

Supporting Information

Generation of Organozinc Reagents from Arylsulfonium Salts Using a Nickel Catalyst and Zinc Dust

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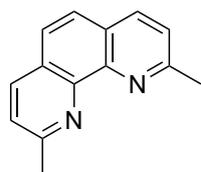
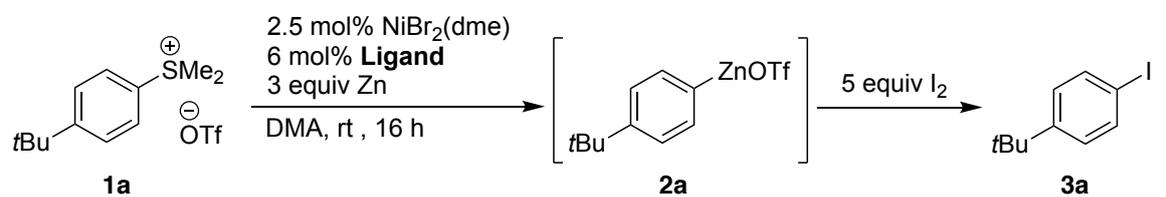
Instrumentation and Chemicals

^1H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{19}F NMR (564 MHz) spectra were recorded on a JEOL ECZ-600 spectrometer. Chemical shifts in ^1H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to residual CHCl_3 ($\delta = 7.26$ ppm), $\text{CD}_2\text{HSOCD}_3$ ($\delta = 2.50$ ppm), or tetramethylsilane ($\delta = 0.00$ ppm). Chemical shifts in ^{13}C NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to CDCl_3 ($\delta = 77.16$ ppm), CD_3SOCD_3 ($\delta = 39.52$ ppm). For the ^{19}F NMR spectra, fluorobenzene (^{19}F : $\delta = -113.50$ ppm) was used as an external standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using “APCI-L Low Concentration Tuning Mix” (Agilent Technologies, Inc.) as the internal standard or Electrospray Ionization (ESI) method using “ESI-L Low Concentration Tuning Mix” (Agilent Technologies, Inc.) as the internal standard. Melting points were determined on a Stanford Research Systems MPA100 melting point apparatus. For all spectroscopic studies, spectroscopic grade solvents were used as purchased unless otherwise noted.

All non-aqueous reactions were carried out under an inert atmosphere of N_2 gas in oven-dried glassware unless otherwise noted. Dehydrated solvents (DMA : *N,N*-dimethylacetamide, NMP : *N*-methylpyrrolidone, DMF : *N,N*-dimethylformamide) were purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Dehydrated THF was purchased from Kanto Chemical Co., Inc. and stored under nitrogen atmosphere. Zn powder was purchased from Tokyo Chemical Industry Co., Ltd. and activated according to the literature¹. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F₂₅₄. Preparative flash chromatography was performed using Silica Gel (Wakosil[®] C-300 purchased from FUJIFILM Wako Pure Chemical Corporation, or Silica Gel 60N, spherical neutral, particle size 100-210 μm , purchased from Kanto Chemical Co., Inc.). Membrane filters (Millex[®]-LCR 33 mm) were purchased from Merck Millipore Ltd.

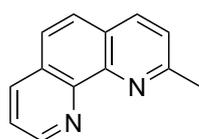
Optimization of Reaction Conditions

Table S1. Screening of ligands^a



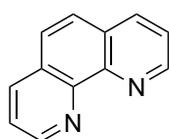
L1

81%



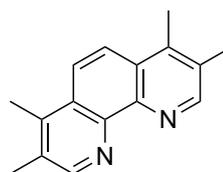
L2

79%



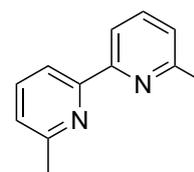
L3

trace



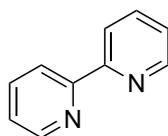
L4

0%



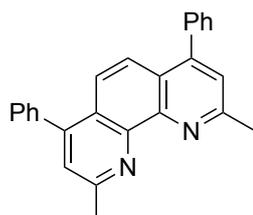
L5

18%



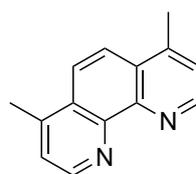
L6

6%



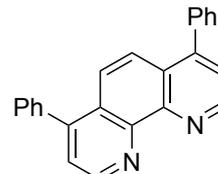
L7

44%



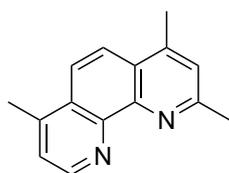
L8

trace



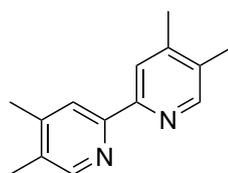
L9

57%



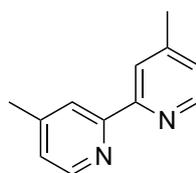
L10

23%



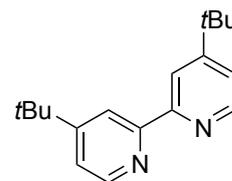
L11

0%



L12

0%

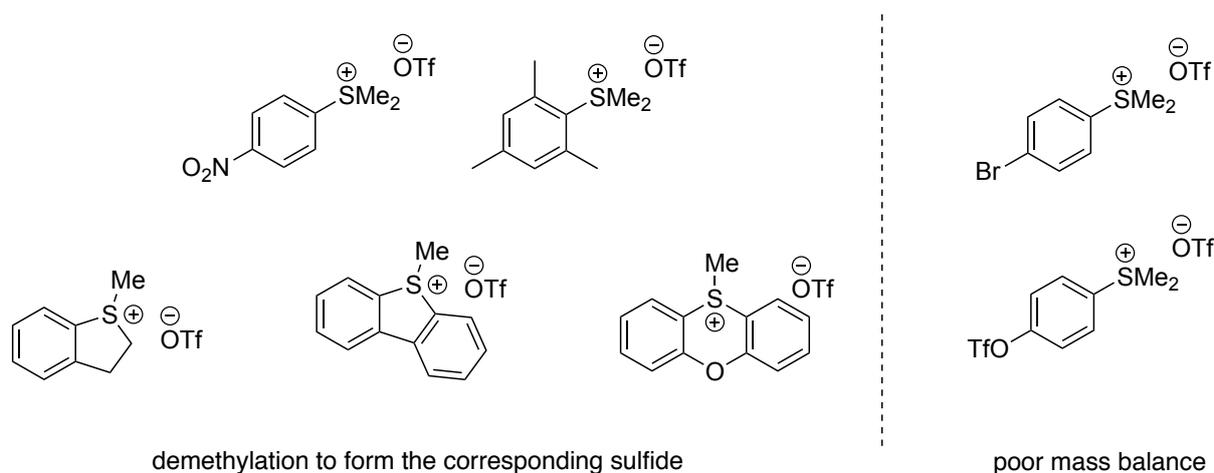


L13

0%

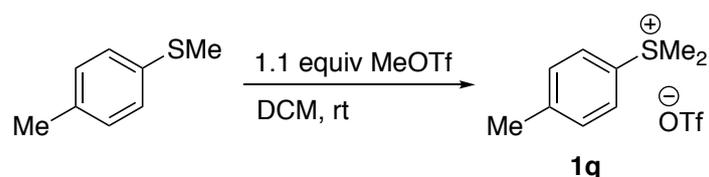
^aYields were determined by ¹H-NMR using 1,1,2,2-tetrabromoethane as an internal standard.

Unsuccessful Substrates



Preparation of Substrates

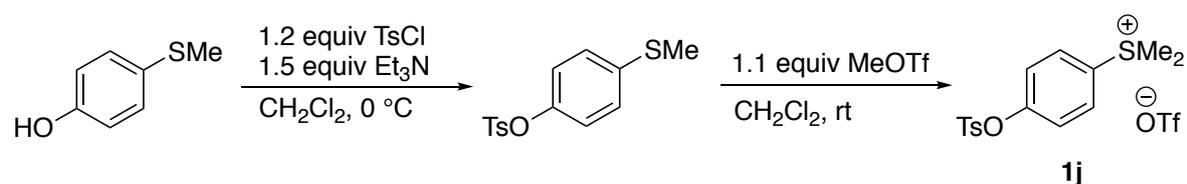
General procedure for the synthesis of aryldimethylsulfonium salts (GP1)



The synthesis of dimethyl(*p*-tolyl)sulfonium trifluoromethanesulfonate (**1q**) is representative. A 300-mL flask was charged with methyl *p*-tolyl sulfide (3.8 g, 28 mmol) and CH_2Cl_2 (30 mL). To the flask was added MeOTf (3.3 mL, 30 mmol), and the resulting solution was stirred at room temperature for 12 h. Et_2O (100 mL) was then added slowly. The precipitates were filtered off and washed with Et_2O (3×20 mL) to afford **1q** (7.6 g, 25 mmol, 91%) as a white solid. All the resonances in ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the reported values.

Arylsulfonium salts **1h**, **1r**, **1s**, and **1t** were also synthesized according to the same procedure from the corresponding aryl sulfides.

General procedure for the synthesis of aryldimethylsulfonium salts (GP2)



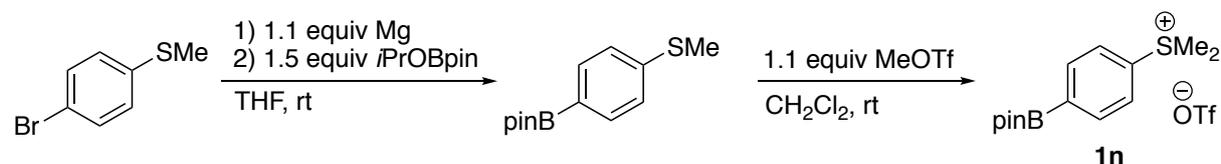
The synthesis of dimethyl(4-(*p*-toluenesulfonyloxy)phenyl)sulfonium trifluoromethanesulfonate (**1j**) is representative. A 300-mL flask was charged with 4-

hydroxyphenyl methyl sulfide (1.4 g, 10 mmol), *p*-toluenesulfonyl chloride (2.3 g, 12 mmol) and CH₂Cl₂ (40 mL). To the flask, Et₃N (2.1 mL, 15 mmol) was added at 0 °C, and the resulting mixture was stirred for 15 h at room temperature. The reaction was quenched with water (100 mL), and the resulting biphasic solution was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 4-(*p*-toluenesulfonyloxy)phenyl methyl sulfide (2.7 g, ca. 9.1 mmol) as a pale yellow solid with small amounts of impurities.

According to **GPI**, the crude sulfide was converted to the corresponding sulfonium salt **1j** (white solid, 3.9 g, 8.5 mmol, 94% from ca. 9.1 mmol of 4-(*p*-toluenesulfonyl)phenyl methyl sulfide).

Arylsulfonium salts **1k** and **1m** were also synthesized according to the same procedure from the corresponding aryl sulfides.

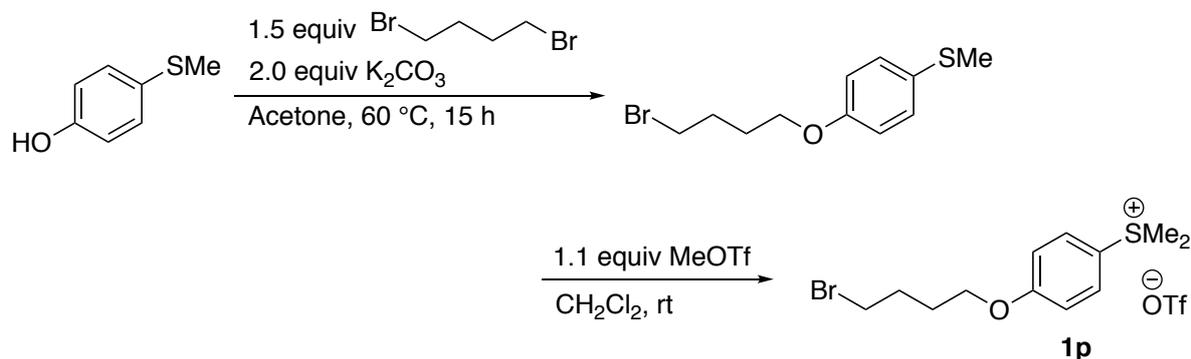
Synthesis of aryl dimethylsulfonium salt **1n**



A 100-mL two-necked flask equipped with a reflux condenser was charged with magnesium turnings (588 mg, 24 mmol) and THF (11 mL). A solution of 4-bromophenyl methyl sulfide (4.5 g, 22 mmol in 11 mL of THF) was then added slowly. The resulting mixture was stirred vigorously for 2 h at room temperature. The resulting solution was added slowly to another 100-mL two-necked flask charged with *i*PrOBpin (6.12 mL, 30 mmol) and THF (15 mL). The resulting mixture was then stirred 2 h at room temperature. The reaction was quenched with 3 M aqueous HCl (20 mL) at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The resulting biphasic solution was extracted with EtOAc (3 × 30 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl methyl sulfide (5.6 g, ca. 21 mmol) as a pale yellow oil with small amounts of impurities.

According to **GPI**, the crude sulfide was converted to the corresponding sulfonium salt **1n** (white solid, 3.5 g, 8.5 mmol, 84% from ca. 10 mmol of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl methyl sulfide).

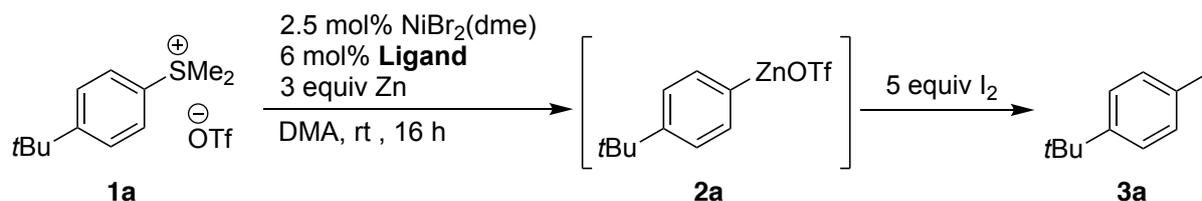
Synthesis of aryldimethylsulfonium salt **1p**



A 100-mL flask was charged with K₂CO₃ (4.2 g, 30 mmol), 4-hydroxyphenyl methyl sulfide (2.1 g, 15 mmol), and acetone (15 mL). To the flask, 1,4-dibromobutane (0.74 mL, 7.5 mmol) was added at 0 °C. The resulting solution was stirred at 60 °C (oil bath) for 15 h before an addition of 3 M aqueous HCl (20 mL). The resulting biphasic solution was extracted with hexane (3 × 30 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to afford 4-(4-bromobutoxy)phenyl methyl sulfide (2.6 g, 9.3 mmol, 62%) as a colorless oil. The obtained sulfide was treated with MeOTf according to **GP1** to afford the corresponding sulfonium salt **1p** as a white solid (3.5 g, 8.0 mmol, 99% from 8.1 mmol of 4-(4-bromobutoxy)phenyl methyl sulfide).

Experimental Procedures

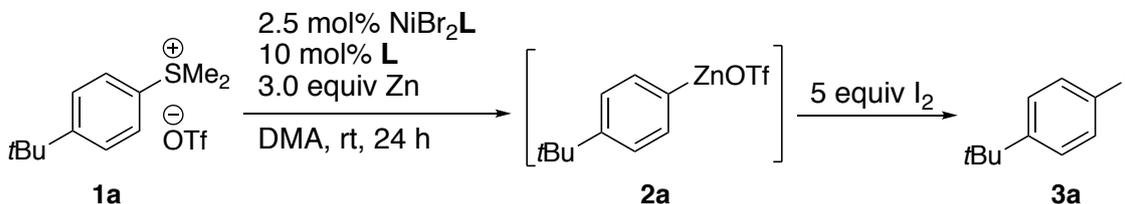
General procedure for ligand screening (GP3, Scheme 4)



The zincation of **1a** with **L1** as a ligand is representative. A 20-mL Schlenk tube was charged with dimethyl(*p*-*tert*-butylphenyl)sulfonium trifluoromethanesulfonate (**1a**, 103.3 mg, 0.30 mmol), **L1** (3.7 mg, 18 μmol), Zn powder (58.8 mg, 0.90 mmol). The tube was then evacuated and refilled with N₂ gas (3 times). A solution of NiBr₂(dme) (11.6 mg, 7.5 μmol in DMA (1.5 mL)) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. The reaction was quenched with iodine (381 mg, 1.5 mmol). After the mixture was stirred for 5 min, saturated aqueous Na₂S₂O₃ was added. The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of

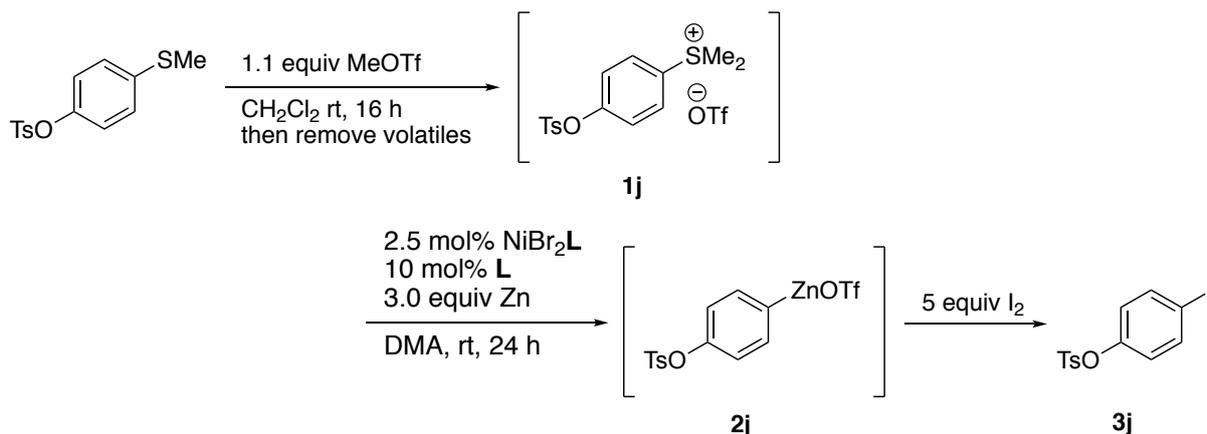
Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The yield of **3a** was determined by NMR analysis using 1,1,2,2-tetrabromoethane as an internal standard.

General procedure for zincation of arylsulfonium salts **1** (GP4, Scheme 4)



The synthesis of **3a** is representative. A 20-mL Schlenk tube was charged with dimethyl(*p*-*tert*-butylphenyl)sulfonium trifluoromethanesulfonate (**1a**, 344.4 mg, 1.0 mmol), NiBr₂**L1** (10.7 mg, 25 μmol), **L1** (20.8 mg, 100 μmol), Zn powder (196.1 mg, 3.0 mmol). The tube was then evacuated and refilled with N₂ gas (3 times). DMA (5 mL) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. The reaction was quenched with iodine (1.3 g, 5.0 mmol). After the mixture was stirred for 5 min, saturated aqueous Na₂S₂O₃ was added. The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with hexane to afford *p*-*tert*-butyliodobenzene (**3a**, 217.3 mg, 0.84 mmol, 84%) as a colorless oil.

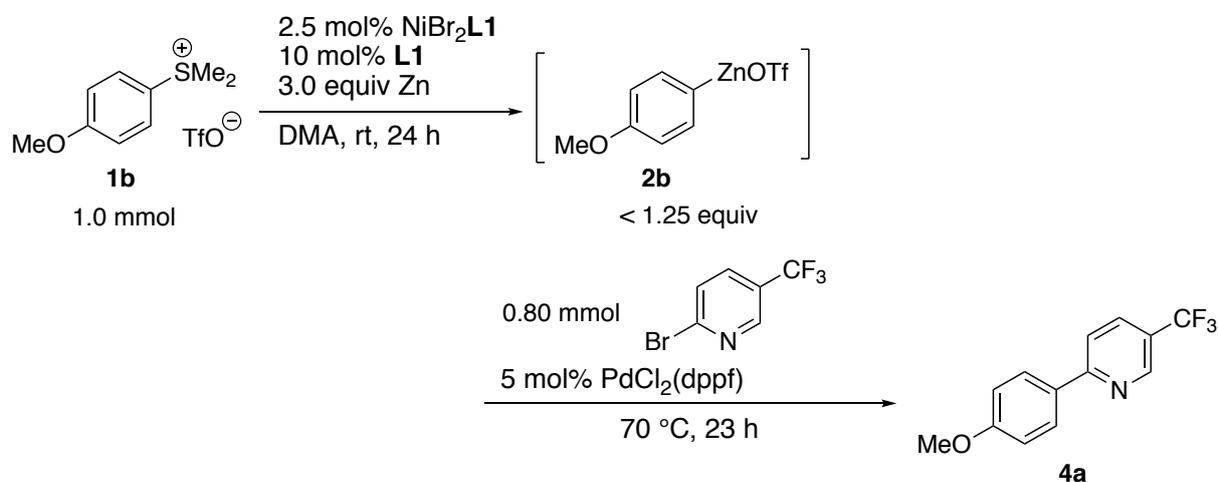
Procedure for one-pot zincation from aryl methyl sulfide (Scheme 4)



A 20-mL Schlenk tube was charged with methyl *p*-tosyloxyphenyl methyl sulfide (294.4 mg, 1.0 mmol) and CH₂Cl₂ (2.0 mL). To this solution, methyl triflate (124 μL, 1.1 mmol) was added, and the resulting mixture was stirred for 16 h at room temperature. All volatiles were removed under reduced pressure to afford the corresponding sulfonium salt **1j**. To the Schlenk tube, Zn powder (196 mg, 3.0 mmol), NiBr₂**L1** (10.7 mg, 25 μmol), and **L1** (20.8 mg, 100 μmol) were

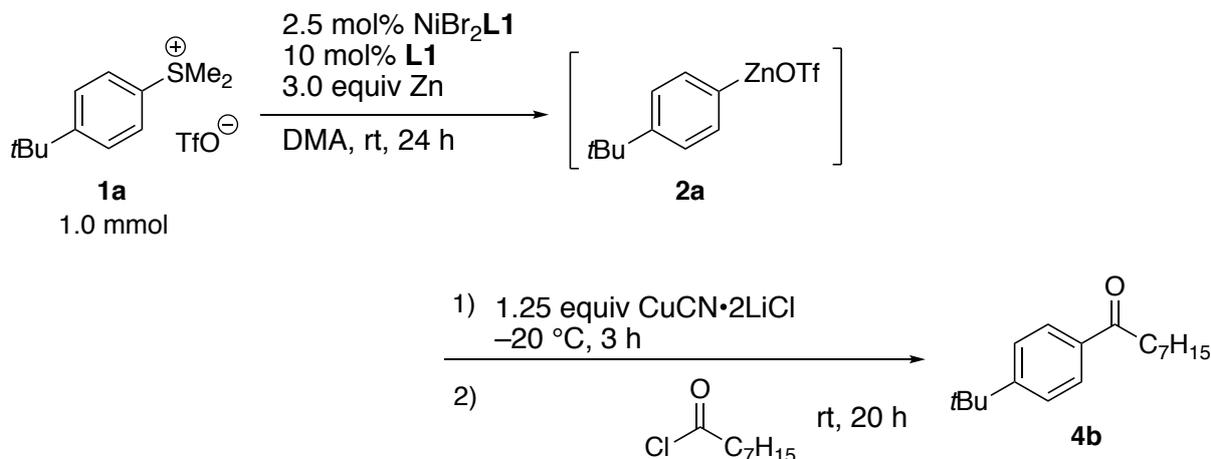
added. The tube was then evacuated and refilled with N₂ gas (3 times). DMA (5 mL) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. The reaction was quenched with iodine (1.3 g, 5.0 mmol). After the mixture was stirred for 5 min, saturated aqueous Na₂S₂O₃ was added. The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/EtOAc = 15/1) to afford *p*-tosyloxyiodobenzene (**3j**, 198.7 mg, 0.53 mmol, 53%) as a white solid.

Procedure for one-pot Negishi coupling (Scheme 5)



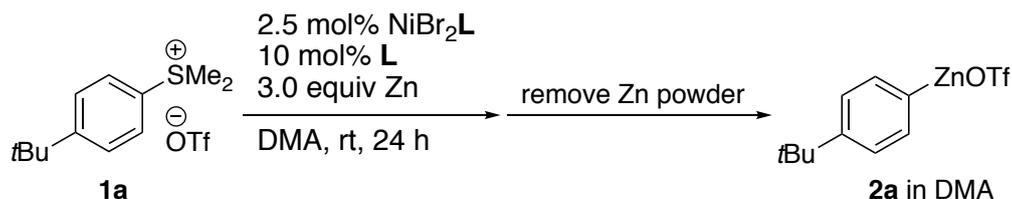
A 20-mL Schlenk tube was charged with dimethyl(*p*-methoxyphenyl)sulfonium trifluoromethanesulfonate (**1a**, 344.4 mg, 1.0 mmol), NiBr₂L1 (10.7 mg, 25 μmol), L1 (20.8 mg, 100 μmol), Zn powder (196.1 mg, 3.0 mmol). The tube was then evacuated and refilled with N₂ gas (3 times). DMA (5 mL) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. To the Schlenk tube, 2-bromo-5-trifluoromethylpyridine (180.8 mg, 0.80 mmol) and PdCl₂(dppf) (32.7 mg, 40 μmol) were added, and the resulting mixture was stirred for 23 h at 70 °C (oil bath). The reaction was quenched with 3 M aqueous HCl (4.0 mL). The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/EtOAc = 30/1) to afford 2-(4-methoxyphenyl)-5-trifluoromethylpyridine (**4a**, 157.2 mg, 0.62 mmol, 78% based on 2-bromo-5-trifluoromethylpyridine) as a white solid.

General procedure for one-pot cross-coupling via transmetalation to copper (GP5, Scheme 5)



The synthesis of **4b** is representative. A 20-mL Schlenk tube was charged with dimethyl(*p*-*tert*-butylphenyl)sulfonium trifluoromethanesulfonate (**1a**, 344.4 mg, 1.0 mmol), NiBr₂L1 (10.7 mg, 25 μmol), L1 (20.8 mg, 100 μmol), and Zn powder (196.1 mg, 3.0 mmol). The tube was then evacuated and refilled with N₂ gas (3 times). DMA (5 mL) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. To the Schlenk tube, a solution of CuCN (89.6 mg, 1.0 mmol) and LiCl (84.8 mg, 2.0 mmol) in THF (2 mL) was then added at -20 °C, and the resulting mixture was stirred for 3 h at the same temperature. Octanoyl chloride (130.1 mg, 0.80 mmol) was then added at -20 °C. The reaction mixture was warmed up to room temperature by leaving the CCl₄/dry ice without adding additional dry ice. After 20 h, the reaction was quenched with saturated aqueous NH₄Cl (4.0 mL). The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/CH₂Cl₂ = 5/1) to afford 1-(4-*tert*-butylphenyl)octan-1-one (**4b**, 121.9 mg, 0.47 mmol, 59% based on octanoyl chloride) as a colorless oil.

General procedure for preparation of arylzinc stock solutions (GP6, Scheme 6)

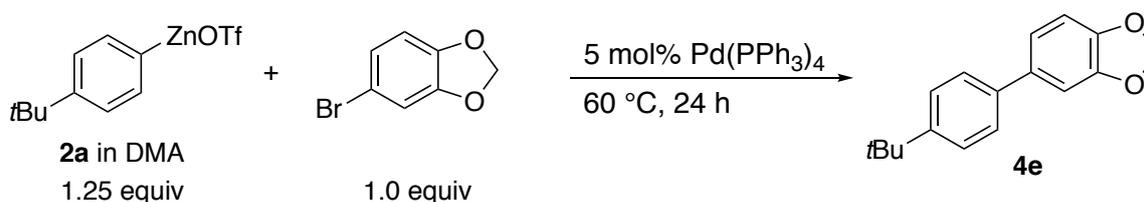


The zincation of **1a** is representative. A 200-mL Schlenk tube was charged with dimethyl(*p*-*tert*-butylphenyl)sulfonium trifluoromethanesulfonate (**1a**, 4.14 g, 12 mmol), NiBr₂L1 (128 mg, 0.30 mmol), L1 (250 mg, 1.2 mmol), and Zn powder (2.35 g, 36 mmol). The tube was then

evacuated and refilled with N₂ gas (3 times). DMA (60 mL) was then added, and the resulting mixture was stirred vigorously for 24 h at room temperature. The residue of zinc powder was removed with a membrane filter, and the filtrate was stored in a Schlenk tube.

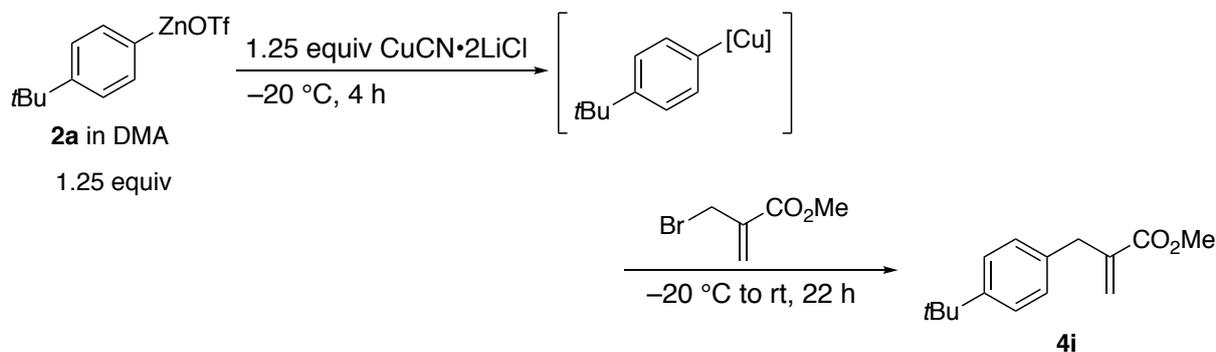
The concentration was determined by ¹H NMR after iodination of 0.50 mL of the arylzinc solution, using 1,1,2,2-tetrabromoethane as an internal standard.

General procedure for cross-coupling reactions with arylzinc stock solutions (GP7, Scheme 6, Condition A)



The synthesis of **4e** is representative. A 20-mL Schlenk tube was charged with Pd(PPh₃)₄ (46.2 mg, 40 μmol) and 4-bromo-1,2-methylenedioxybenzene (160.8 mg, 0.80 mmol). The arylzinc stock solution prepared from **1a** according to **GP6** was then added (0.18 M, 5.6 mL, 1.0 mmol). The resulting mixture was stirred for 24 h at 60 °C (oil bath). The reaction was quenched with 3 M aqueous HCl (4.0 mL). The resulting biphasic solution was extracted with Et₂O (3 × 20 mL). The combined organic layer was passed through pads of Na₂SO₄ and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/CH₂Cl₂ = 10/1) to afford 5-(4-*tert*-butylphenyl)-1,3-benzodioxole (**4e**, 183.1 mg, 0.72 mmol, 90% based on 4-bromo-1,2-methylenedioxybenzene) as a white solid.

General procedure for cross-coupling reactions with arylzinc stock solutions (GP8, Scheme 6, Condition B)



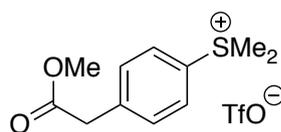
The synthesis of **4i** is representative. A 20-mL Schlenk tube was charged with an arylzinc stock solution prepared from **1a** according to **GP6** (0.16 M, 6.3 mL, 1.0 mmol). A solution of

CuCN (89.6 mg, 1.0 mmol) and LiCl (84.8 mg, 2.0 mmol) in THF (2 mL) was then added at $-20\text{ }^{\circ}\text{C}$, and the resulting mixture was stirred for 4 h at the same temperature. Methyl 2-(bromomethyl)acrylate (147.0 mg, 0.82 mmol) was then added at $-20\text{ }^{\circ}\text{C}$. The reaction mixture was warmed up to room temperature by leaving the CCl_4 /dry ice without adding additional dry ice. After 22 h, the reaction was quenched with saturated aqueous NH_4Cl (4.0 mL). The resulting biphasic solution was extracted with Et_2O ($3 \times 20\text{ mL}$). The combined organic layer was passed through pads of Na_2SO_4 and silica gel. All volatiles were then removed under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/ $\text{EtOAc} = 20/1$) to afford methyl 2-(4-*tert*-butylbenzyl)acrylate (**4i**, 185.8 mg, 0.80 mmol, 97% based on methyl 2-(bromomethyl)acrylate) as a colorless oil.

Characterization Data

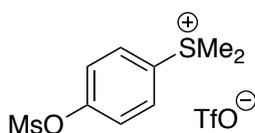
Aryl sulfides which are precursors for arylsulfonium salts **1r**², **1s**³, **1t**⁴ and sulfonium salts **1a**², **1b**², **1c**², **1d**⁵, **1e**⁶, **1f**⁶, **1g**⁶, **1i**², **1j**⁵, **1l**⁵, **1o**², **1q**², **1q-BF₄**², **1q-PF₆**², **1q-SbF₆**², **1b**⁷ were synthesized according to the literature, and showed ¹H and ¹³C{¹H} NMR spectra identical to the reported ones, respectively. Iodoarene **3a**⁸, **3b**⁸, **3c**⁹, **3d**¹⁰, **3e**¹¹, **3f**⁸, **3g**¹², **3h**¹³, **3i**⁸, **3j**¹⁴, **3k**¹⁴, **3l**⁸, **3m**¹⁵, **3n**¹⁶ and biaryl **4a**¹⁷, **4f**¹⁸ also showed ¹H NMR and ¹³C NMR spectra identical to the reported ones.

