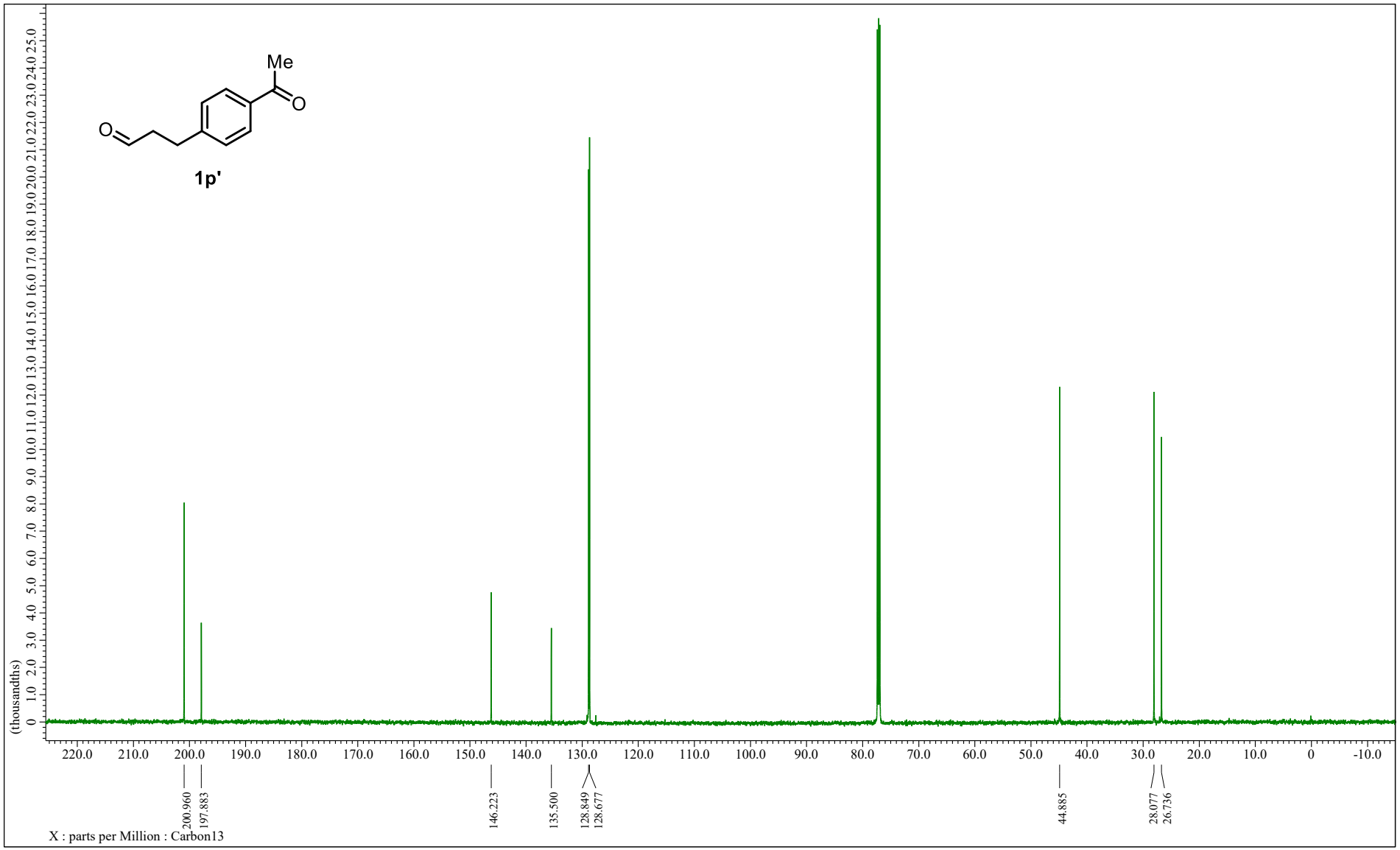

Figure S12. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1p'**.

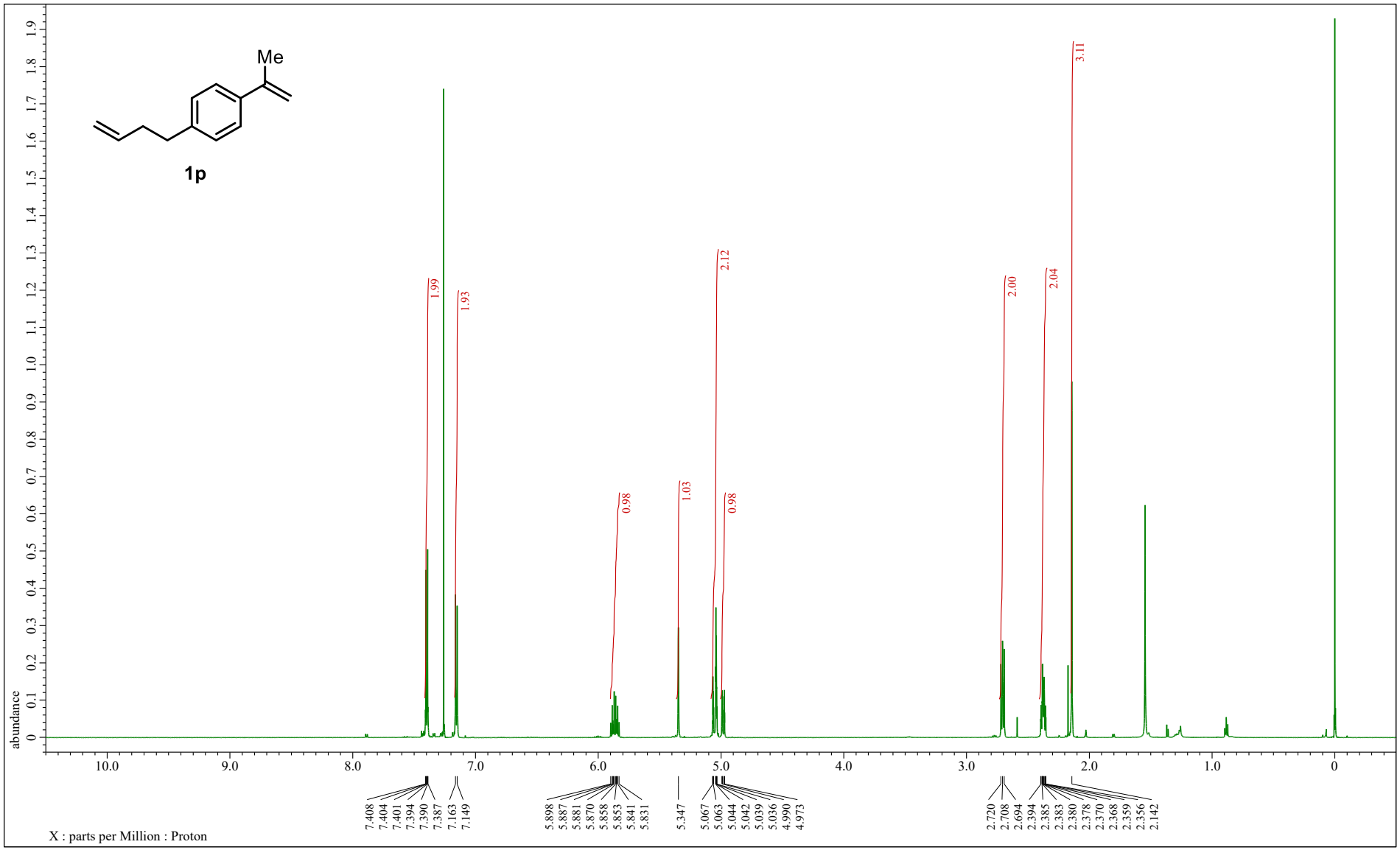

Figure S13. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1p**.

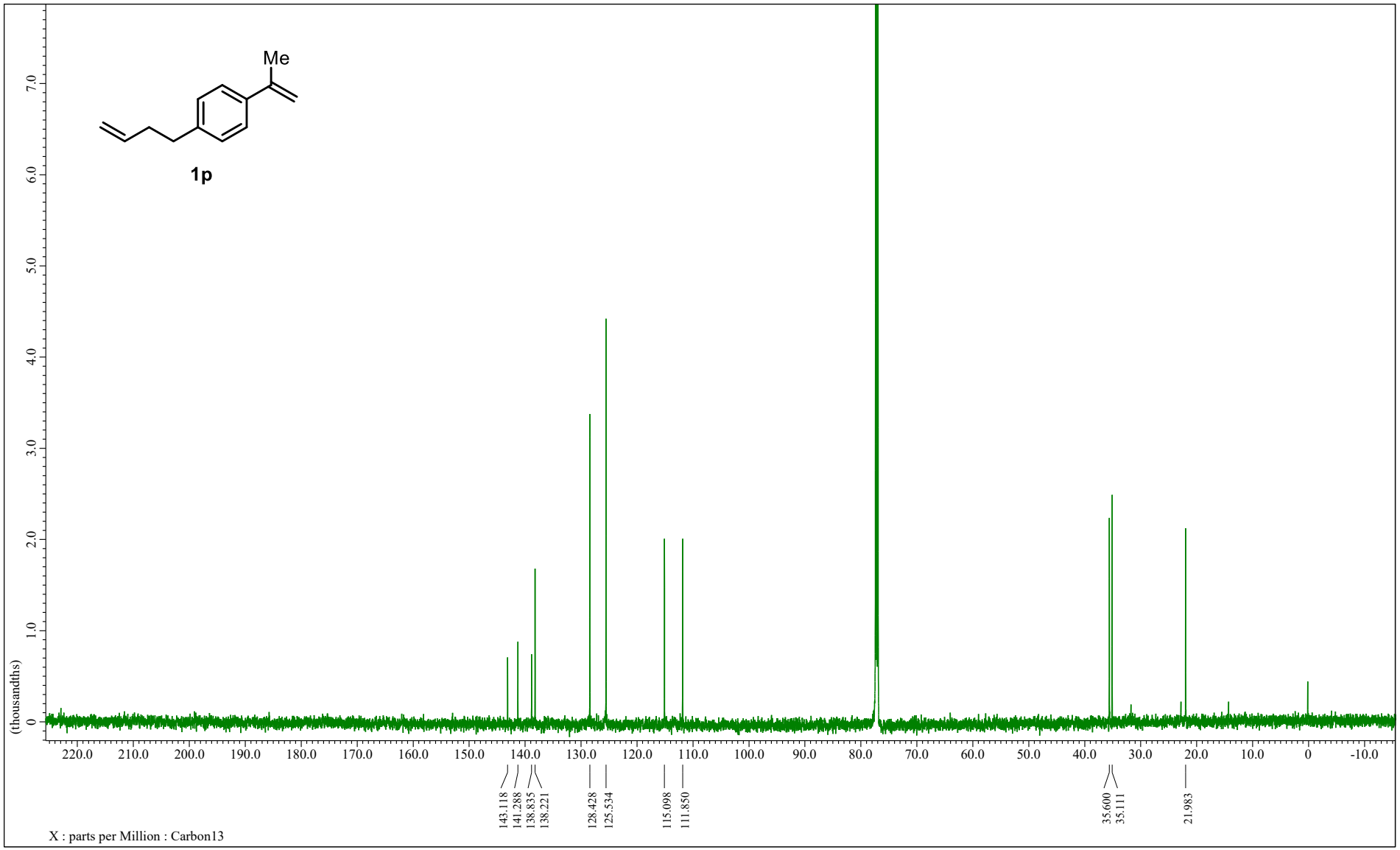

Figure S14. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1p**.

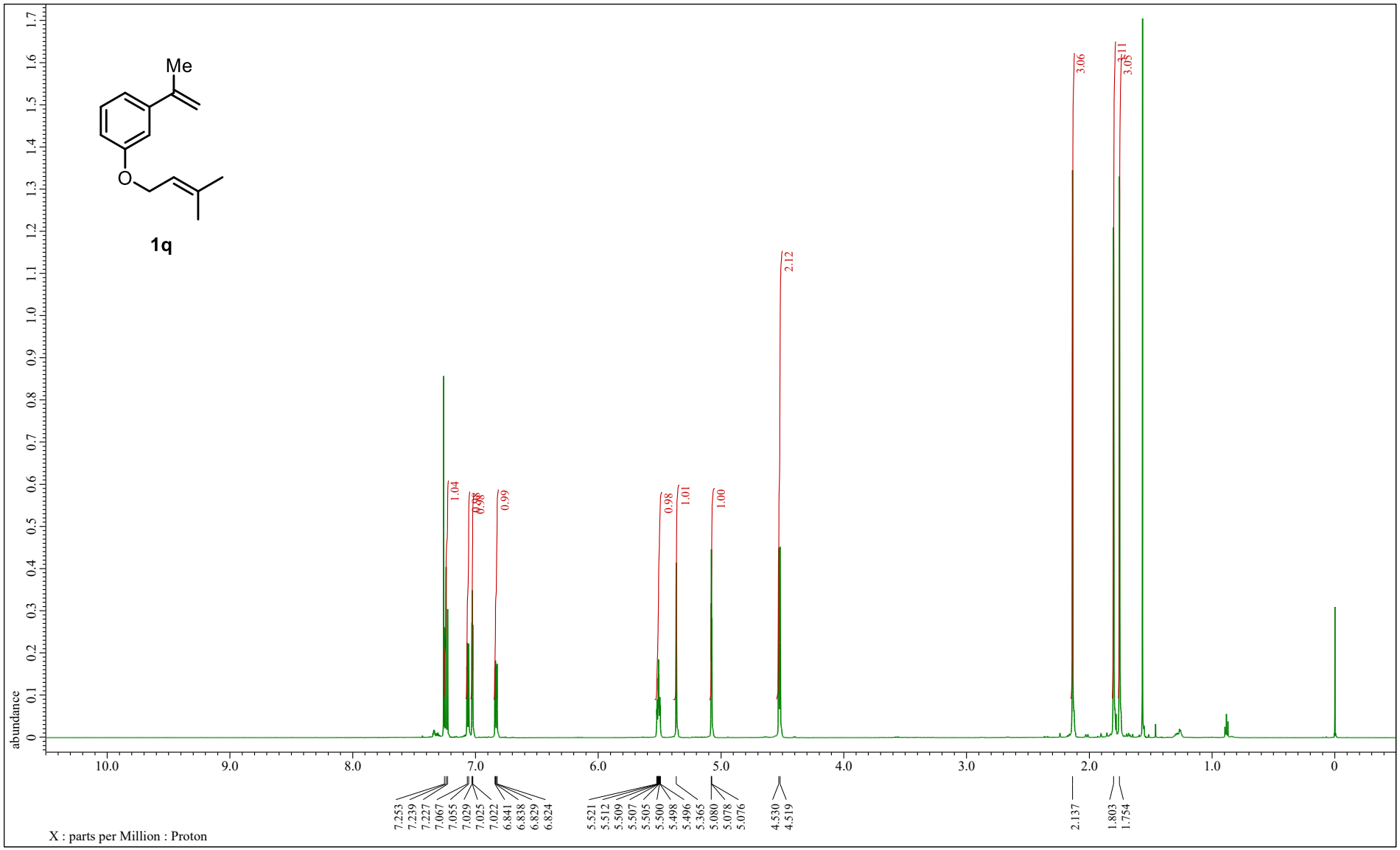

Figure S15. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1q**.

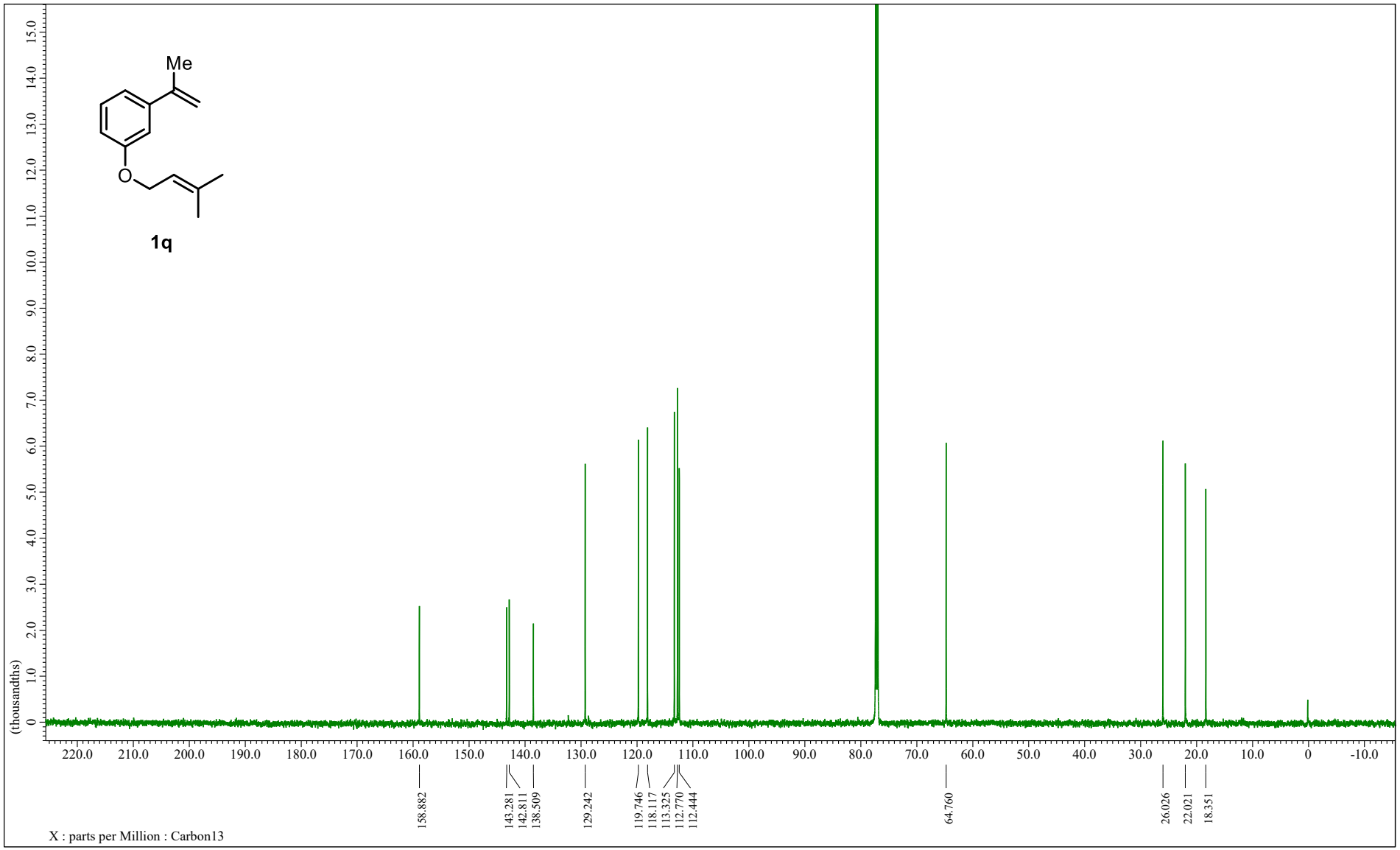

Figure S16. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1q**.

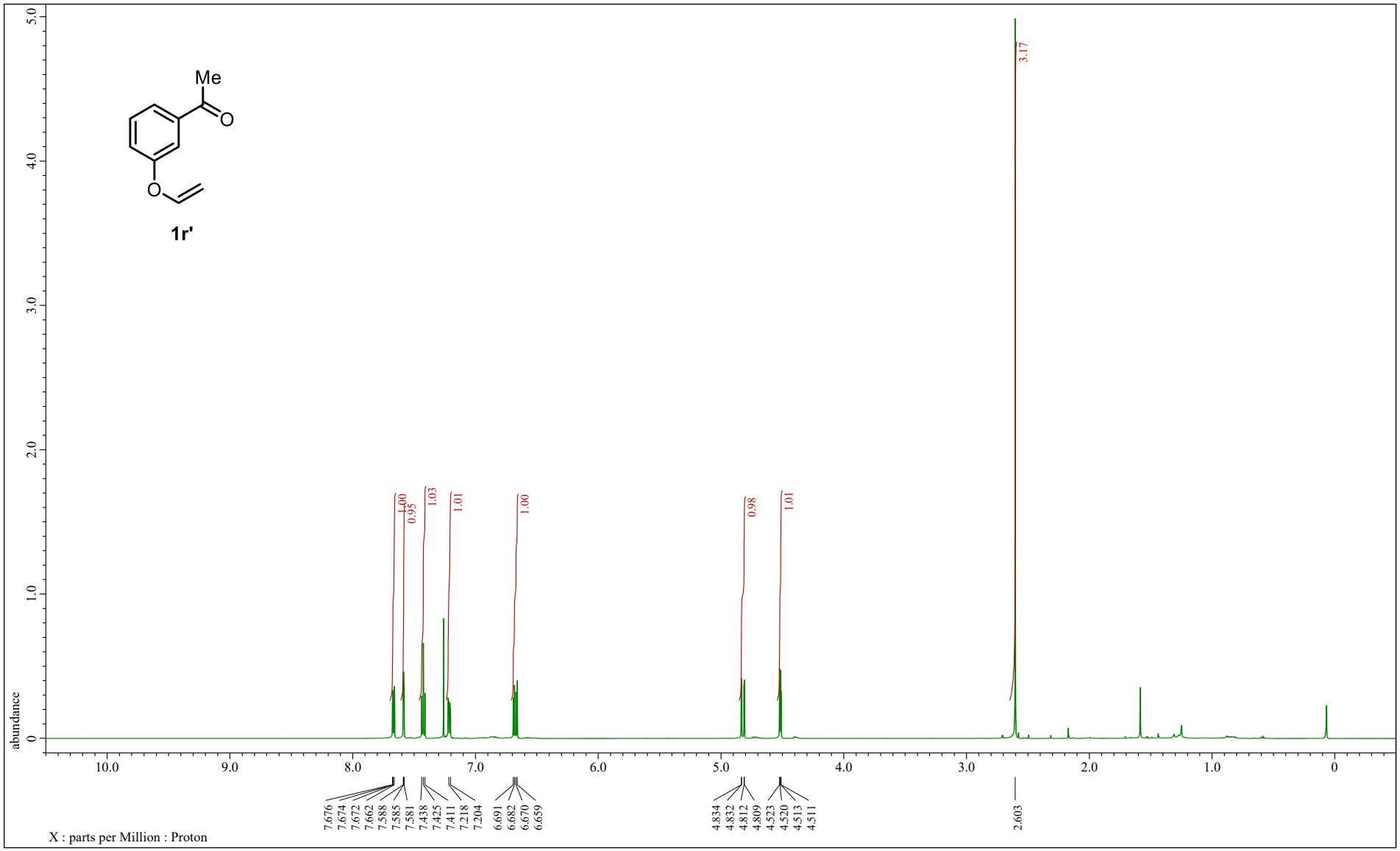

Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1r'**.