(4-(2-methoxy-2-oxoethyl)phenyl)dimethylsulfonium trifluoromethanesulfonate (**1h**):



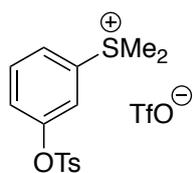
White solid (4.93 g, 13.6 mmol, 99% from the corresponding sulfide (2.71 g, 13.8 mmol)). mp: $90.5\text{--}91.8\text{ }^{\circ}\text{C}$; ¹H NMR ($\text{DMSO-}d_6$): δ 8.02 (d, $J = 8.2\text{ Hz}$, 2H), 7.62 (d, $J = 8.2\text{ Hz}$, 2H), 3.86 (s, 2H), 3.63 (s, 3H), 3.26 (s, 6H); ¹³C NMR ($\text{DMSO-}d_6$): δ 170.9, 140.6, 131.5 (2C), 129.8, 124.9, 120.7 (q, C-F, $^1J_{\text{C-F}} = 322.2\text{ Hz}$), 51.9, 28.2; ¹⁹F NMR ($\text{DMSO-}d_6$): δ -78.2 ; HRMS (ESI-MS, positive): m/z $[\text{M-OTf}]^+$ Calcd for $\text{C}_{11}\text{H}_{15}\text{O}_2\text{S}$ 211.0787; Found 211.0783.

dimethyl(4-(methylsulfonyloxy)phenyl)sulfonium trifluoromethanesulfonate (**1k**):



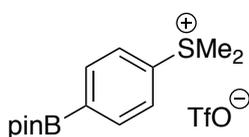
White solid (3.72 g, 9.74 mmol, 94% from the corresponding sulfide (2.26 g, 10.3 mmol) prepared according to **GP2** using MsCl instead of TsCl). mp: $91.9\text{--}93.3\text{ }^{\circ}\text{C}$; ¹H NMR ($\text{DMSO-}d_6$): δ 8.20 (d, $J = 8.9\text{ Hz}$, 2H), 7.71 (d, $J = 8.9\text{ Hz}$, 2H), 3.50 (s, 3H), 3.28 (s, 6H); ¹³C NMR ($\text{DMSO-}d_6$): δ 152.5, 132.4, 125.6, 124.3, 120.7 (q, C-F, $^1J_{\text{C-F}} = 321.7\text{ Hz}$), 38.0, 28.4; ¹⁹F NMR ($\text{DMSO-}d_6$): δ -78.2 ; HRMS (ESI-MS, positive): m/z $[\text{M-OTf}]^+$ Calcd for $\text{C}_9\text{H}_{13}\text{O}_3\text{S}_2$ 233.0301; Found 233.0304.

dimethyl(3-tosyloxyphenyl)sulfonium trifluoromethanesulfonate (1m):



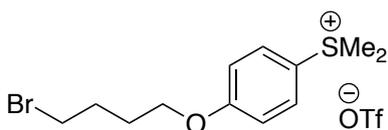
White solid (1.39 g, 3.0 mmol, 99% from the corresponding sulfide (882 mg, 3.0 mmol)). mp: 104.9–106.3 °C; ¹H NMR (DMSO-*d*₆): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.77–7.71 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 3.22 (s, 6H), 2.43 (s, 3H); ¹³C NMR (DMSO-*d*₆): δ 149.5, 146.5, 132.0, 130.8, 130.5, 129.3, 128.7, 128.4, 127.3, 123.8, 120.7 (q, C–F, ¹*J*_{C–F} = 322.2 Hz), 28.2, 21.2; ¹⁹F NMR (DMSO-*d*₆): δ –78.2; HRMS (ESI-MS, positive): *m/z* [M–OTf]⁺ Calcd for C₁₅H₁₇O₃S₂ 309.0614; Found 309.0606.

dimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)sulfonium trifluoromethanesulfonate (1n):



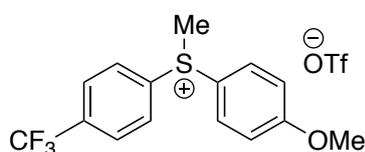
White solid (3.51 g, 8.48 mmol, 84% from the corresponding sulfide (2.65 g, 10.1 mmol)). Decomposed around 196 °C; ¹H NMR (DMSO-*d*₆): δ 8.07 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H), 3.27 (s, 6H), 1.32 (s, 12H); ¹³C NMR (DMSO-*d*₆): δ 135.8, 130.0, 129.1, 120.7 (q, C–F, ¹*J*_{C–F} = 322.2 Hz), (the signal of the carbon at the ipso position of the boron atom was not observed), 84.4, 28.0, 24.6; ¹⁹F NMR (DMSO-*d*₆): δ –78.2; HRMS (ESI-MS, positive): *m/z* [M–OTf]⁺ Calcd for C₁₄H₂₂O₂BS 265.1431; Found 265.1431.

[4-(4-bromobutoxy)phenyl]dimethylsulfonium trifluoromethanesulfonate (1p):



White solid (3.53 g, 8.04 mmol, 99% from the corresponding sulfide (2.23 g, 8.1 mmol)). mp: 119.4–120.4 °C; ¹H NMR (DMSO-*d*₆): δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 2H), 4.13 (t, *J* = 6.9 Hz, 2H), 3.61 (t, *J* = 6.9 Hz, 2H), 3.21 (s, 6H), 1.97 (t, *J* = 6.9 Hz, 2H), 1.87 (t, *J* = 6.9 Hz, 2H); ¹³C NMR (DMSO-*d*₆): δ 162.7, 132.0, 120.7 (q, C–F, ¹*J*_{C–F} = 322.2 Hz), 116.3, 116.2, 67.5, 34.7, 28.9, 28.7, 27.1; ¹⁹F NMR (DMSO-*d*₆): δ –78.2; HRMS (ESI-MS, positive): *m/z* [M–OTf]⁺ Calcd for C₁₂H₁₈⁸¹BrOS 291.0236; Found 291.0235.

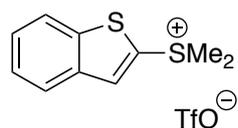
methyl(*p*-methoxyphenyl)(*p*-trifluorophenyl)sulfonium trifluoromethanesulfonate (1r):



White solid (1.86 g, 4.14 mmol, 83% from the corresponding sulfide (1.43 g, 5.0 mmol)). mp: 74.6–77.2 °C; ¹H NMR (DMSO-*d*₆): δ 8.16 (d, *J* = 8.2 Hz, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ¹³C NMR (DMSO-

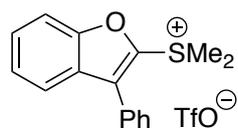
d_6): δ 164.3, 134.6, 133.5, 133.4 (q, C–F, $^2J_{C-F} = 32.8$ Hz), 130.8, 127.9, 123.7 (q, C–F, $^1J_{C-F} = 273.1$ Hz), 121.2 (q, C–F, $^1J_{C-F} = 322.2$ Hz), 117.0 (q, C–F, $^3J_{C-F} = 12.0$ Hz), 116.4, 56.5, 27.7; ^{19}F NMR (DMSO- d_6): δ –62.4, –78.3; HRMS (ESI-MS, positive): m/z [M–OTf] $^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{F}_3\text{OS}$ 299.0712; Found 299.0698.

benzo[*b*]thiophen-2-yl dimethylsulfonium trifluoromethanesulfonate (1s):



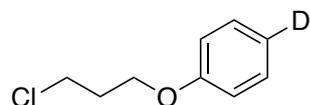
White solid (3.11 g, 9.04 mmol, 90% from the corresponding sulfide (1.80 g, 10.2 mmol)). mp: 113.6–115.1 °C; ^1H NMR (DMSO- d_6): δ 8.44 (s, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 8.08 (d, $J = 8.2$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 3.42 (s, 6H); ^{13}C NMR (DMSO- d_6): δ 141.8, 137.4, 135.0, 127.8, 126.0, 125.6, 125.3, 123.2, 120.7 (q, C–F, $^1J_{C-F} = 322.2$ Hz), 30.8; ^{19}F NMR (DMSO- d_6): δ –78.1; HRMS (ESI-MS, positive): m/z [M–OTf] $^+$ Calcd for $\text{C}_{10}\text{H}_{11}\text{S}_2$ 195.0297; Found 195.0305.

dimethyl(3-phenylbenzofuran-2-yl)sulfonium trifluoromethanesulfonate (1t):



White solid (1.05 g, 2.59 mmol, 95% from the corresponding sulfide (653 mg, 2.72 mmol)). mp: 128.0–129.5 °C; ^1H NMR (DMSO- d_6): δ 7.89 (d, $J = 8.9$ Hz, 1H), 7.84 (d, $J = 8.2$ Hz, 1H), 7.77–7.76 (m, 2H), 7.72–7.62 (m, 4H), 7.54 (t, $J = 7.5$ Hz, 1H), 3.50 (s, 6H); ^{13}C NMR (DMSO- d_6): δ 156.4, 133.3, 131.1, 130.0, 129.7, 129.5, 129.4, 127.6, 125.9, 125.3, 122.1, 120.8 (q, C–F, $^1J_{C-F} = 322.2$ Hz), 112.6, 28.7; ^{19}F NMR (DMSO- d_6): δ –78.2; HRMS (ESI-MS, positive): m/z [M–OTf] $^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{OS}$ 255.0838; Found 255.0845.

3-chloropropyl 4-deuteriophenyl ether (3o')

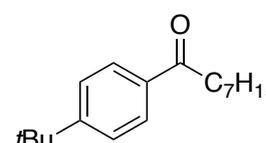


Colorless oil (127 mg, 0.74 mmol, 74% (94%D)) from the corresponding arylsulfonium salt **3o** (381 mg, 1.0 mmol) according to **GP4** quenching with D_2O (2 mL) instead of iodine). Purification was done by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 10/1$). ^1H NMR (CDCl_3): δ 7.35 (d, $J = 8.6$ Hz, 2H), 7.02 (t, $J = 7.3$ Hz, 1H×0.06), 6.98 (d, $J = 8.6$ Hz, 2H), 4.16 (t, $J = 5.8$ Hz, 2H), 3.79 (t, $J = 6.4$ Hz, 2H), 2.30–2.26 (m, 2H); ^{13}C NMR (CDCl_3): δ 158.8, 129.4, 120.7 (t, $J = 24.6$ Hz) 114.6, 64.2, 41.6, 32.4; HRMS (APCI-MS, positive): m/z [M] $^+$ Calcd for $\text{C}_9\text{H}_{10}\text{D}^{35}\text{ClO}$ 171.0556; Found 171.0561.

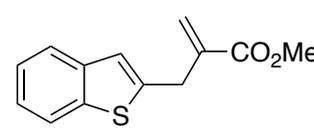
4-bromobutyl 4-deuteriophenyl ether (**3p'**) and 4-deuteriobutyl 4-deuteriophenyl ether (**3p''**):

Before purification, a 74:26 mixture of **3p'** and **3p''** with 89%D at the 4 position of **3p'** and **3p''** and with 31%D for the replacement of the initial Br group in **3p''** was obtained from the corresponding arylsulfonium salt **3p** (381 mg, 1.0 mmol) according to **GP4** quenching with D₂O (2 mL) instead of iodine. After purification, a 97:3 mixture of **3p'** and **3p''** with 89%D at the 4 position of **3p'** and **3p''** and with 31%D for the replacement of the initial Br group in **3p''** was obtained. The 97:3 mixture was a colorless oil (107 mg). Purification was done by column chromatography on silica gel (hexane/CH₂Cl₂ = 10/1). ¹H NMR (CDCl₃): δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.93 (t, *J* = 7.8 Hz, 1H×0.11), 6.88 (d, *J* = 9.0 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H×0.97), 3.91 (t, *J* = 6.6 Hz, 2H×0.03), 3.47 (t, *J* = 6.6 Hz, 2H×0.97), 2.07–2.01 (m, 2H×0.97), 1.94–1.88 (m, 2H×0.97), 1.79–1.73 (m, 2H×0.03), 1.52–1.46 (m, 2H×0.03), 0.96 (t, *J* = 7.8 Hz, 3H×0.03); ¹³C NMR for **3p'** (CDCl₃): δ 158.9, 129.4, 120.5 (t, *J* = 24.6 Hz), 114.5, 66.8, 33.6, 29.6, 28.0; HRMS (APCI-MS, positive): *m/z* [protonated phenoxy]⁺ Calcd for C₆H₅DO 95.0476; Found 95.0473, *m/z* [bromobutyl]⁺ Calcd for C₄H₈⁷⁹Br 134.9804; Found 134.9802.

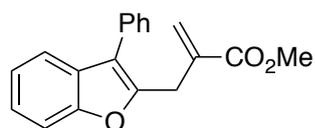
1-(4-*tert*-butylphenyl)octan-1-one (**4b**):

 Colorless oil (122 mg, 0.47 mmol, 59% from the corresponding chloride (130 mg, 0.80 mmol) according to **GP5**). Purification was done by column chromatography on silica gel (hexane/CH₂Cl₂ = 5/1). ¹H NMR (CDCl₃): δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 1.74–1.72 (m, 2H), 1.38–1.27 (m, 17H), 0.88 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃): δ 200.3, 156.5, 134.6, 128.1, 125.5, 38.6, 35.1, 31.8, 31.2, 29.5, 29.2, 24.6, 22.7, 14.2; HRMS (APCI-MS, positive): *m/z* [M+H]⁺ Calcd for C₁₈H₂₉O 261.2213; Found 261.2207.

methyl 2-(benzo[*b*]thiophen-2-ylmethyl)acrylate (**4c**):

 White solid (144 mg, 0.62 mmol, 78% from the corresponding bromide (141 mg, 0.79 mmol) according to **GP5**). Purification was done by column chromatography on silica gel (hexane/EtOAc = 30/1). ¹H NMR (CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.32–7.25 (m, 2H), 7.07 (s, 1H), 6.32 (s, 1H), 5.71 (s, 1H), 3.91 (s, 2H), 3.77 (s, 3H); ¹³C NMR (CDCl₃): δ 167.0, 142.4, 140.2, 139.9, 138.8, 127.1, 124.3, 123.9, 123.1, 122.5, 122.3, 52.2, 33.2; HRMS (APCI-MS, positive): *m/z* [M]⁺ Calcd for C₁₃H₁₂O₂S 232.0553; Found 232.0560.

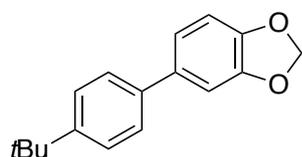
methyl 2-((3-phenylbenzofuran-2-yl)methyl)acrylate (4d):



Colorless oil (167 mg, 0.57 mmol, 71% from the corresponding bromide (145.1 mg, 0.81 mmol) according to **GP5**). Purification was done by column chromatography on silica gel (hexane/CH₂Cl₂ = 3/1).

¹H NMR (CDCl₃): δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.55–7.53 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.43 (s, 1H), 5.64 (s, 1H), 3.98 (s, 2H), 3.80 (s, 3H); ¹³C NMR (CDCl₃): δ 166.8, 154.4, 150.6, 136.7, 132.3, 128.9, 128.8, 128.6, 127.4, 127.1, 124.1, 122.9, 119.8, 118.9, 111.1, 52.1, 29.4; HRMS (APCI-MS, positive): *m/z* [M]⁺ Calcd for C₁₉H₁₆O₃ 292.1094; Found 292.1087.

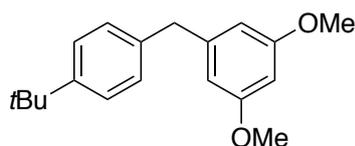
5-(4-*tert*-butylphenyl)benzo[*d*][1,3]dioxole (4e):



White solid (183 mg, 0.72 mmol, 90% from the corresponding bromide (162 mg, 0.80 mmol) according to **GP7**). Purification was done by column chromatography on silica gel (hexane/CH₂Cl₂ = 10/1).

¹H NMR (CDCl₃): δ 7.57–7.52 (m, 4H), 7.18–7.14 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H), 1.46 (s, 9H); ¹³C NMR (CDCl₃): δ 150.0, 148.2, 147.0, 138.1, 135.5, 126.6, 125.8, 120.5, 108.6, 107.6, 101.1, 34.6, 31.5; HRMS (APCI-MS, positive): *m/z* [M]⁺ Calcd for C₁₇H₁₈O₂ 254.1301; Found 254.1307.

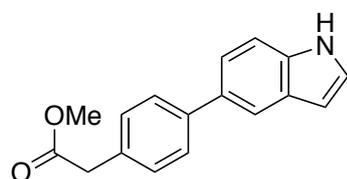
1-(4-*tert*-butylbenzyl)-3,5-dimethoxybenzene (4g):



Colorless oil (222 mg, 0.78 mmol, 97% from the corresponding bromide (185 mg, 0.80 mmol) according to **GP7**). Purification was done by column chromatography on silica gel

(hexane/CH₂Cl₂ = 3/2). ¹H NMR (CDCl₃): δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 8.2 Hz, 2H), 6.52 (s, 2H), 6.47 (s, 1H), 4.02 (s, 2H), 3.86 (s, 6H), 1.45 (s, 9H); ¹³C NMR (CDCl₃): δ 160.9, 148.9, 143.6, 137.8, 128.5, 125.4, 107.2, 97.9, 55.2, 41.7, 34.4, 31.5; HRMS (APCI-MS, positive): *m/z* [M+H]⁺ Calcd for C₁₉H₂₅O₂ 285.1849; Found 285.1855.

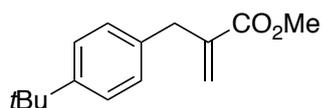
methyl 2-(4-(1*H*-indol-5-yl)phenyl)acetate (4h):



White solid (138 mg, 0.52 mmol, 65% from the corresponding iodide (195 mg, 0.80 mmol) according to **GP7**). Purification was done by column chromatography on silica gel (hexane/EtOAc = 3/1). ¹H NMR (CDCl₃): δ 8.36 (s, 1H), 7.96 (s, 1H), 7.72 (d, *J* =

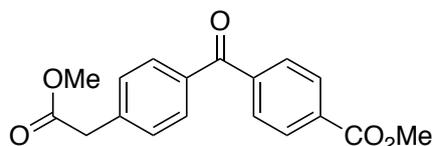
8.2 Hz, 2H), 7.51 (d, $J = 8.9$ Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.9$ Hz, 1H), 7.18 (s, 1H), 6.66 (s, 1H), 3.82 (s, 3H), 3.78 (s, 2H); ^{13}C NMR (CDCl_3): δ 172.5, 141.5, 135.4, 132.7, 131.9, 129.6, 128.4, 127.5, 125.1, 121.6, 119.0, 111.4, 102.7, 52.1, 40.8; HRMS (APCI-MS, positive): m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{NO}_2$ 266.1176; Found 266.1170.

methyl 2-(4-*tert*-butylbenzyl)acrylate (4i):



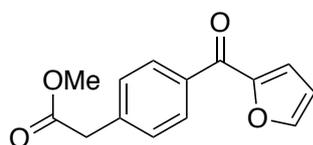
Colorless oil (180 mg, 0.78 mmol, 97% from the corresponding bromide (147 mg, 0.82 mmol) according to **GP8**). Purification was done by column chromatography on silica gel (hexane/EtOAc = 20/1). ^1H NMR (CDCl_3): δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 6.28 (s, 1H), 5.52 (s, 1H), 3.78 (s, 3H), 3.67 (s, 2H), 1.37 (s, 9H); ^{13}C NMR (CDCl_3): δ 167.4, 149.1, 140.3, 135.6, 128.7, 126.1, 125.4, 51.8, 37.5, 34.4, 31.4; HRMS (APCI-MS, positive): m/z $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ 232.1458; Found 232.1456.

methyl 4-(4-(2-methoxy-2-oxoethyl)benzoyl)benzoate (4j):



White solid (145 mg, 0.47 mmol, 58% from the corresponding chloride (159 mg, 0.80 mmol) according to **GP8**). Purification was done by column chromatography on silica gel (hexane/EtOAc = 4/1). ^1H NMR (CDCl_3): δ 8.09 (d, $J = 8.2$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 3.91 (s, 3H), 3.68 (s, 2H), 3.68 (s, 3H); ^{13}C NMR (CDCl_3): δ 195.4, 171.2, 166.2, 141.3, 139.3, 135.8, 133.2, 130.4, 129.7, 129.5 (2C), 52.4, 52.2, 41.0; HRMS (APCI-MS, positive): m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_5$ 313.1071; Found 313.1070.

methyl 2-(4-(furan-2-carbonyl)phenyl)acetate (4k):



Colorless oil (112 mg, 0.50 mmol, 57% from the corresponding chloride (104 mg, 0.80 mmol) according to **GP8**). Purification was done by column chromatography on silica gel (hexane/EtOAc = 4/1). ^1H NMR (CDCl_3): δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 2.1$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 3.4$ Hz, 1H), 6.55 (dd, $J = 3.4, 2.1$ Hz, 1H), 3.68 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (CDCl_3): δ 182.0, 171.3, 152.3, 147.1, 138.8, 136.1, 129.6, 129.4, 120.5, 112.3, 52.2, 41.1; HRMS (ESI-MS, positive): m/z $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{13}\text{O}_4$ 245.0808; Found 245.0813.

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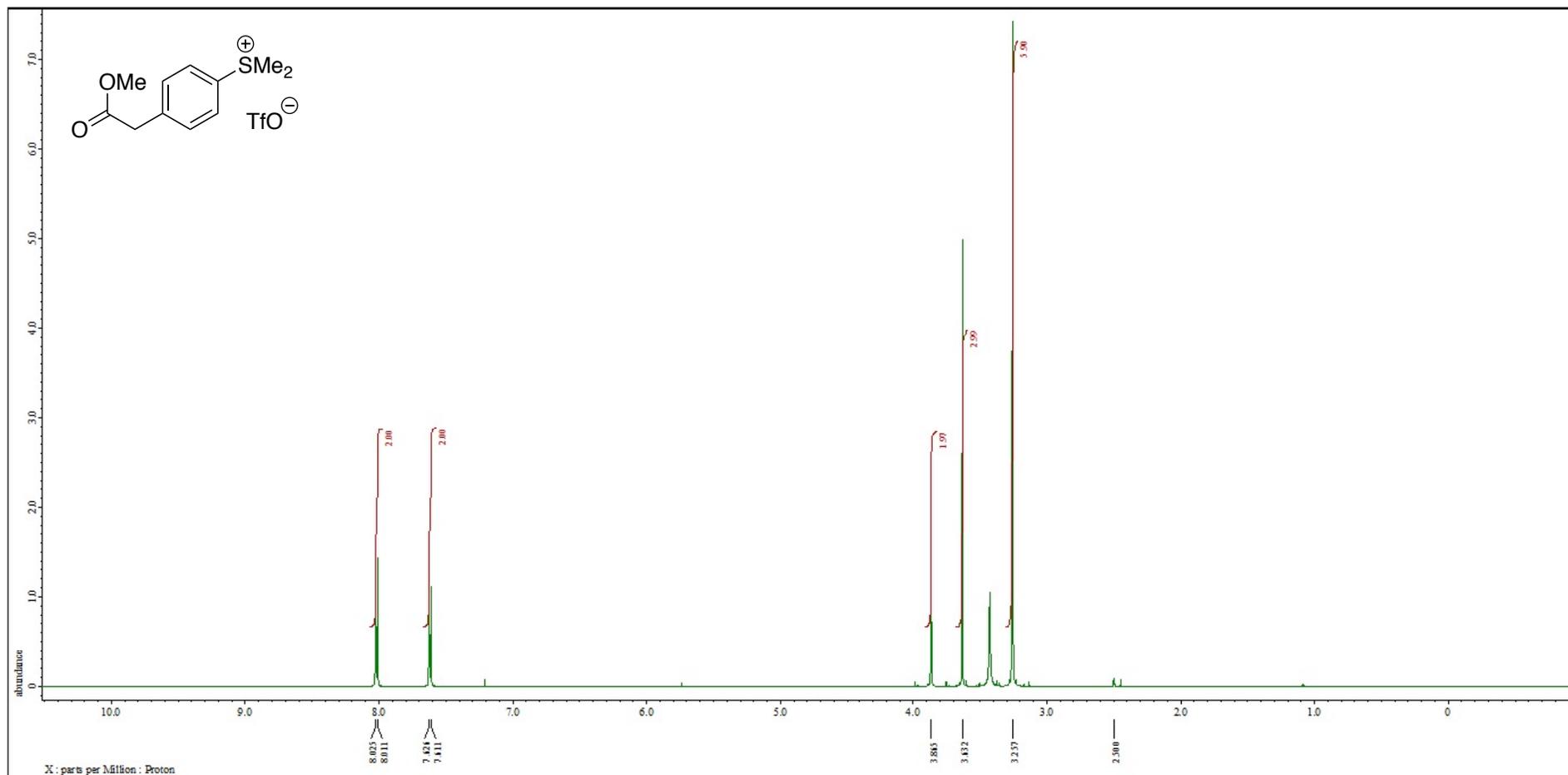