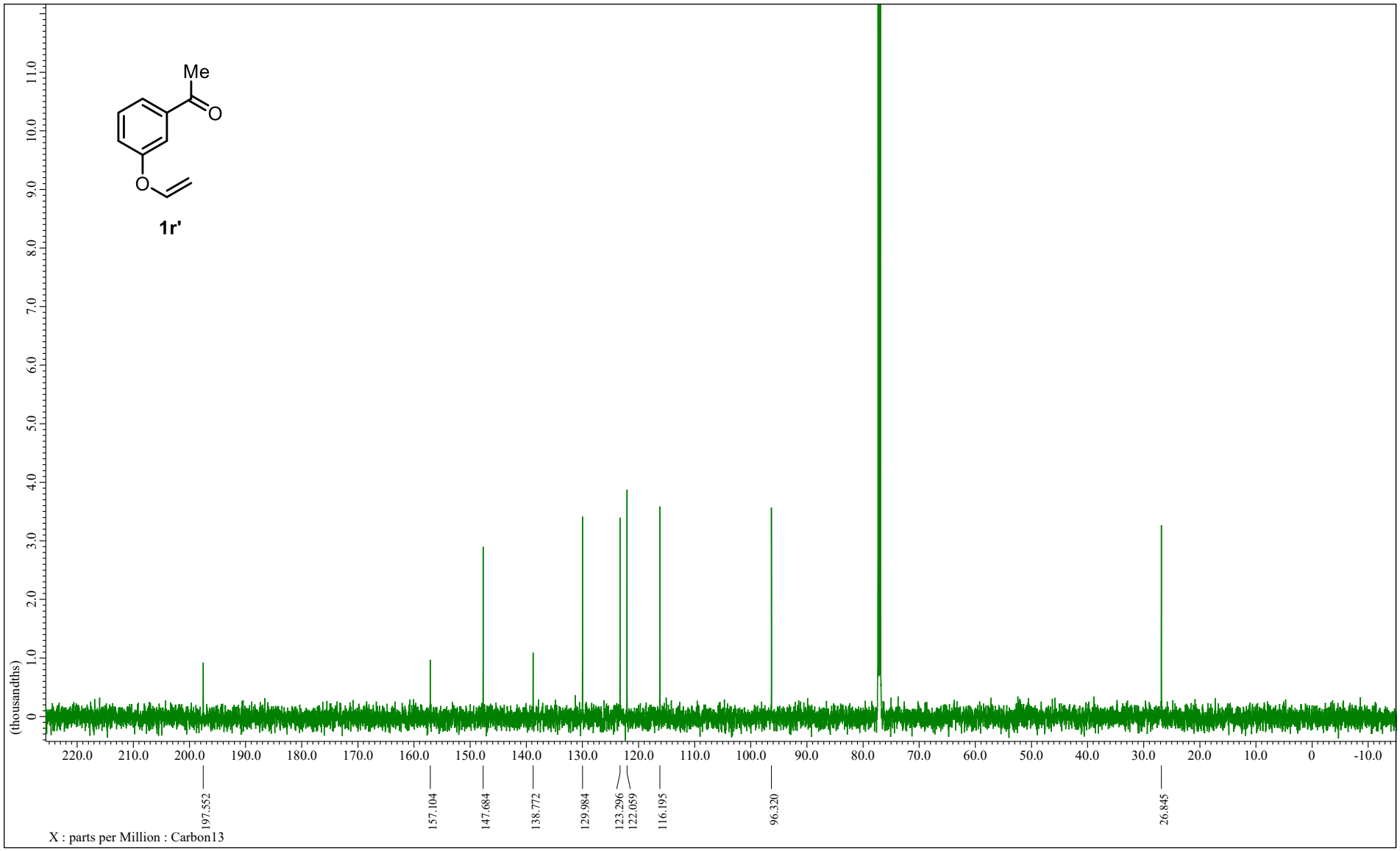

Figure S18. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1r'**.

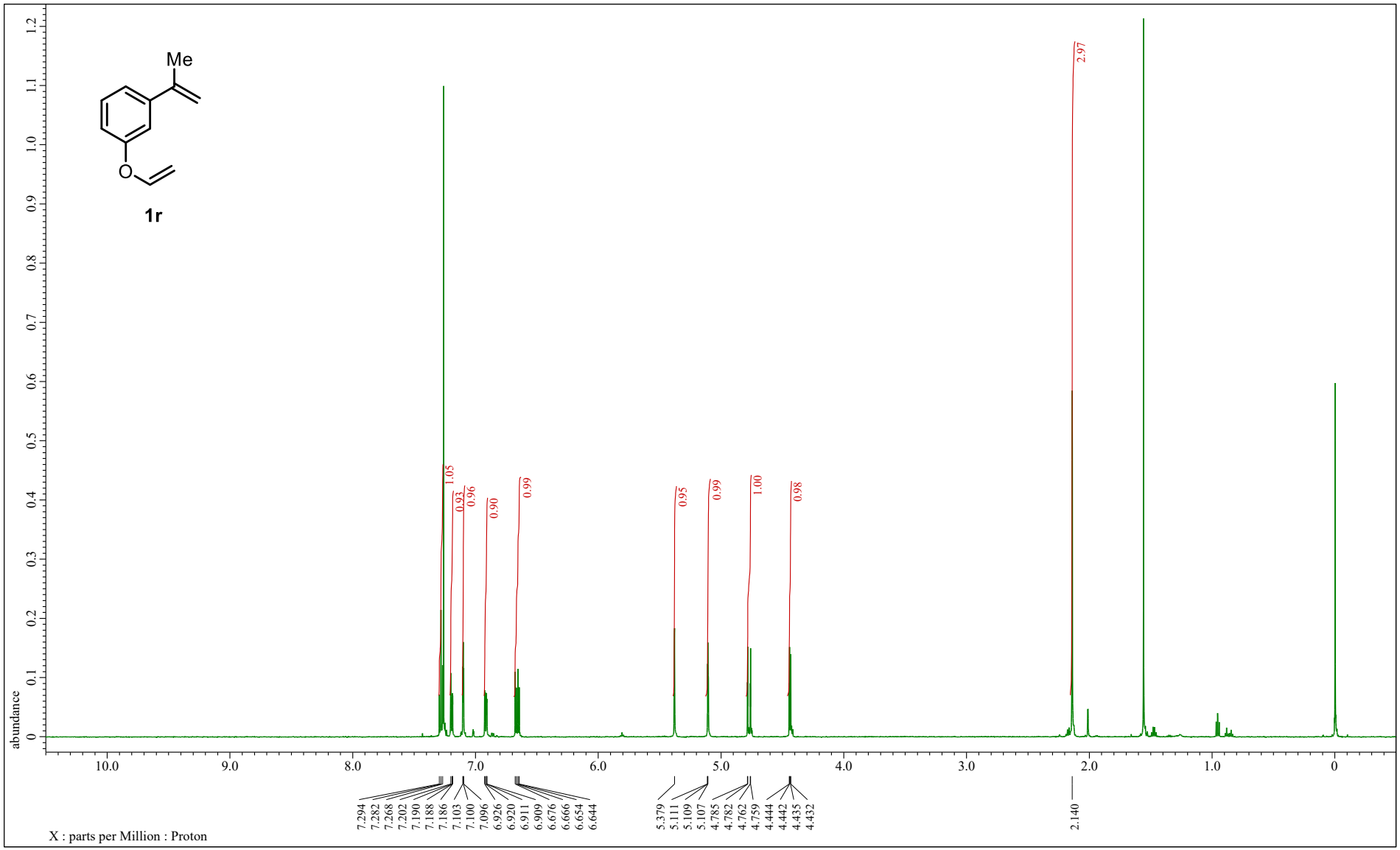

Figure S19. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1r**.

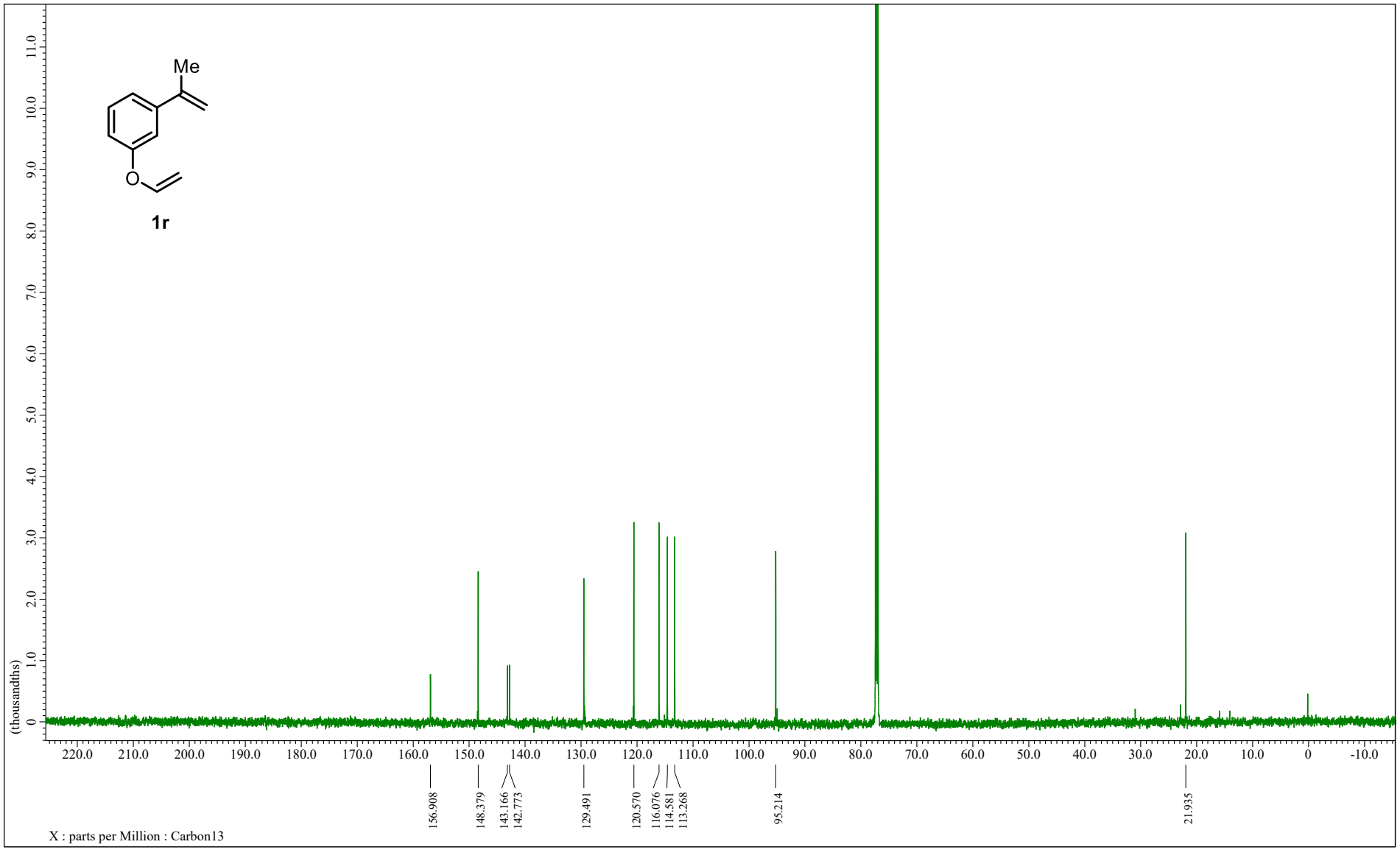

Figure S20. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1r**.

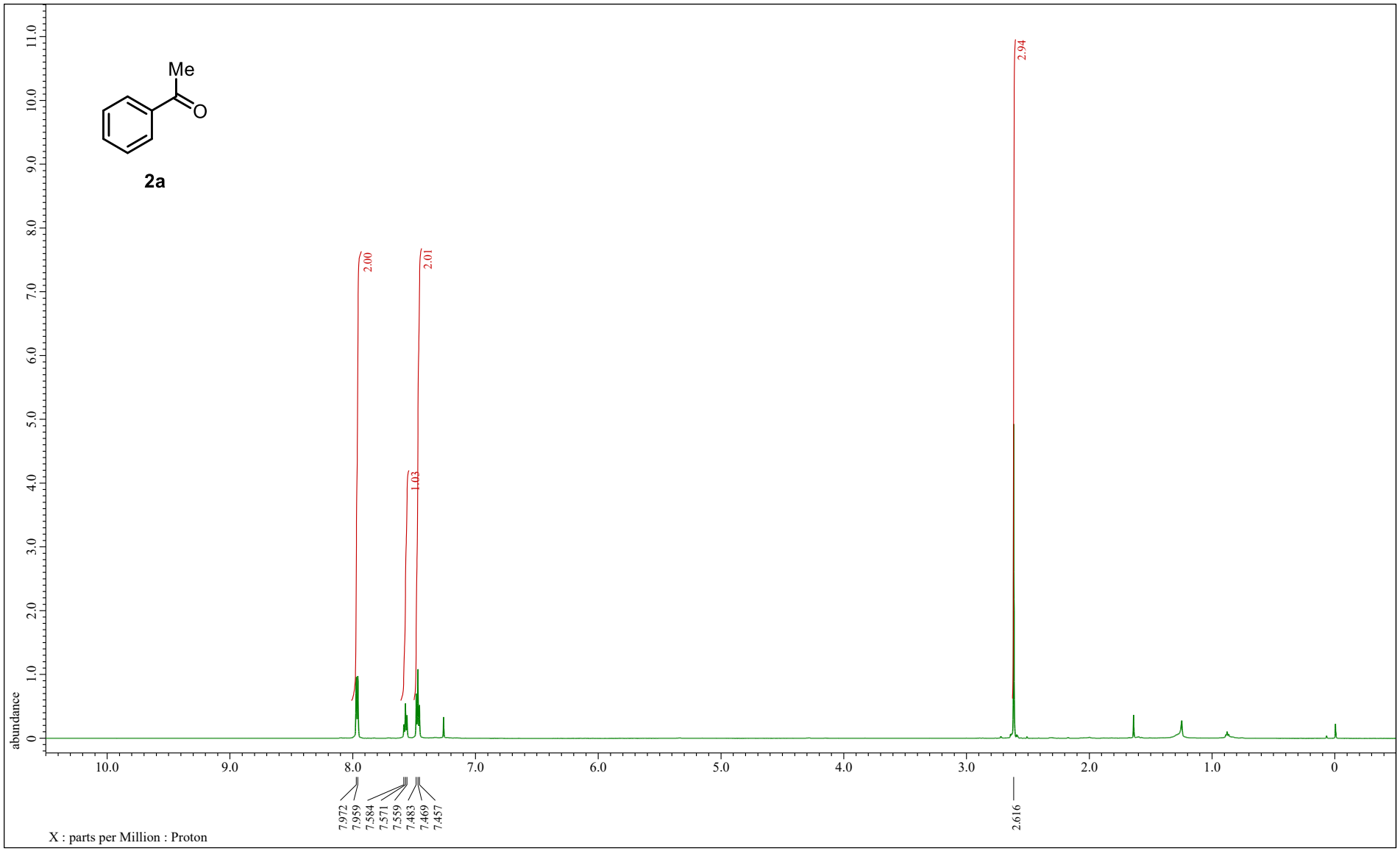

Figure S21. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a**.

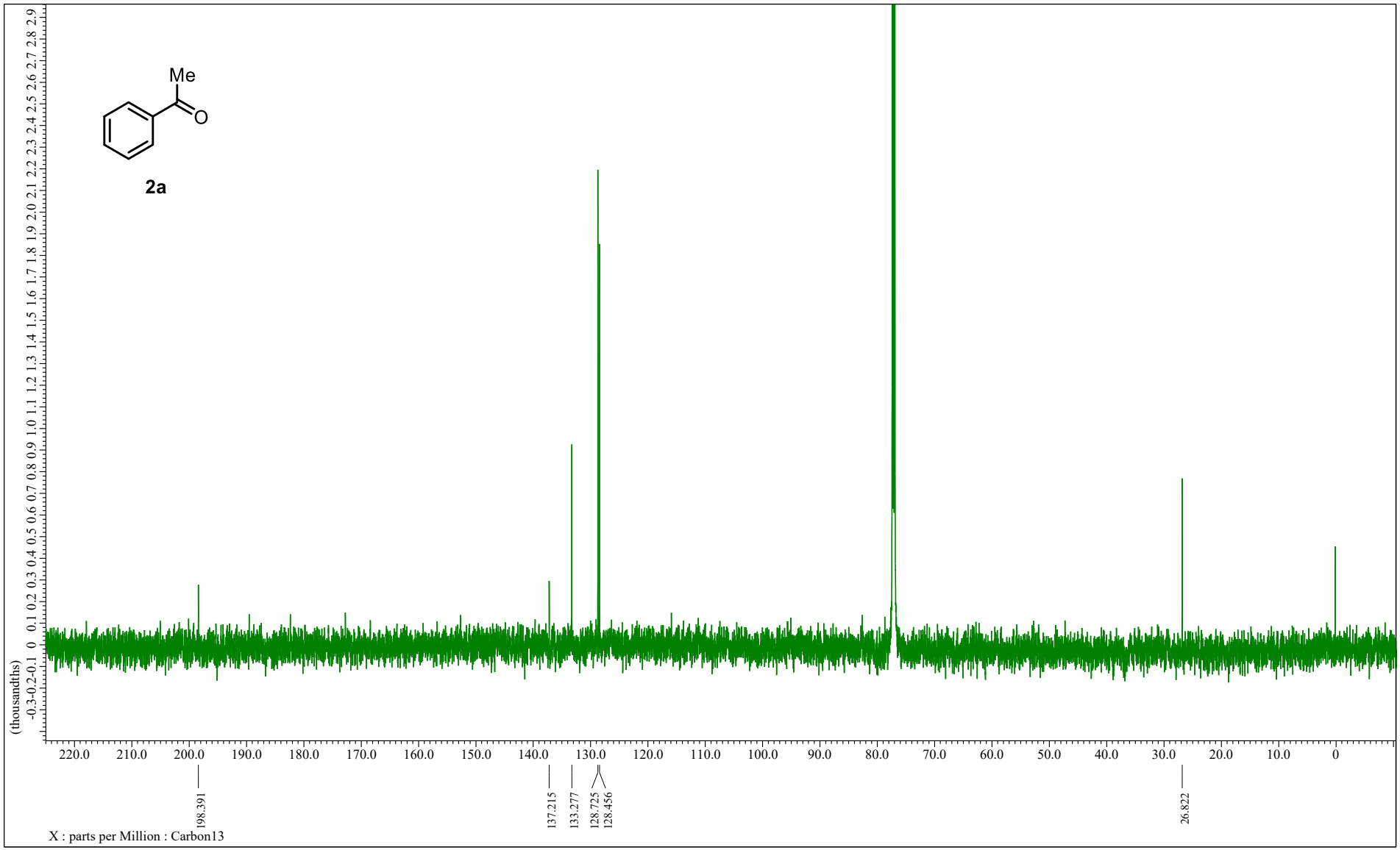

Figure S22. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2a**.

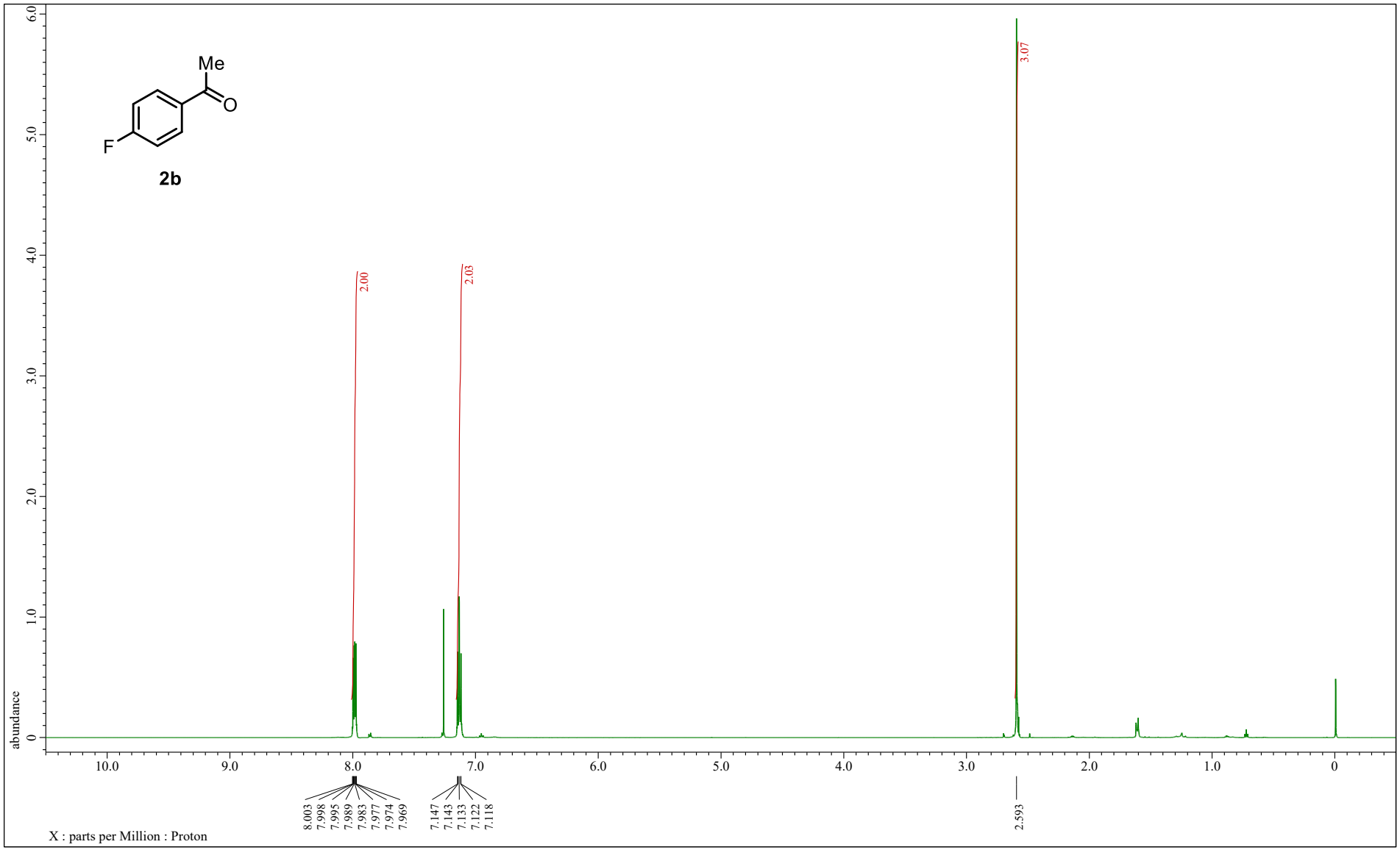

Figure S23. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b**.

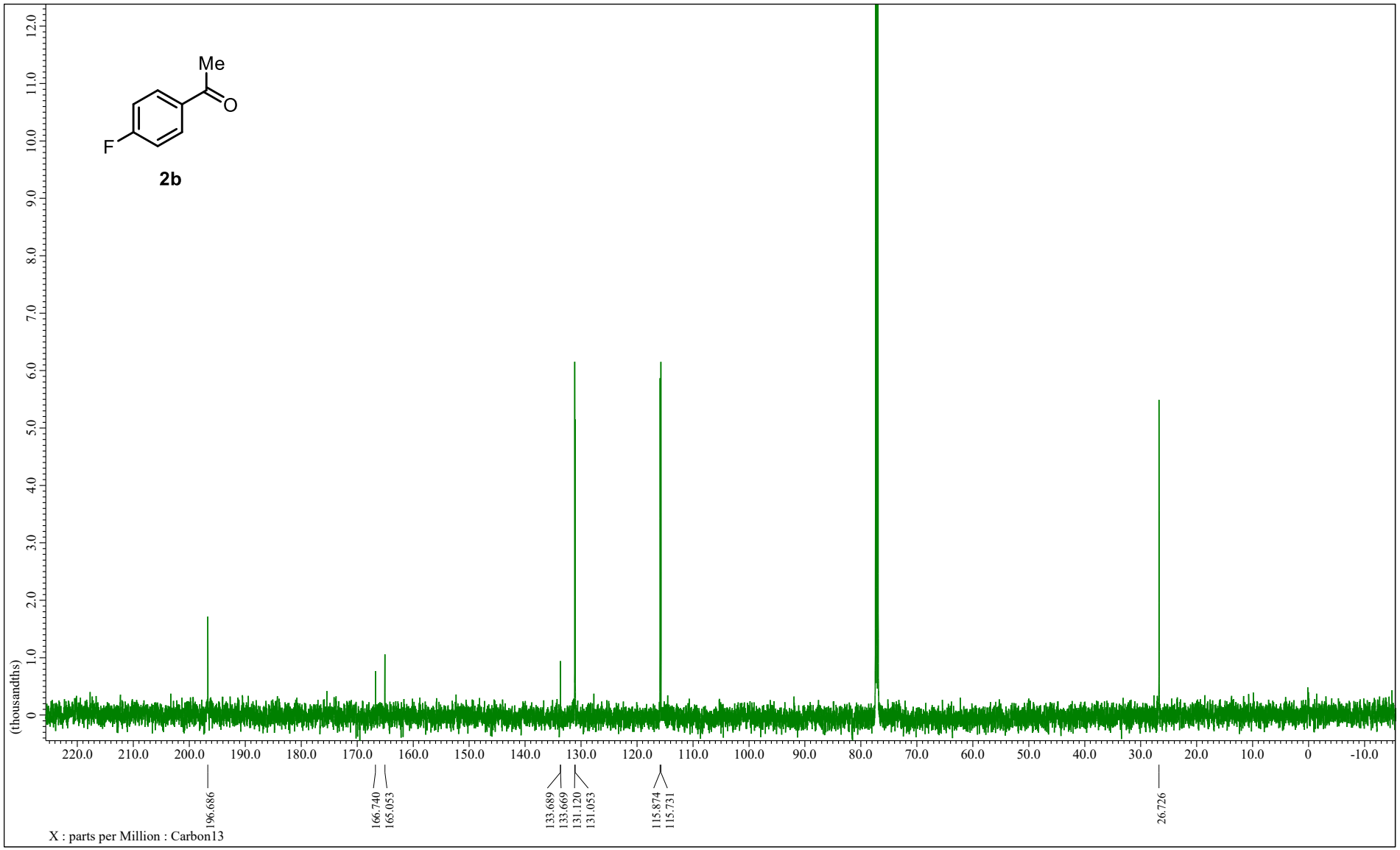

Figure S24. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2b**.

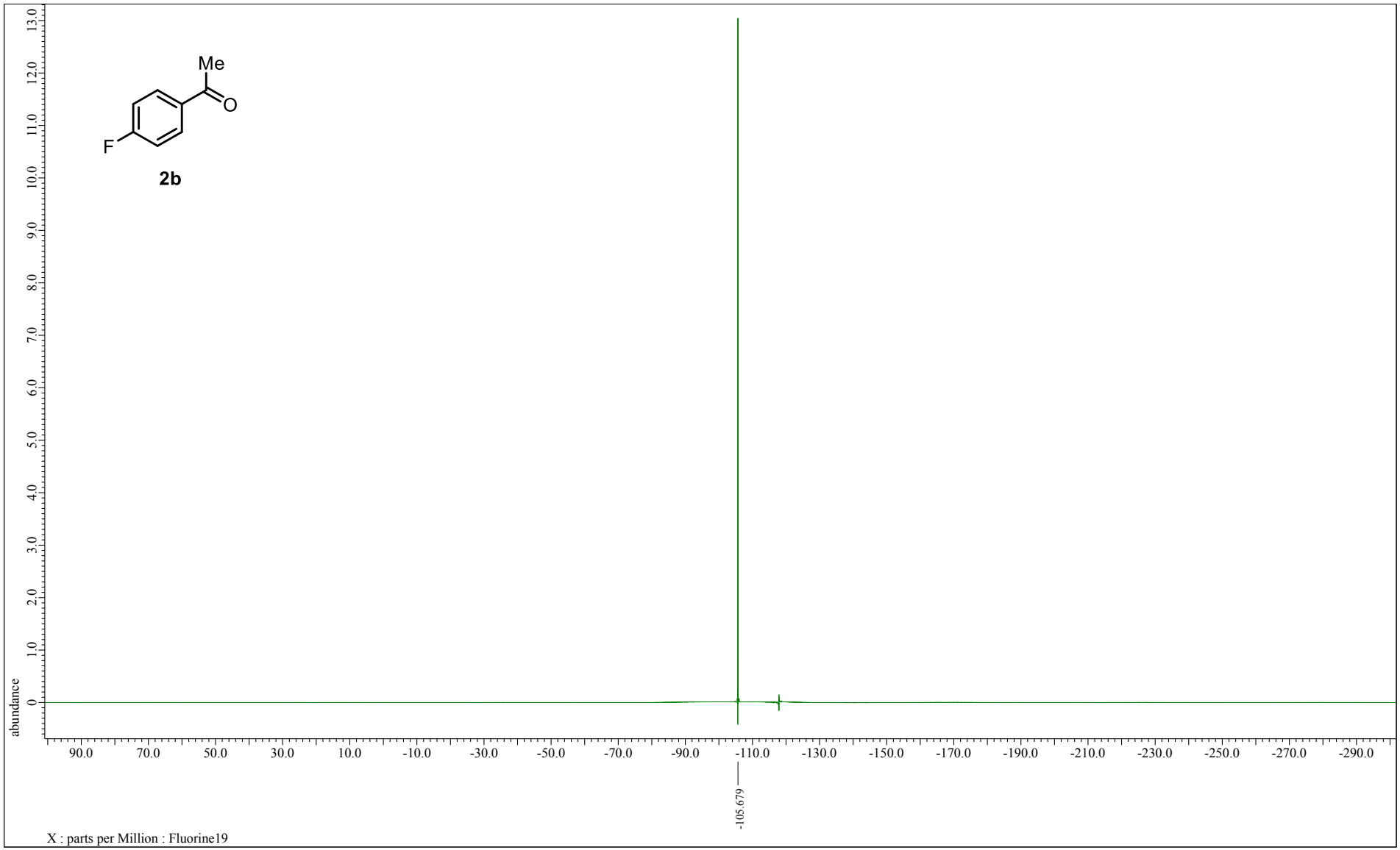

Figure S25. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2b**.

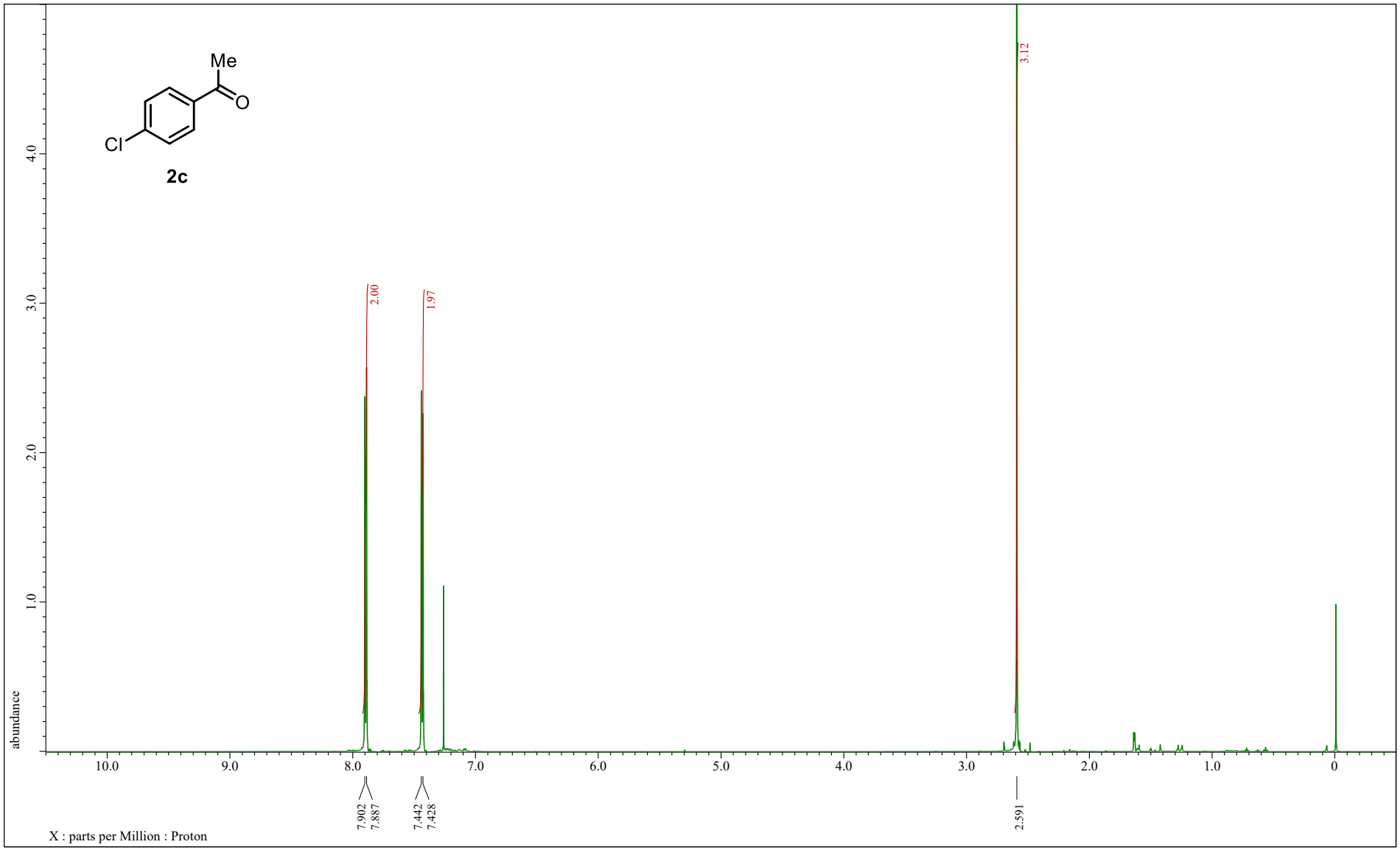

Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c**.

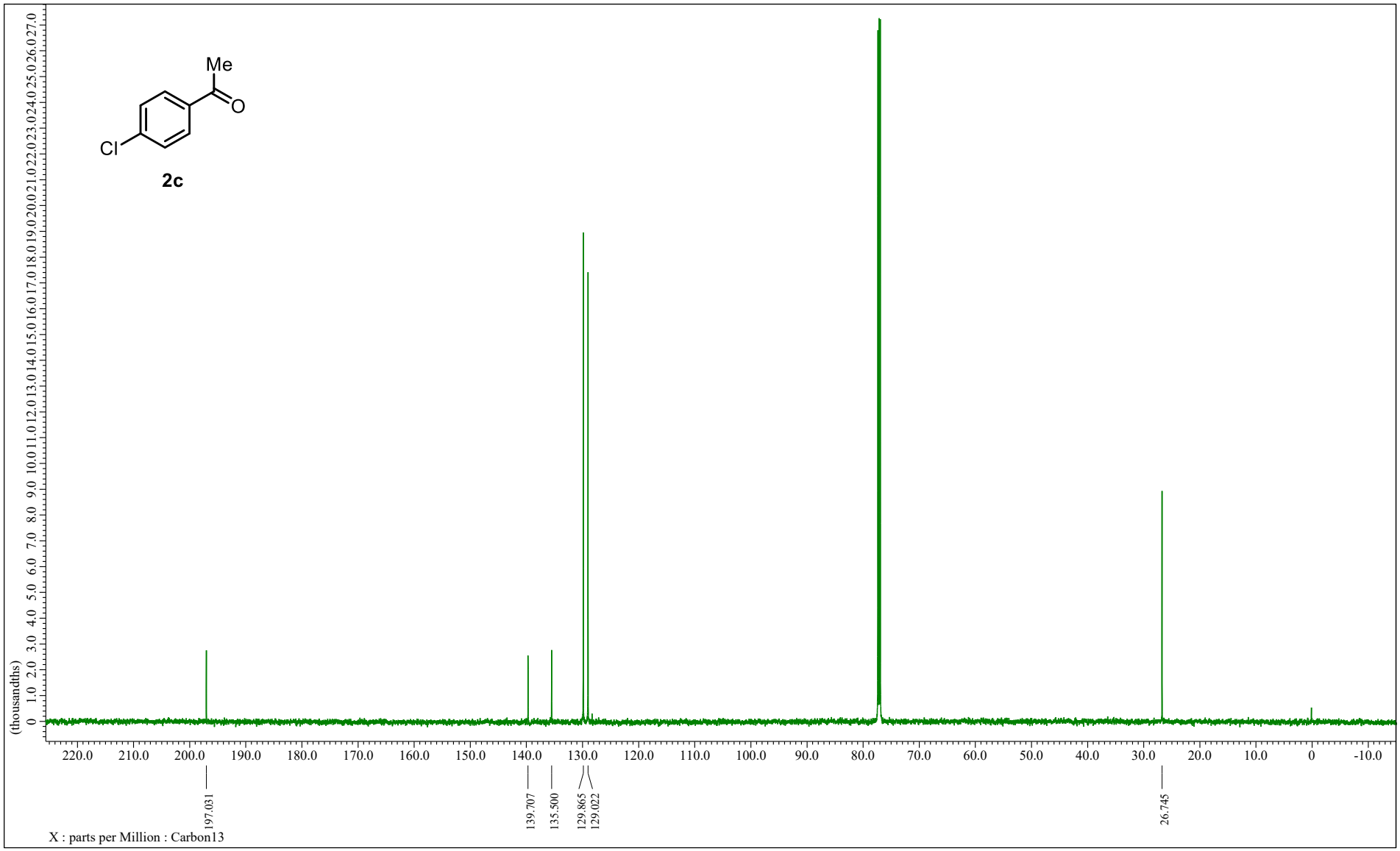

Figure S27. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2c**.

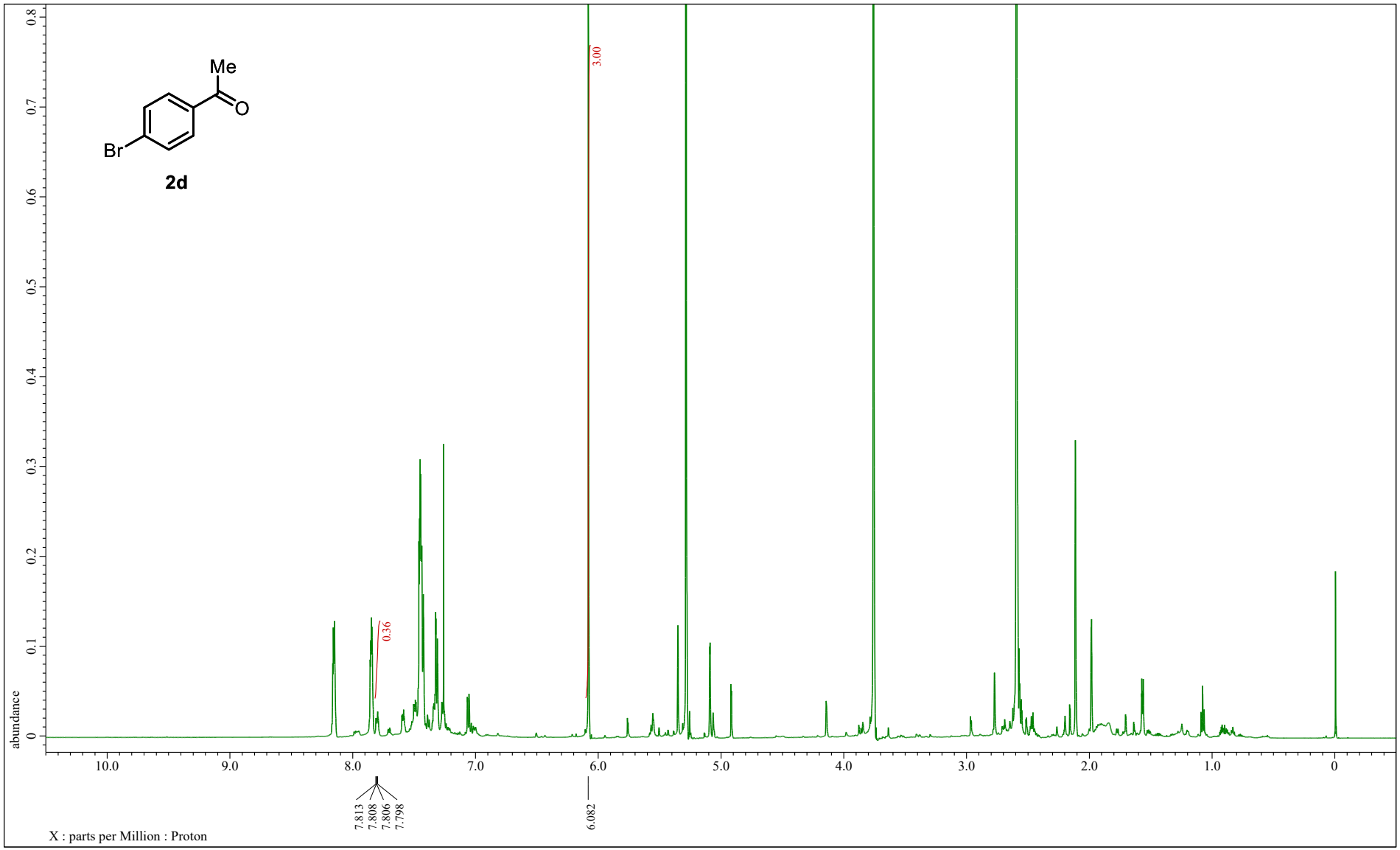

Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the crude mixture containing **2d**.

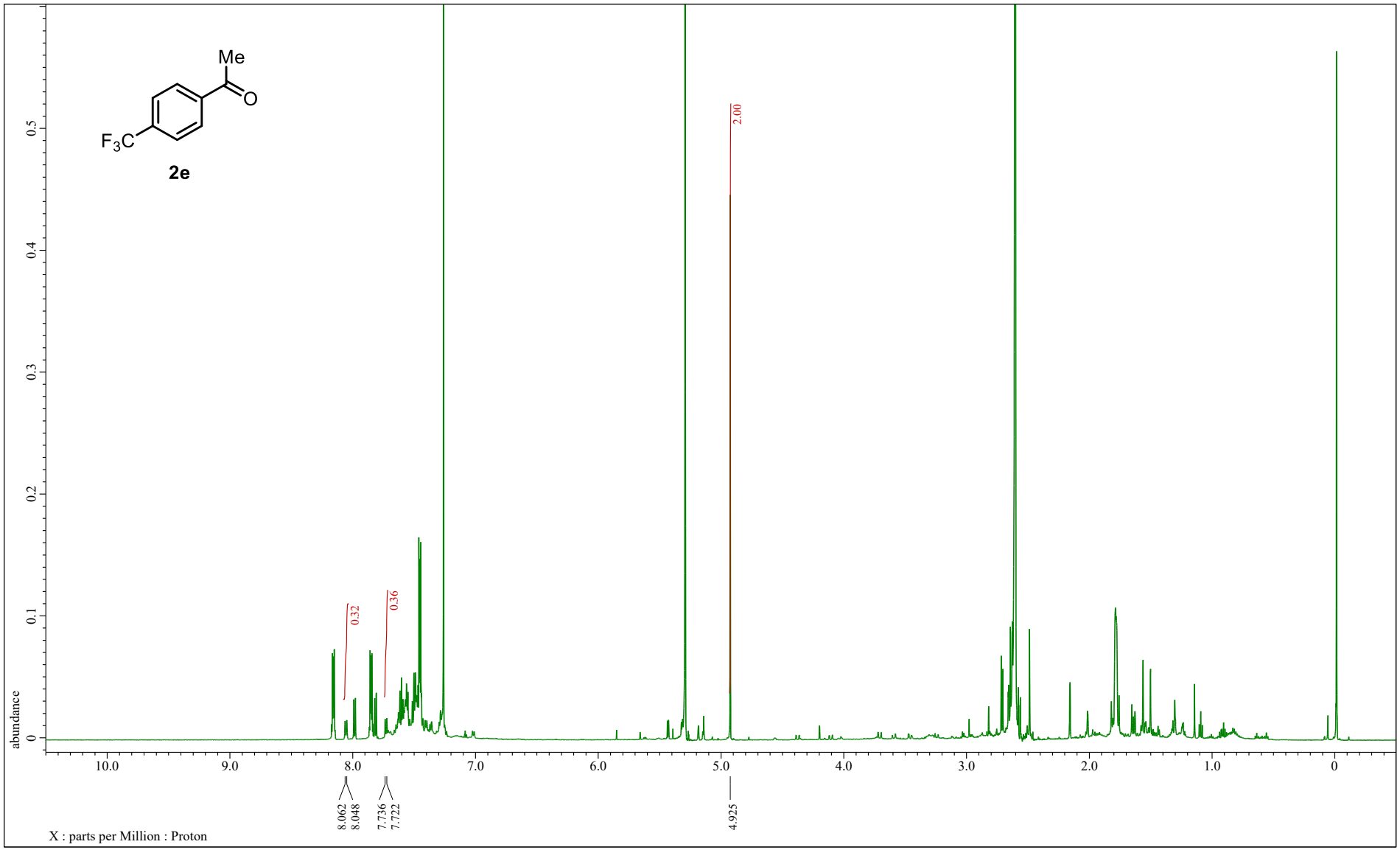

Figure S29. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the crude mixture containing **2e**.