Figure S1. ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of **1h**

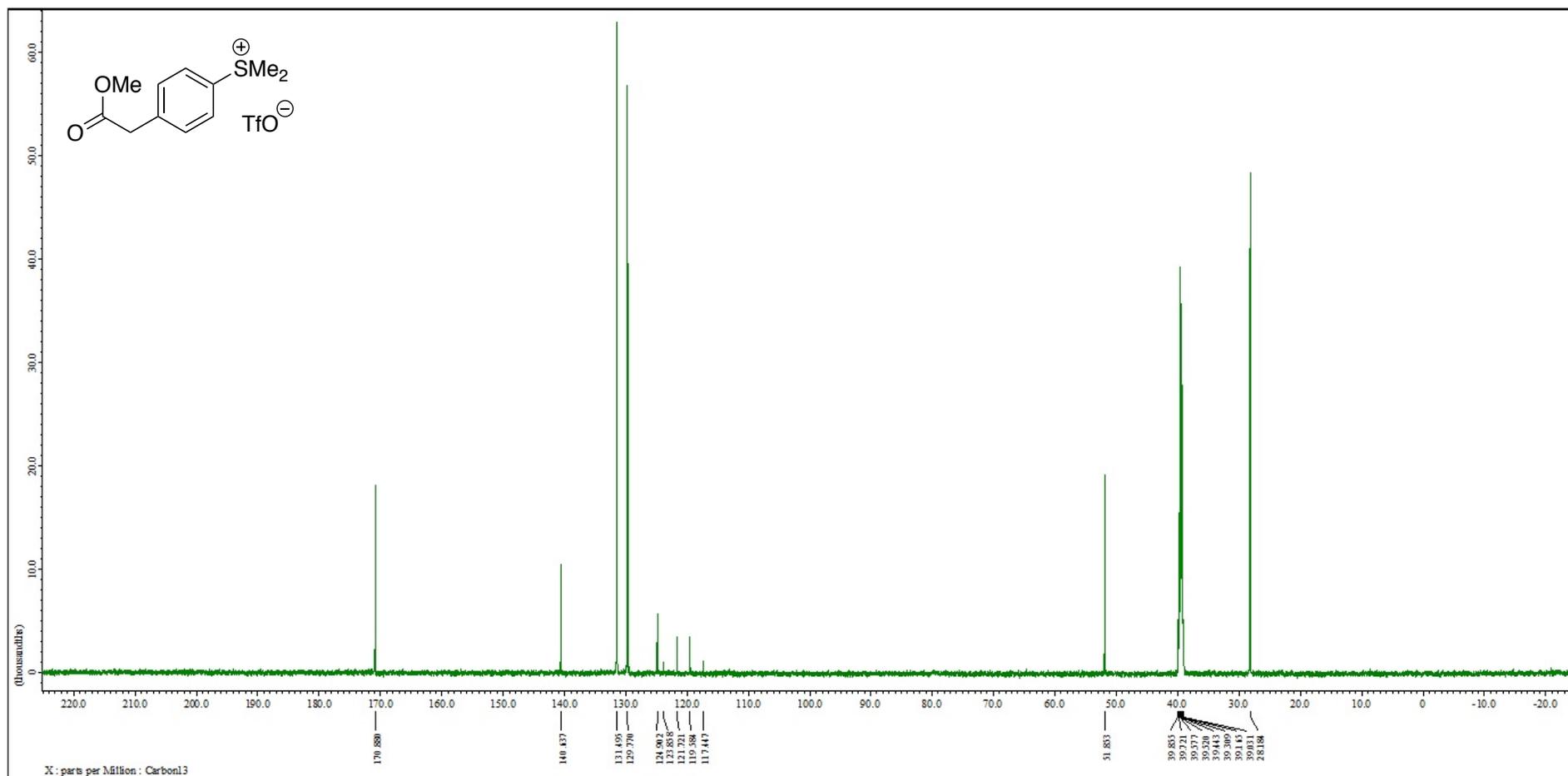


Figure S2. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1h**

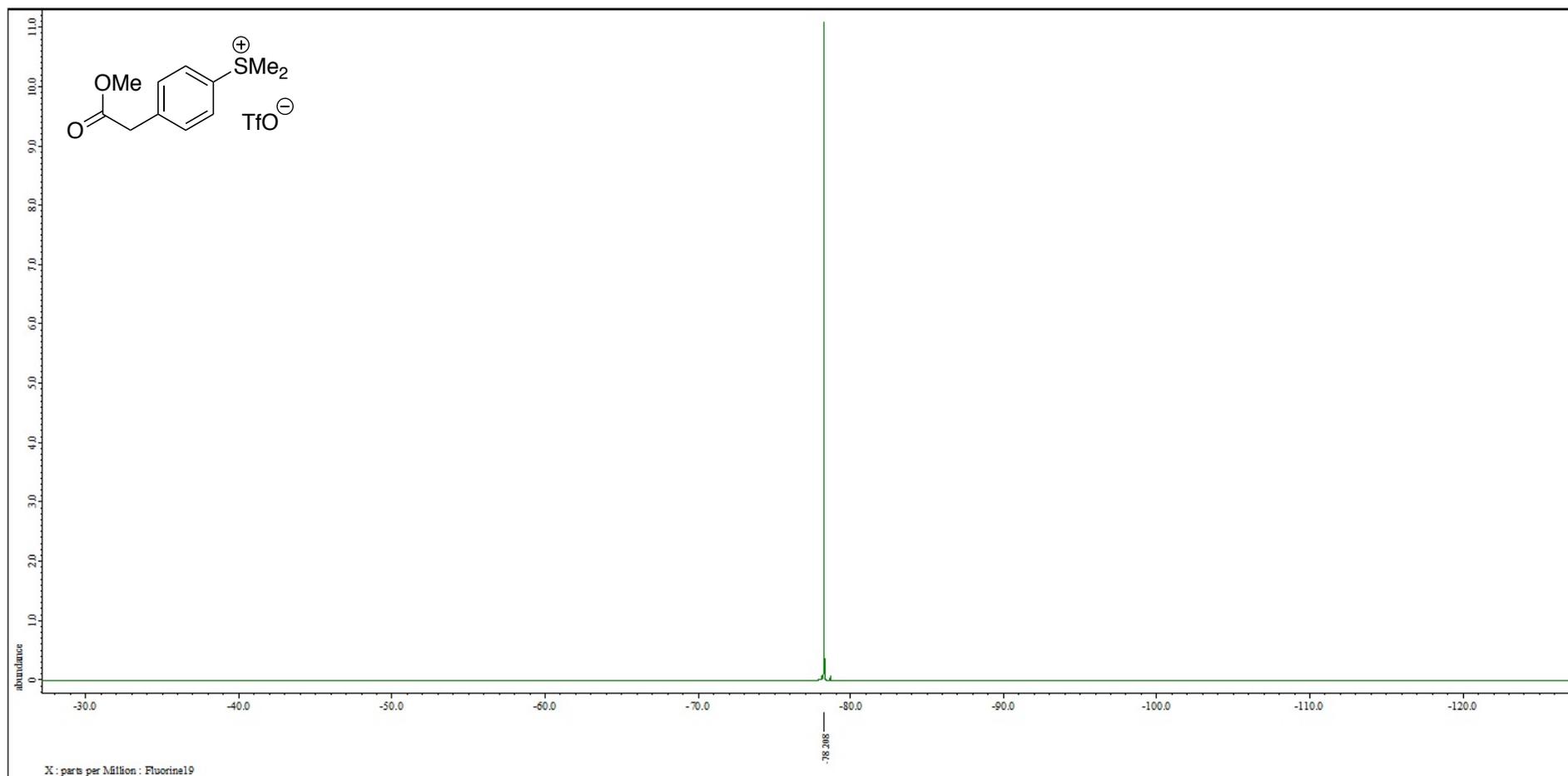


Figure S3. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1h**

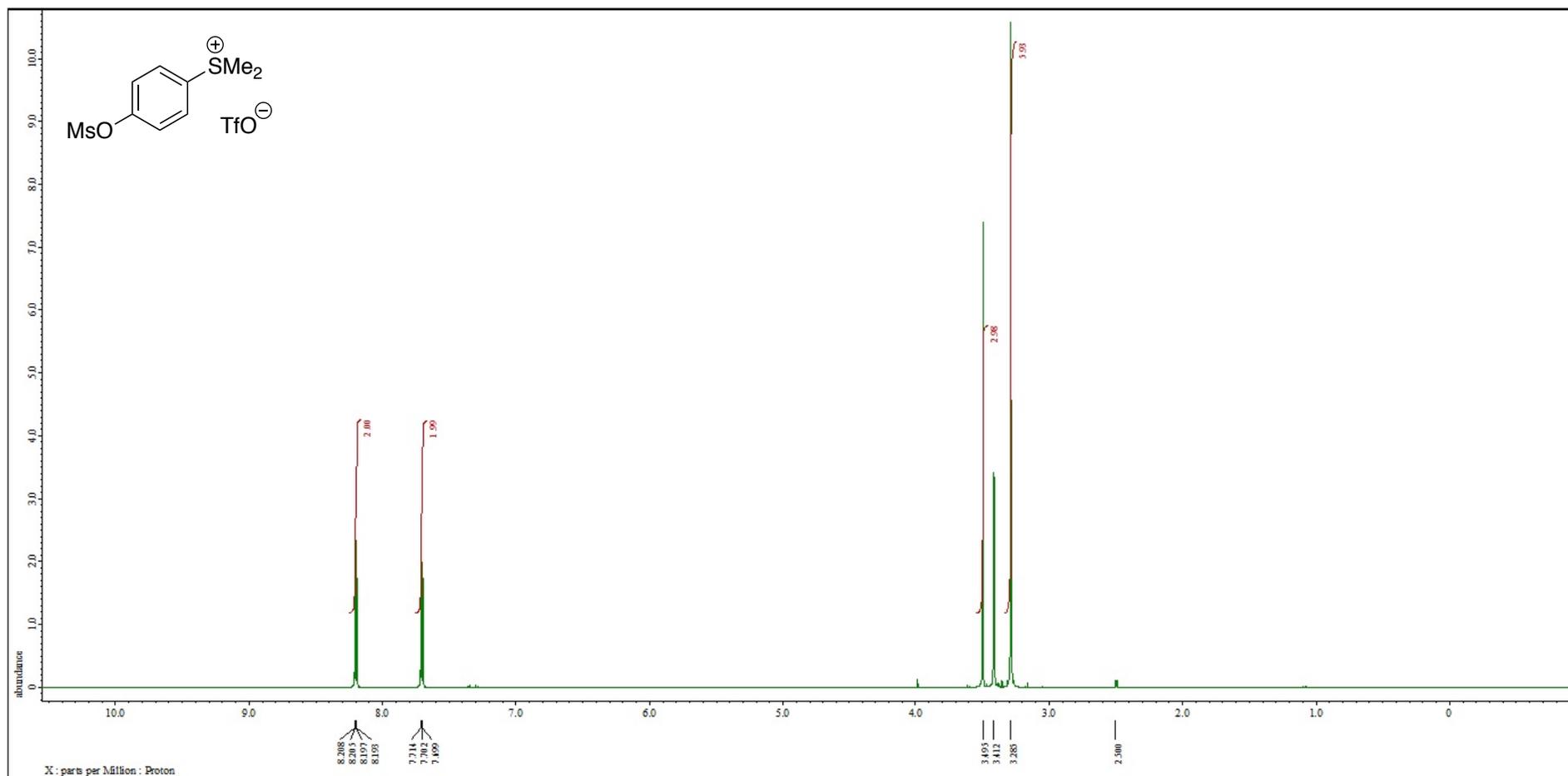


Figure S4. ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of **1k**

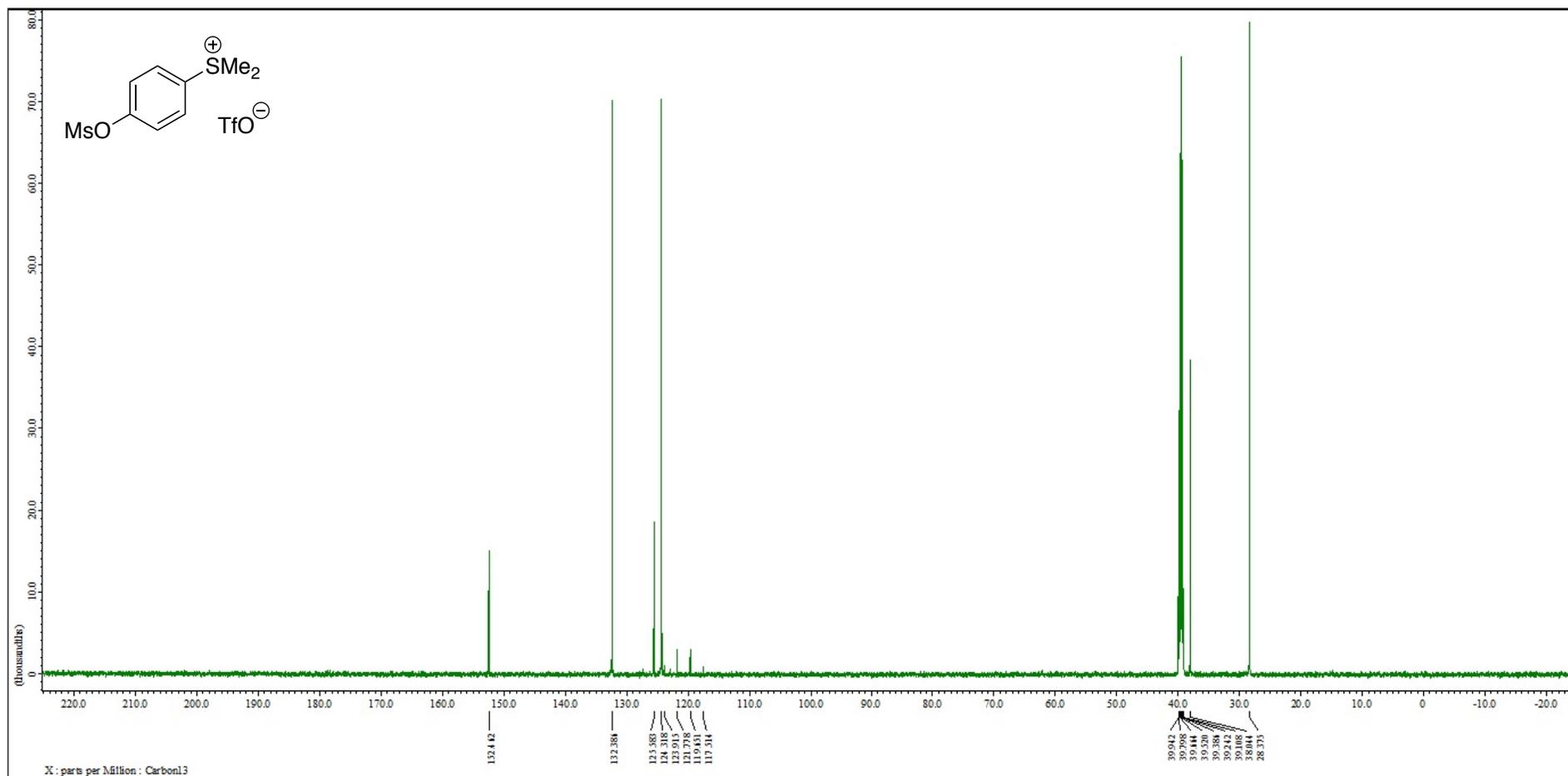


Figure S5. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1k**

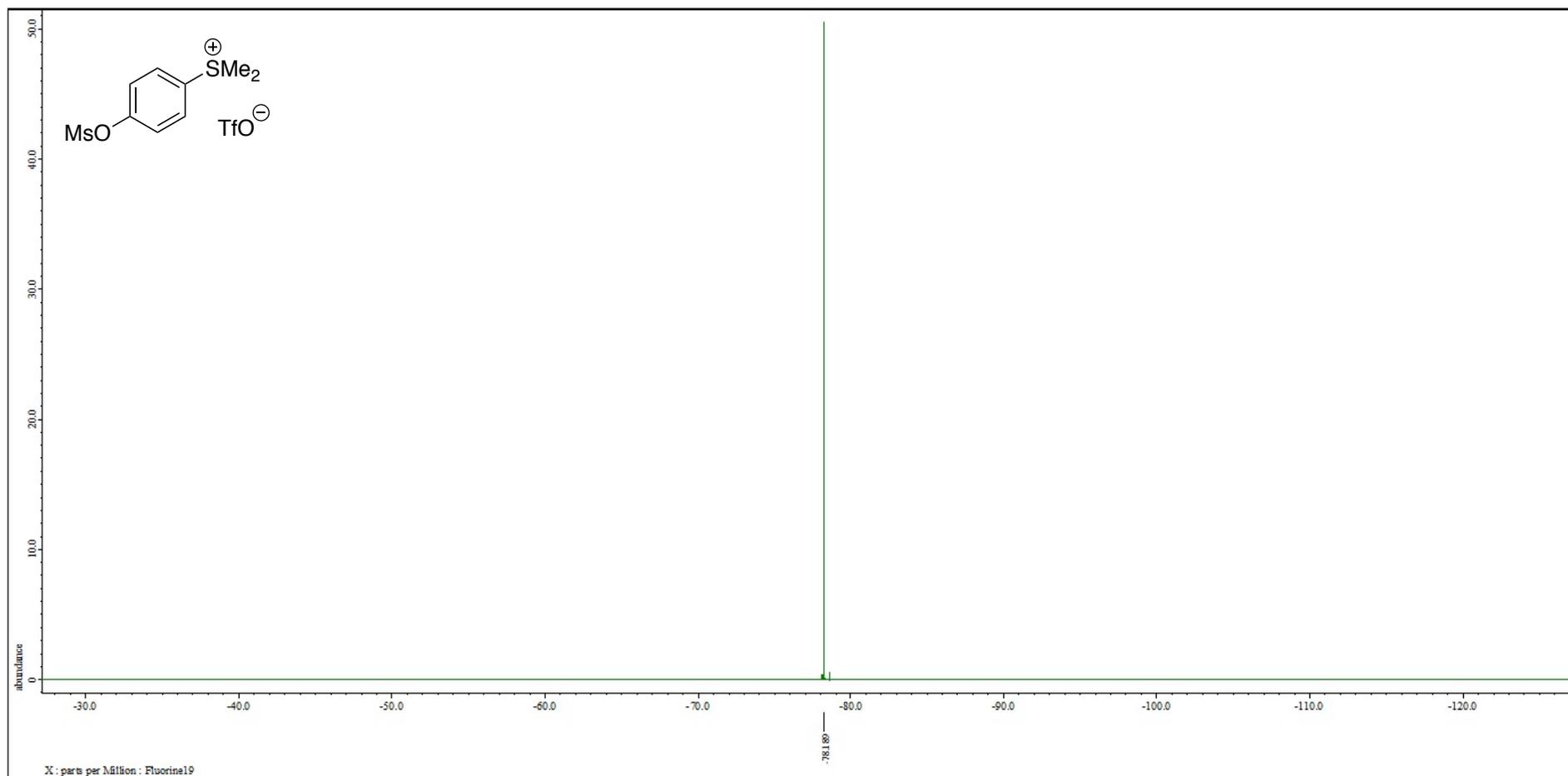


Figure S6. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1k**

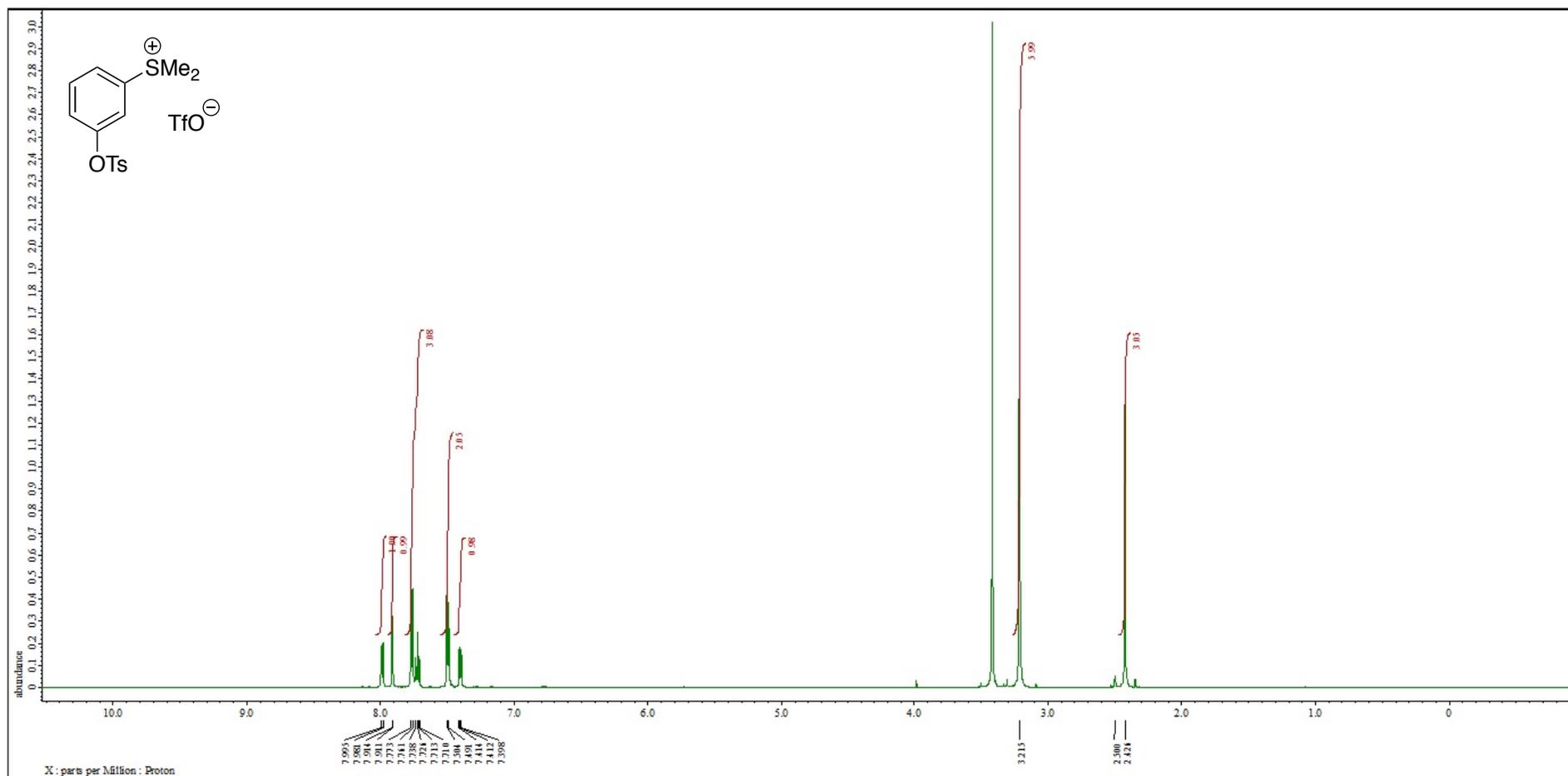


Figure S7. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) spectrum of **1m**

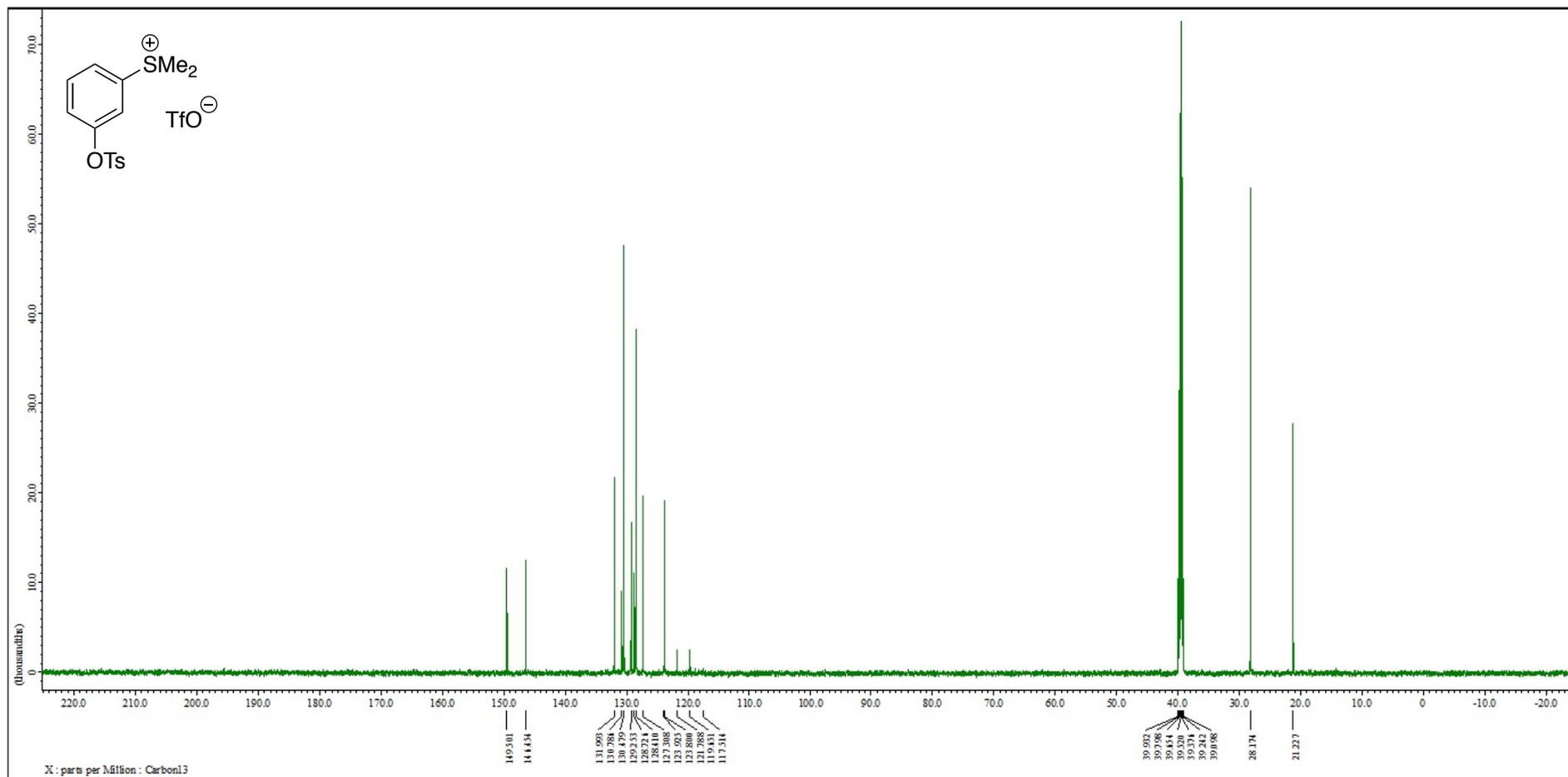


Figure S8. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1m**

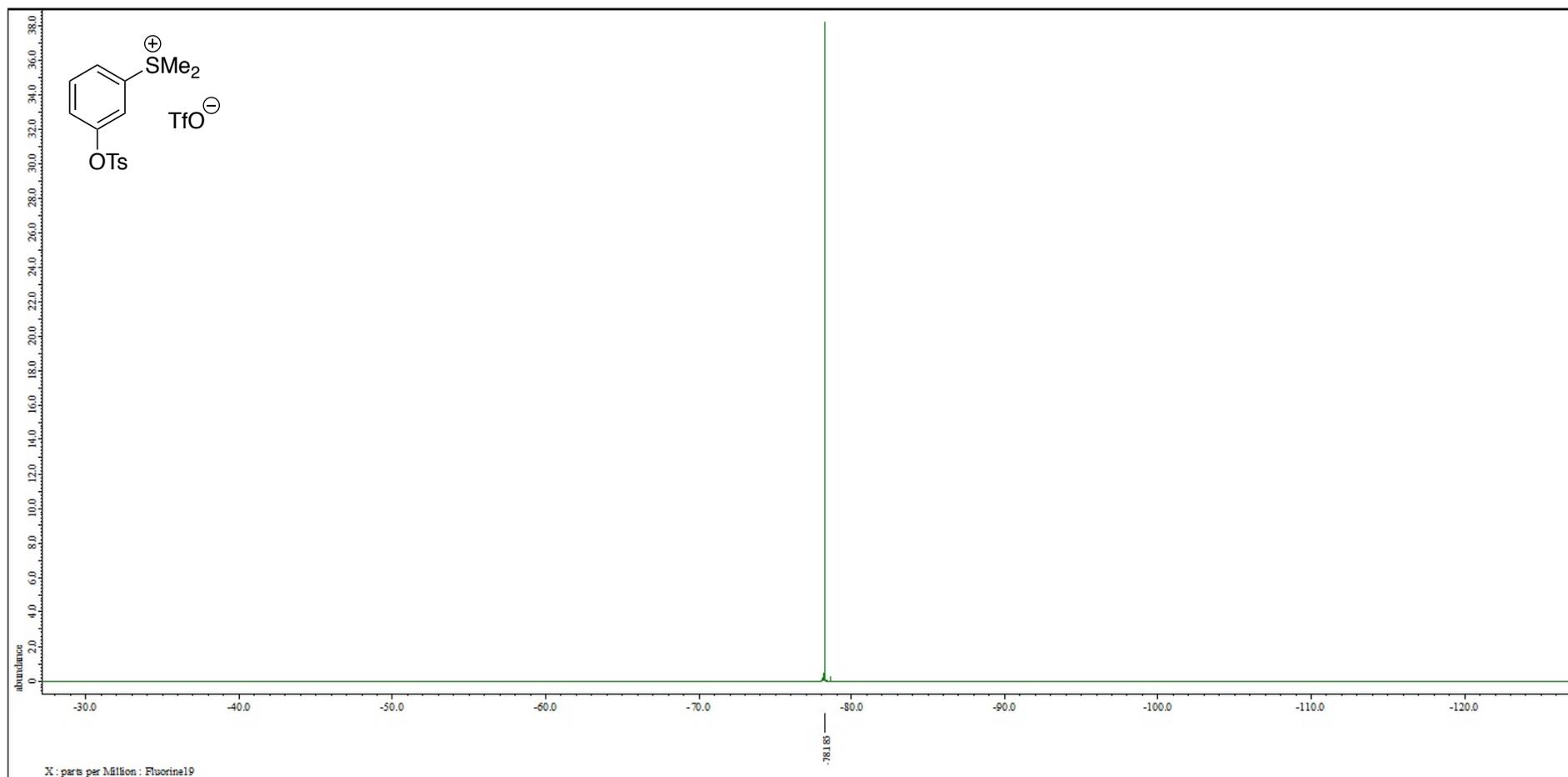


Figure S9. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1m**

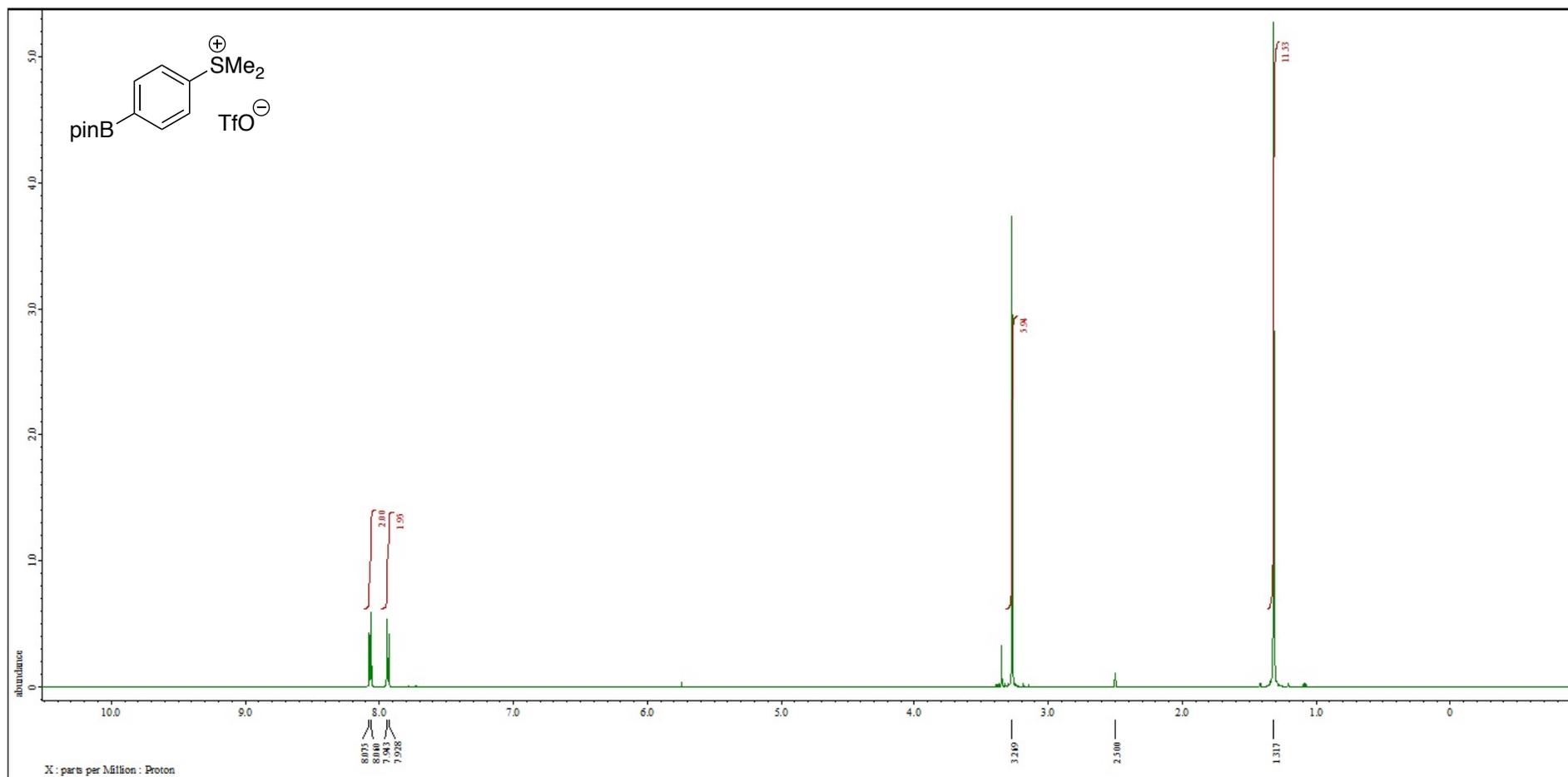


Figure S10. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) spectrum of **1n**