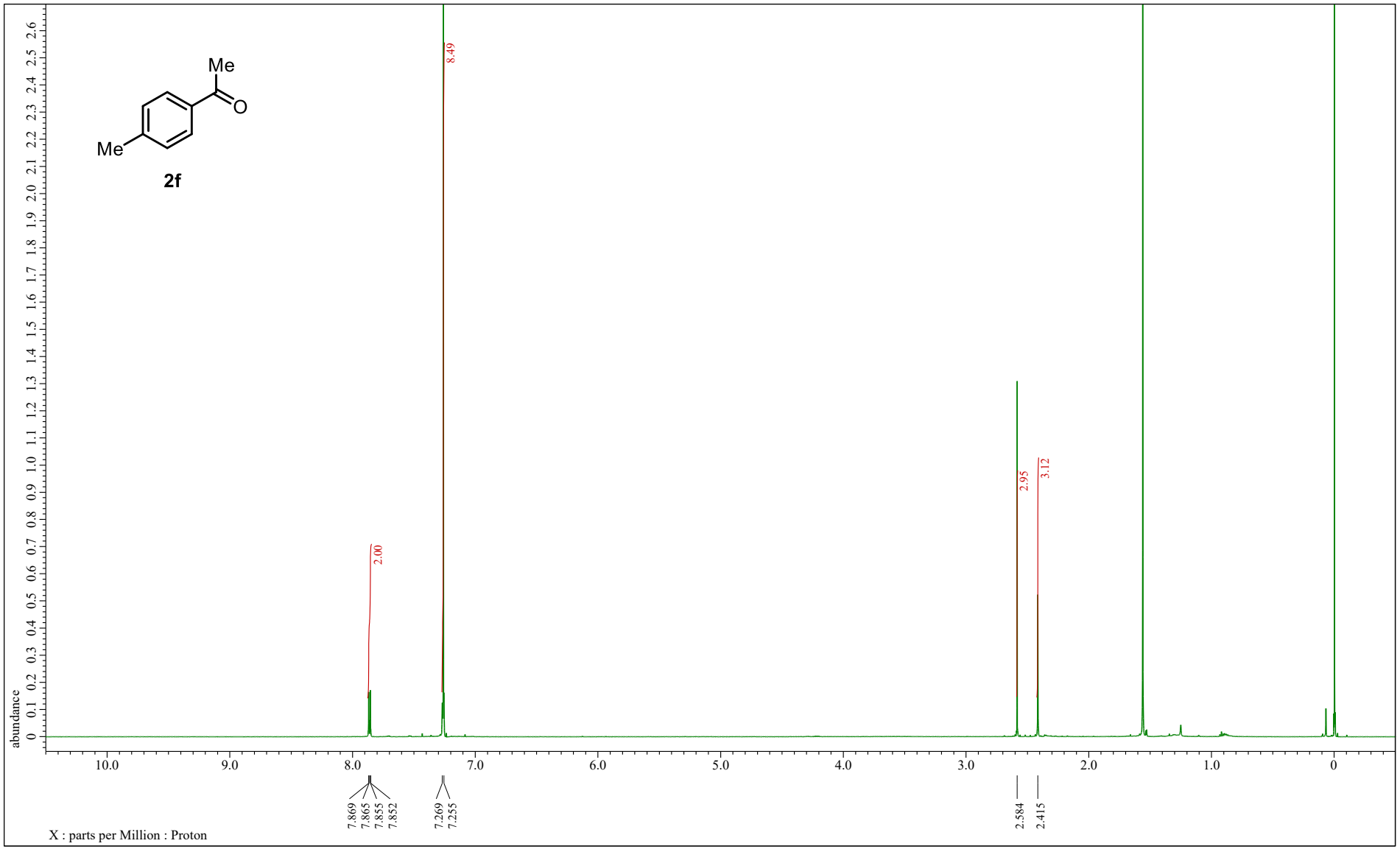

Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2f**.

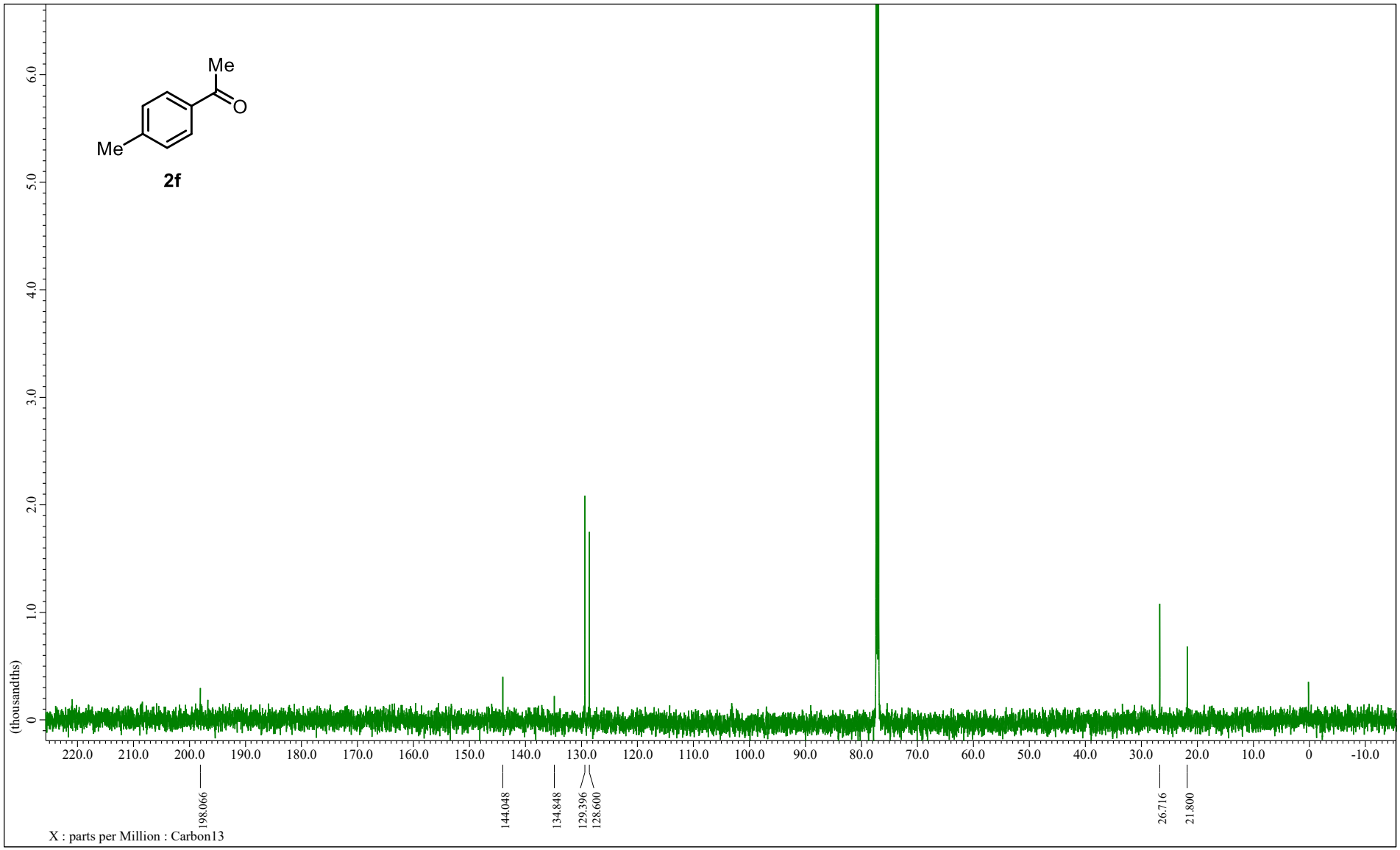

Figure S31. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2f**.

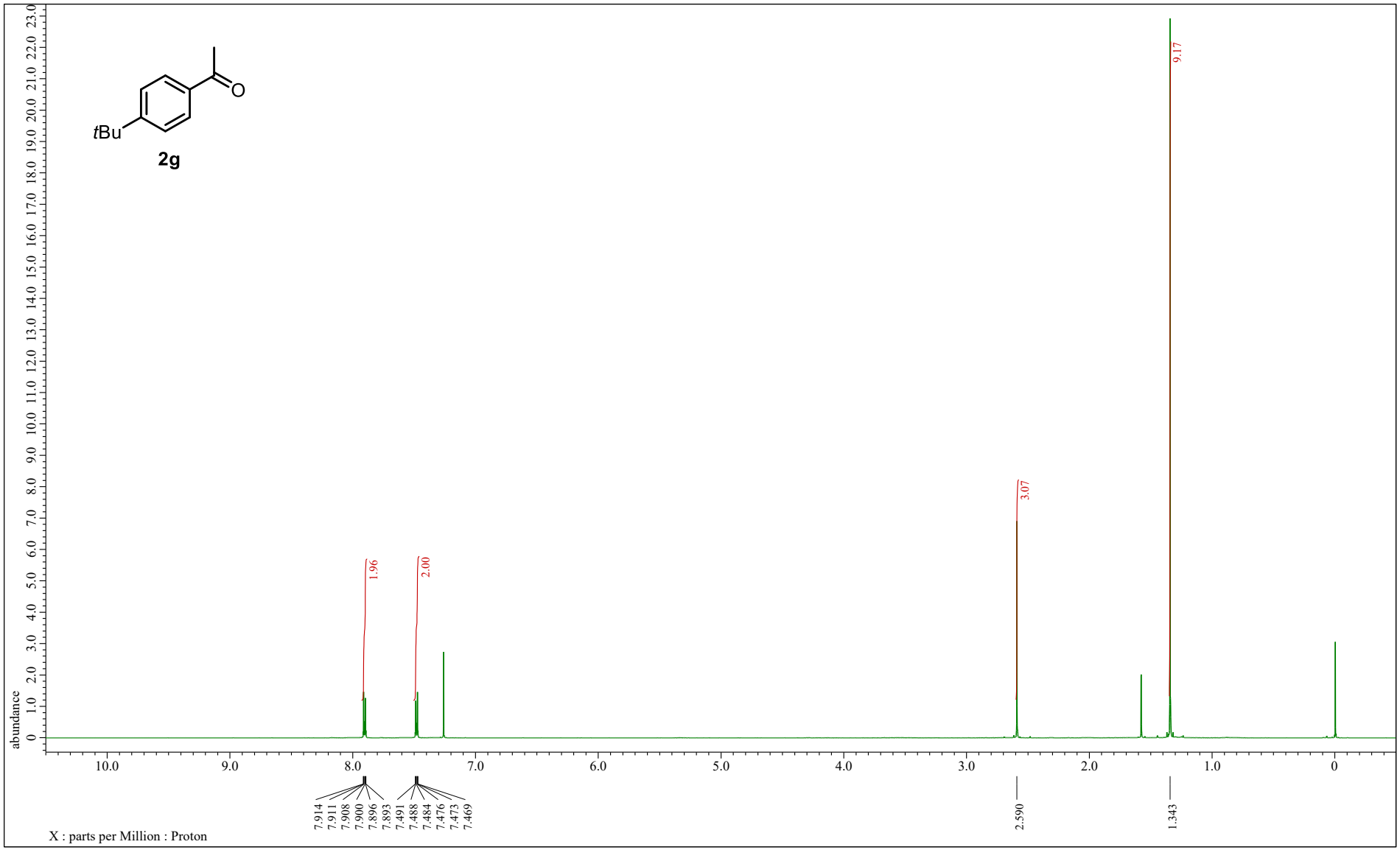

Figure S32. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2g**.

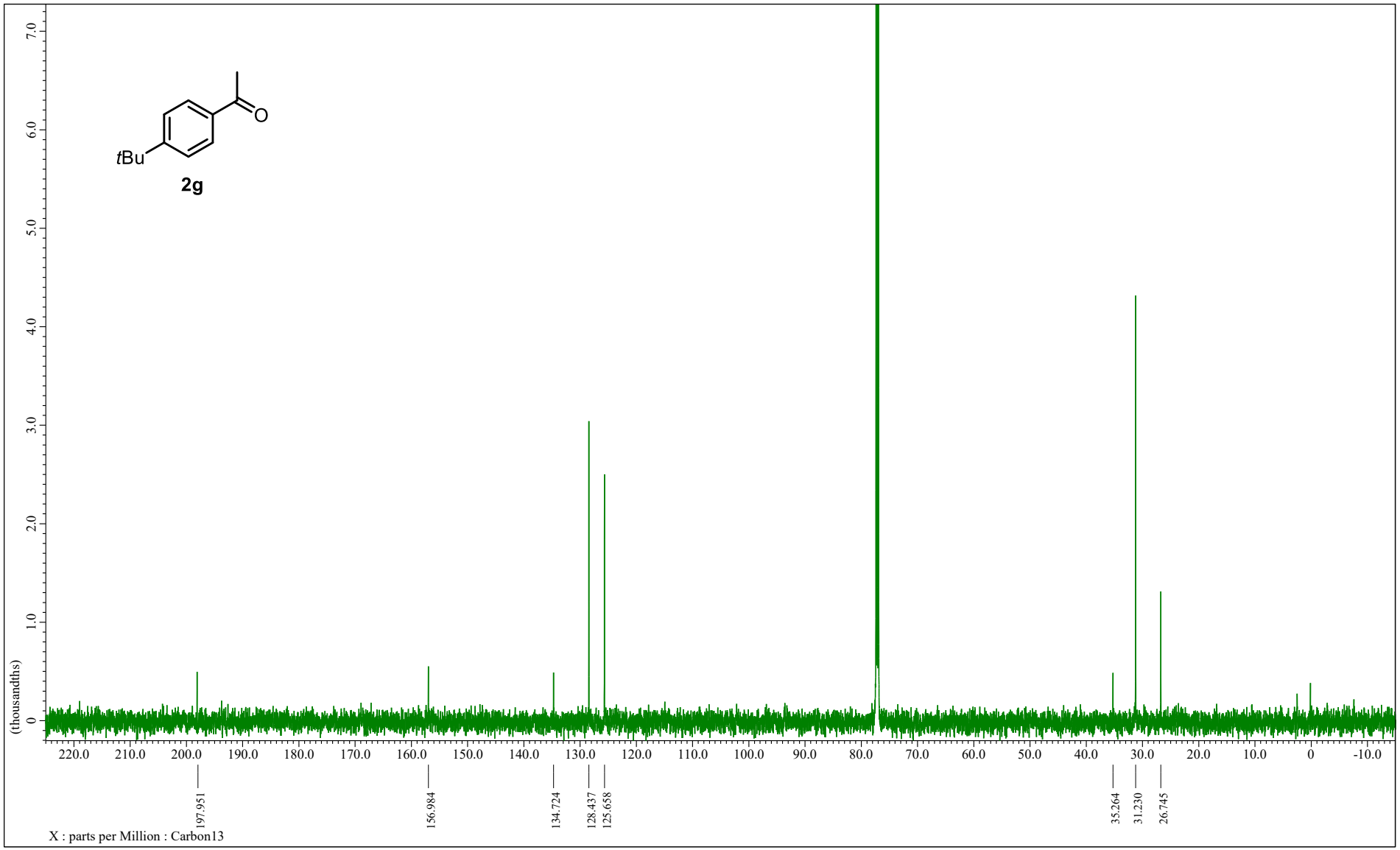

Figure S33. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2g**.

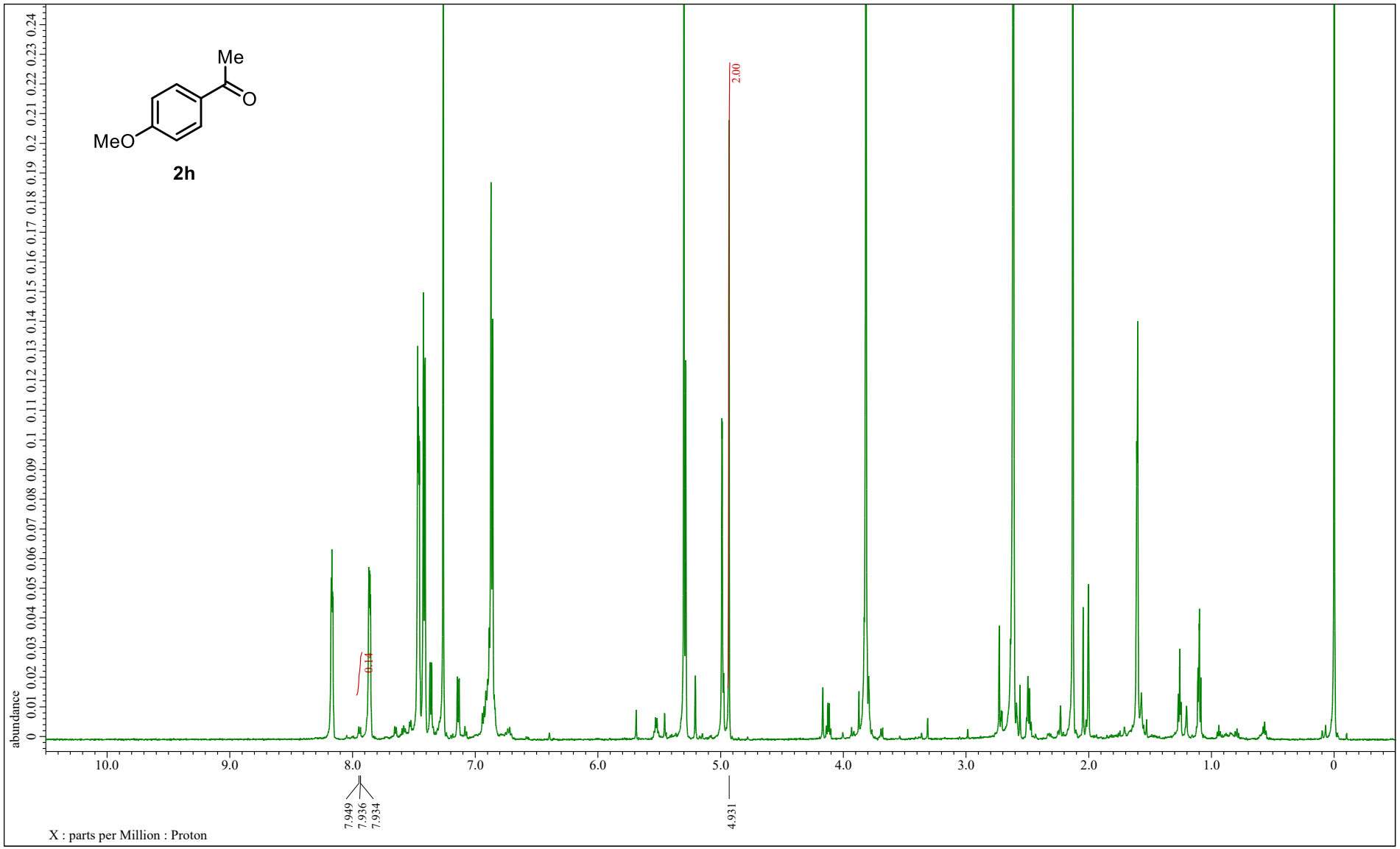

Figure S34. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the crude mixture containing **2h**.

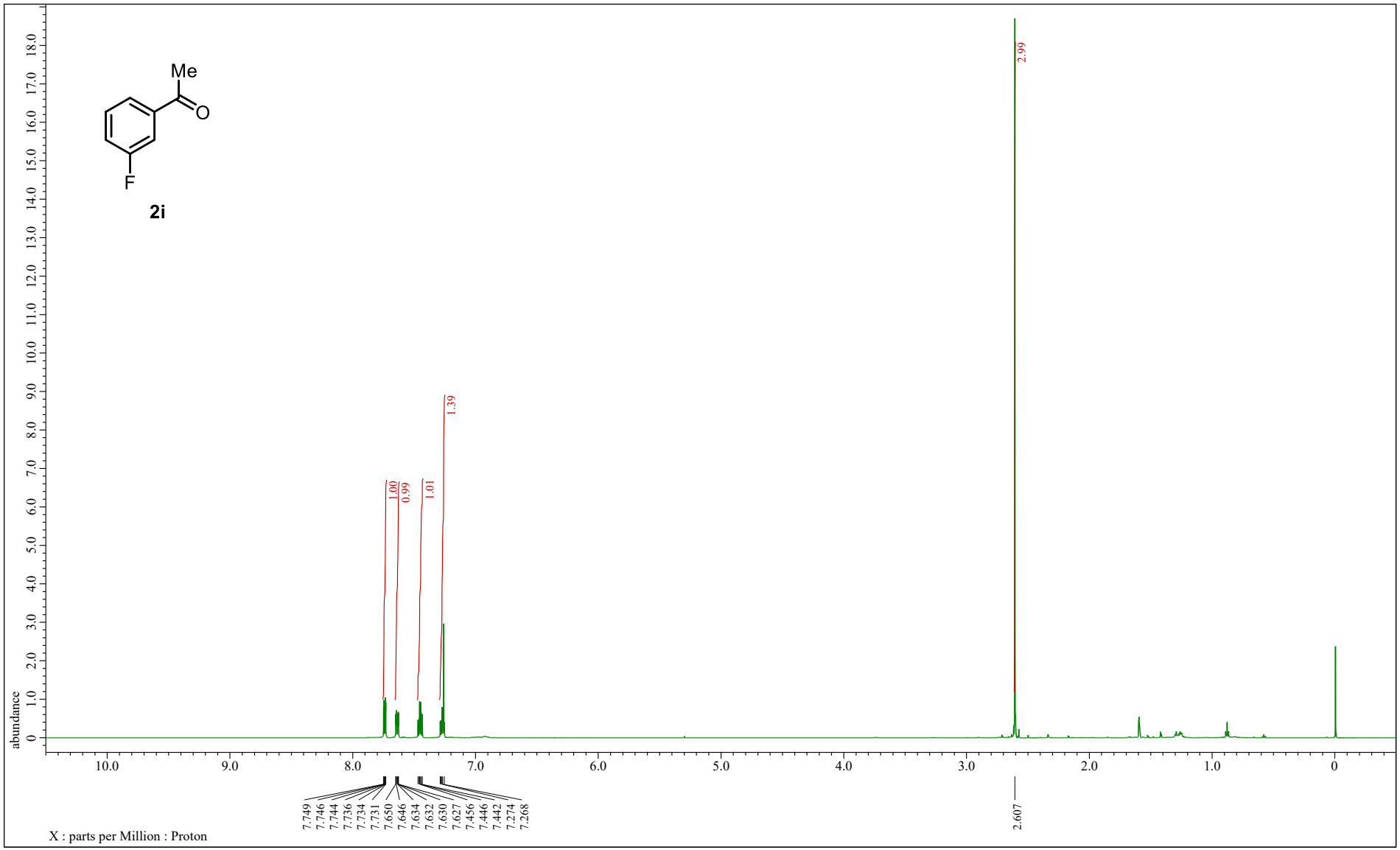

Figure S35. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2i**.

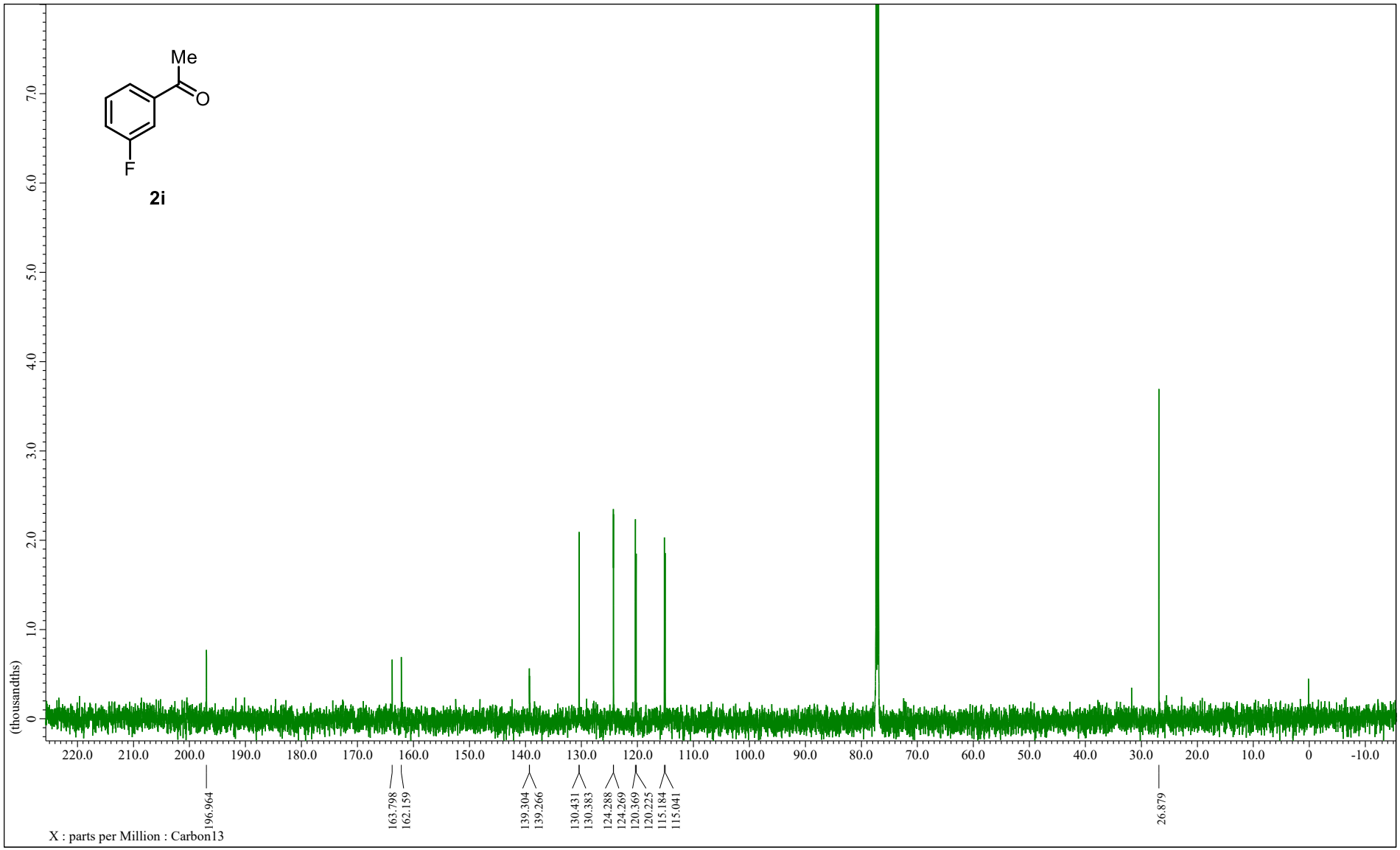

Figure 36. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2i**.

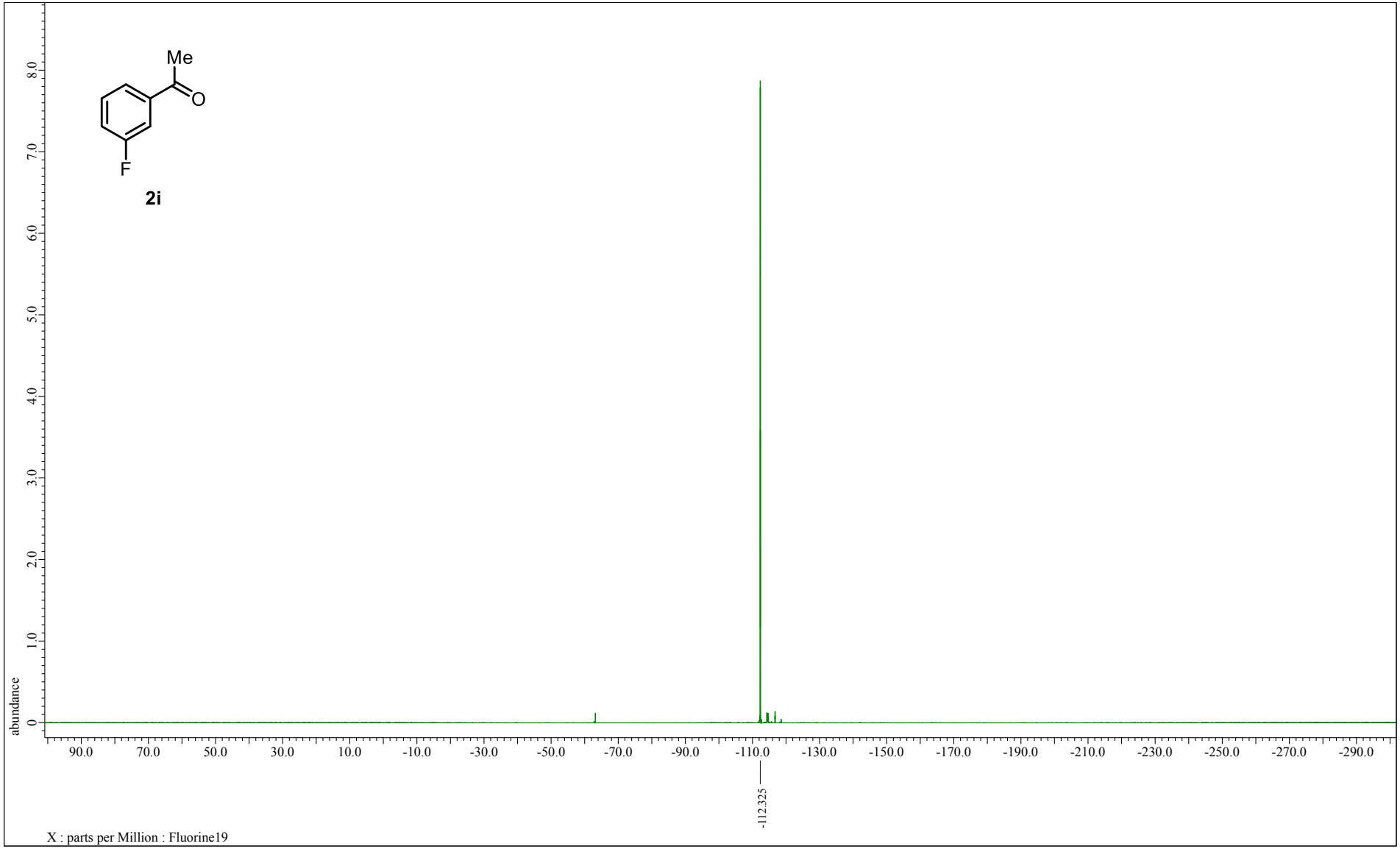

Figure S37. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2i**.

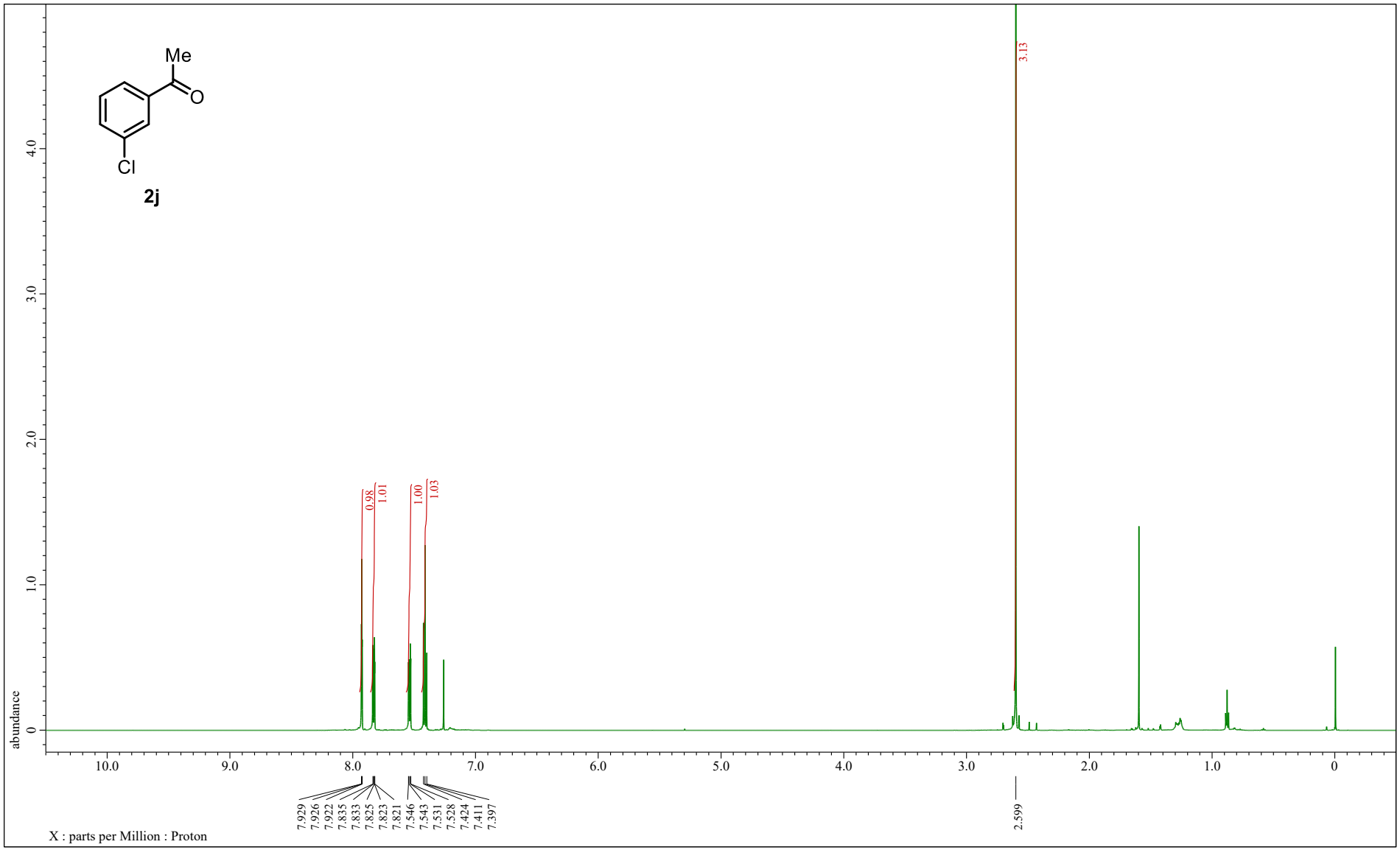

Figure S38. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2j**.

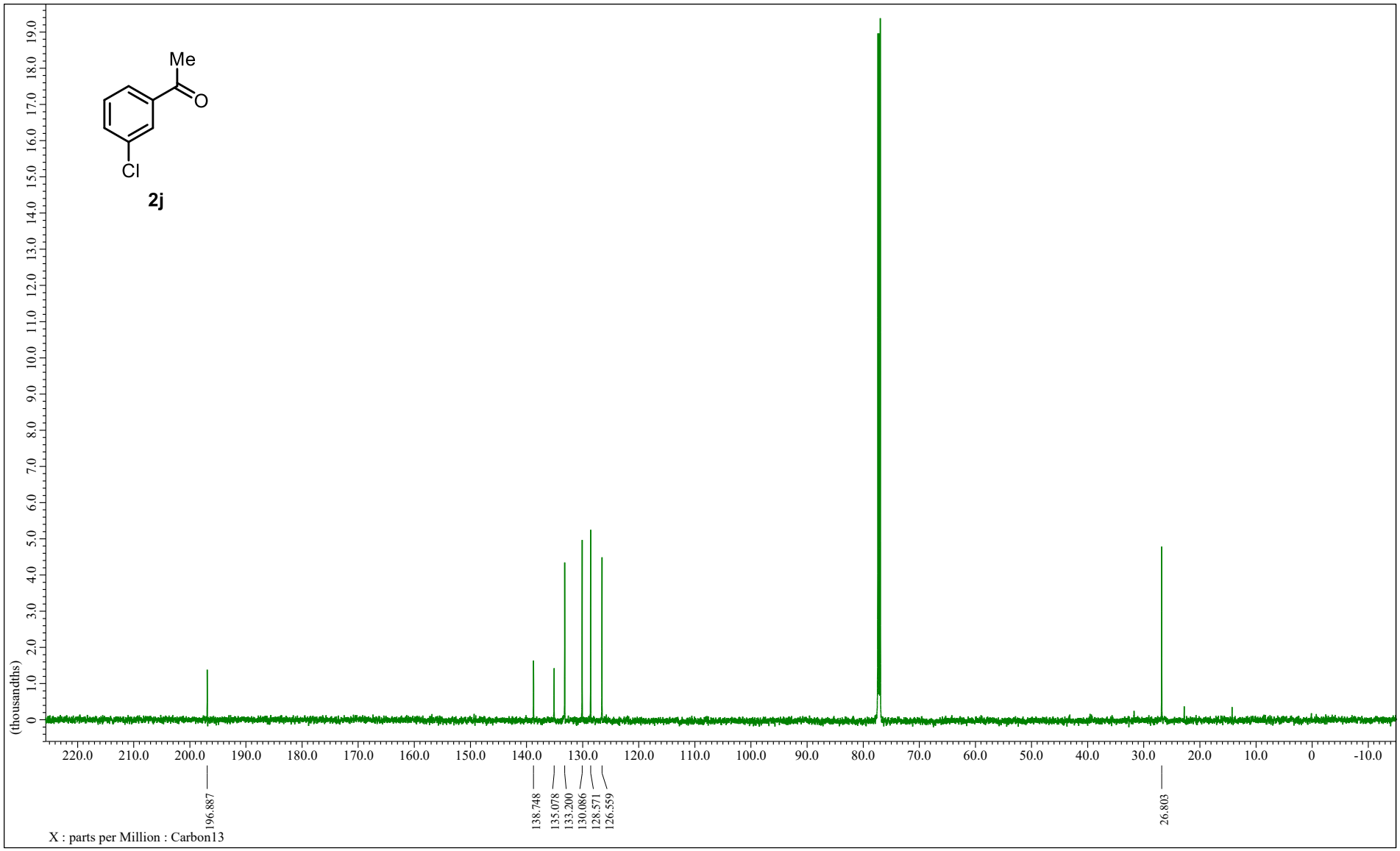

Figure S39. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2j**.

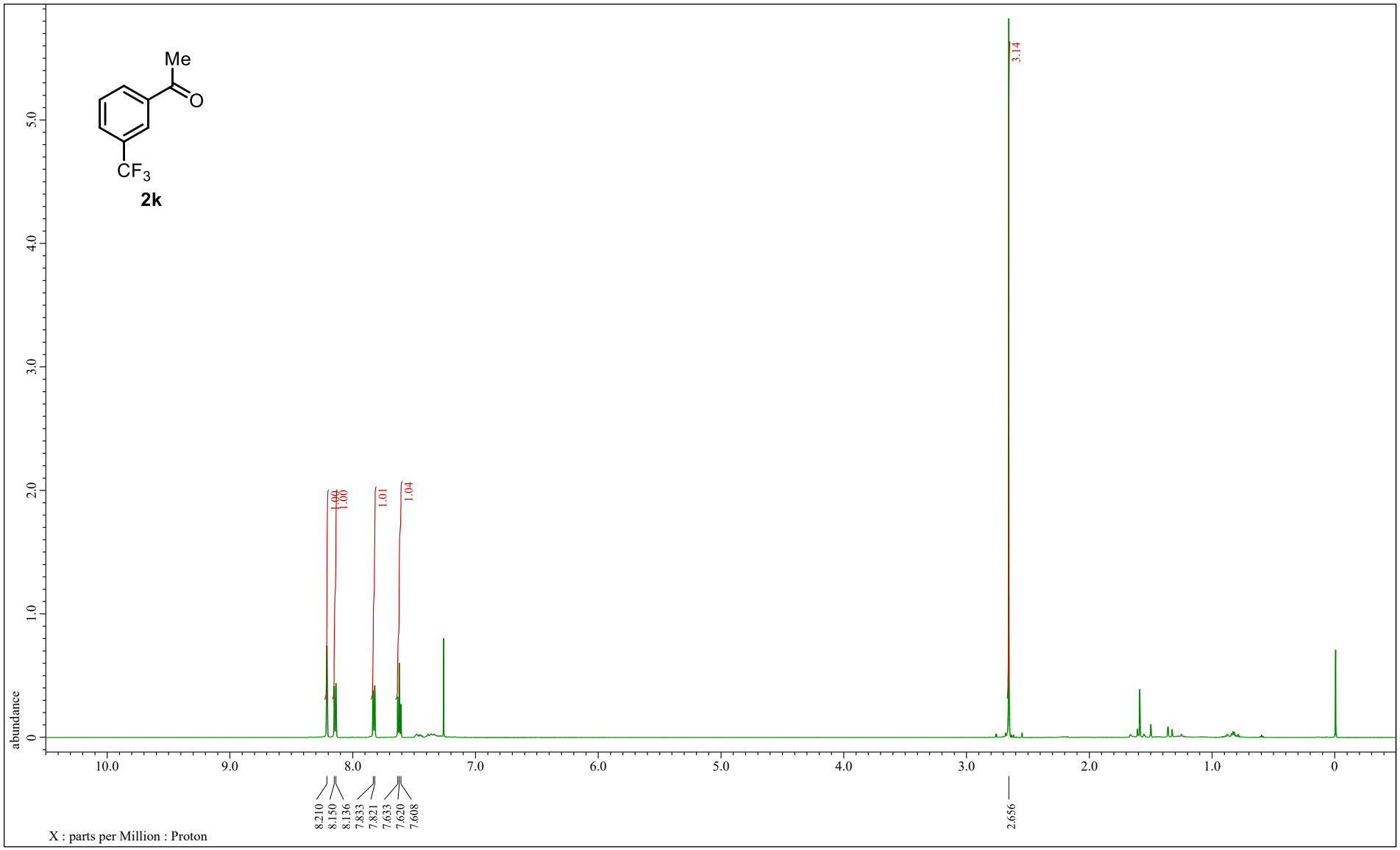

Figure S40. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2k**.