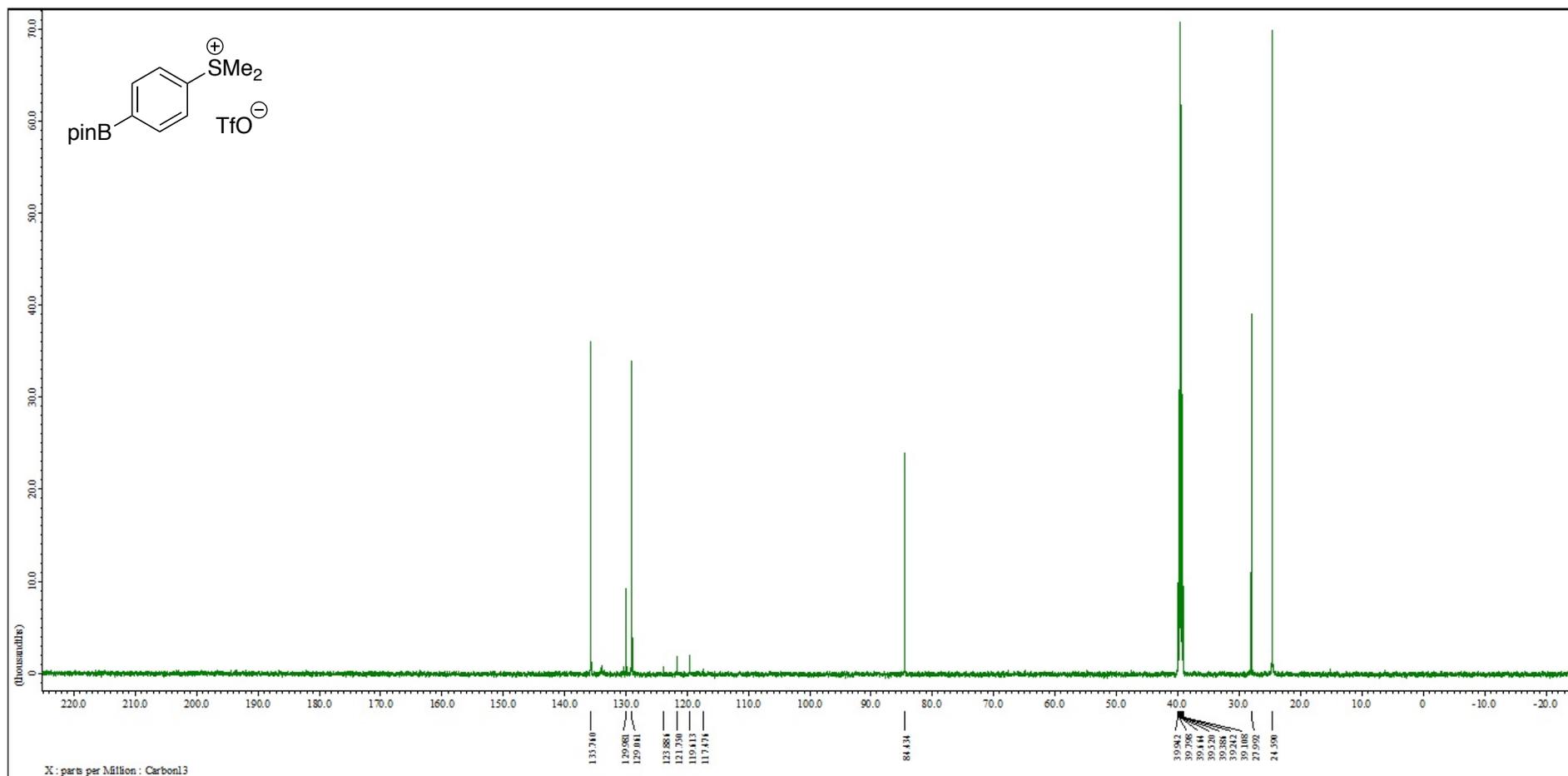


Figure S11. ¹³C NMR (151 MHz, DMSO-*d*₆) spectrum of **1n**

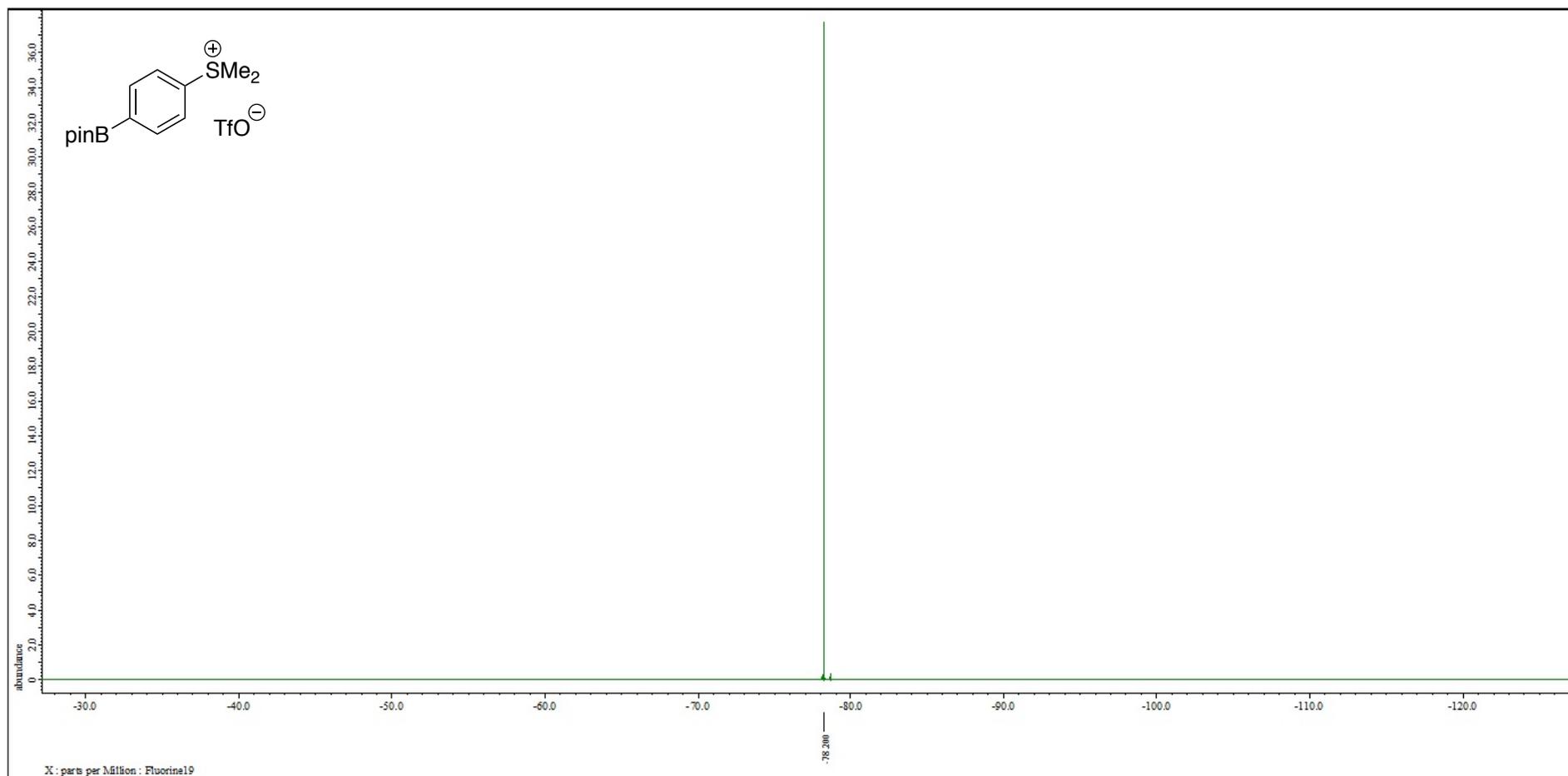


Figure S12. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1n**

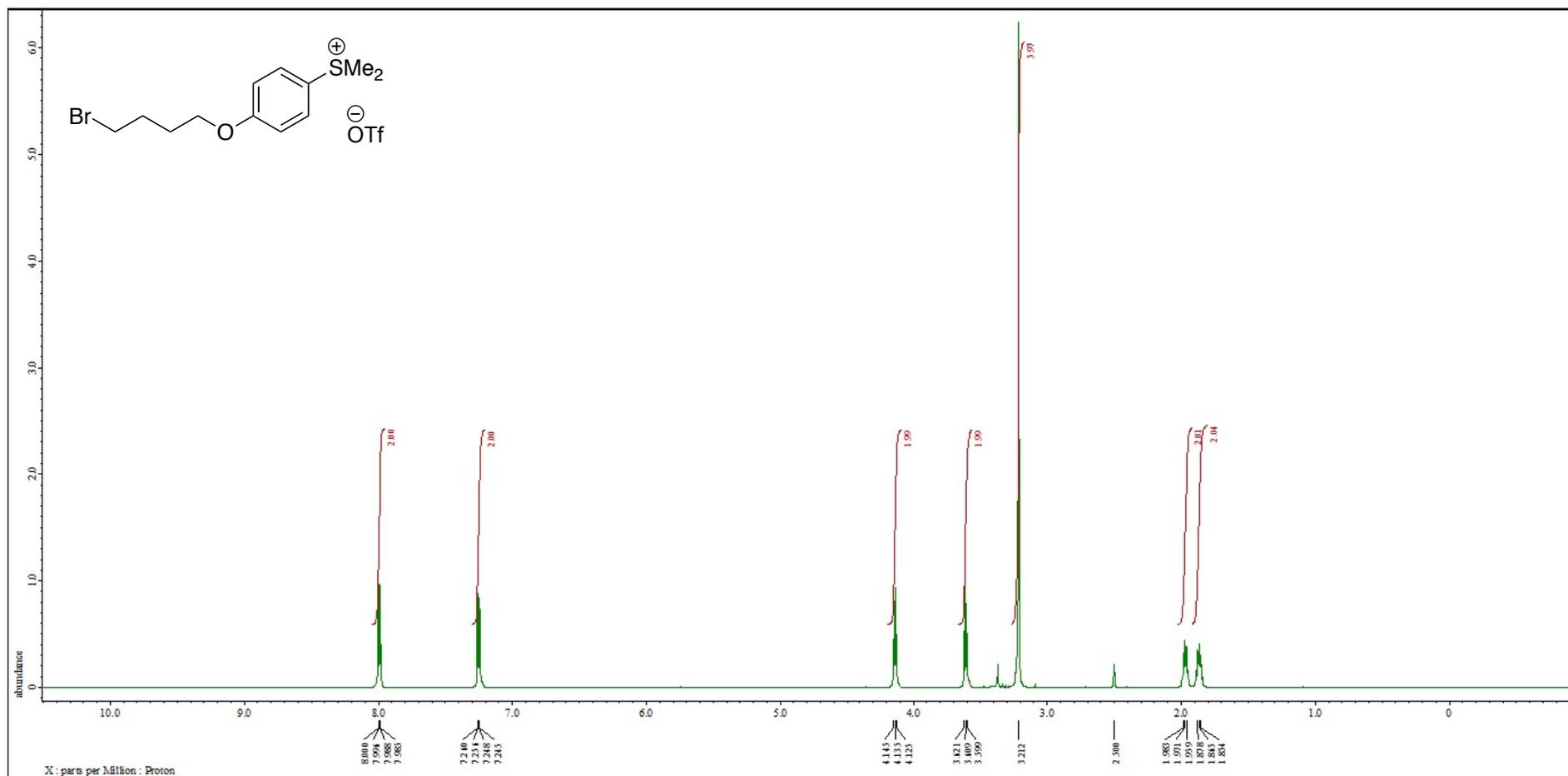


Figure S13. ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of **1p**

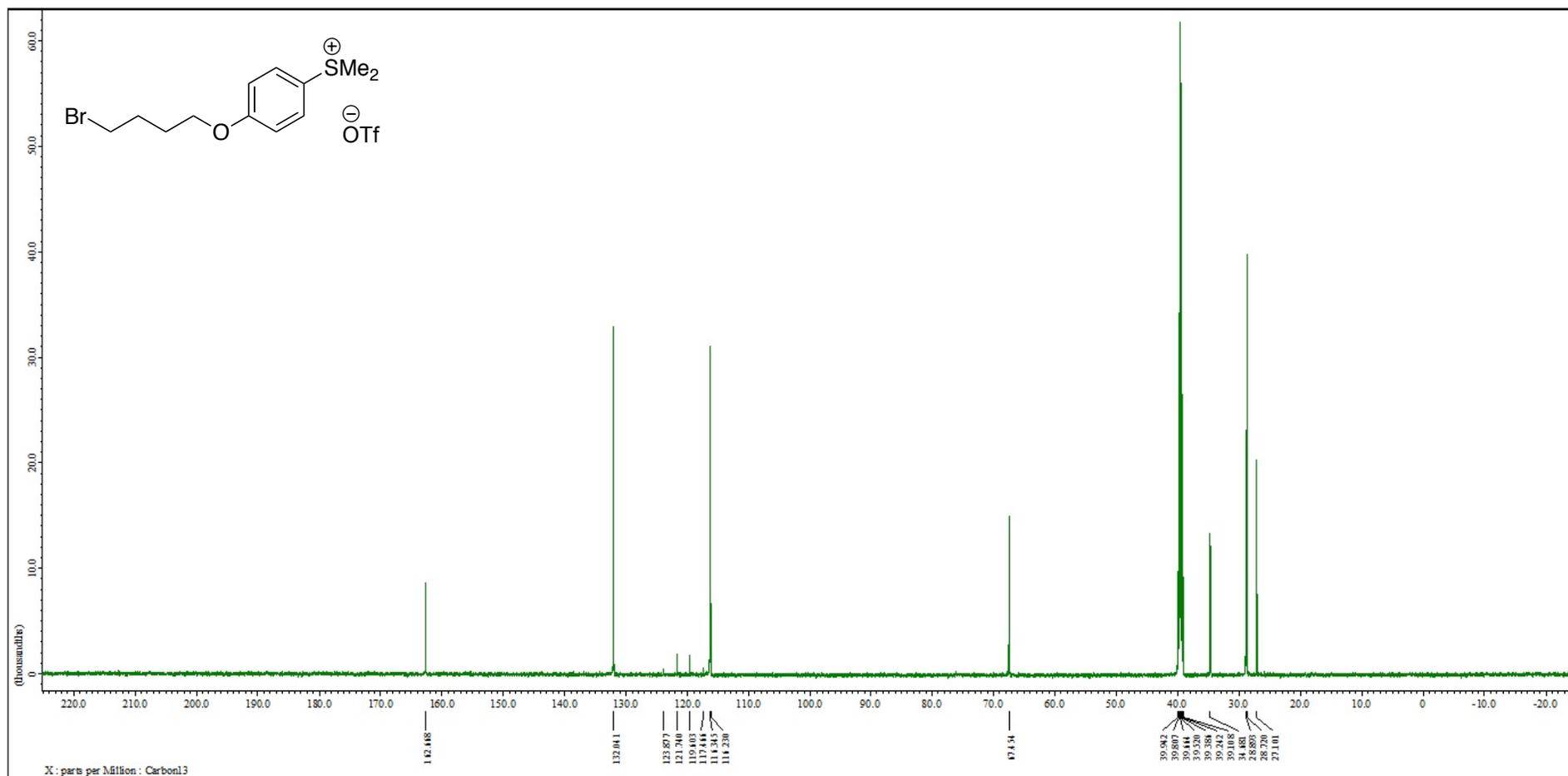


Figure S14. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1p**

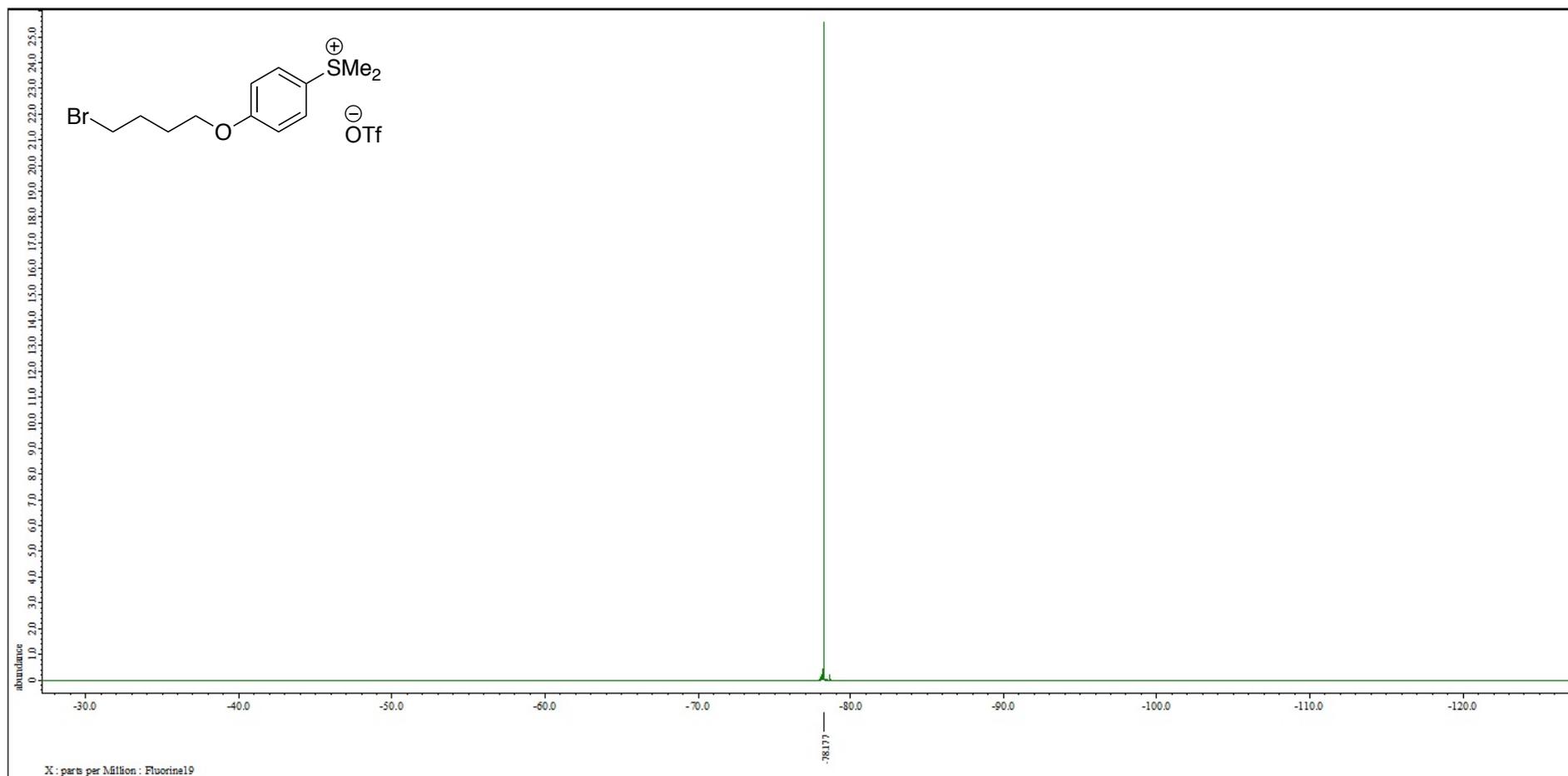


Figure S15. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1p**

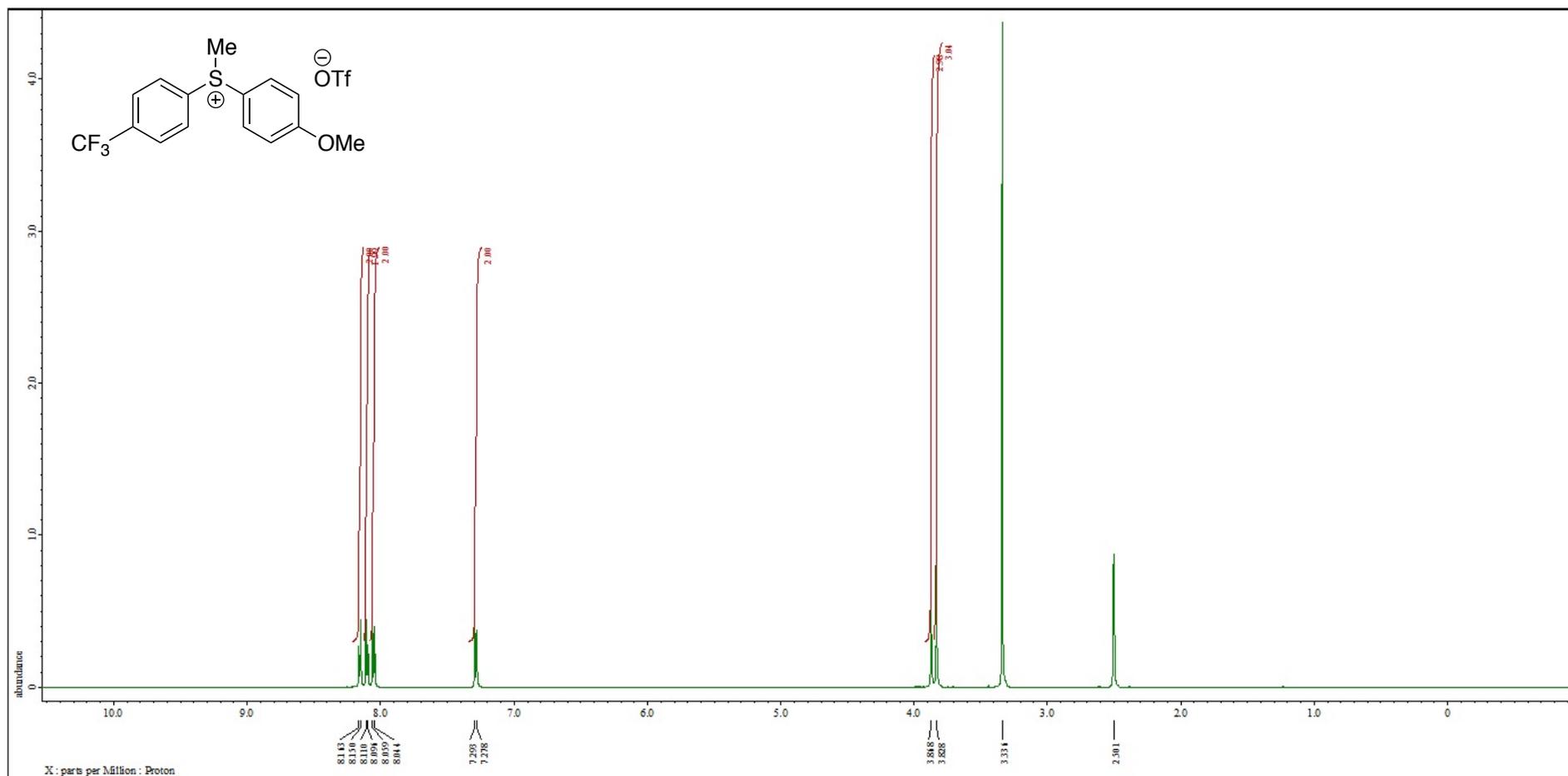


Figure S16. ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of **1r**

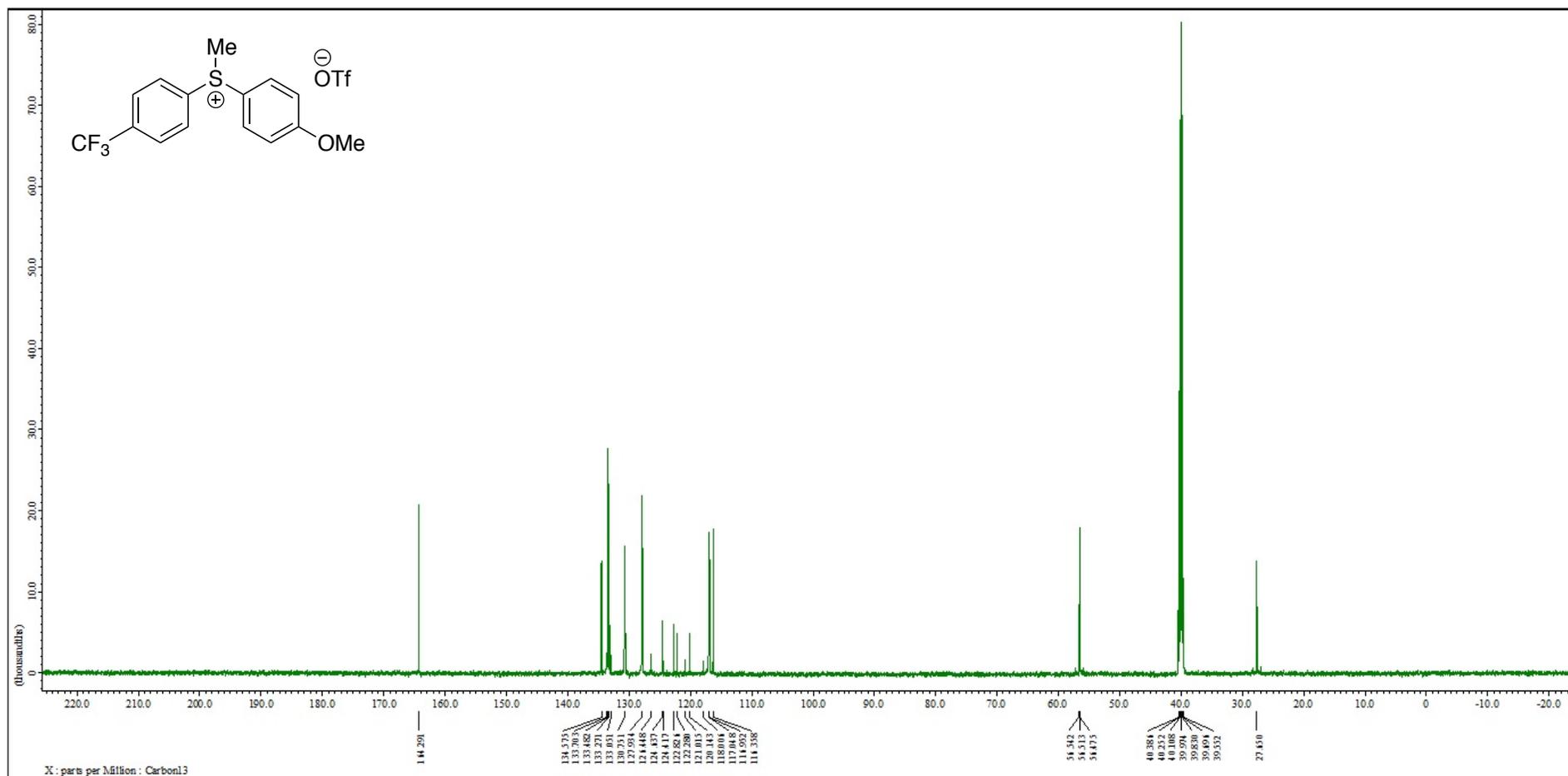


Figure S17. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1r**

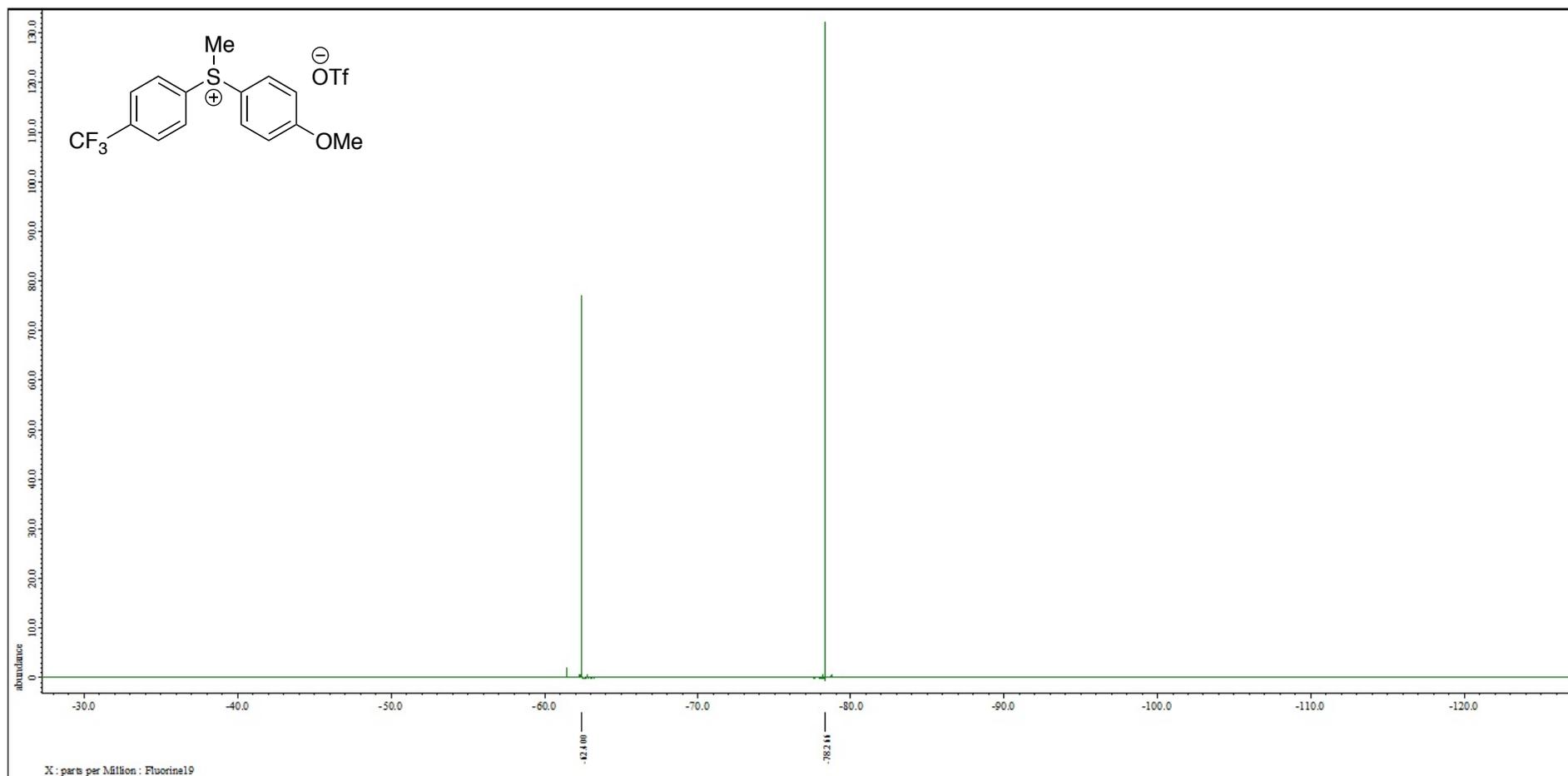


Figure S18. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1r**

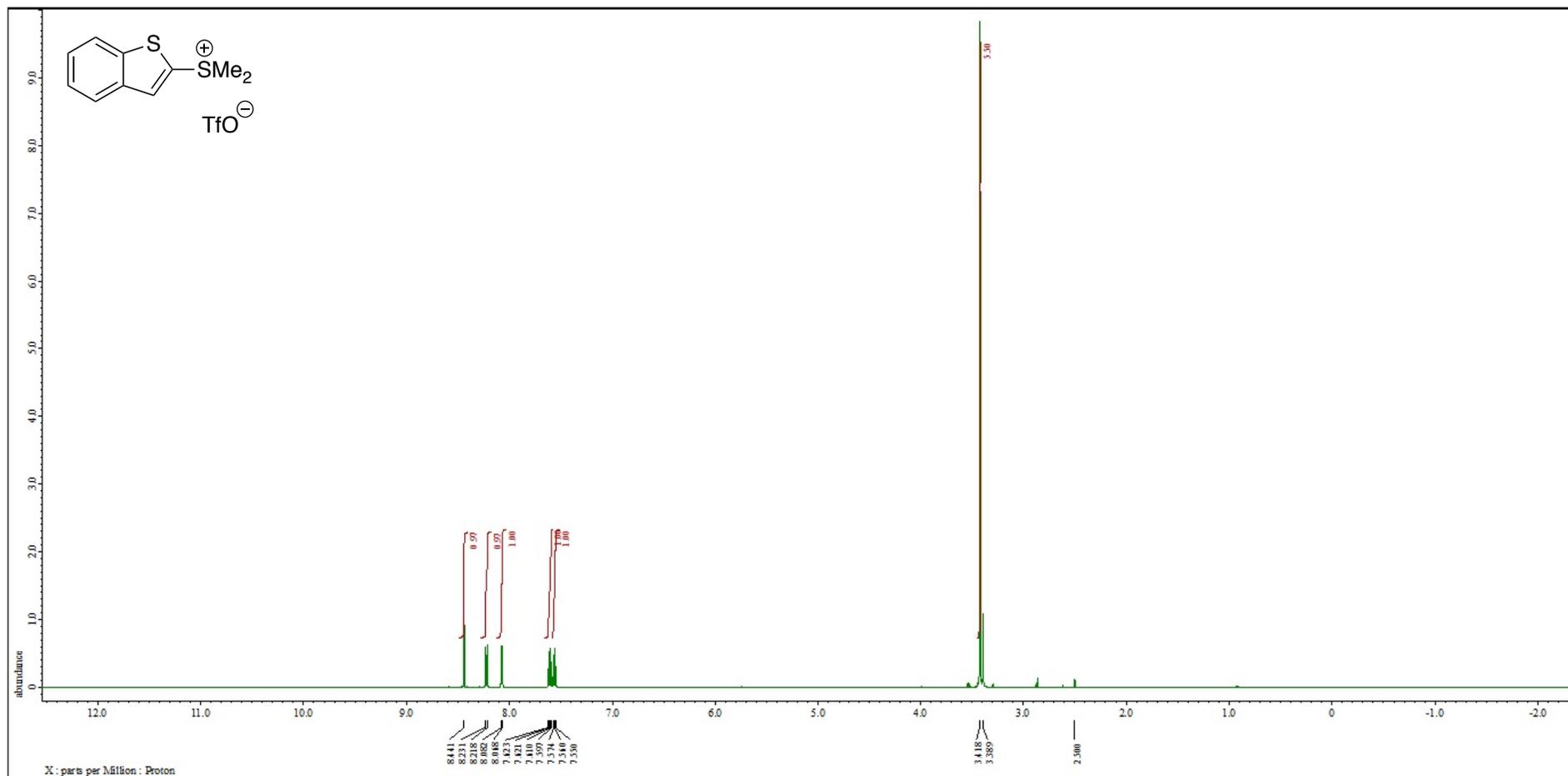


Figure S19. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) spectrum of **1s**

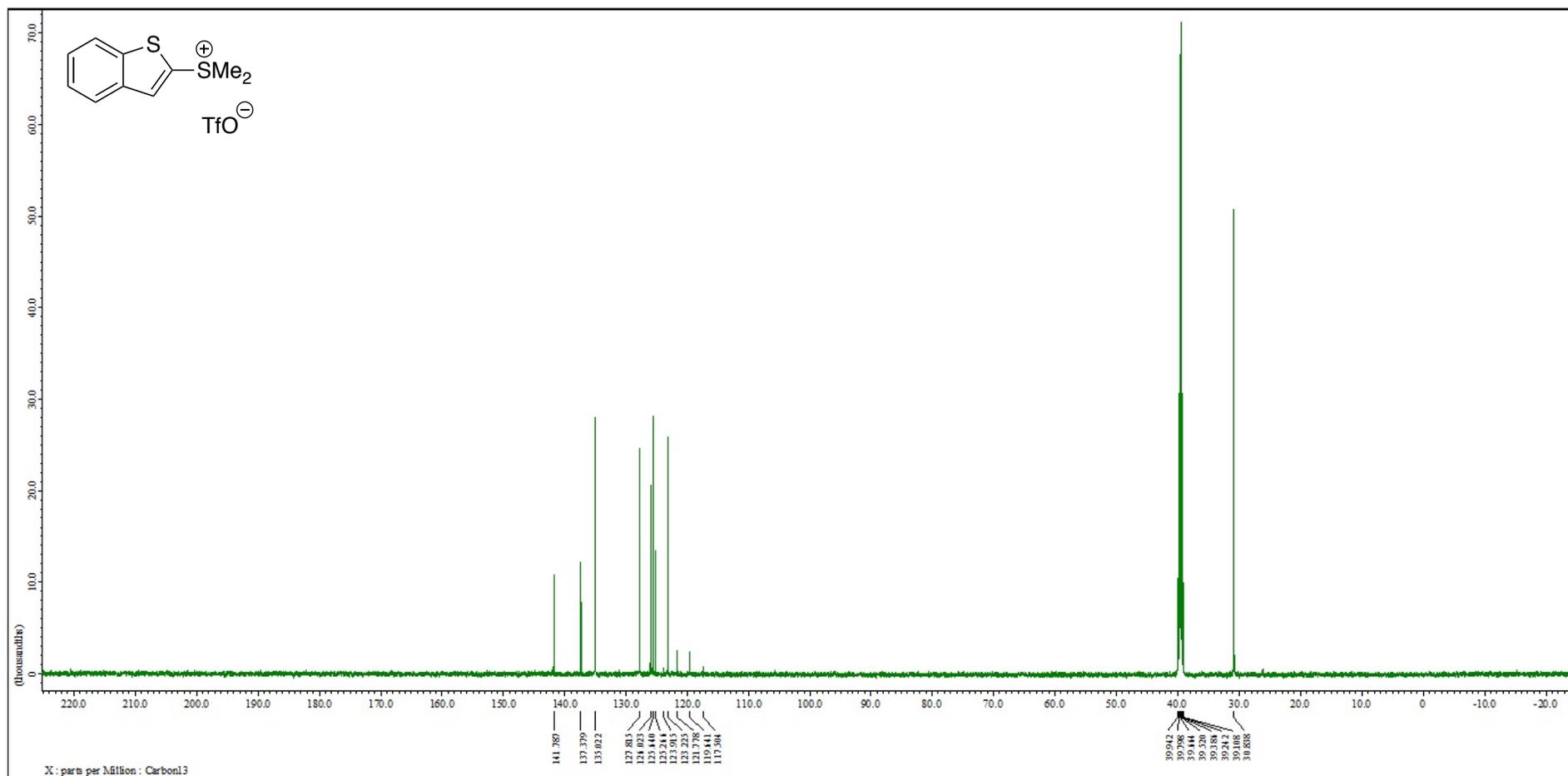


Figure S20. ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) spectrum of **1s**

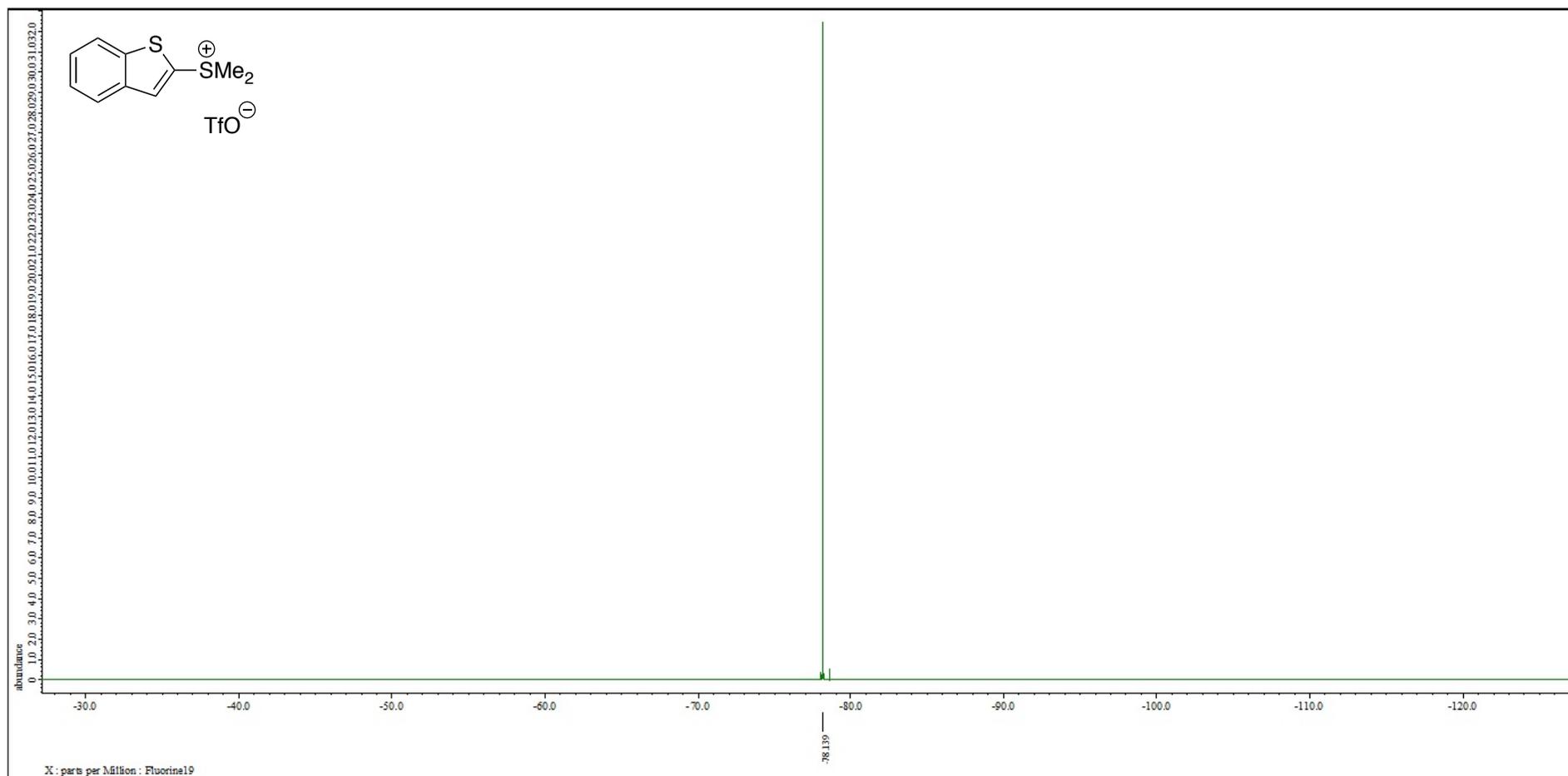


Figure S21. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1s**

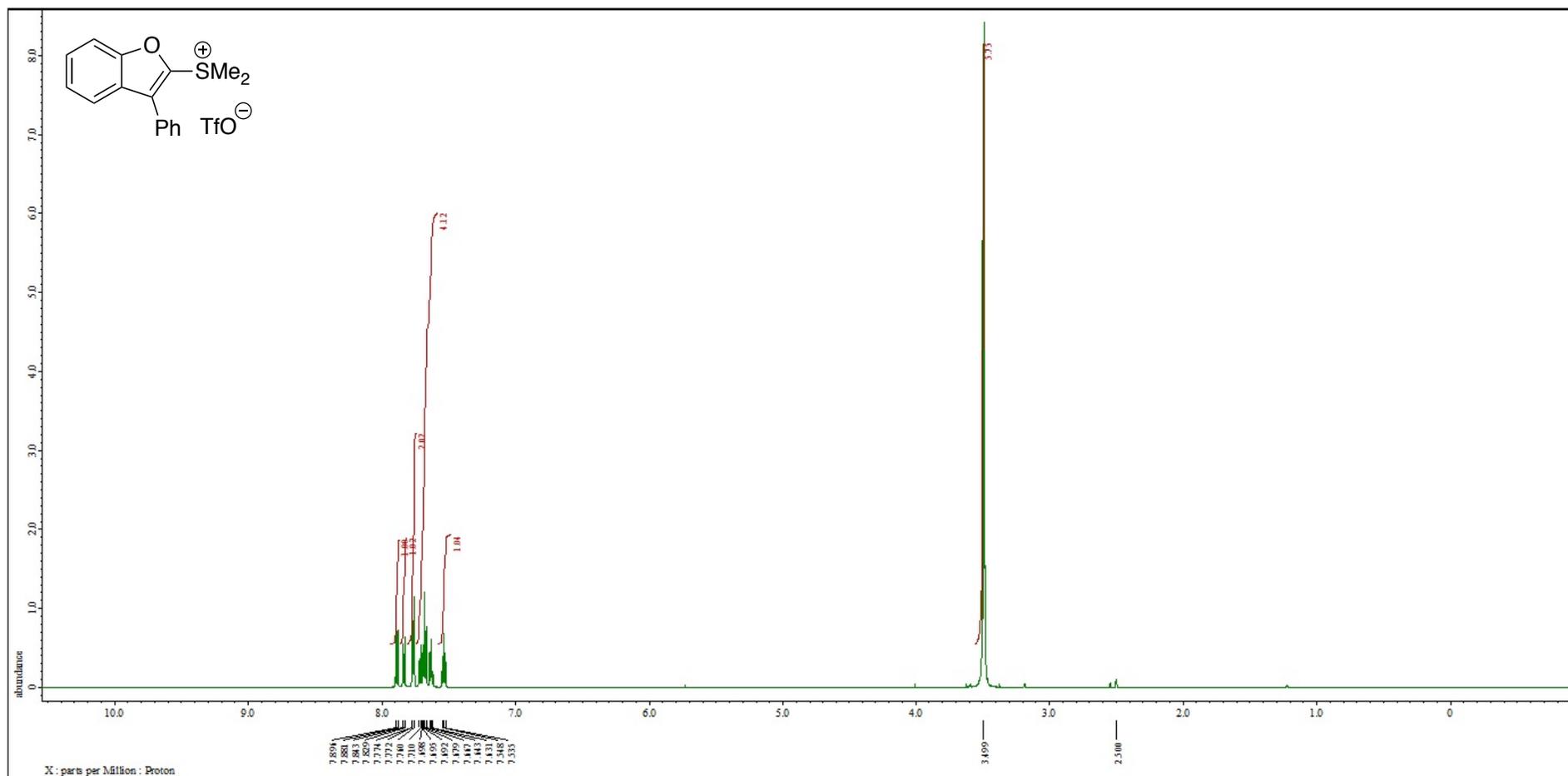


Figure S22. ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of **1t**

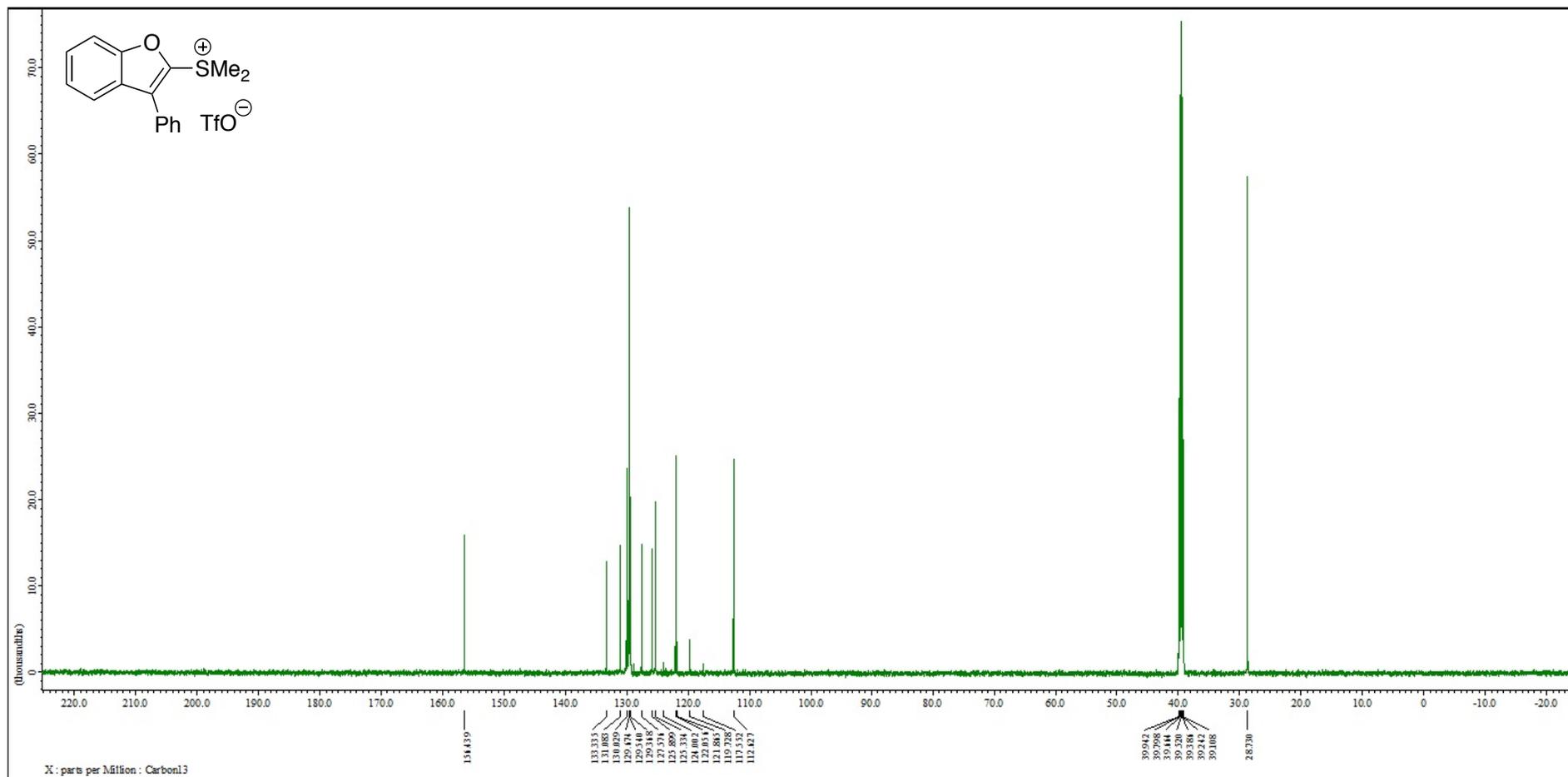


Figure S23. ¹³C NMR (151 MHz, DMSO-*d*₆) spectrum of **1t**

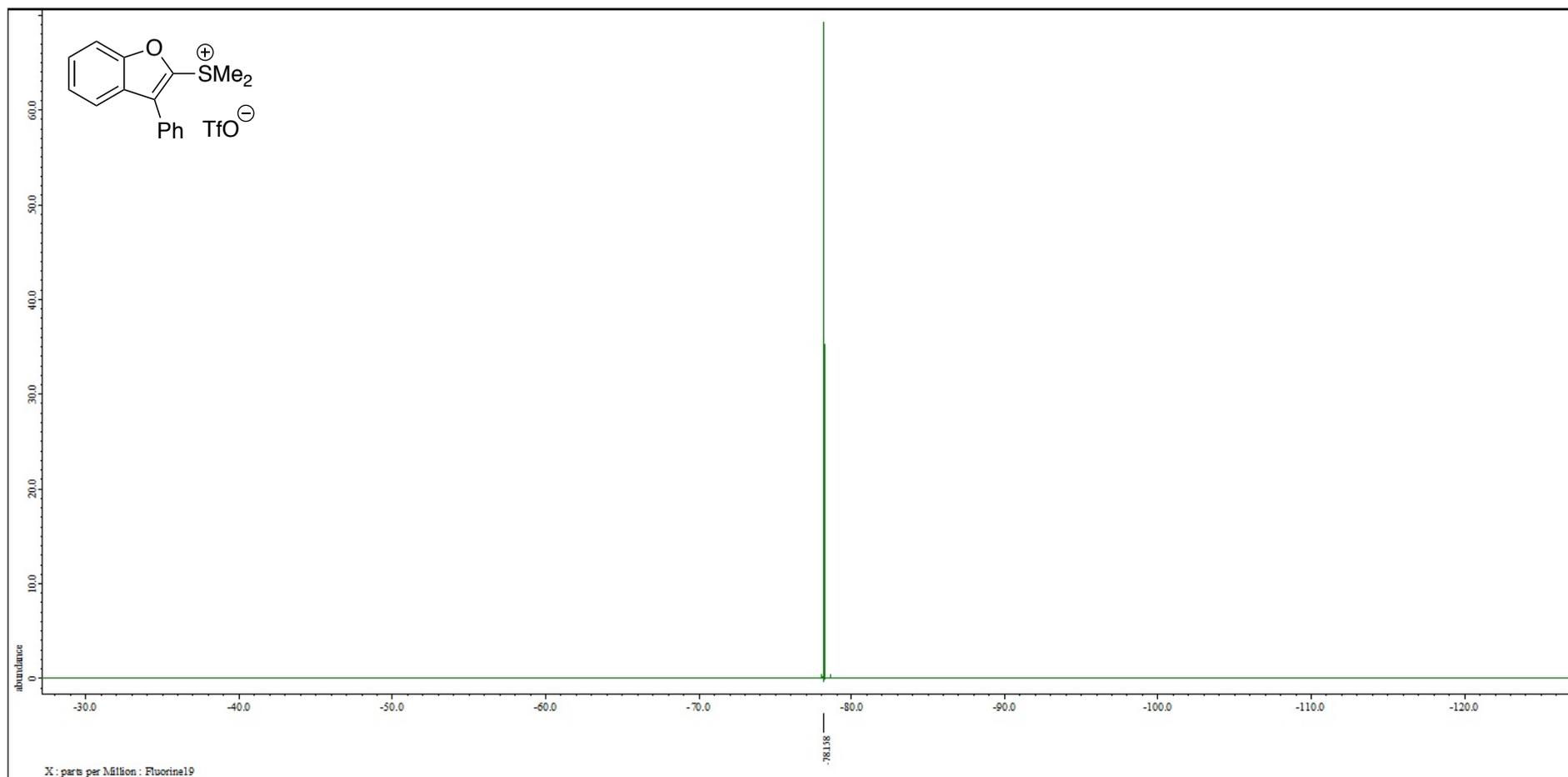


Figure S24. ^{19}F NMR (564 MHz, $\text{DMSO-}d_6$) spectrum of **1t**

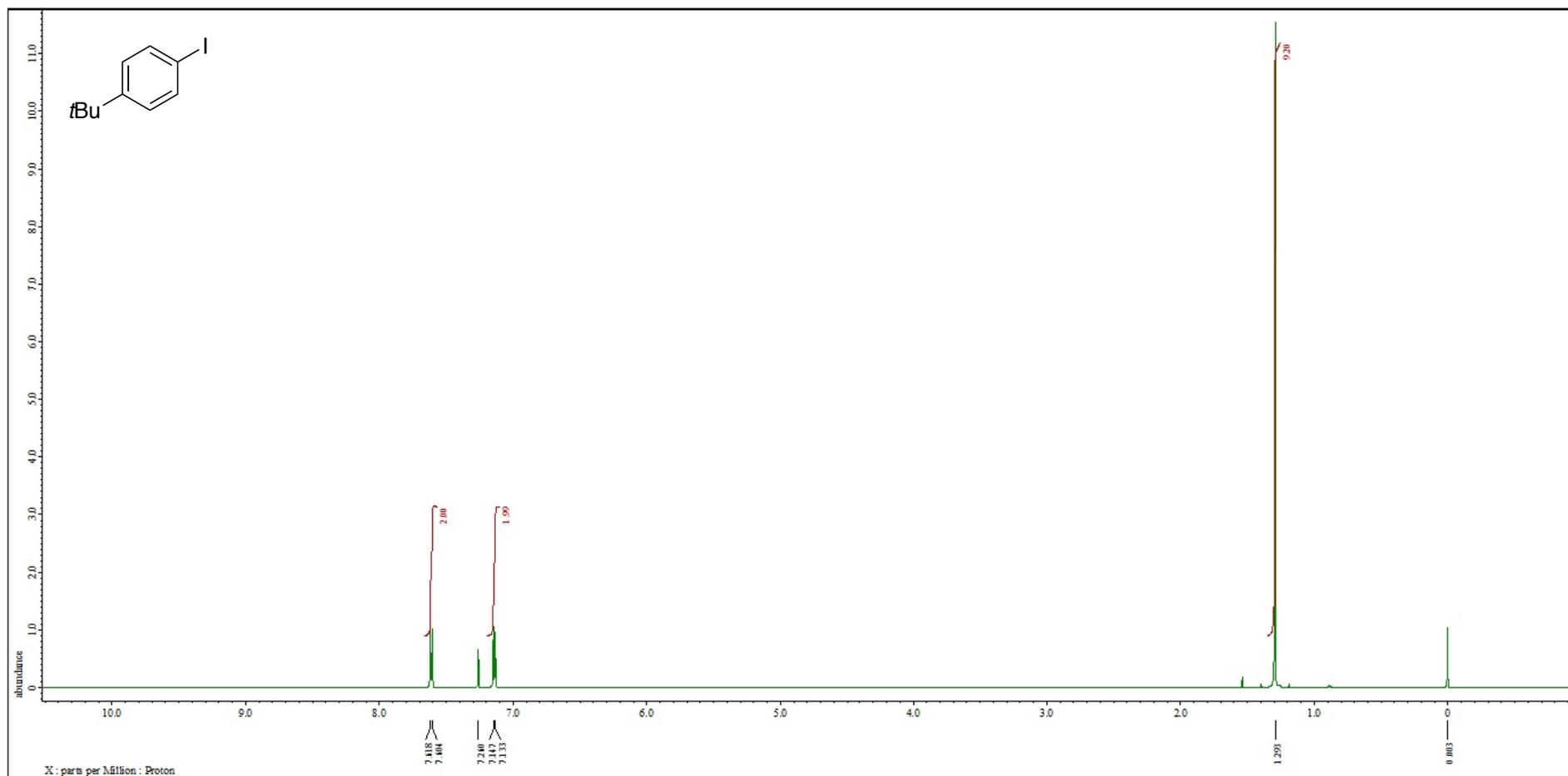


Figure S25. ¹H NMR (600 MHz, CDCl₃) spectrum of **3a**

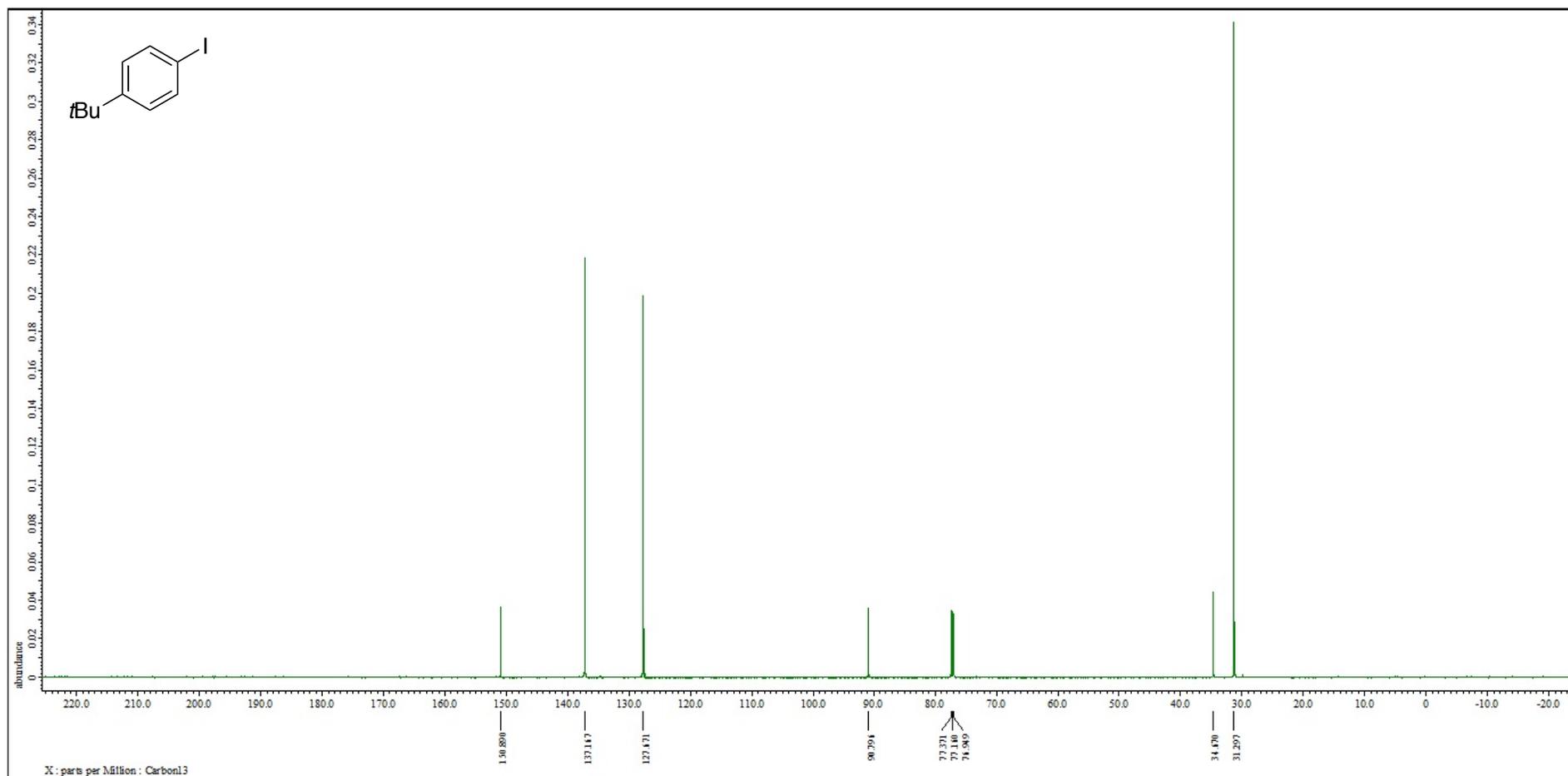


Figure S26. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3a**

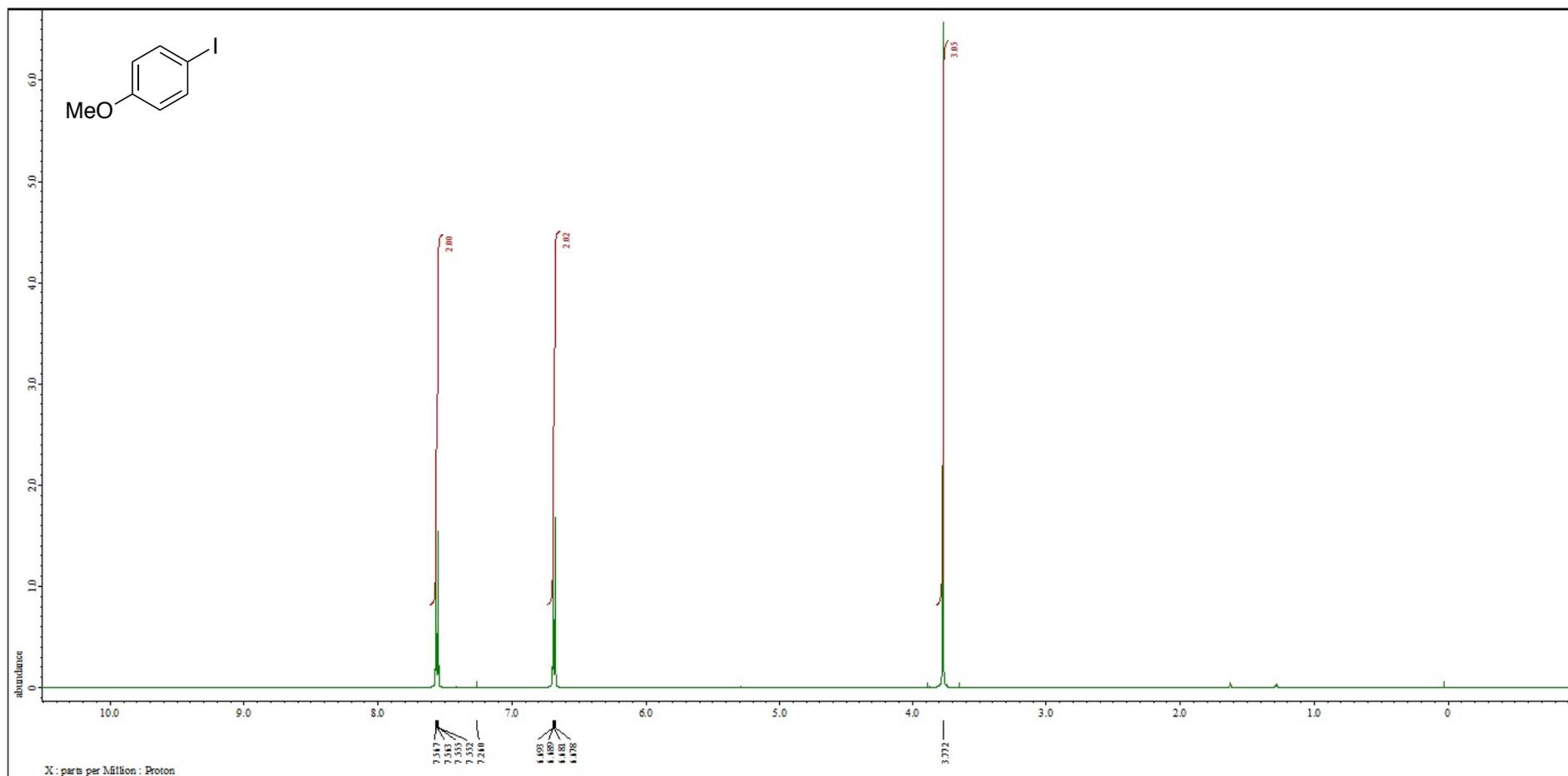


Figure S27. ¹H NMR (600 MHz, CDCl₃) spectrum of **3b**

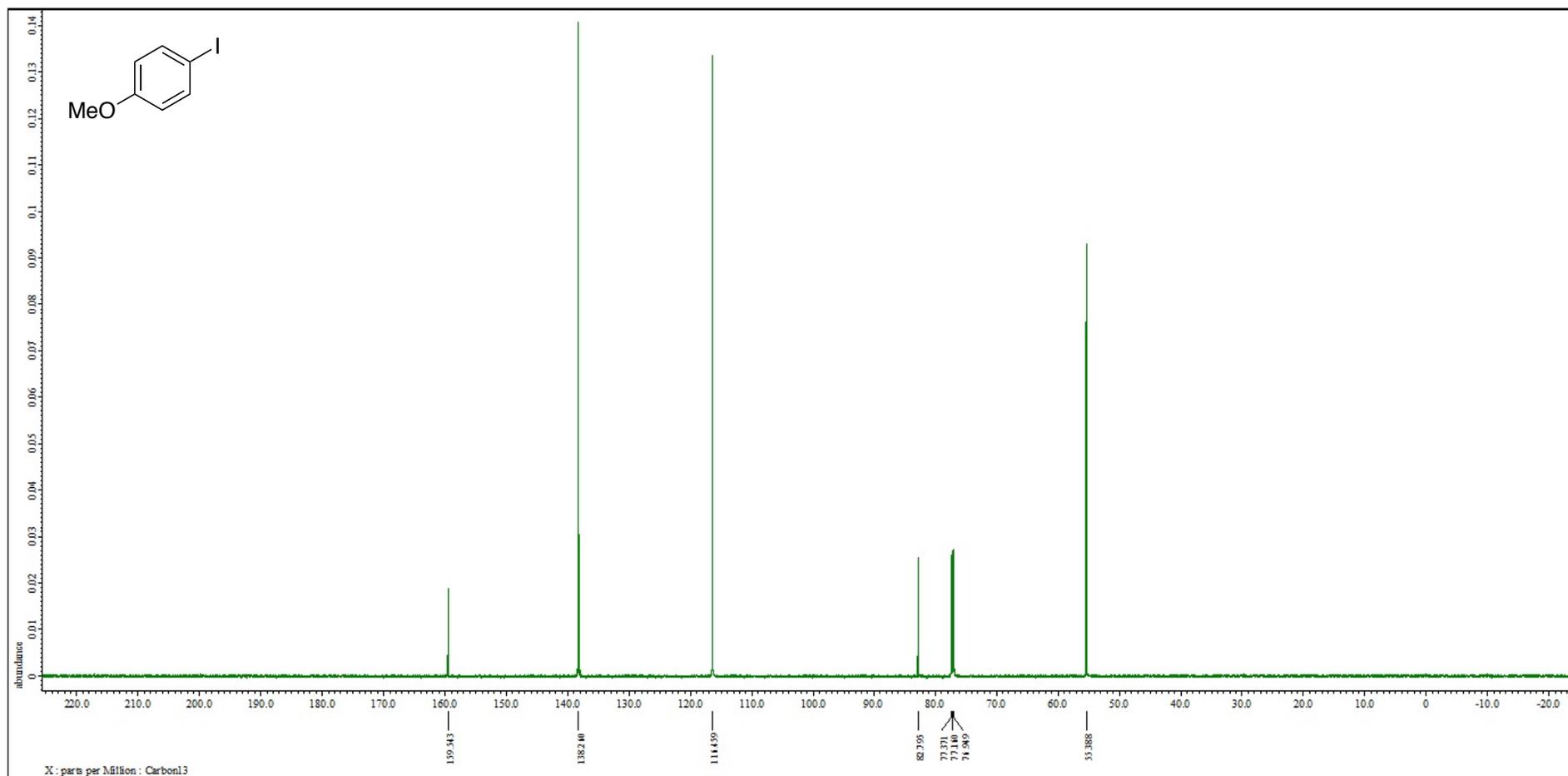


Figure S28. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3b**

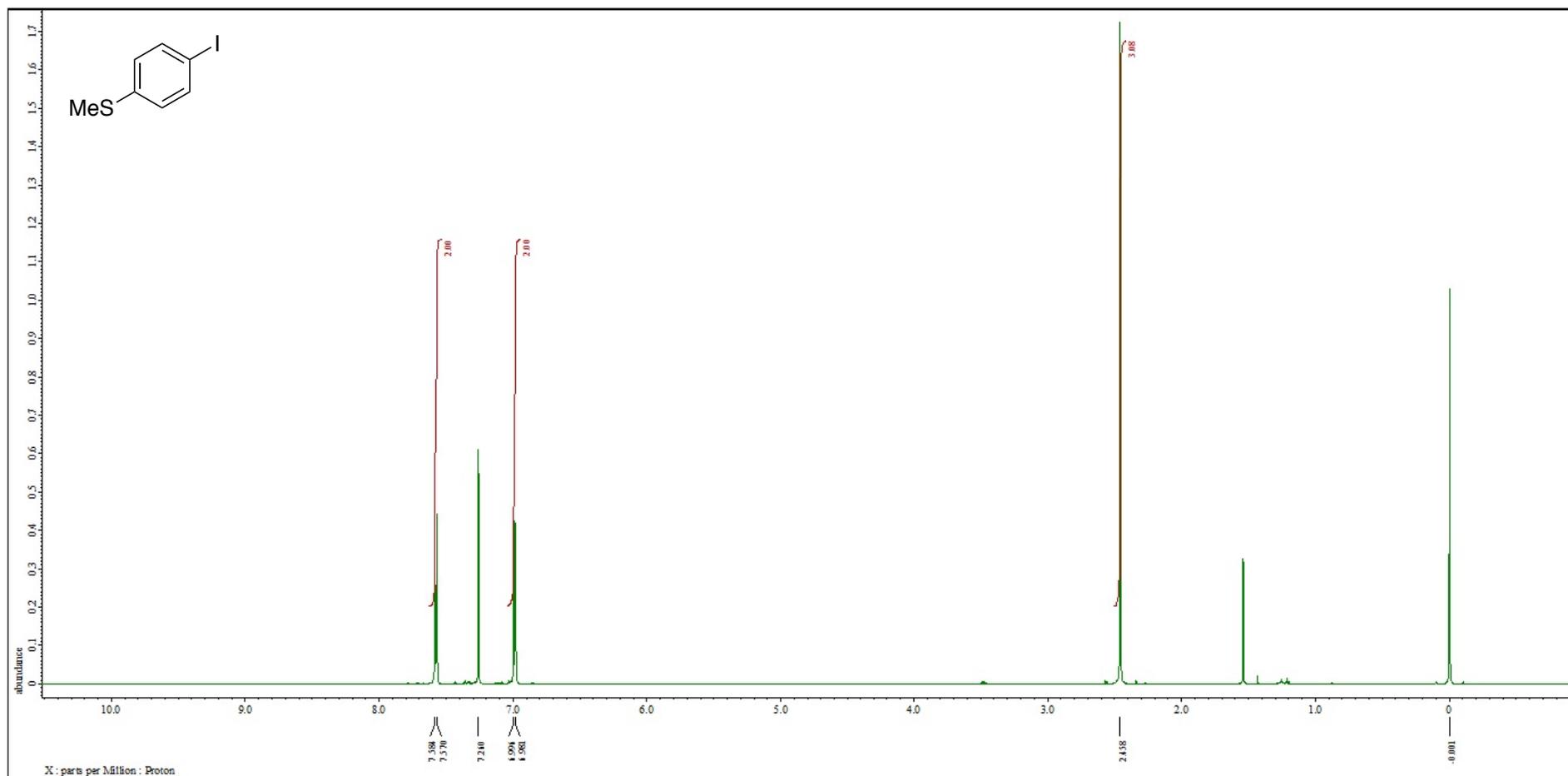