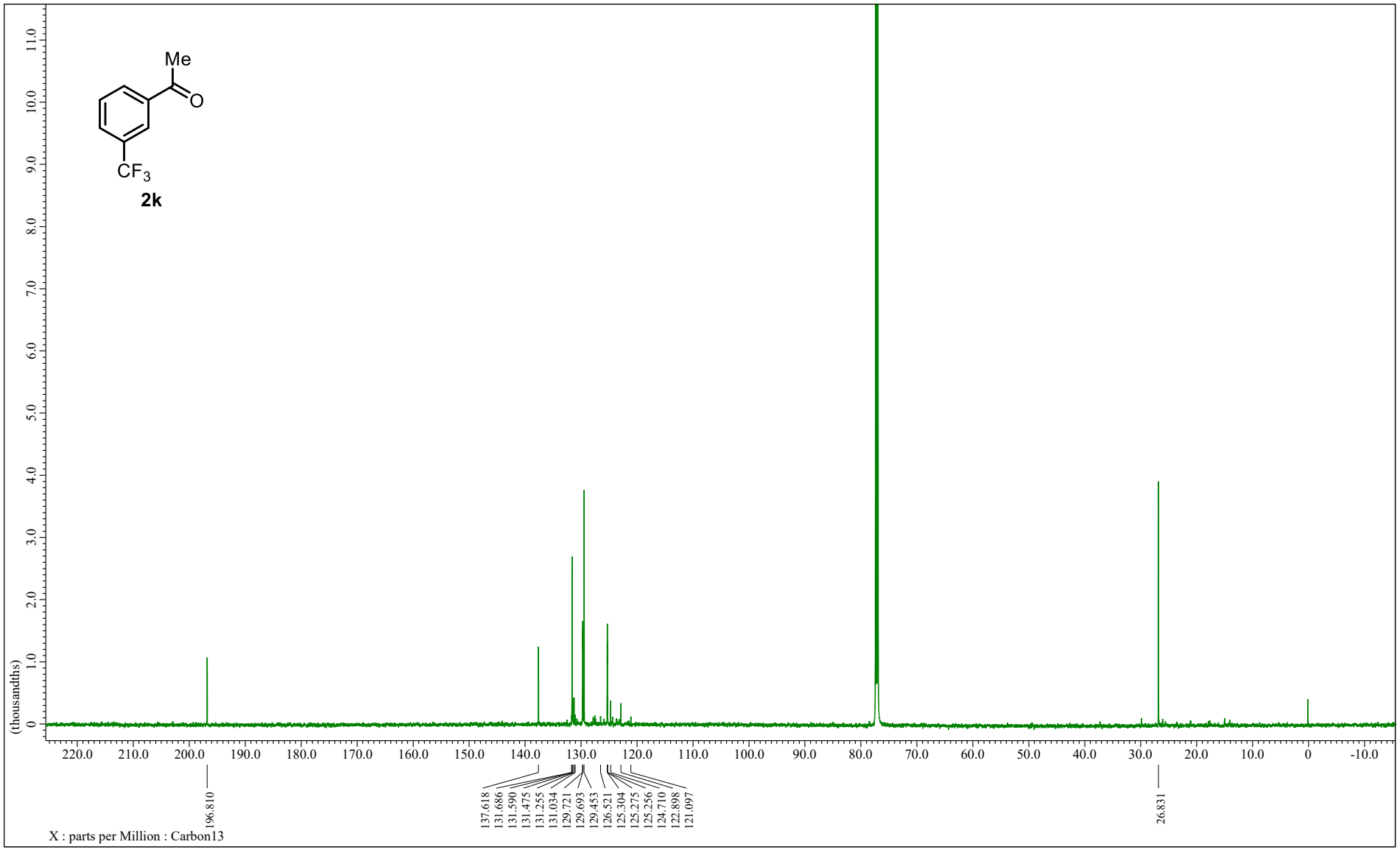

Figure S41. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2k**.

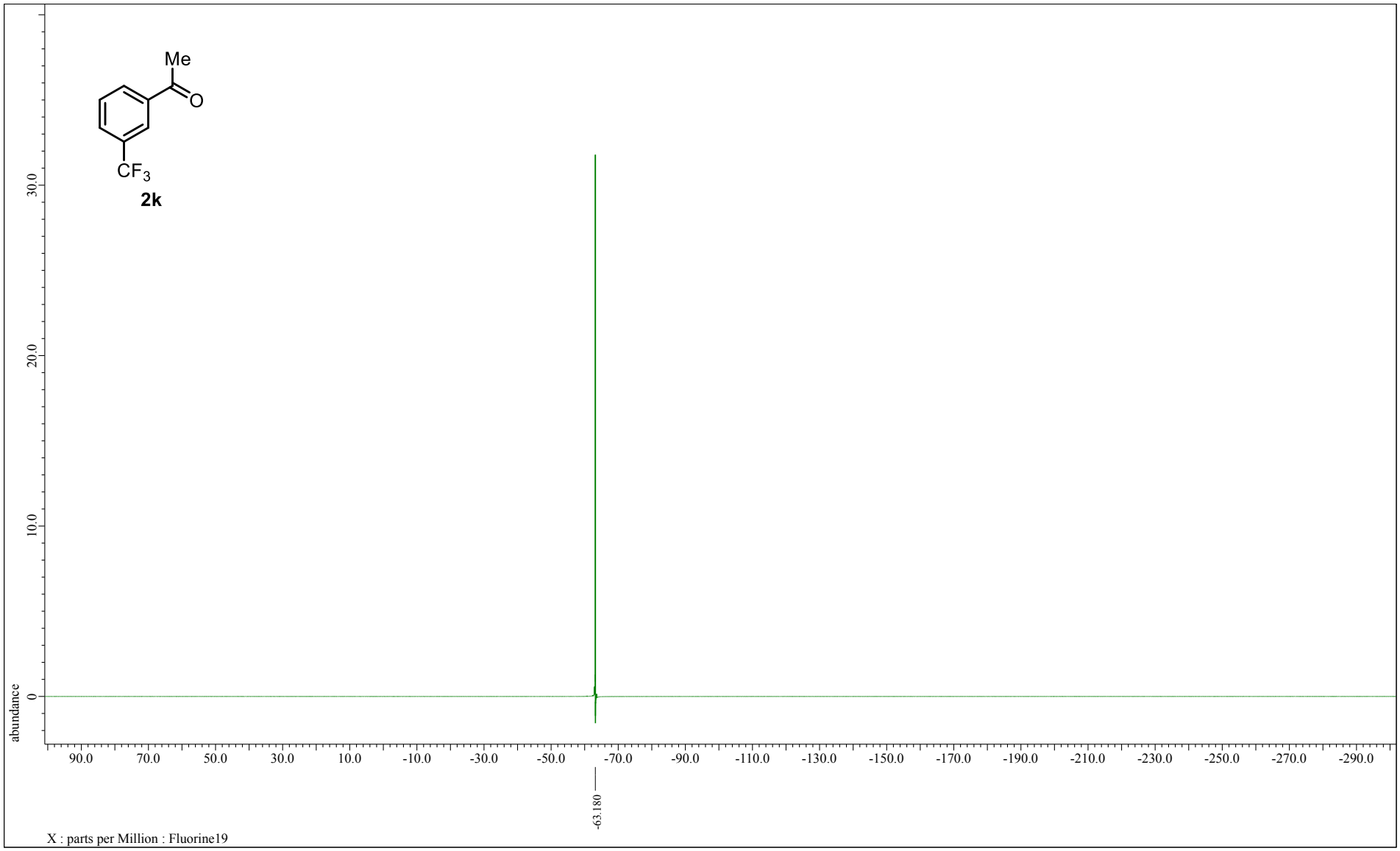

Figure S42. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2k**.

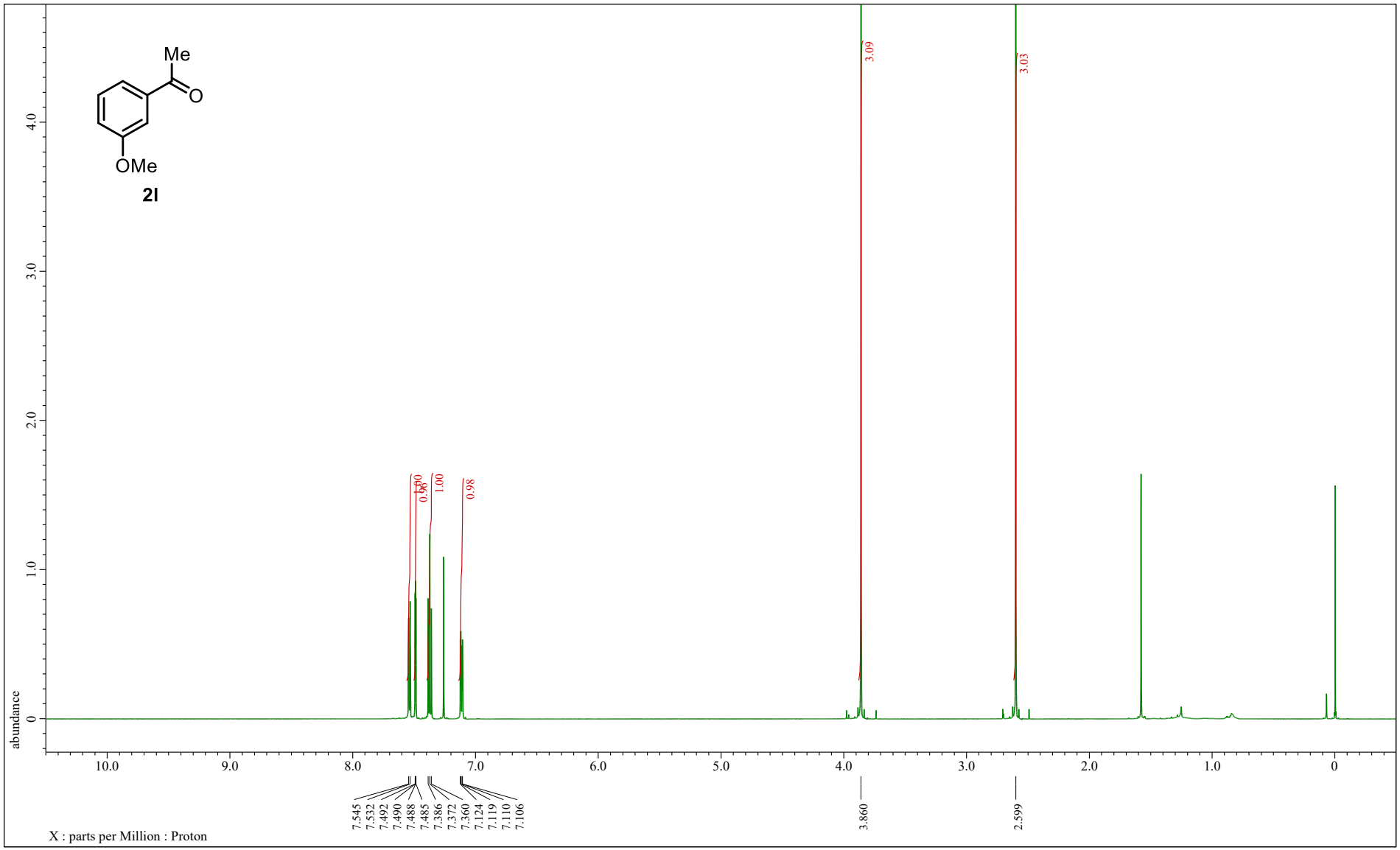

Figure S43. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2l**.

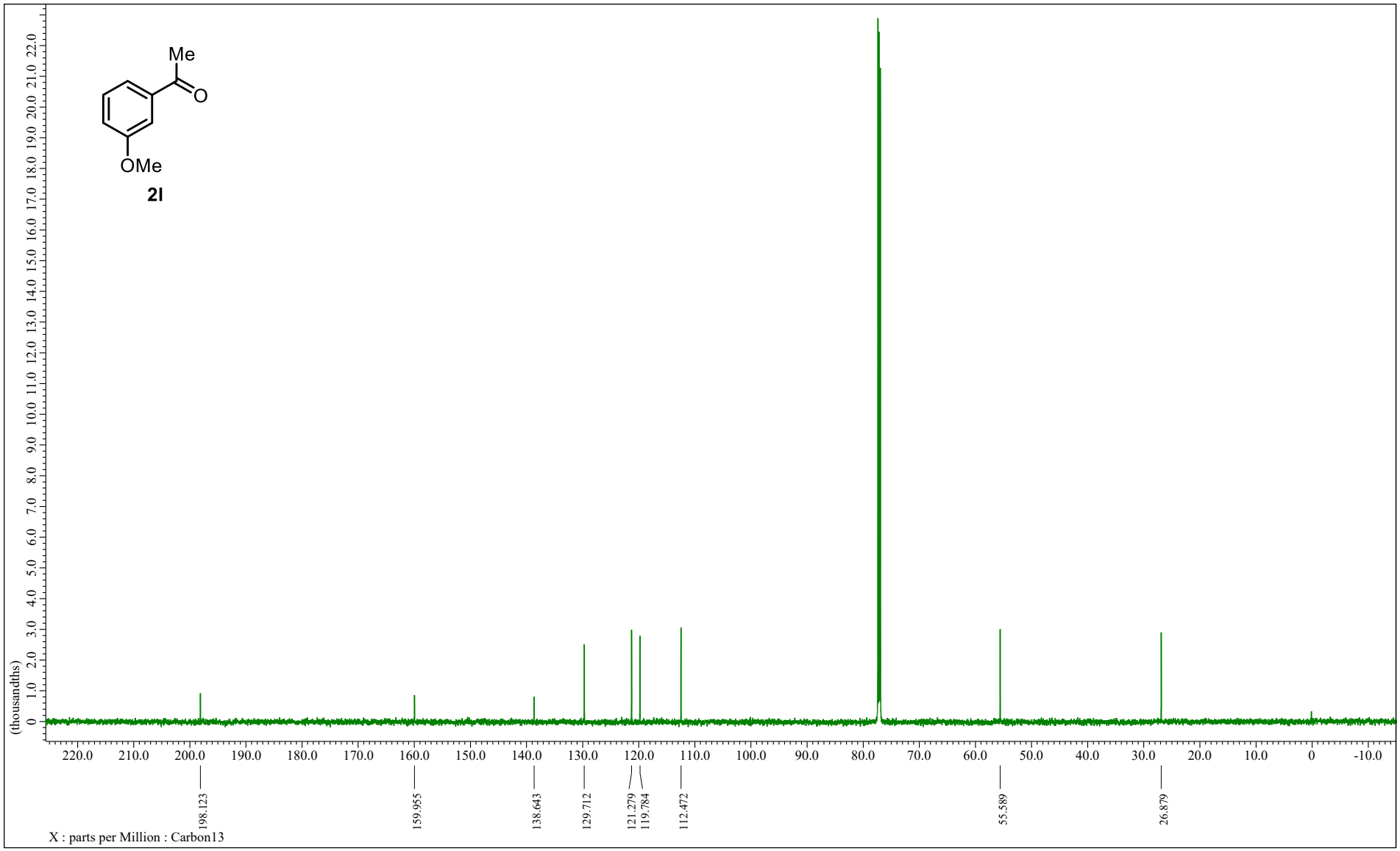

Figure S44. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2l**.

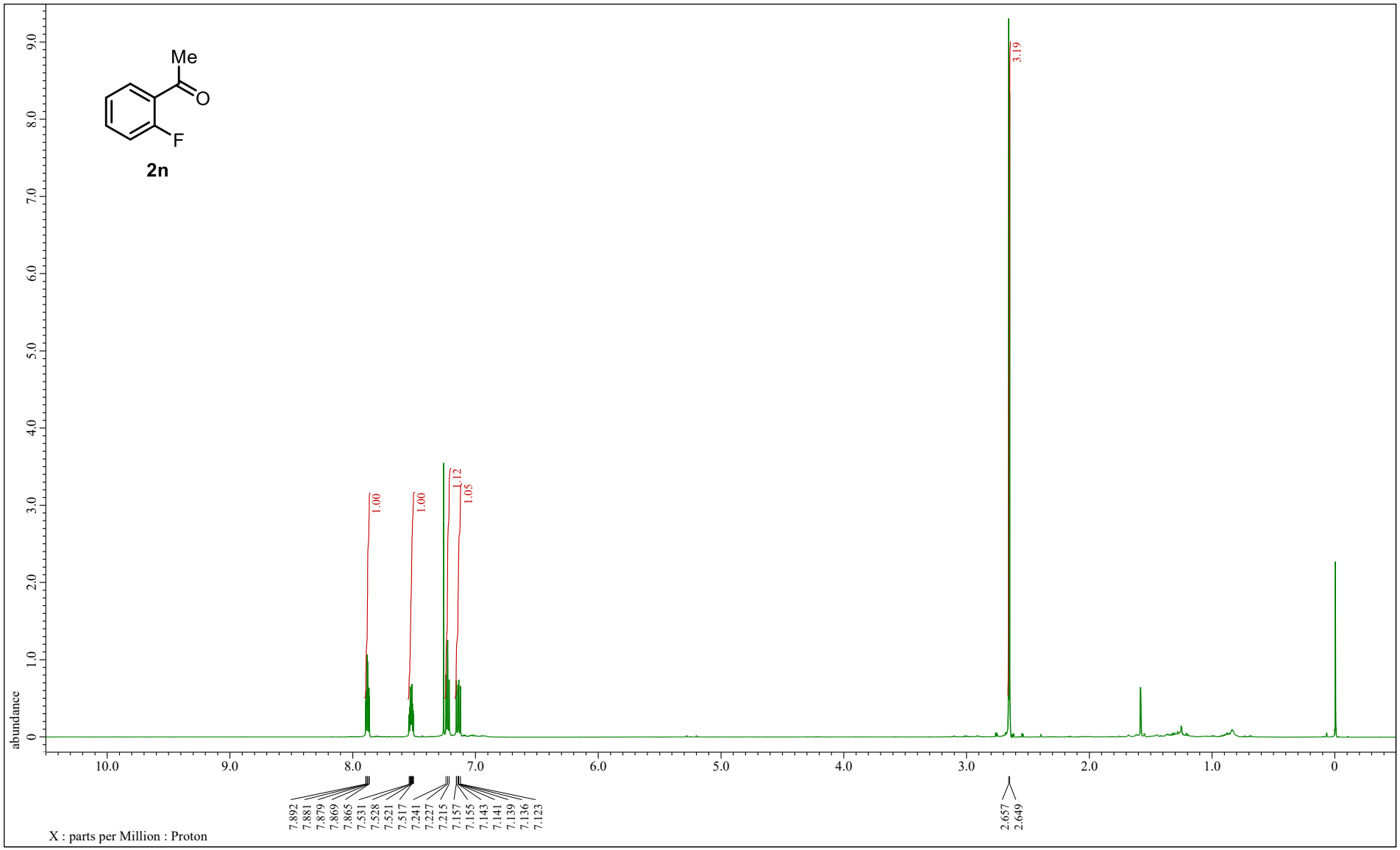

Figure S45. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2n**.

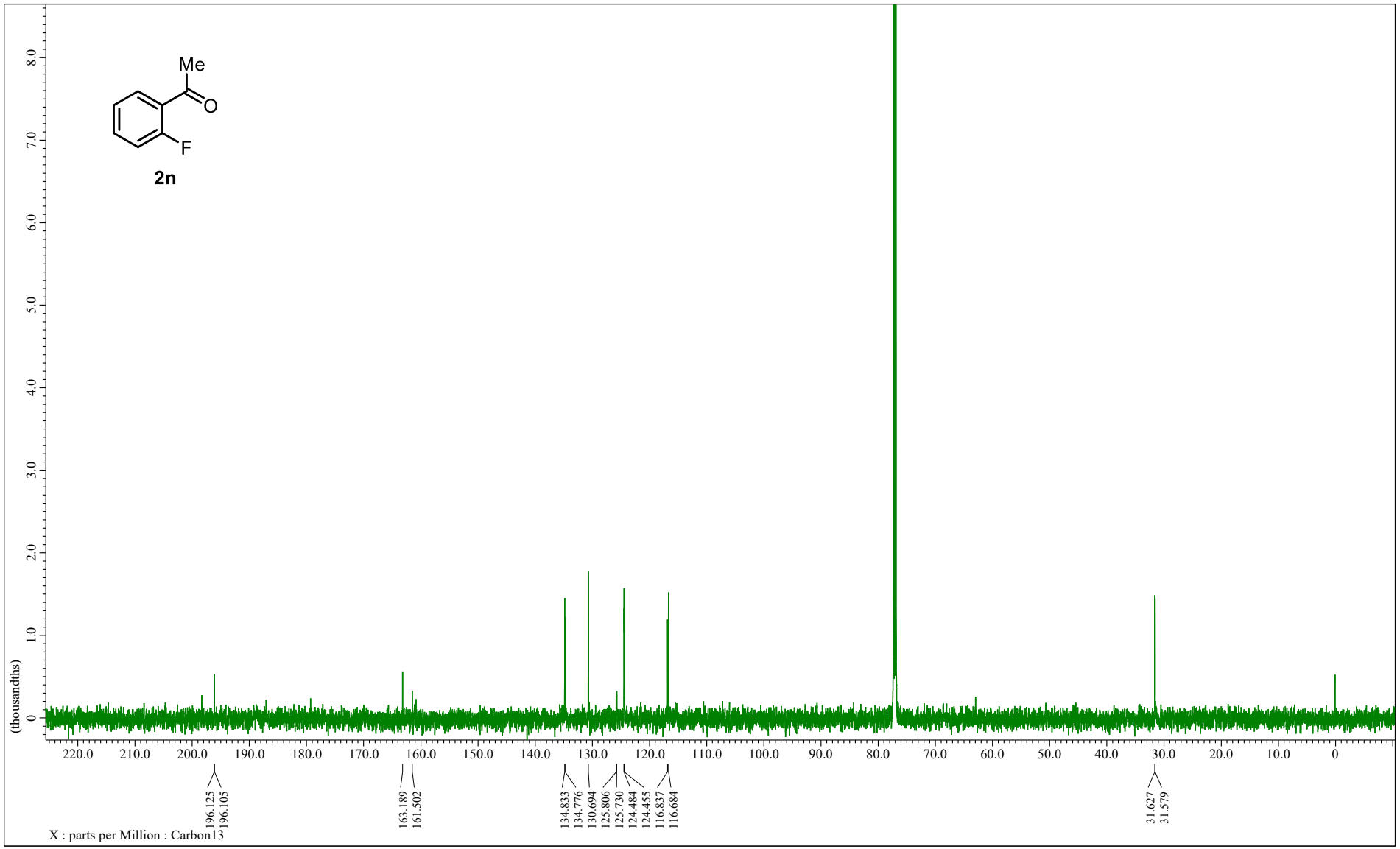

Figure S46. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2n**.