Figure S29. ^1H NMR (600 MHz, CDCl_3) spectrum of **3c**

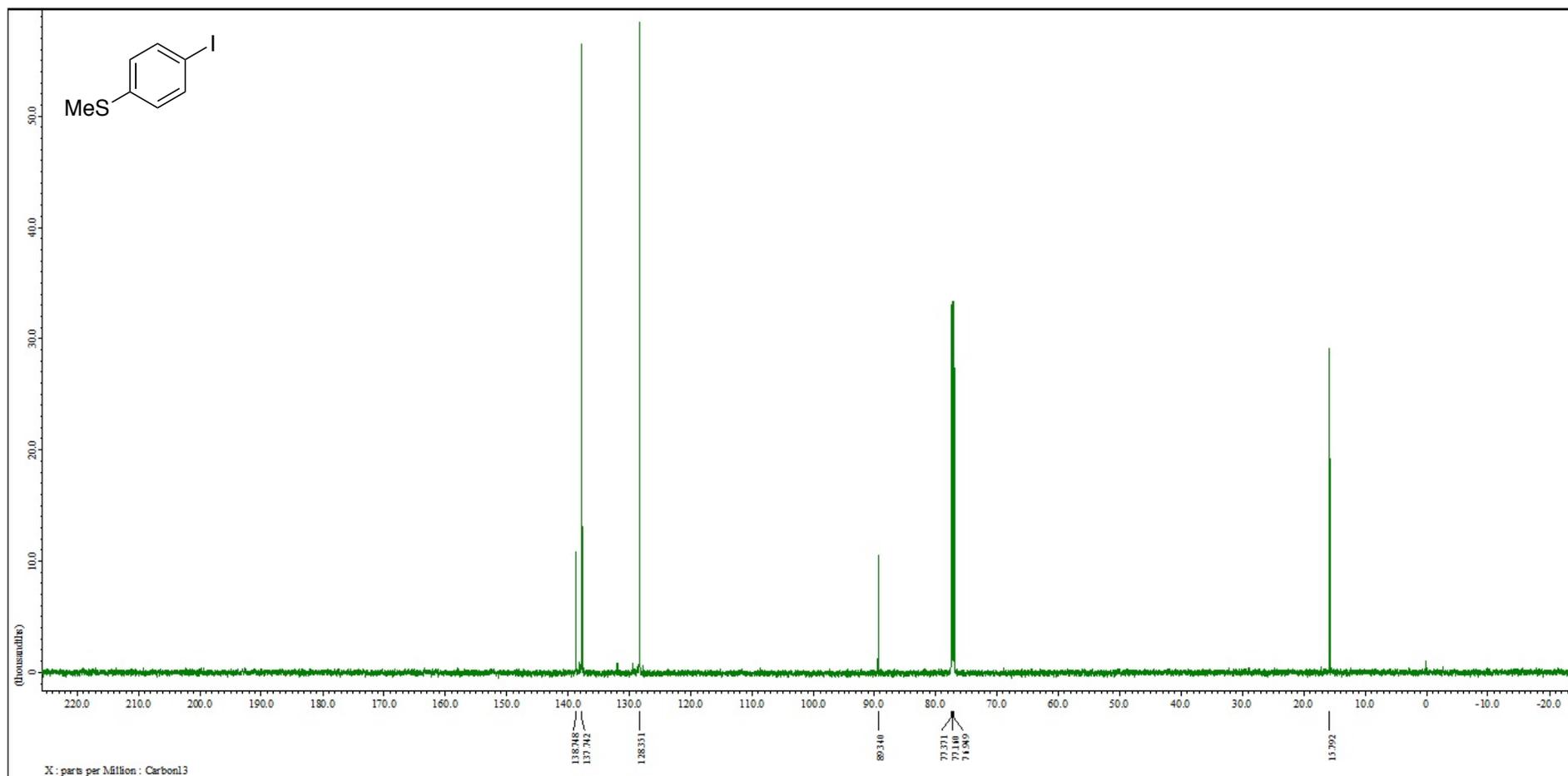


Figure S30. ¹³C NMR (151 MHz, CDCl₃) spectrum of **3c**

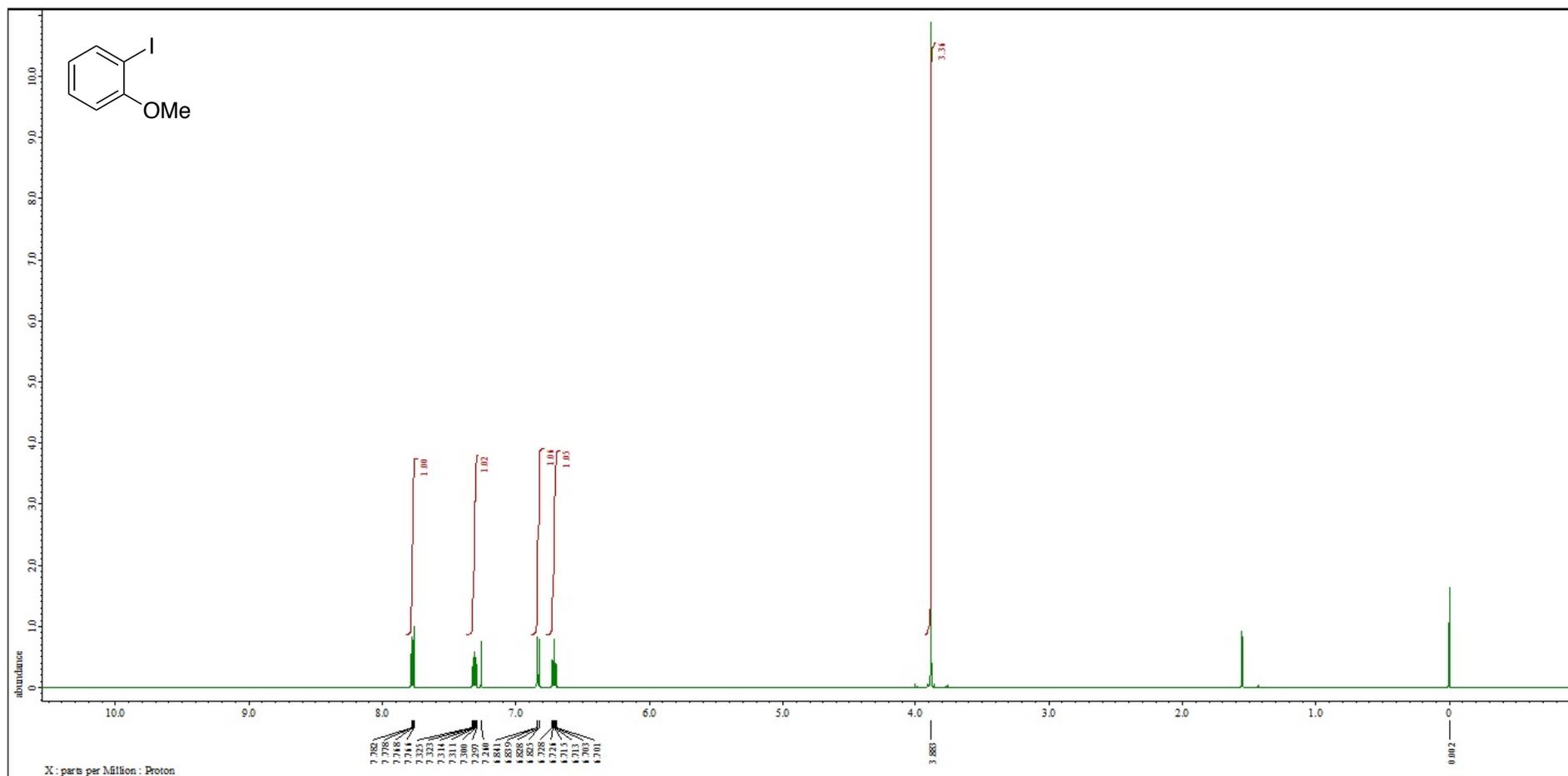


Figure S31. ^1H NMR (600 MHz, CDCl_3) spectrum of **3d**

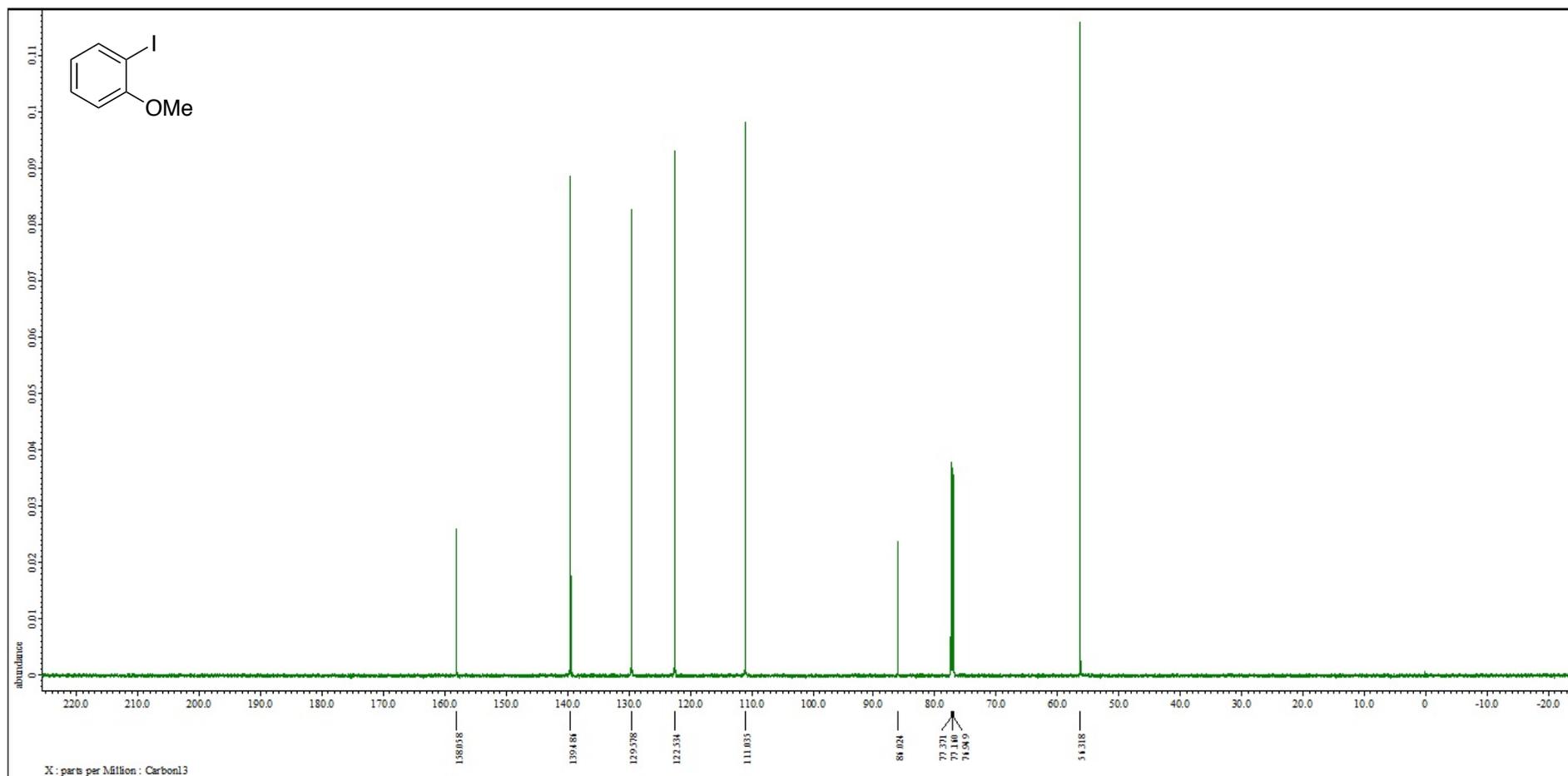


Figure S32. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3d**

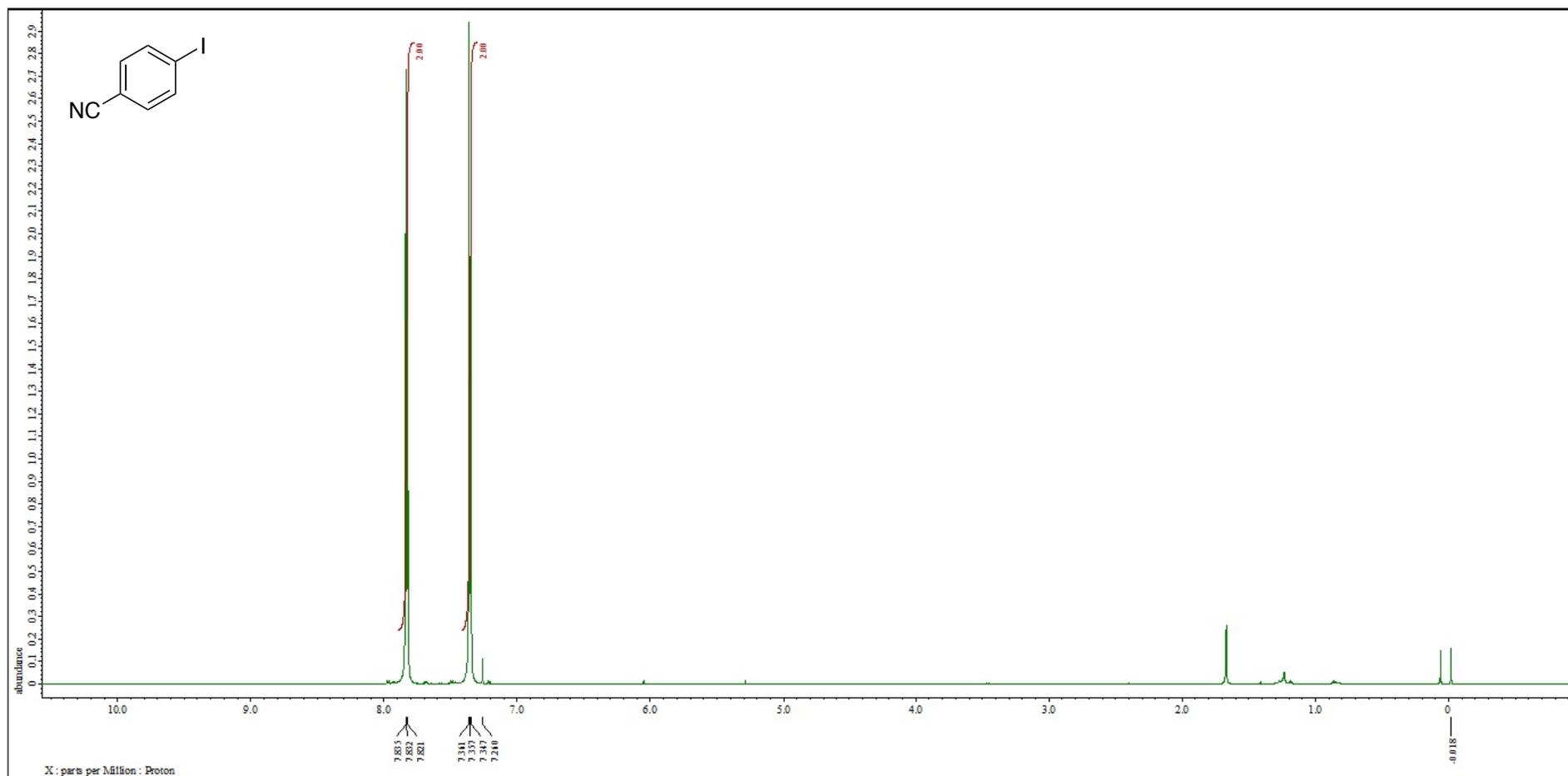


Figure S33. ¹H NMR (600 MHz, CDCl₃) spectrum of **3e**

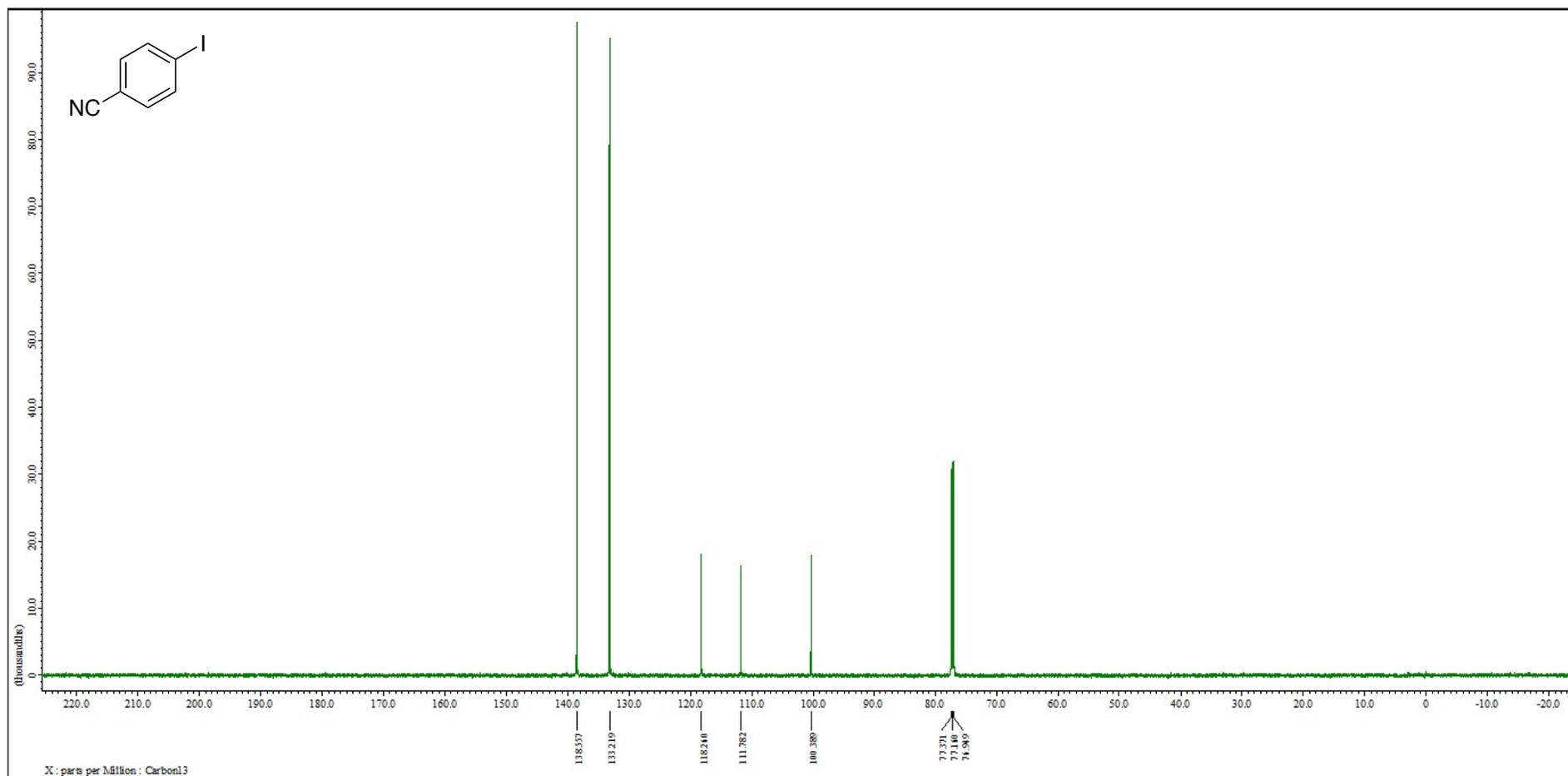


Figure S34. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3e**

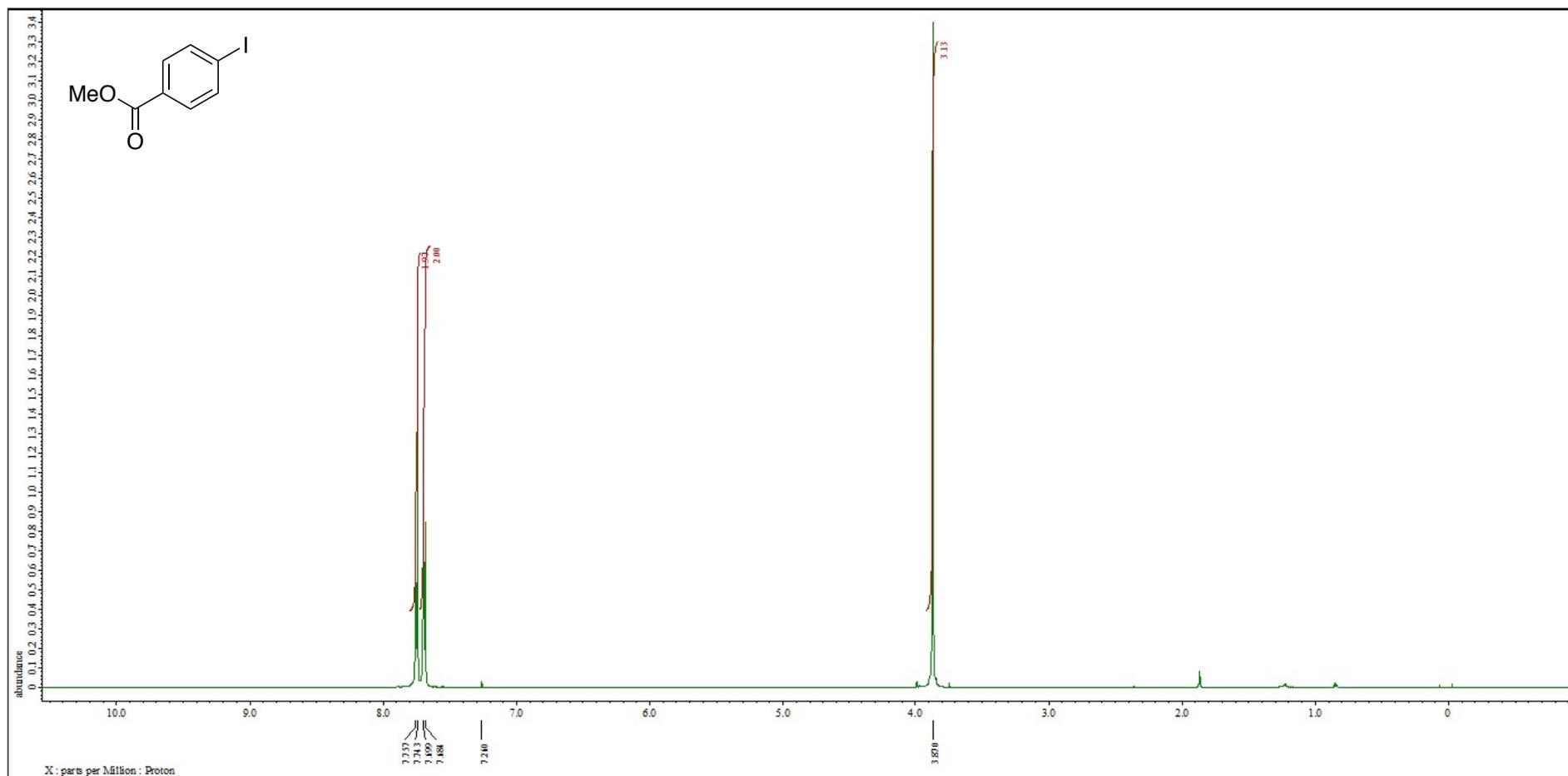


Figure S35. ^1H NMR (600 MHz, CDCl_3) spectrum of **3f**

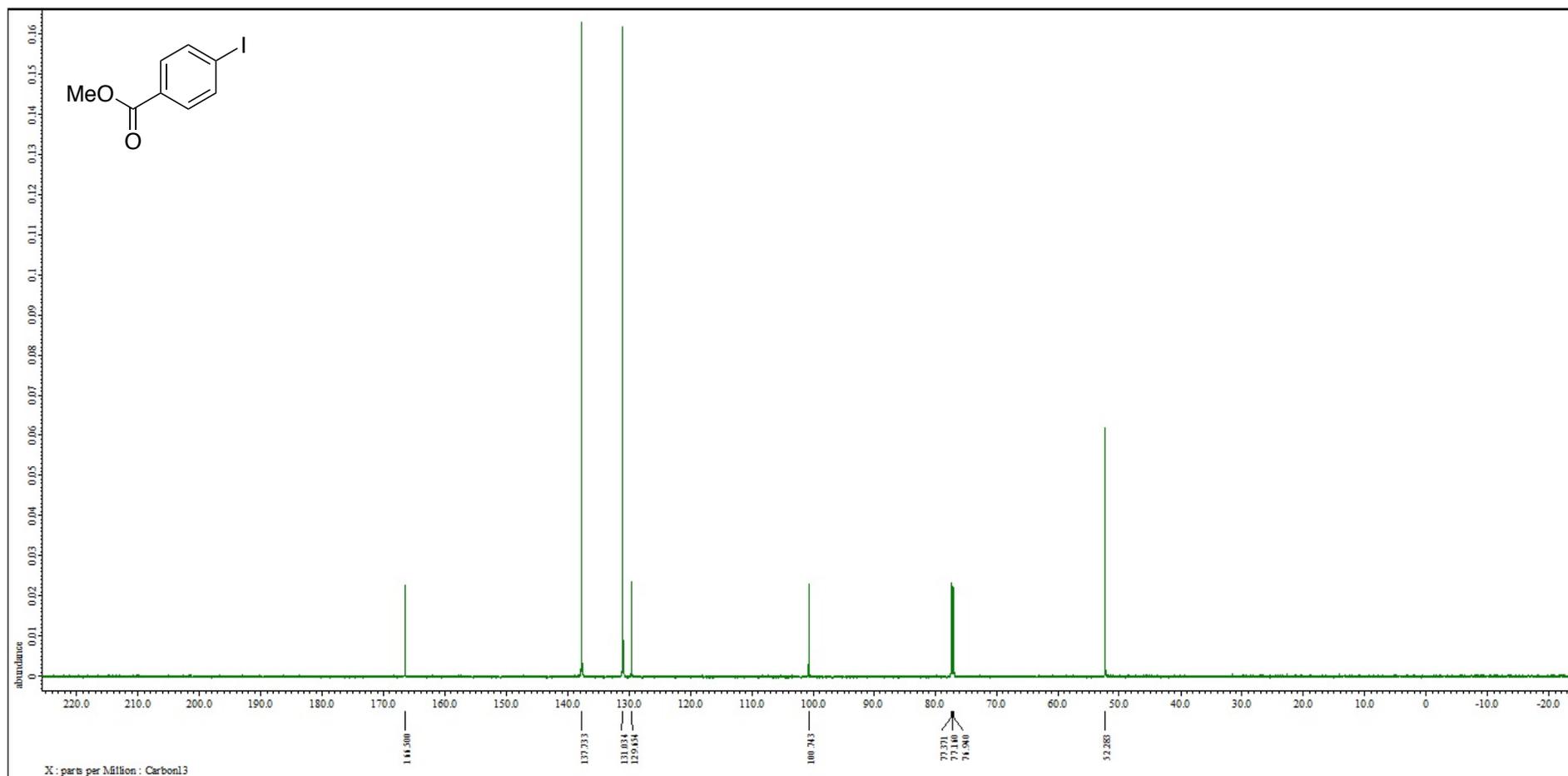


Figure S36. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3f**

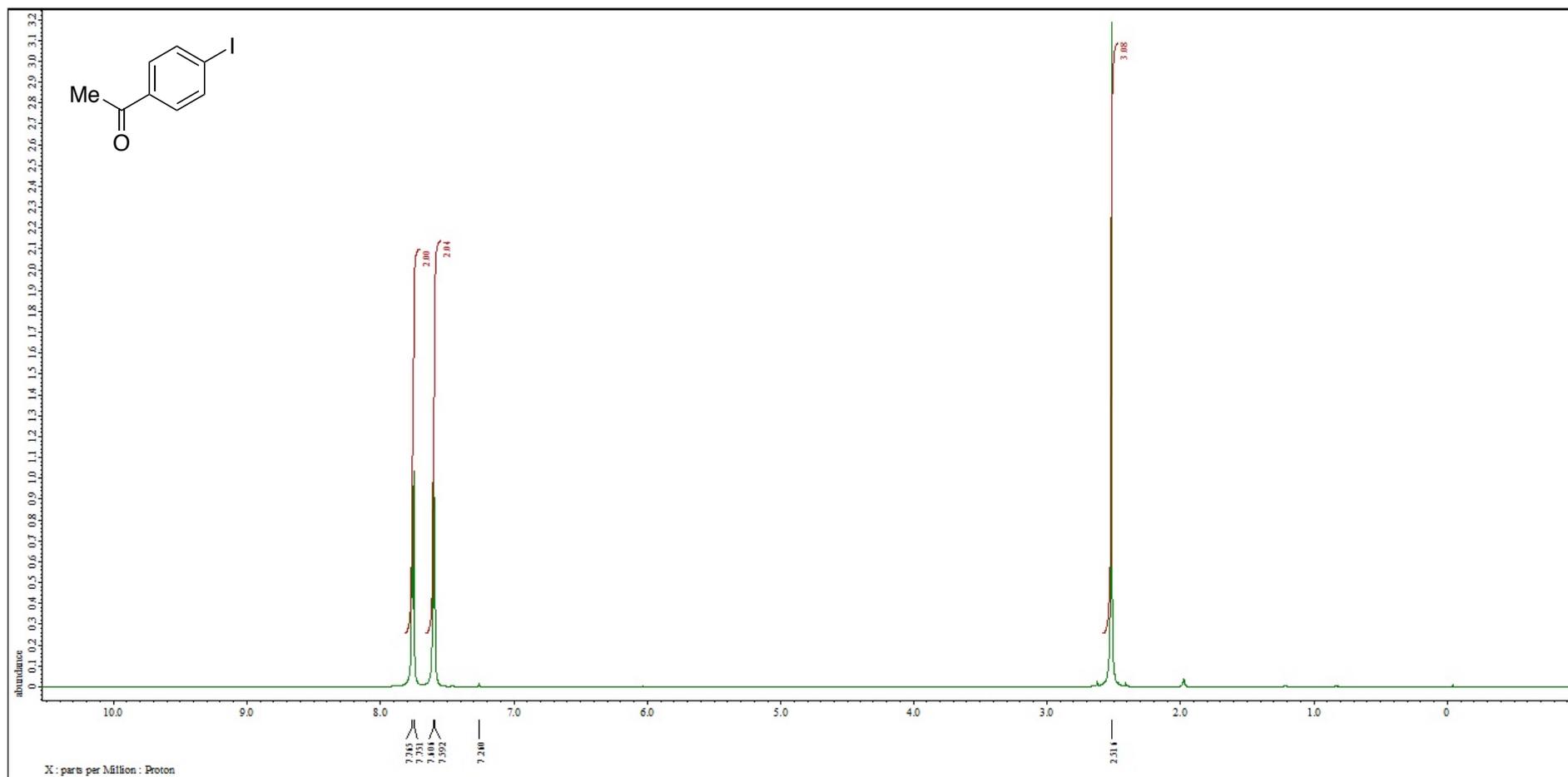


Figure S37. ^1H NMR (600 MHz, CDCl_3) spectrum of **3g**

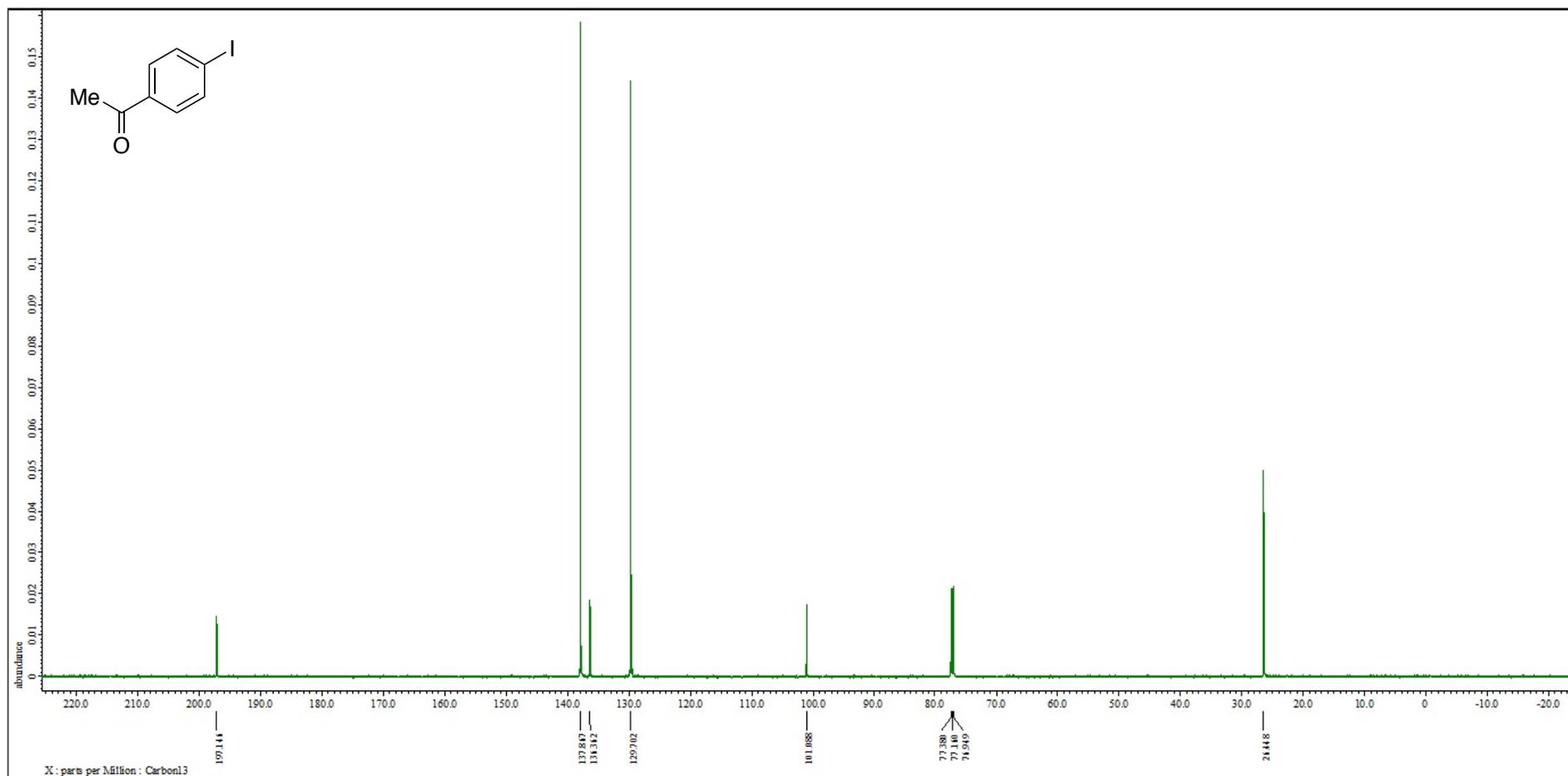


Figure S38. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3g**

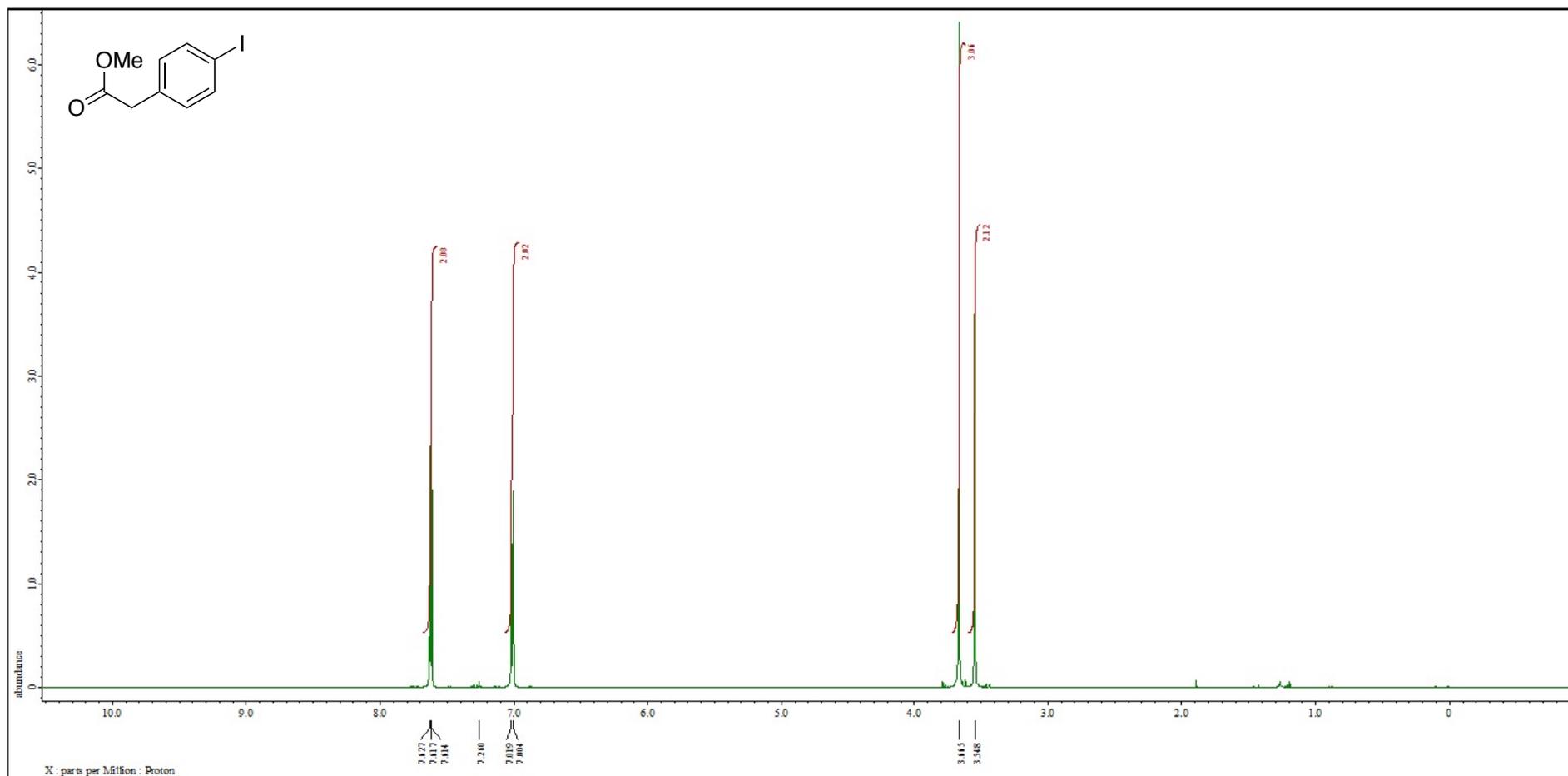


Figure S39. ¹H NMR (600 MHz, CDCl₃) spectrum of **3h**

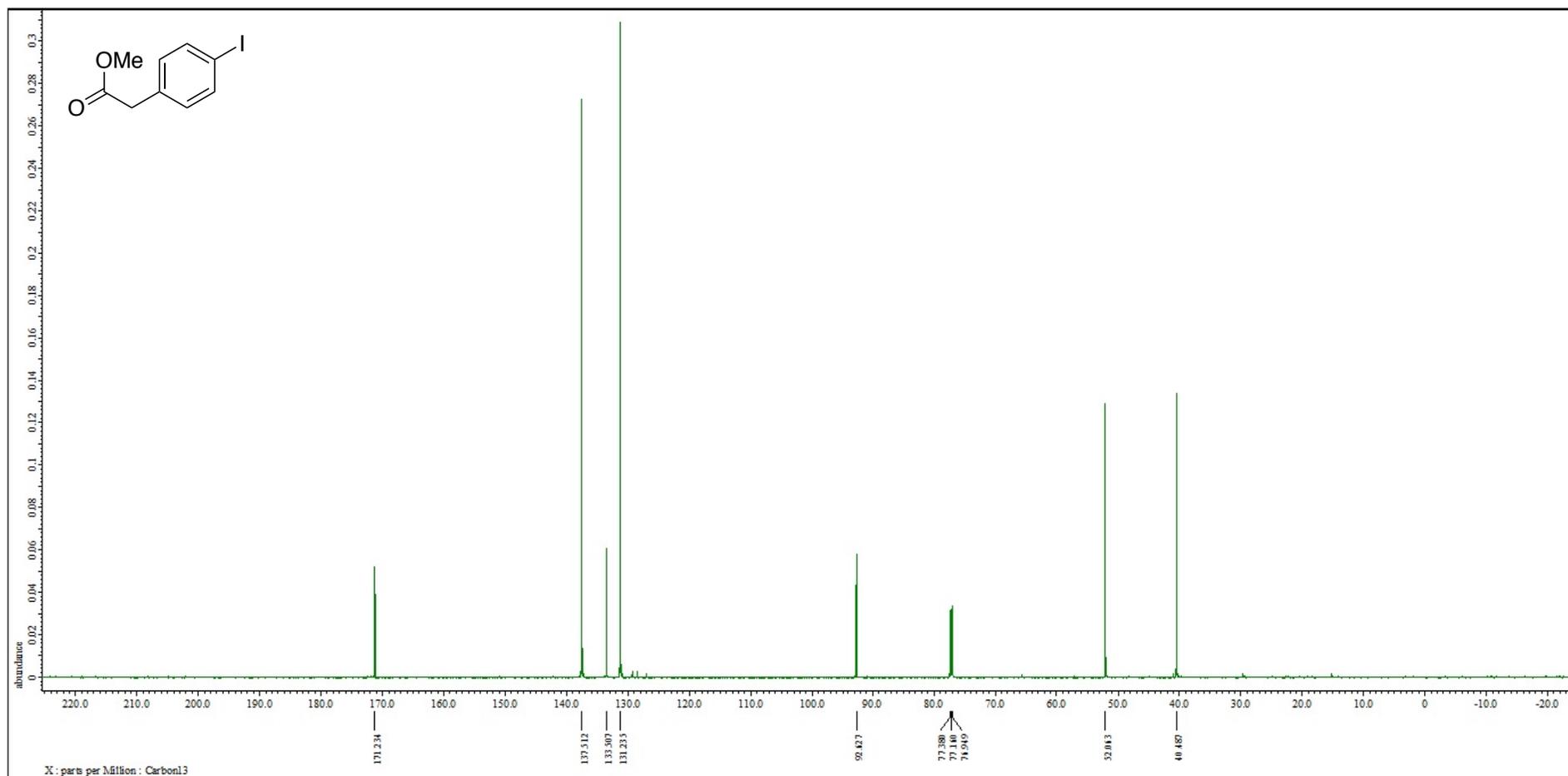


Figure S40. ¹³C NMR (151 MHz, CDCl₃) spectrum of 3h

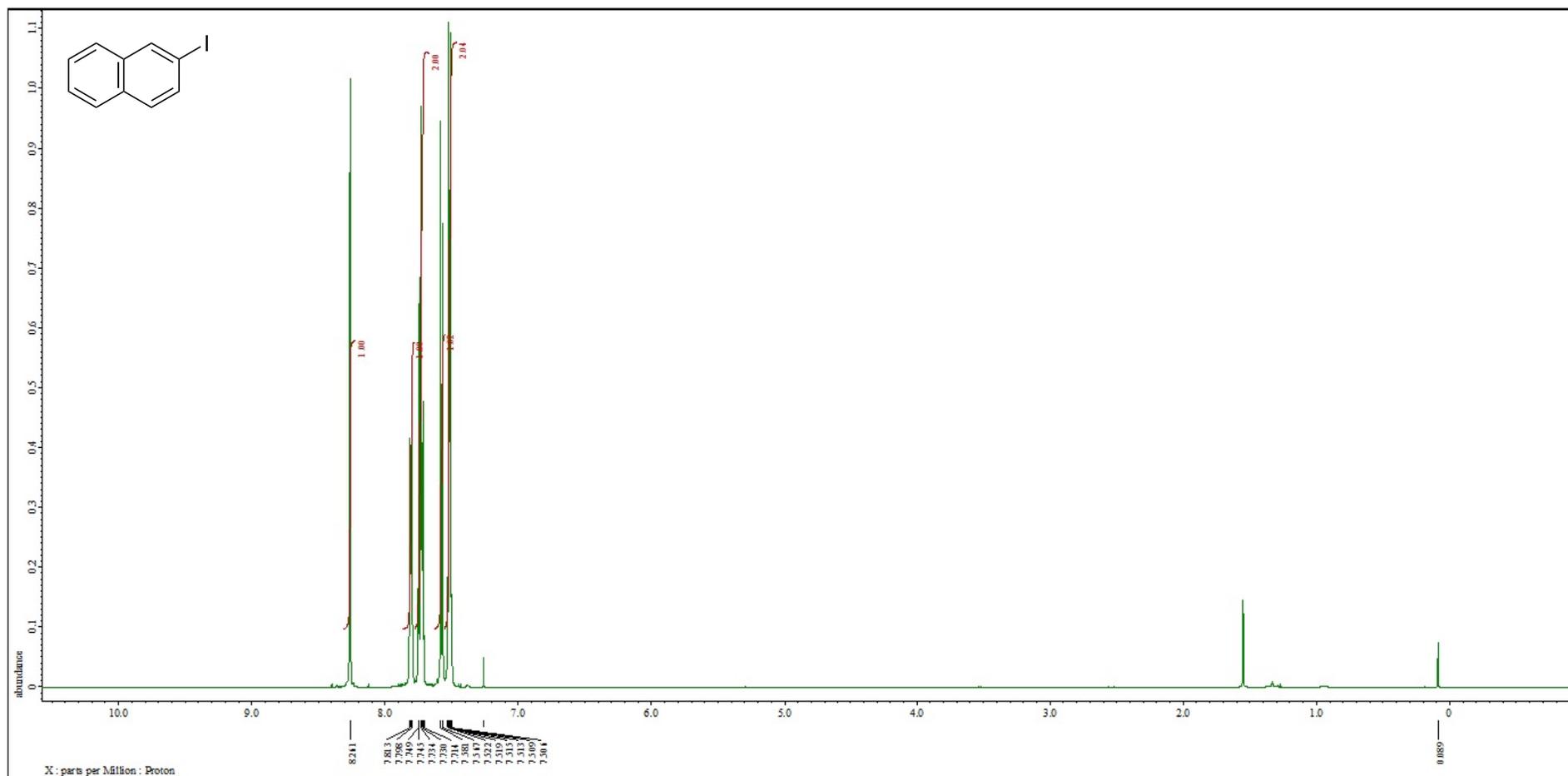


Figure S41. ¹H NMR (600 MHz, CDCl₃) spectrum of **3i**

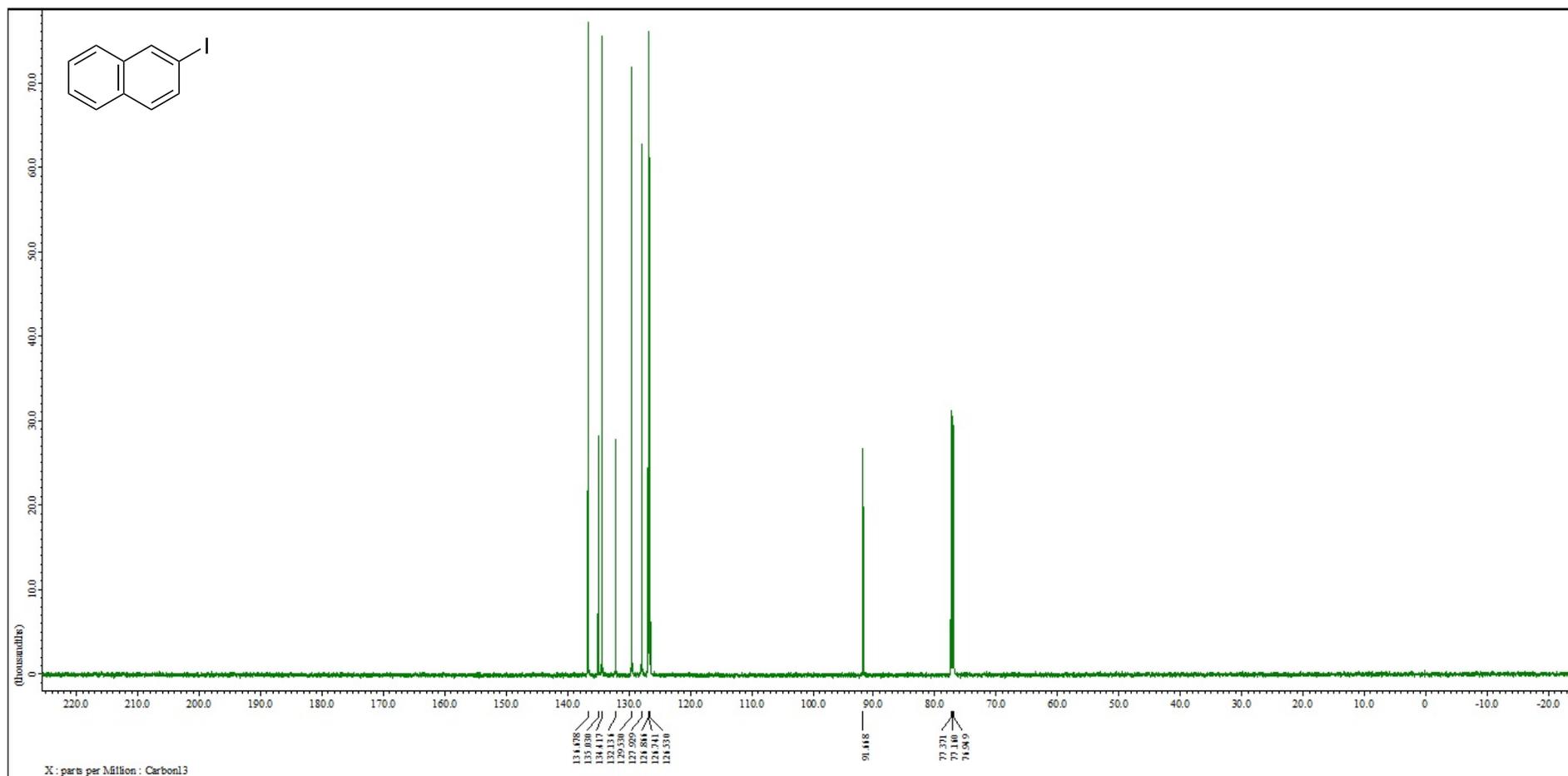


Figure S42. ¹³C NMR (151 MHz, CDCl₃) spectrum of 3i

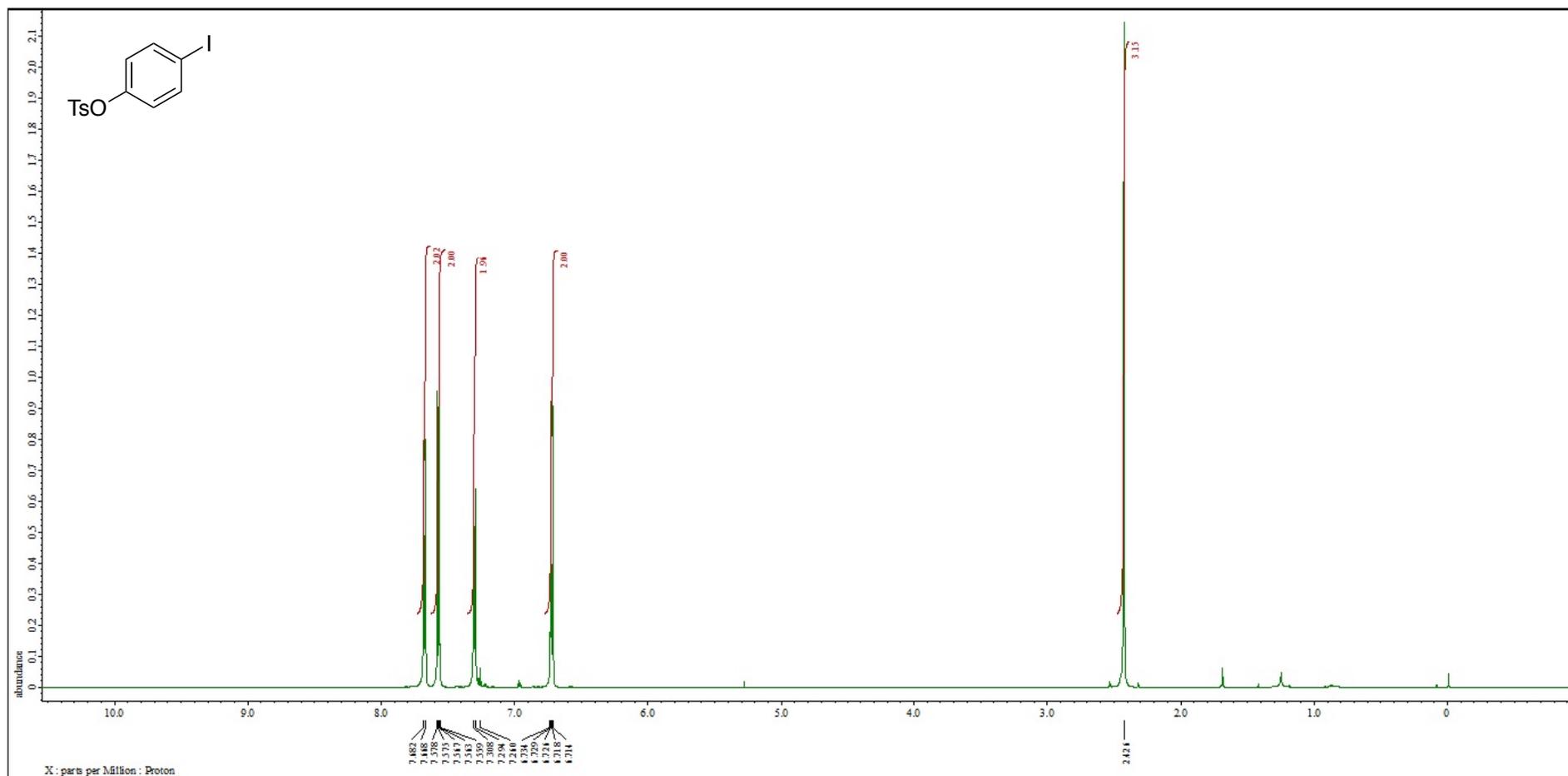


Figure S43. ¹H NMR (600 MHz, CDCl₃) spectrum of **3j**

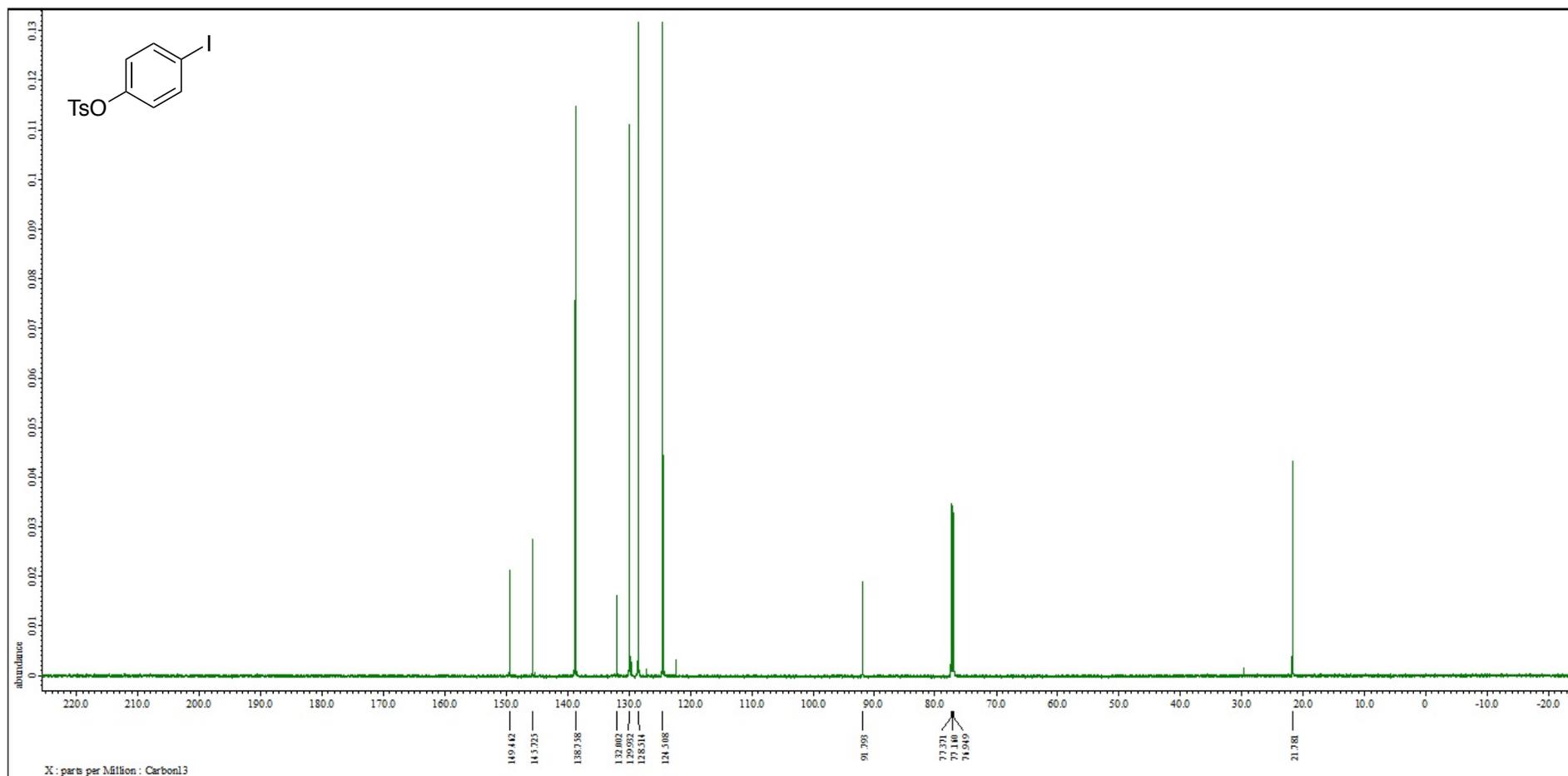


Figure S44. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **3j**

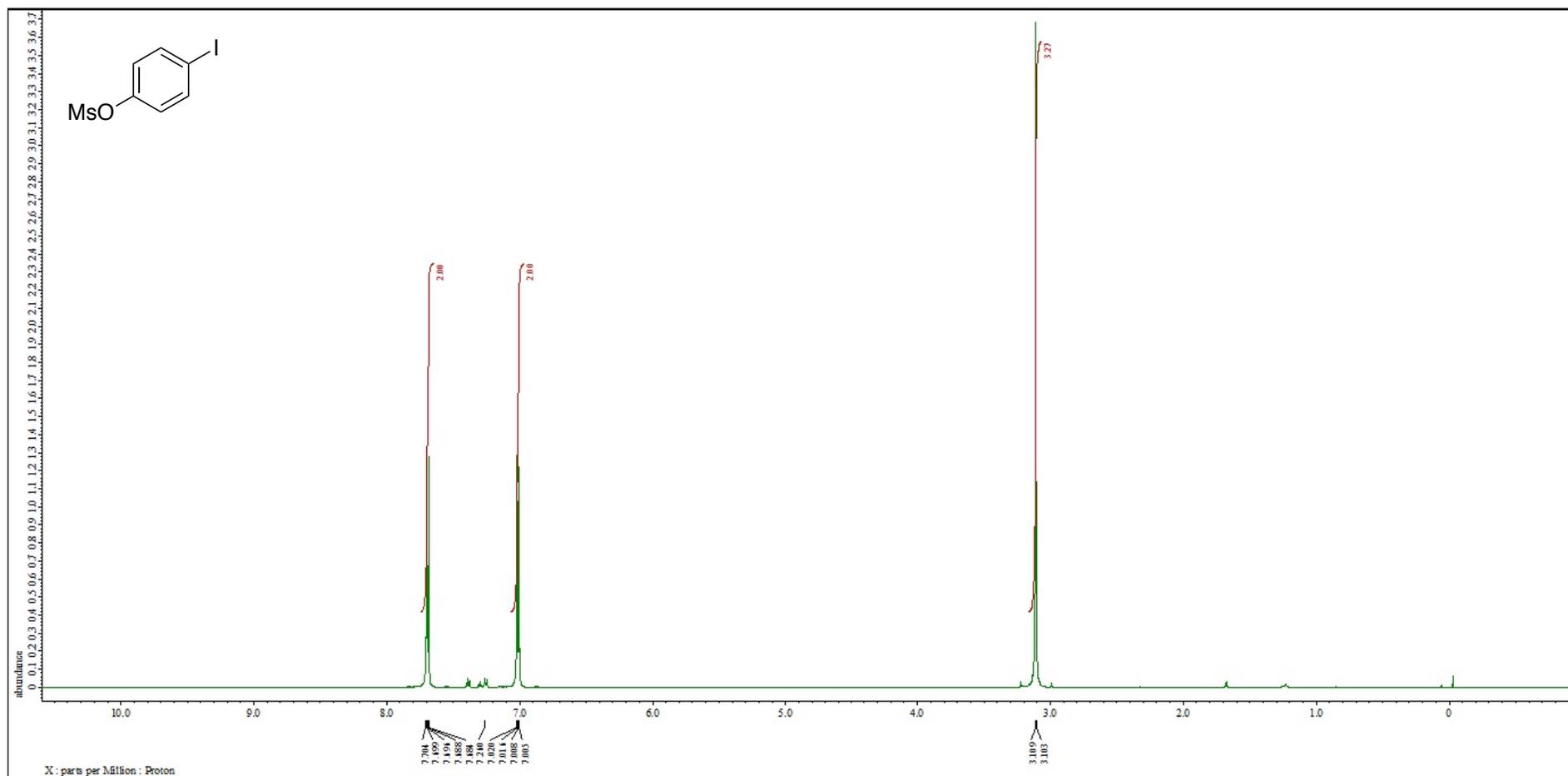


Figure S45. ¹H NMR (600 MHz, CDCl₃) spectrum of 3k

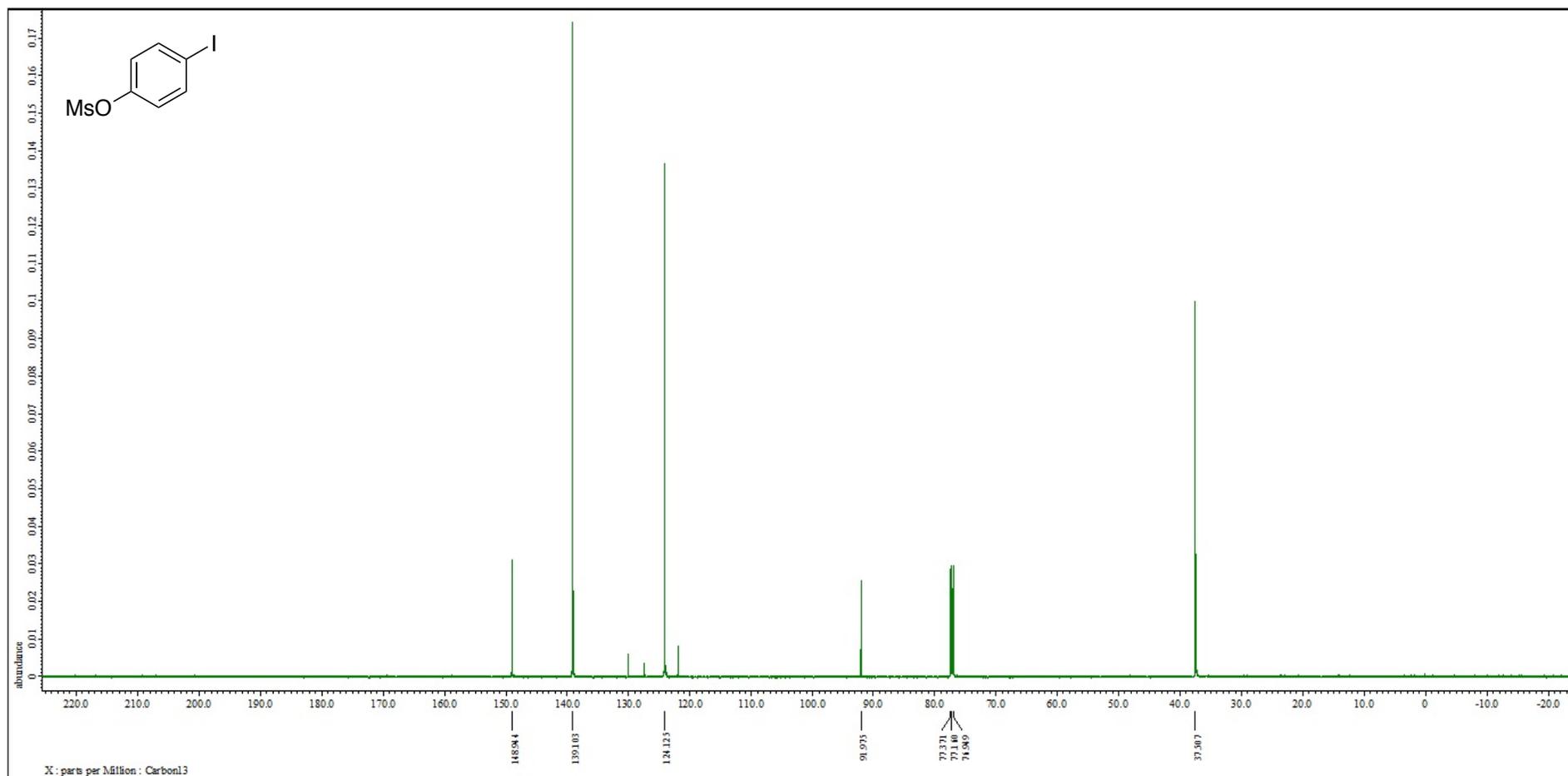
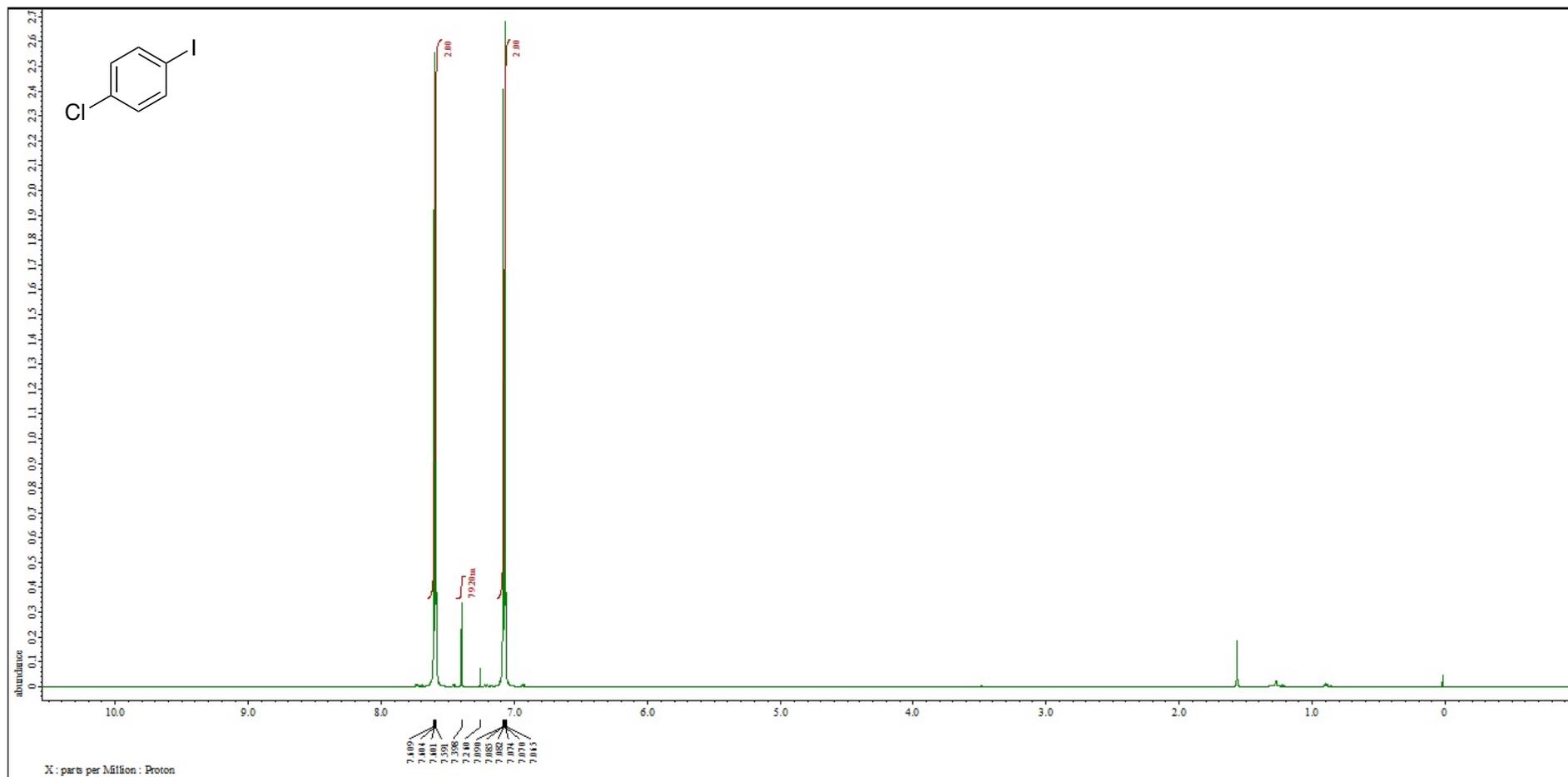