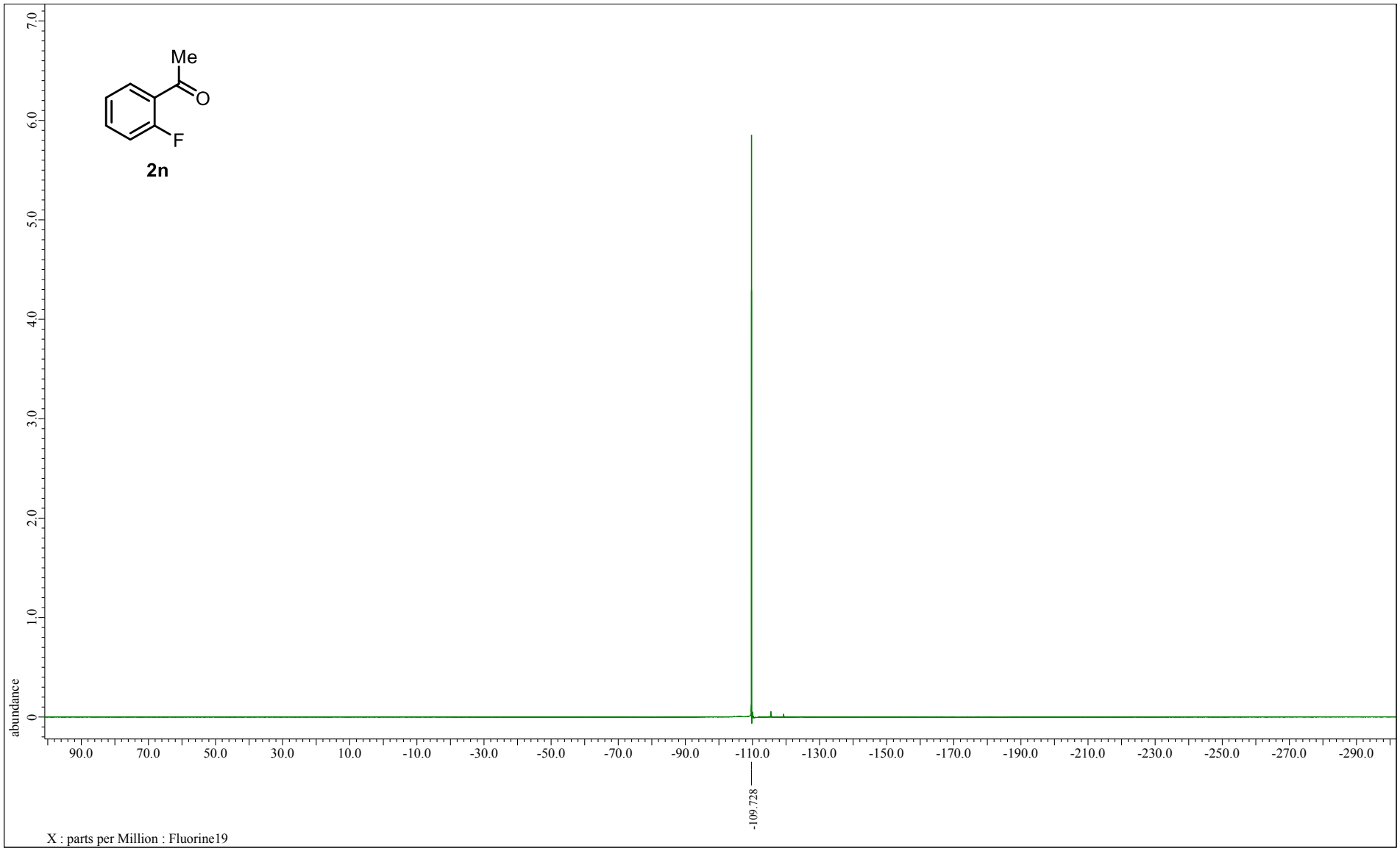

Figure S47. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2n**.

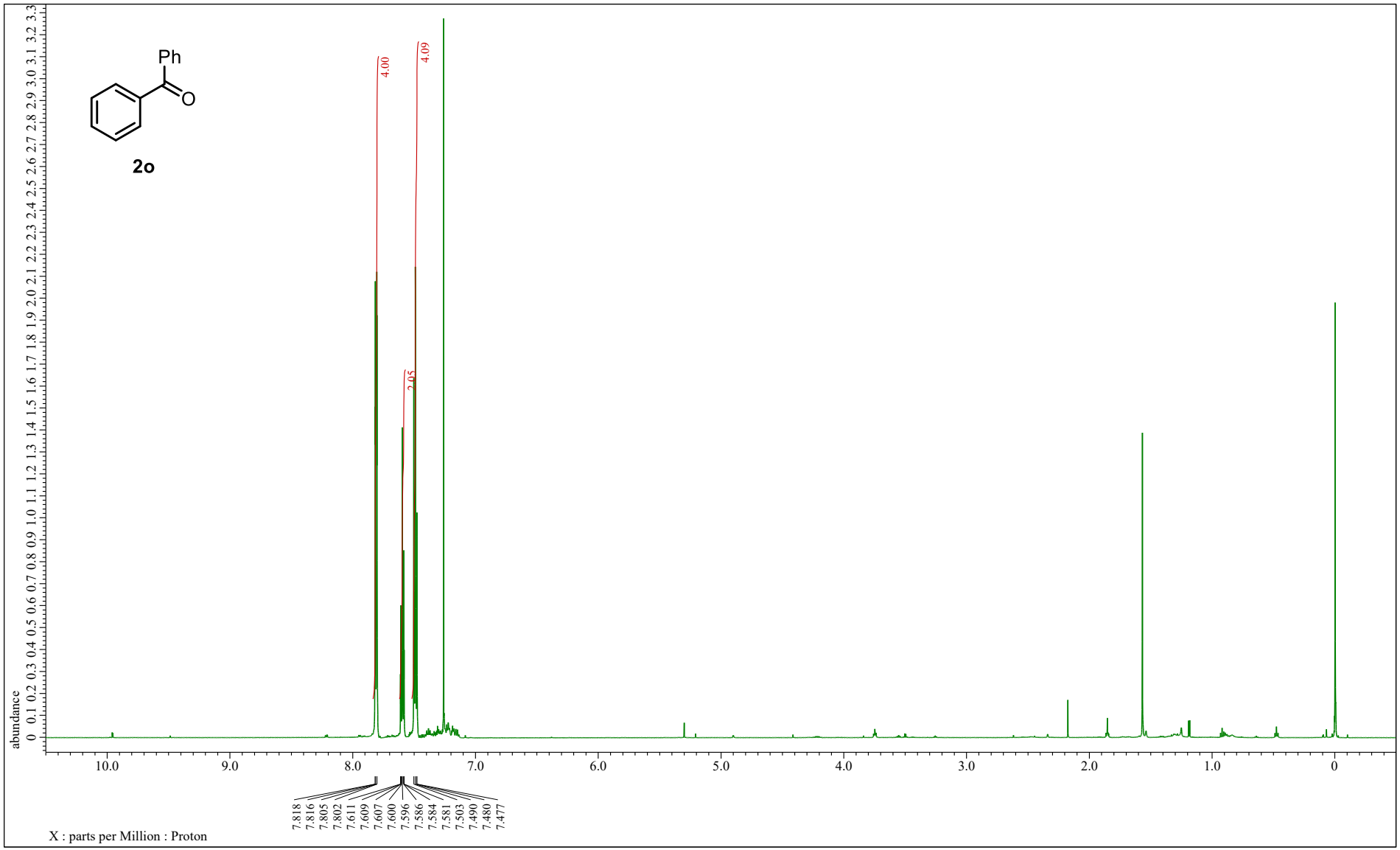

Figure S48. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2o**.

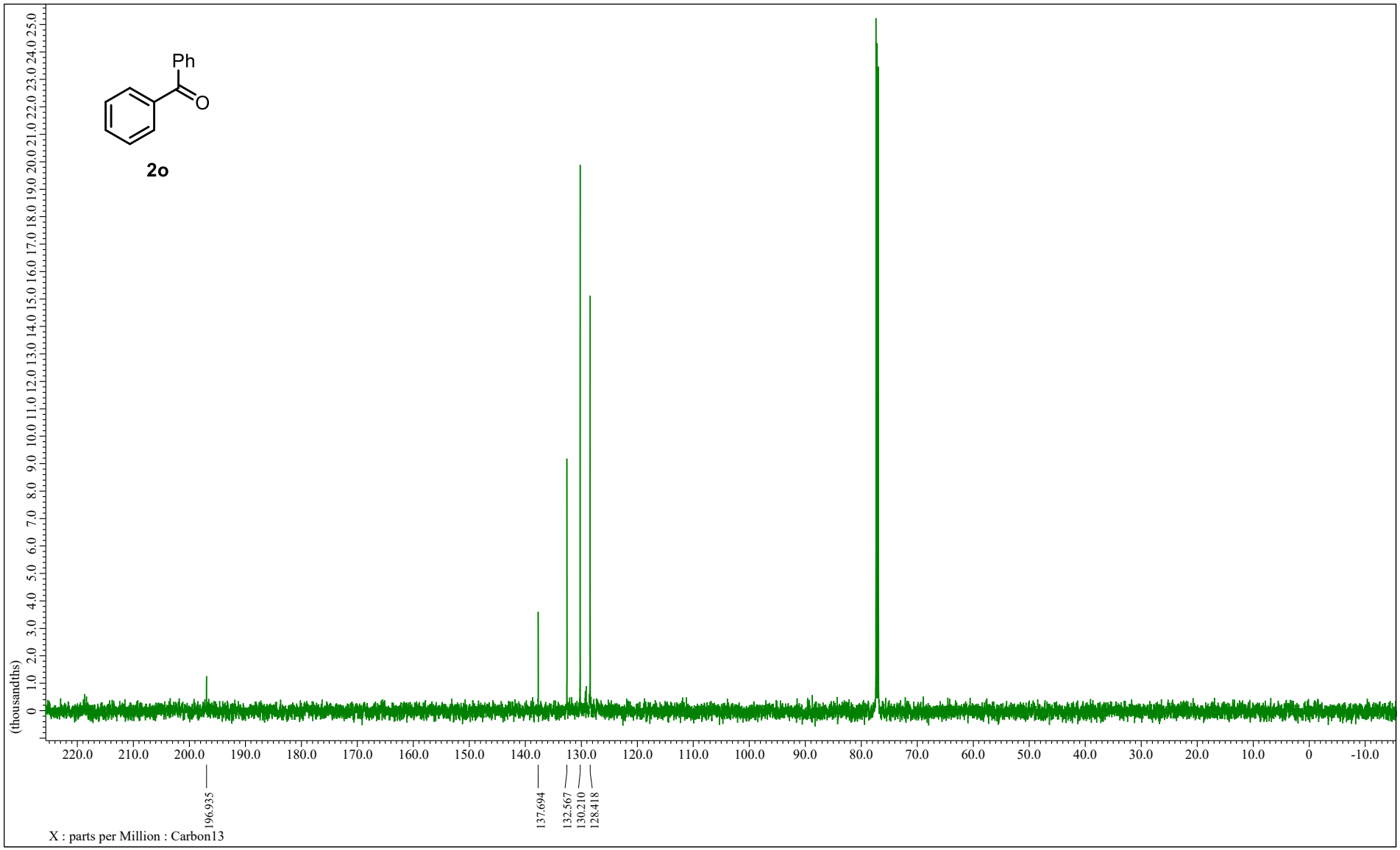

Figure S49. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2o**.

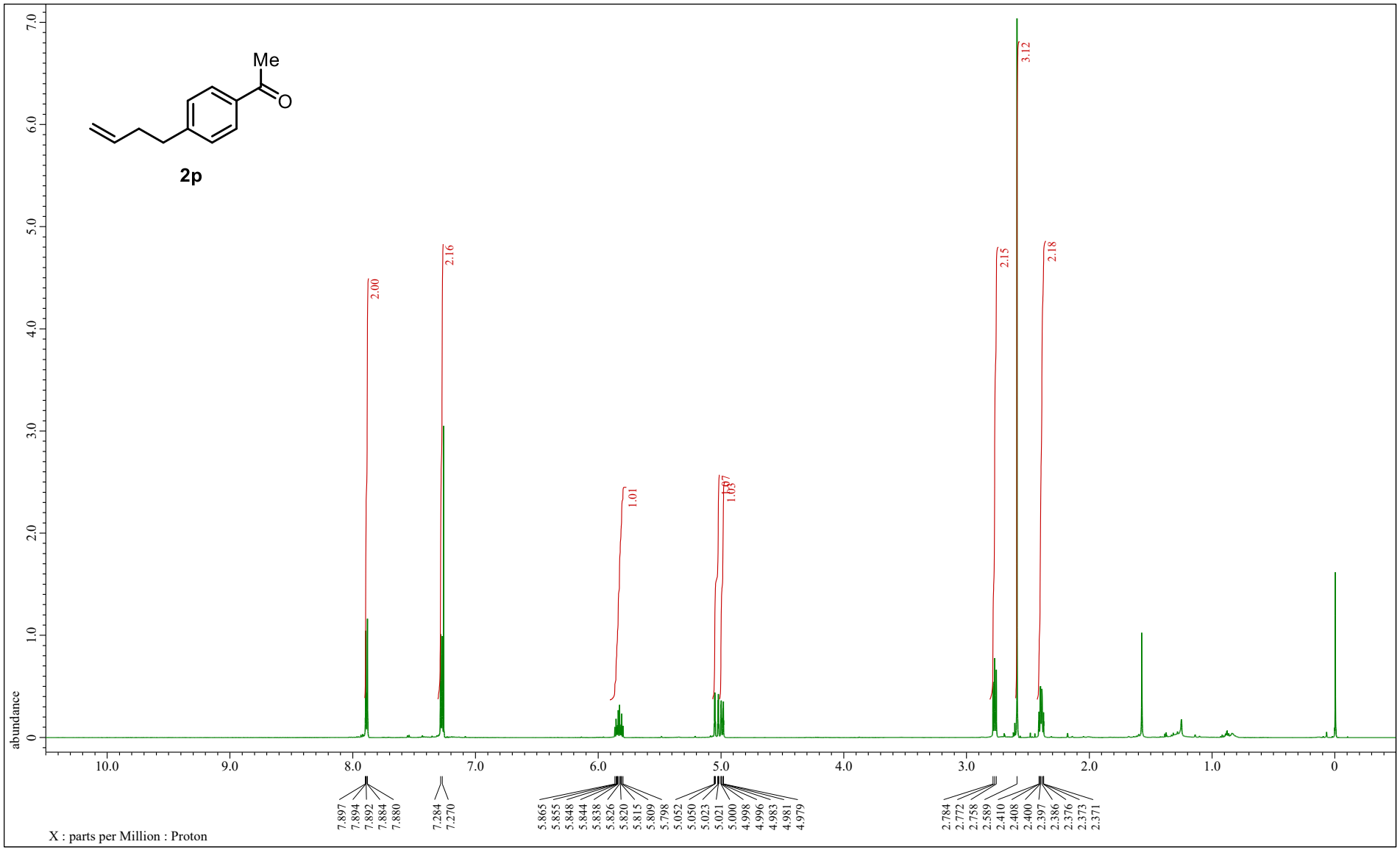

Figure S50. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2p**.

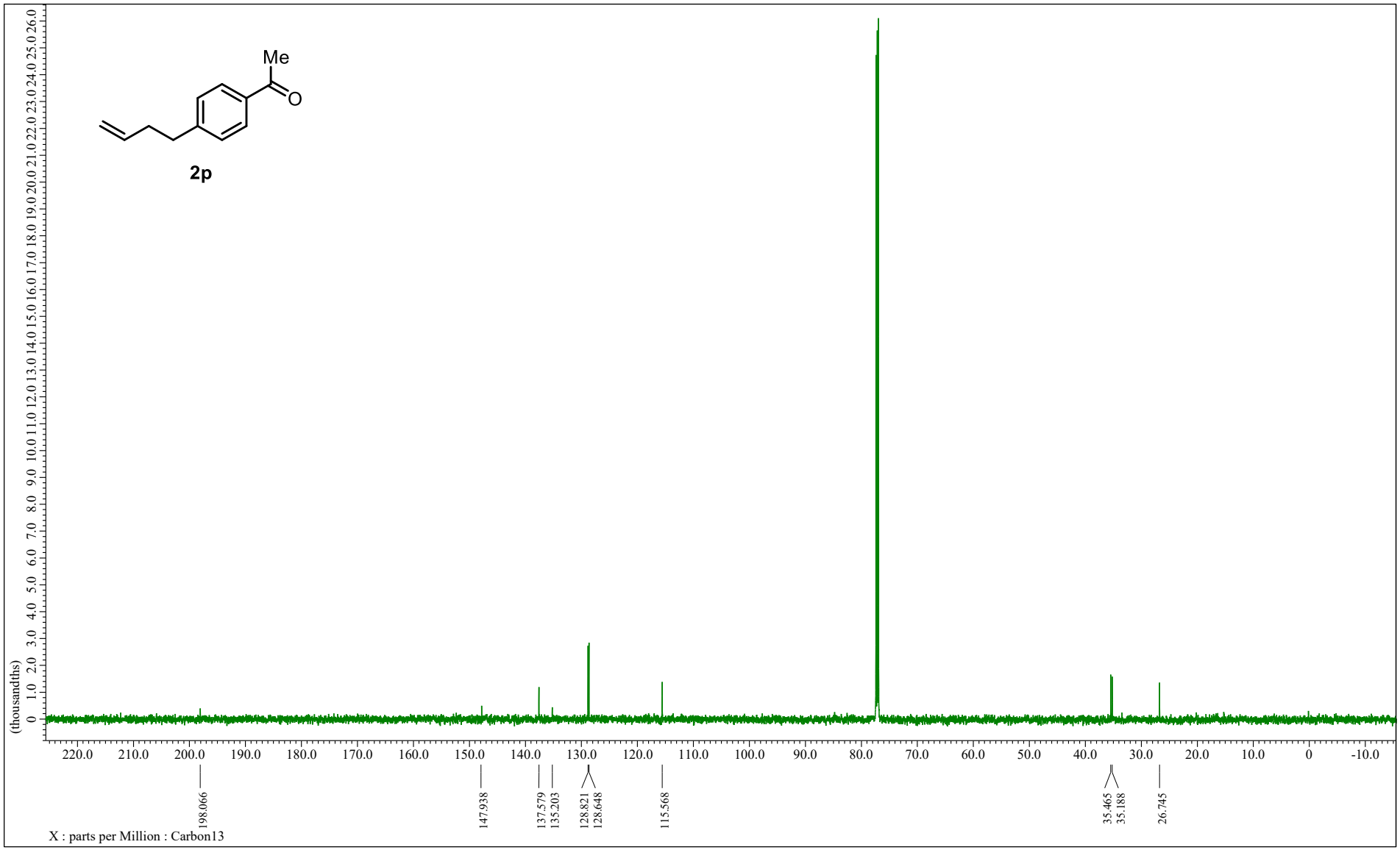

Figure S51. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2p**.

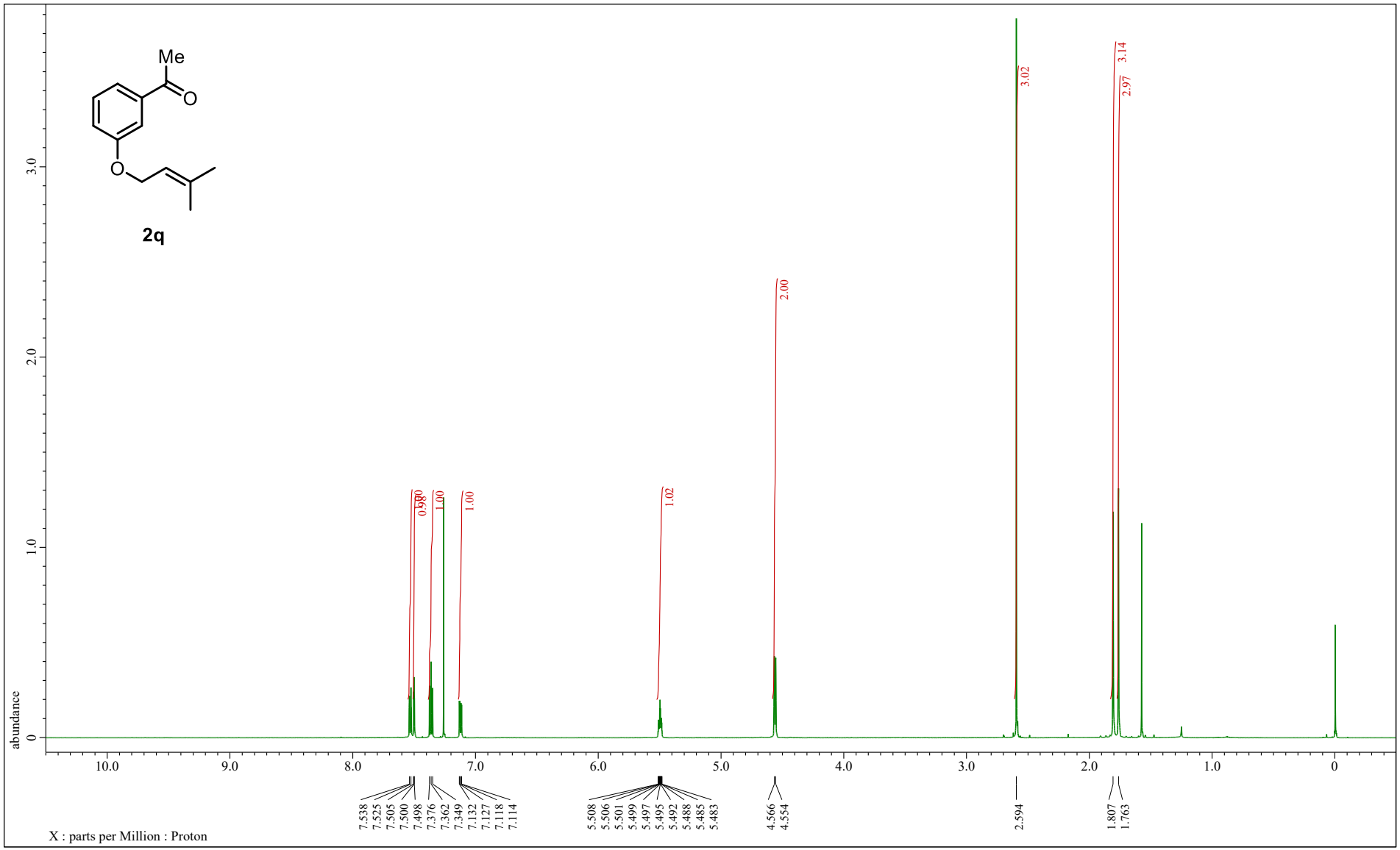

Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2q**.

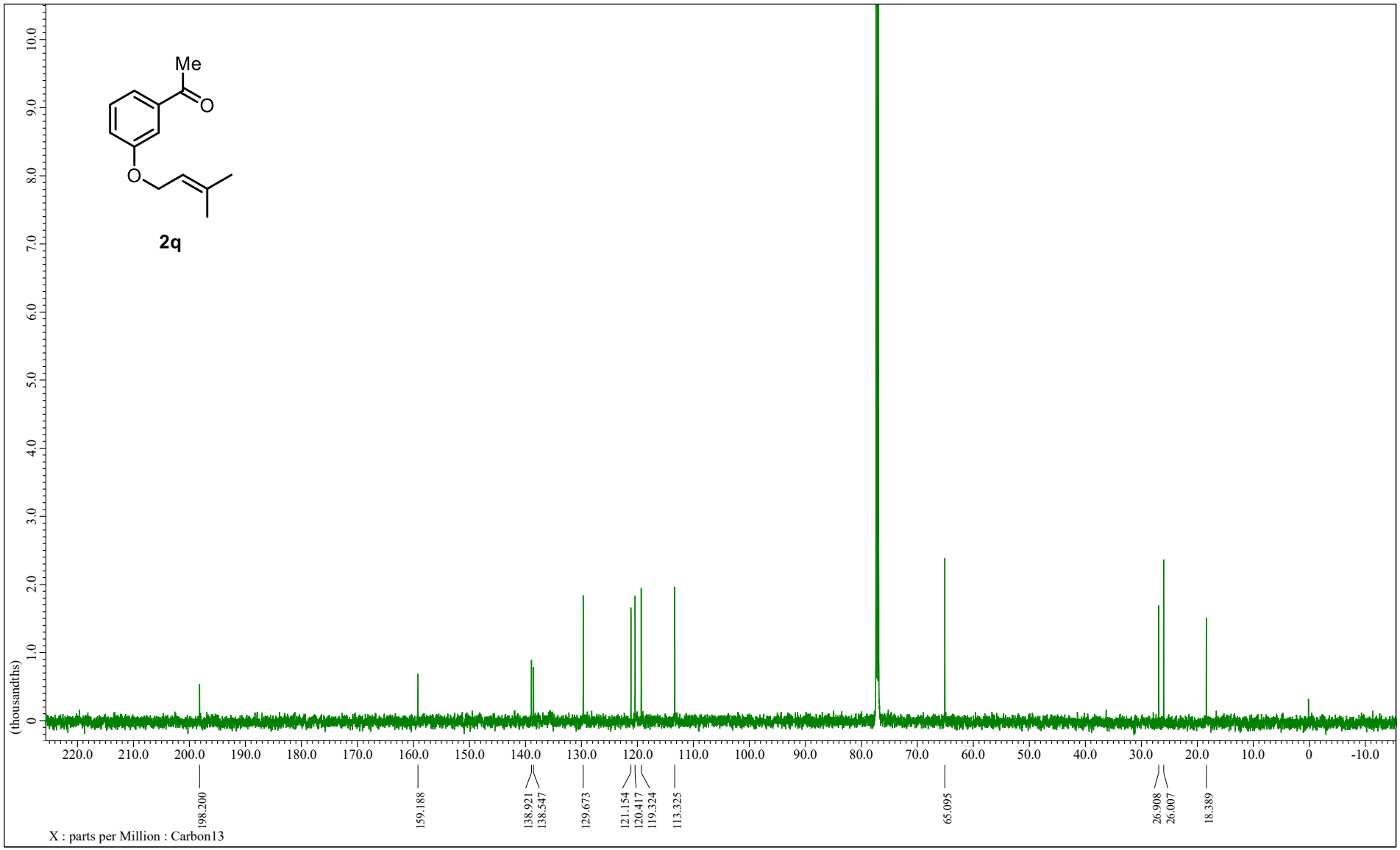

Figure S53. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2q**.

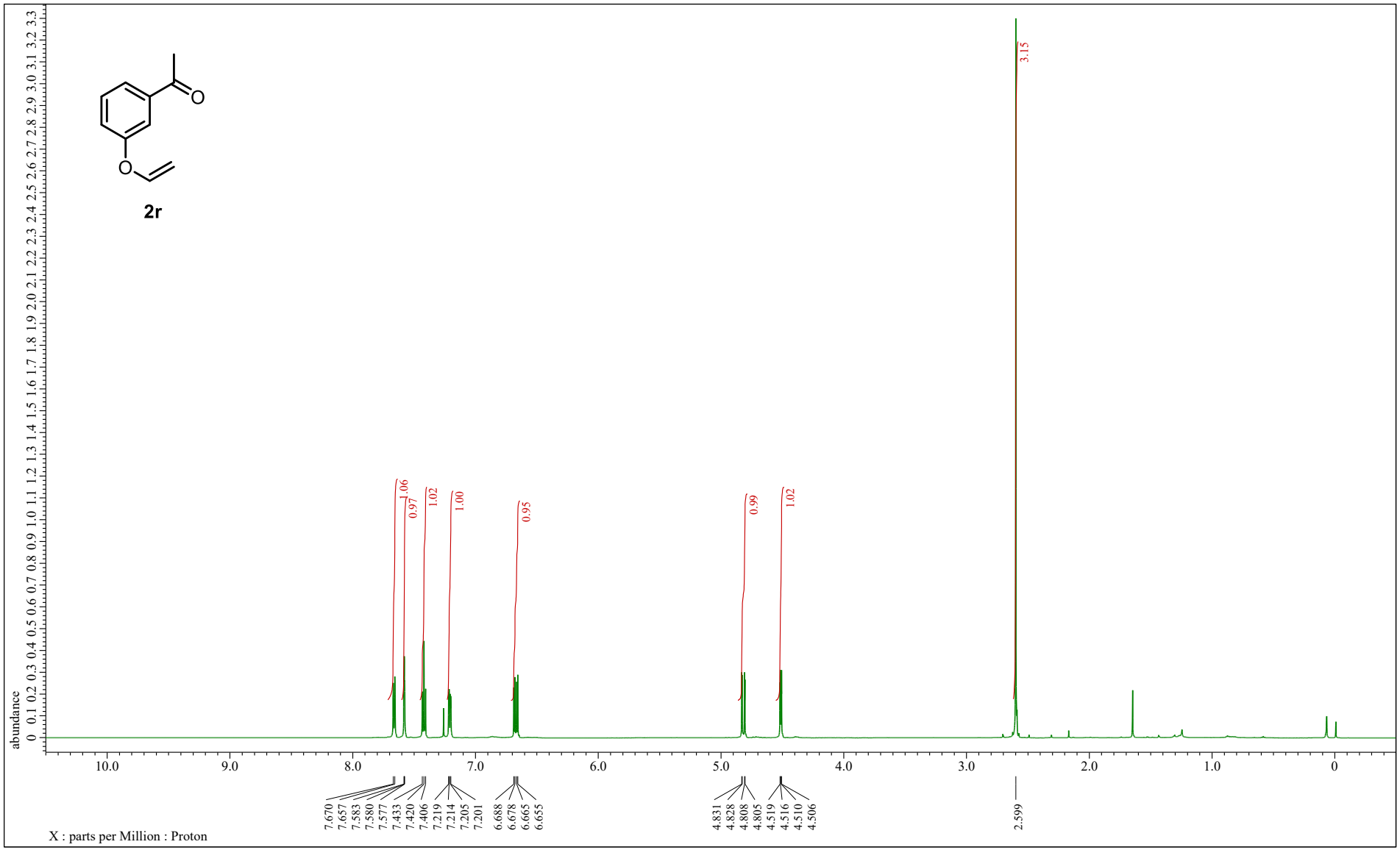

Figure S54. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2r**.

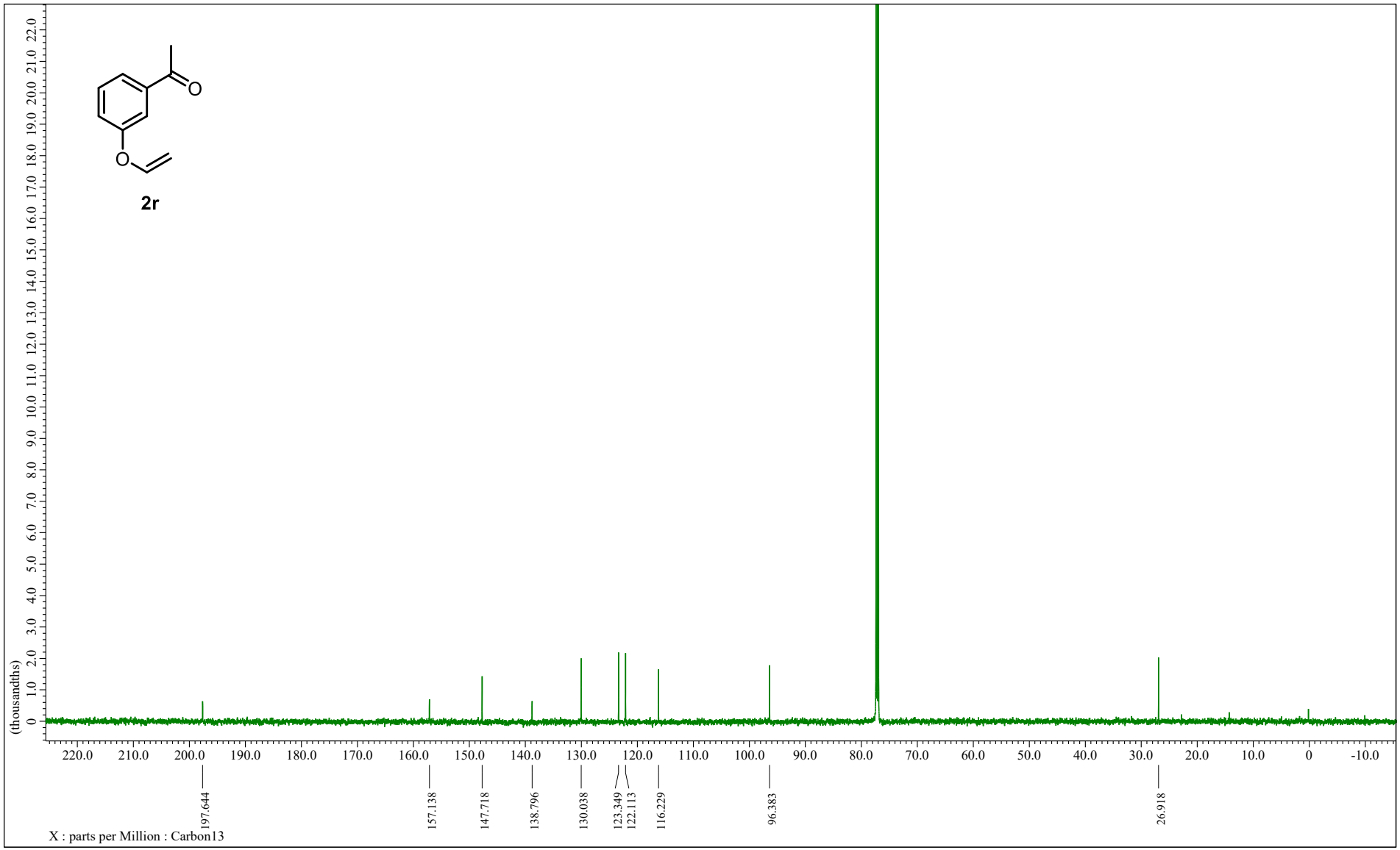

Figure S55. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2r**.

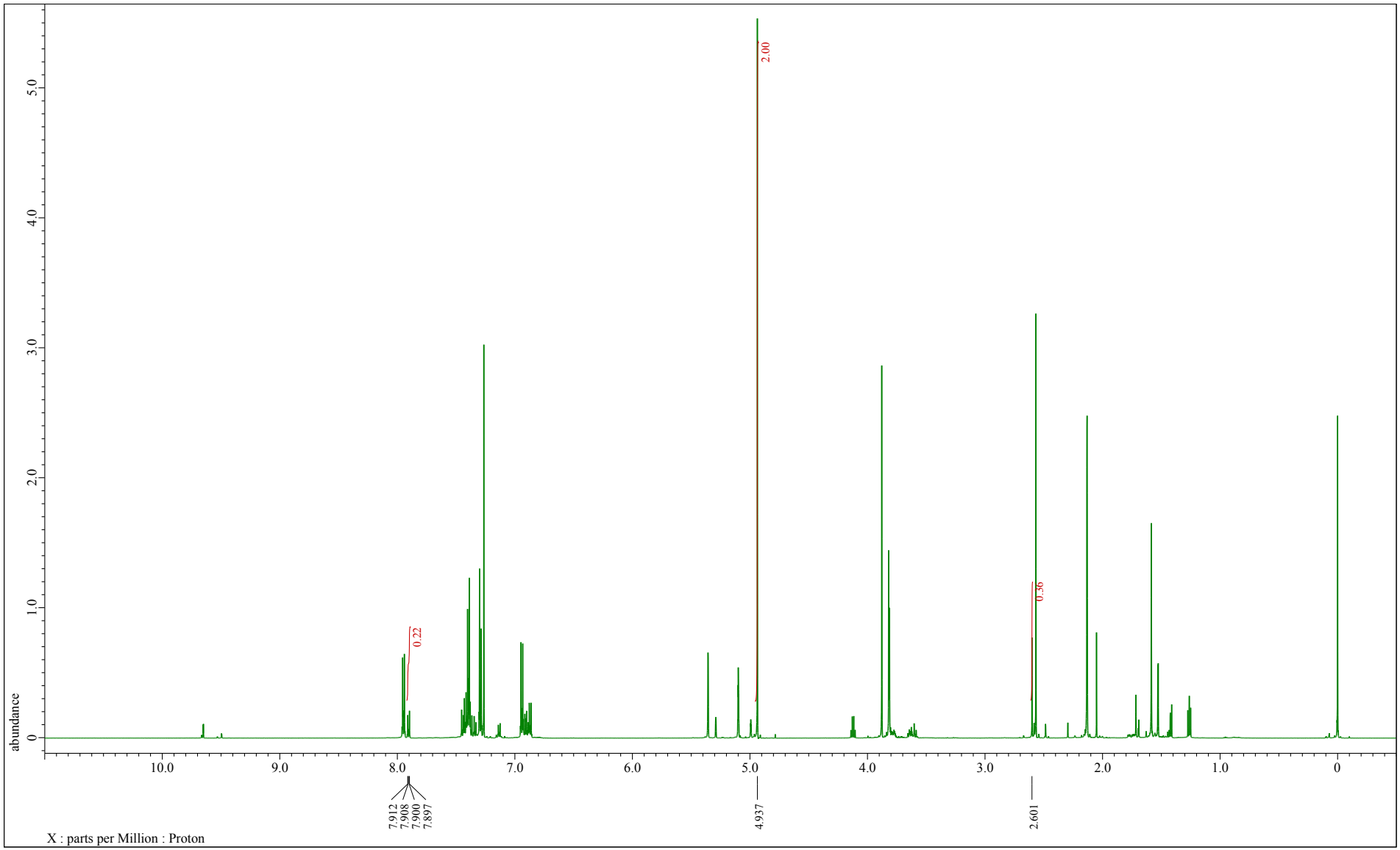

Figure S56. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the crude mixture containing **2c**.

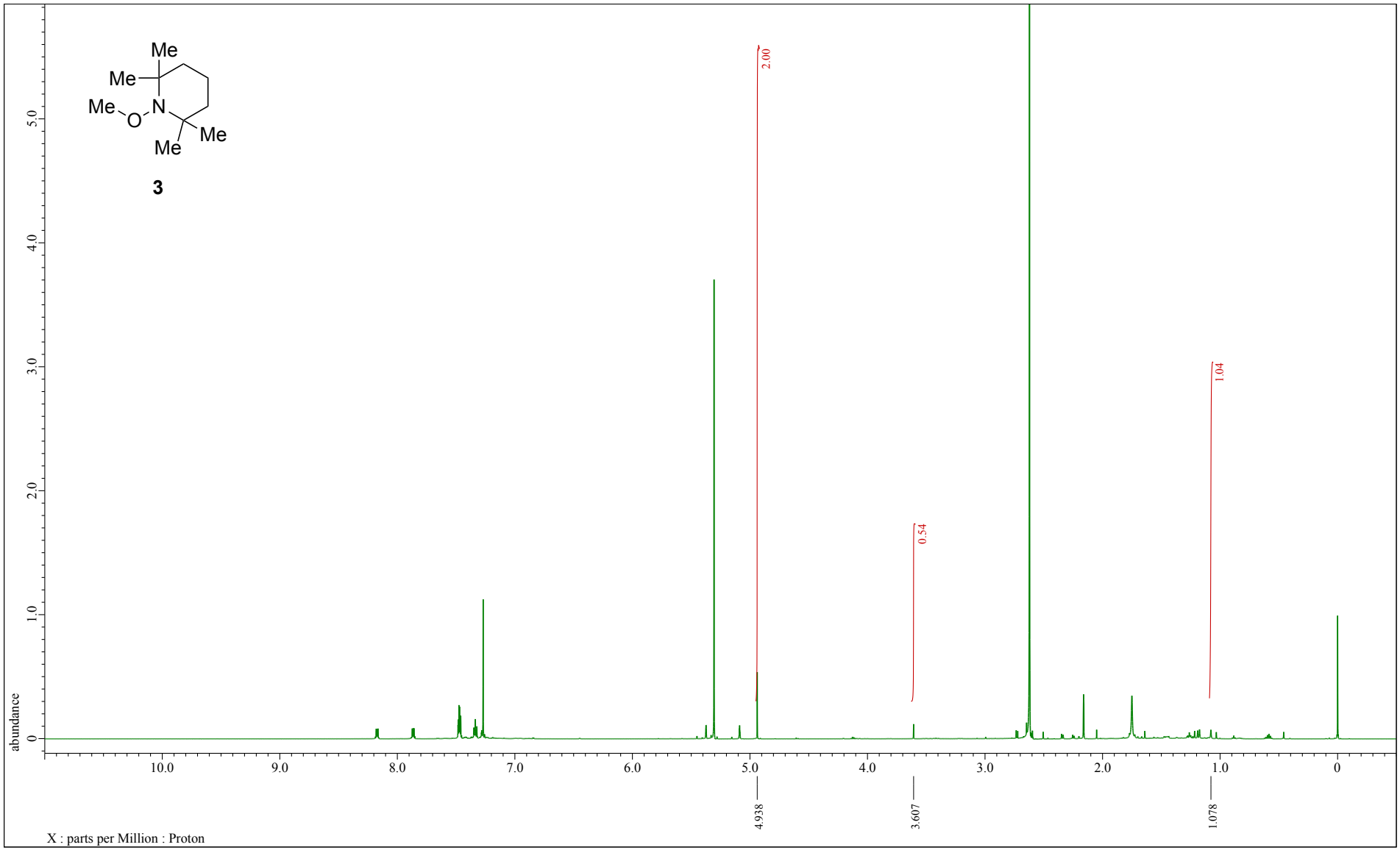

Figure S57. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the crude mixture containing **3**.

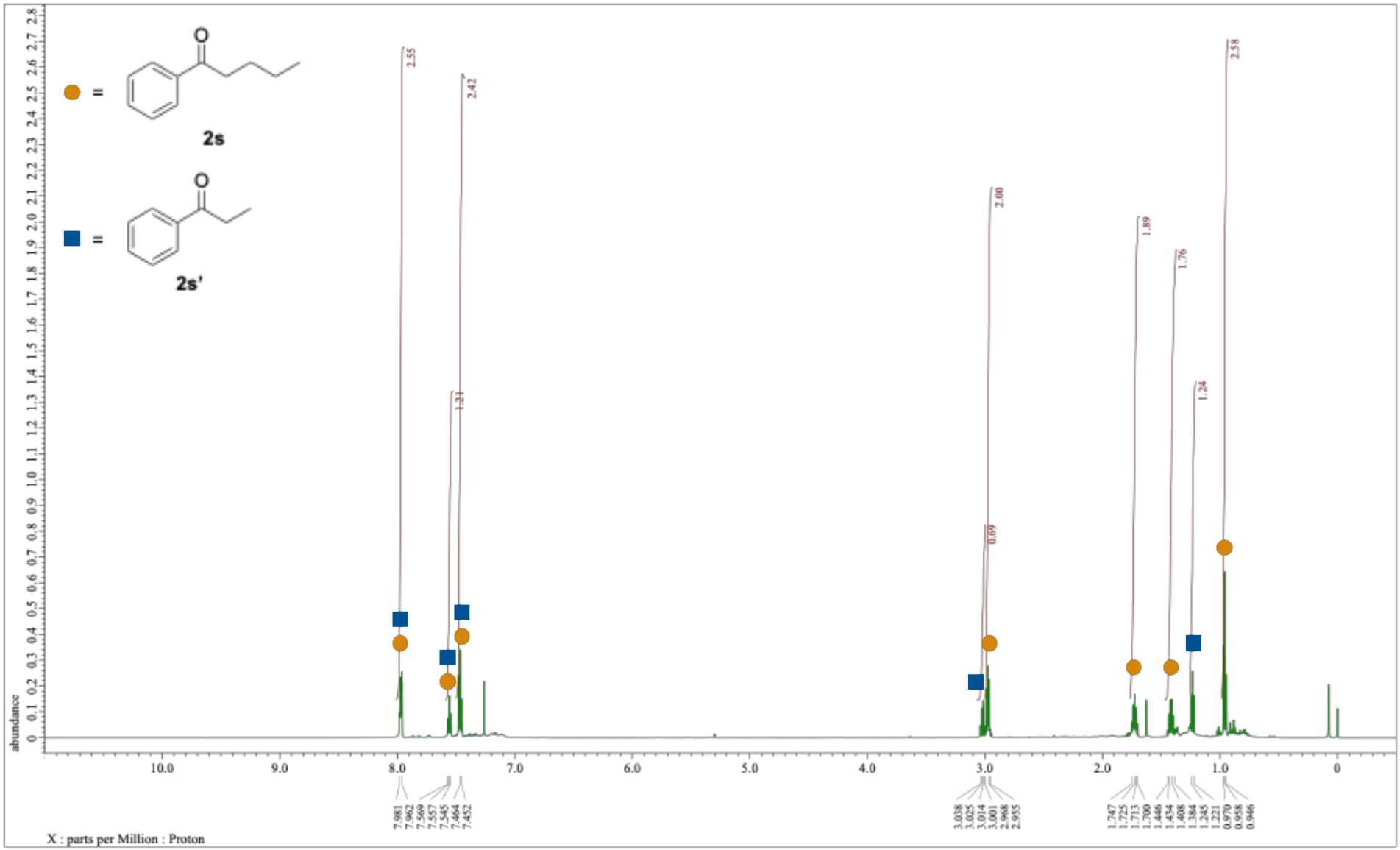

Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of the mixture containing **2s and 2s'**.