Figure S46. ¹³C NMR (151 MHz, CDCl₃) spectrum of **3k**



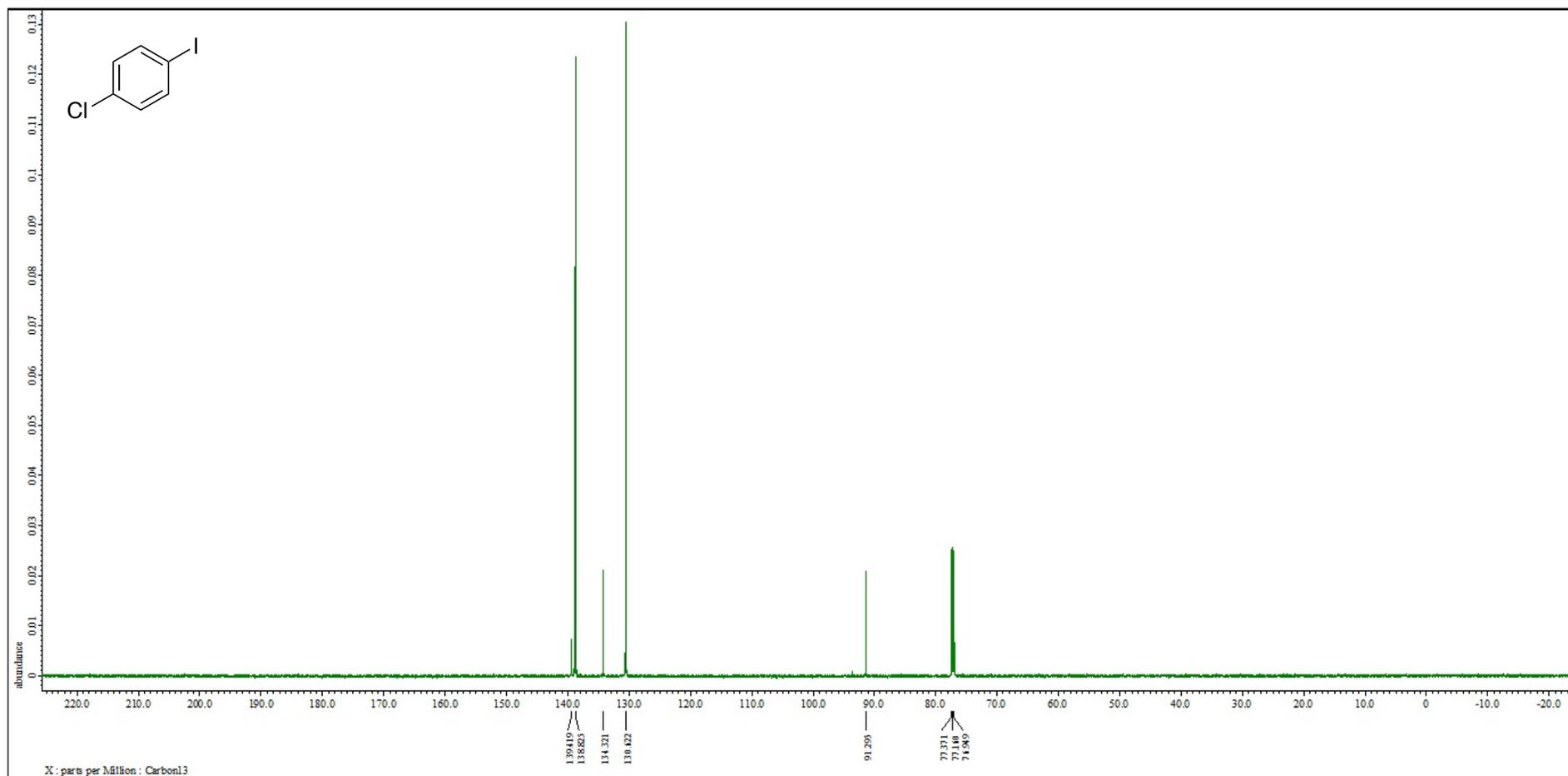


Figure S48. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 31

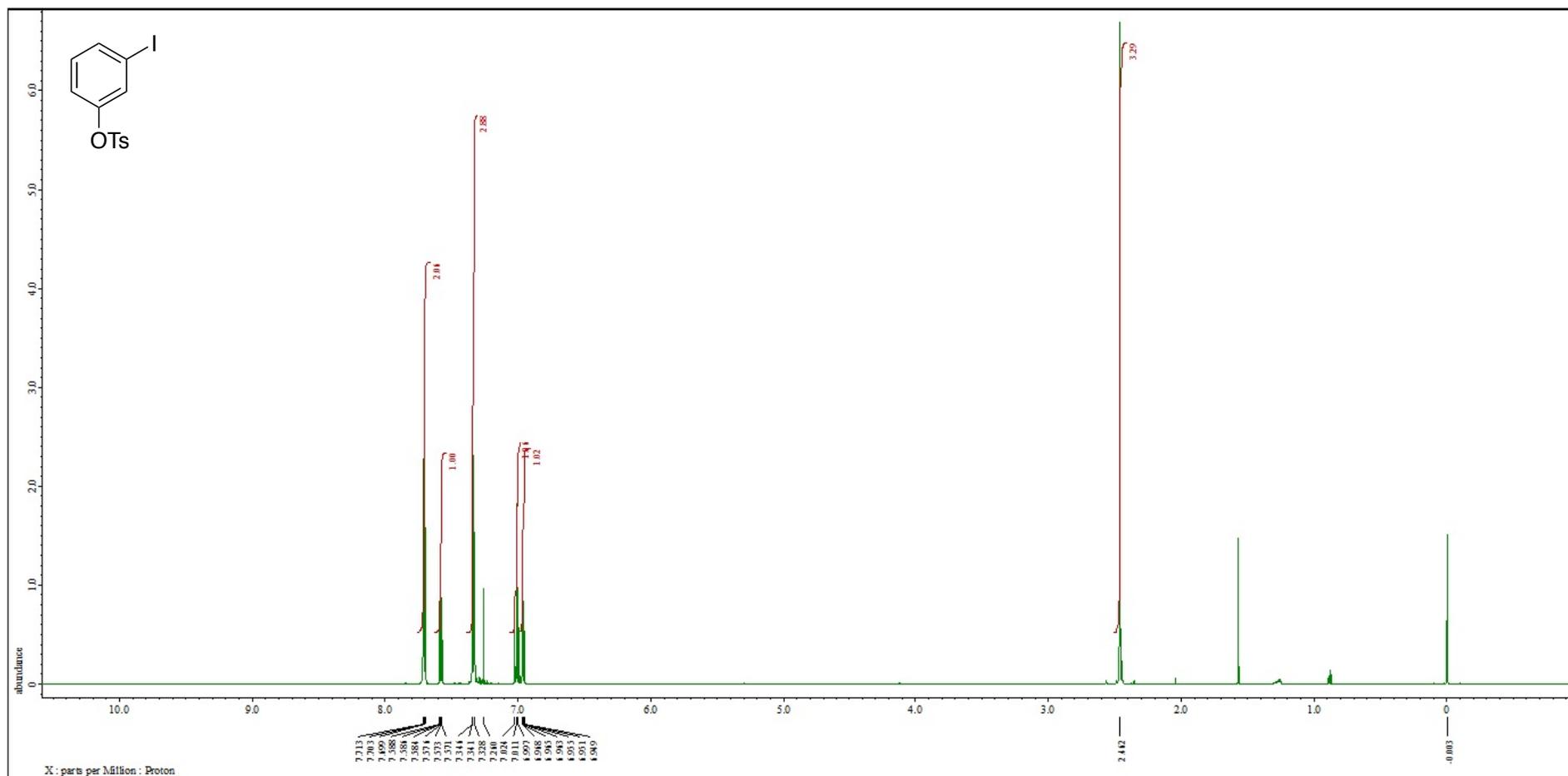


Figure S49. ¹H NMR (600 MHz, CDCl₃) spectrum of **3m**

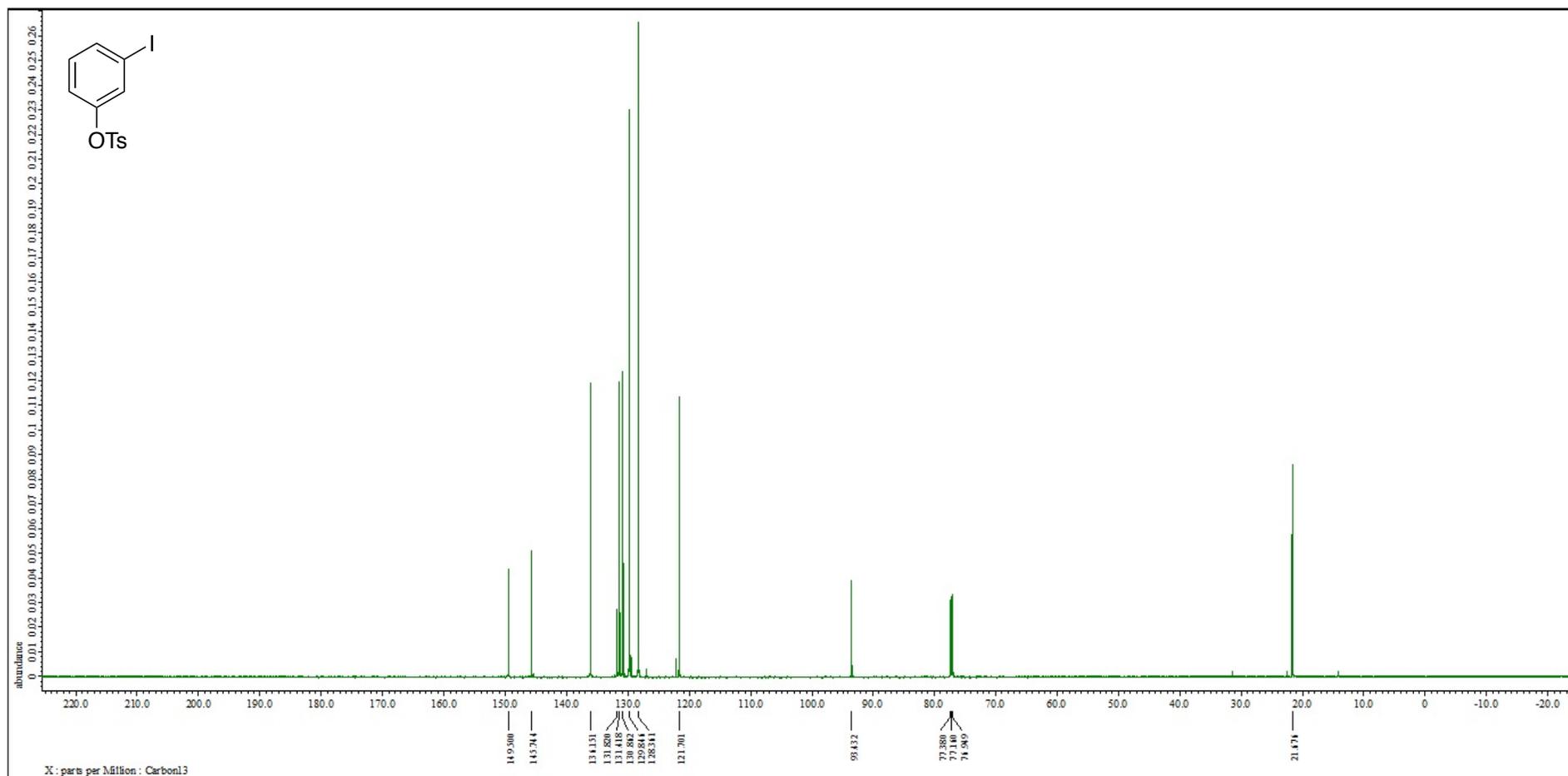


Figure S50. ¹³C NMR (151 MHz, CDCl₃) spectrum of **3m**

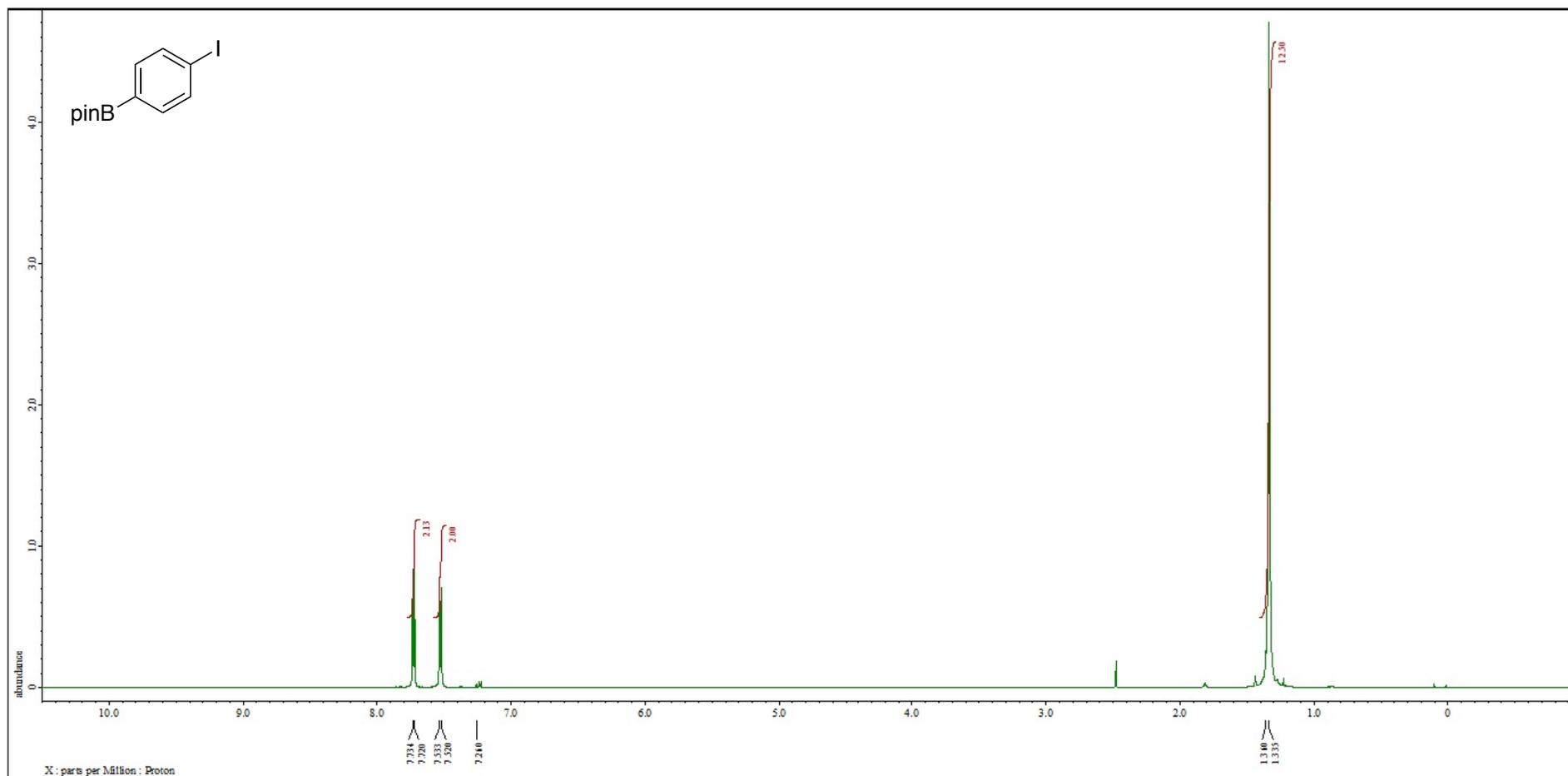


Figure S51. ^1H NMR (600 MHz, CDCl_3) spectrum of **3n**

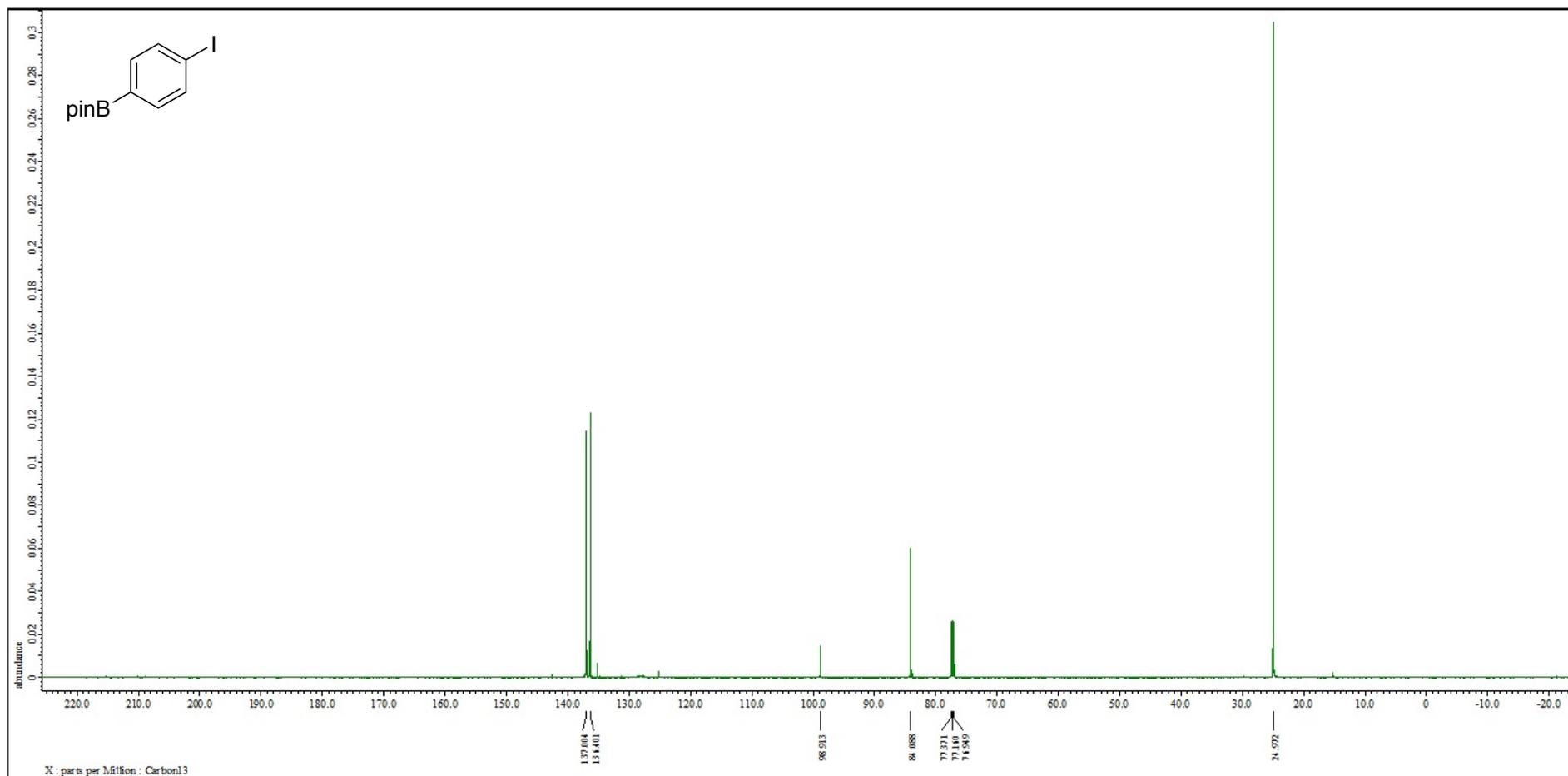


Figure S52. ¹³C NMR (151 MHz, CDCl₃) spectrum of **3n**

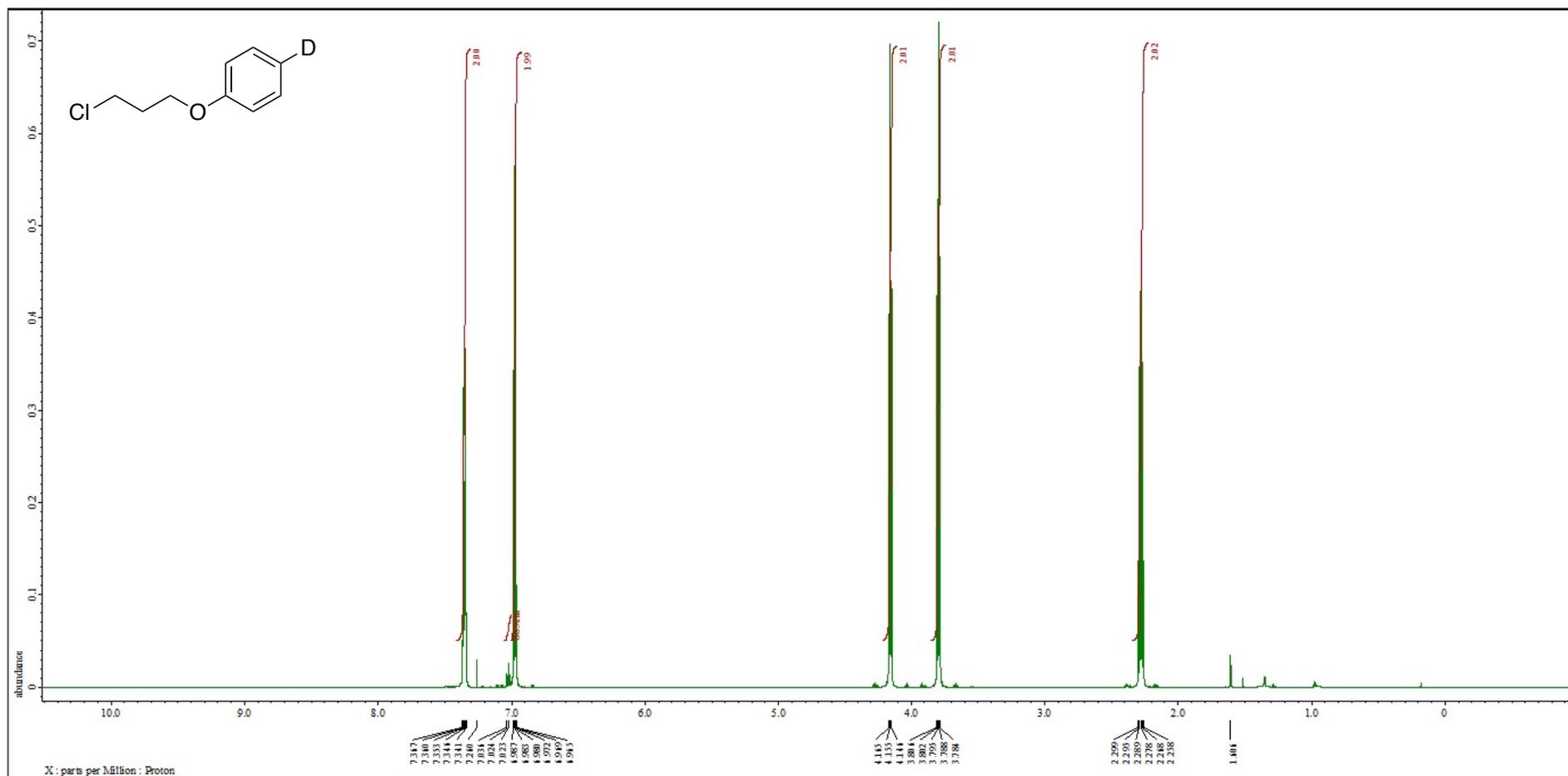


Figure S53. ¹H NMR (600 MHz, CDCl₃) spectrum of 30'

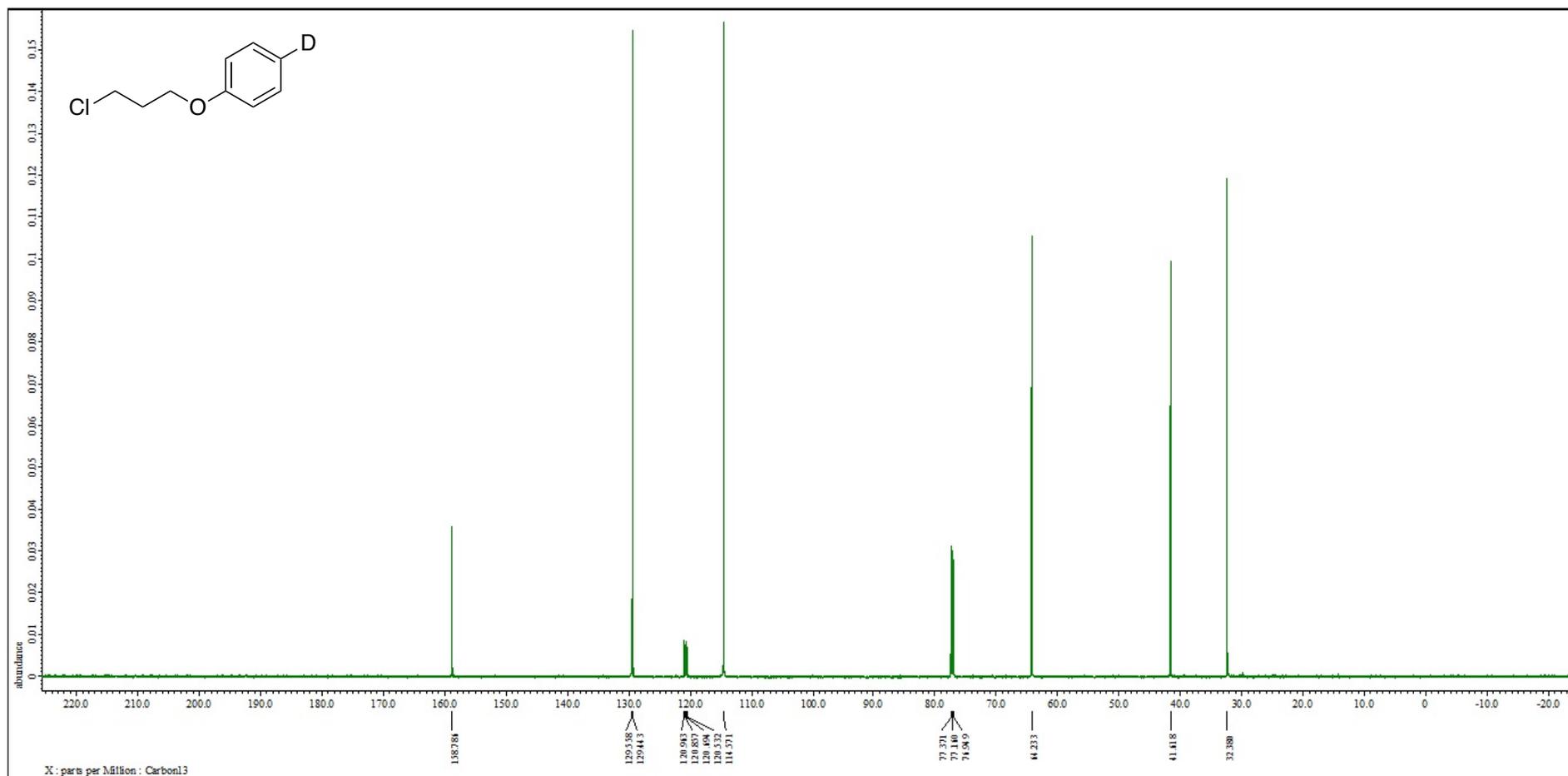


Figure S54. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **30'**

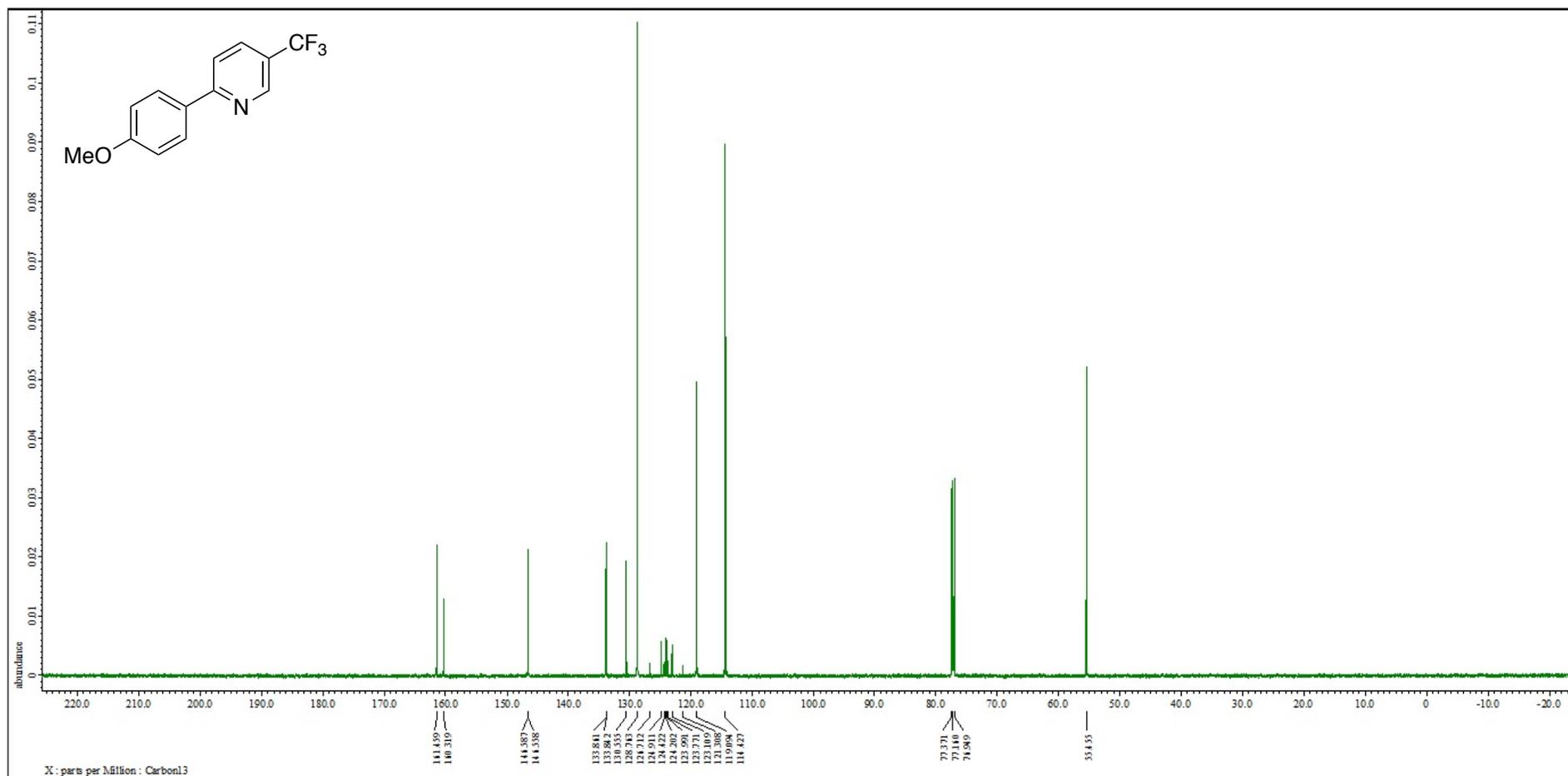


Figure S56. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4a

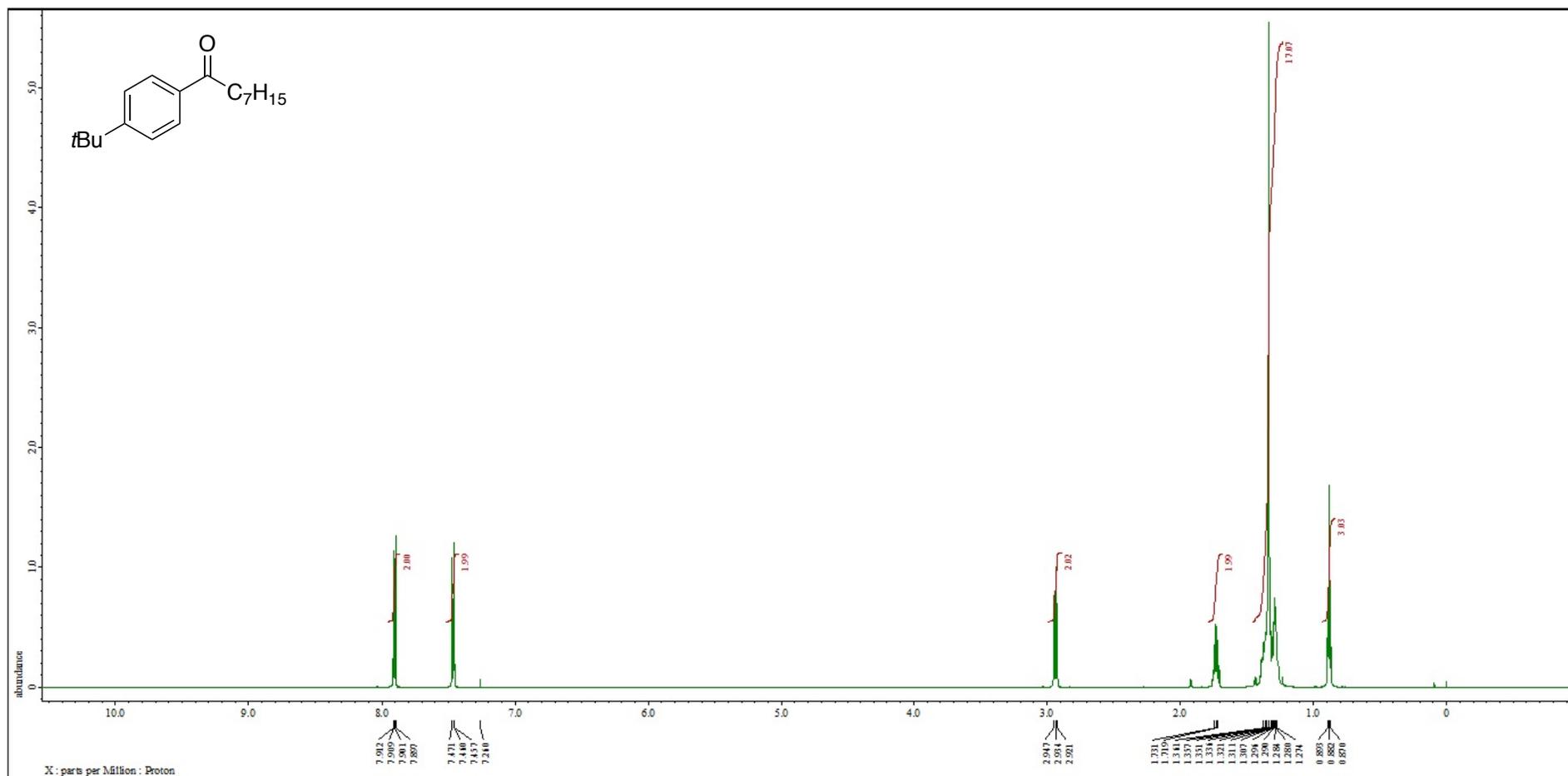


Figure S57. ¹H NMR (600 MHz, CDCl₃) spectrum of **4b**

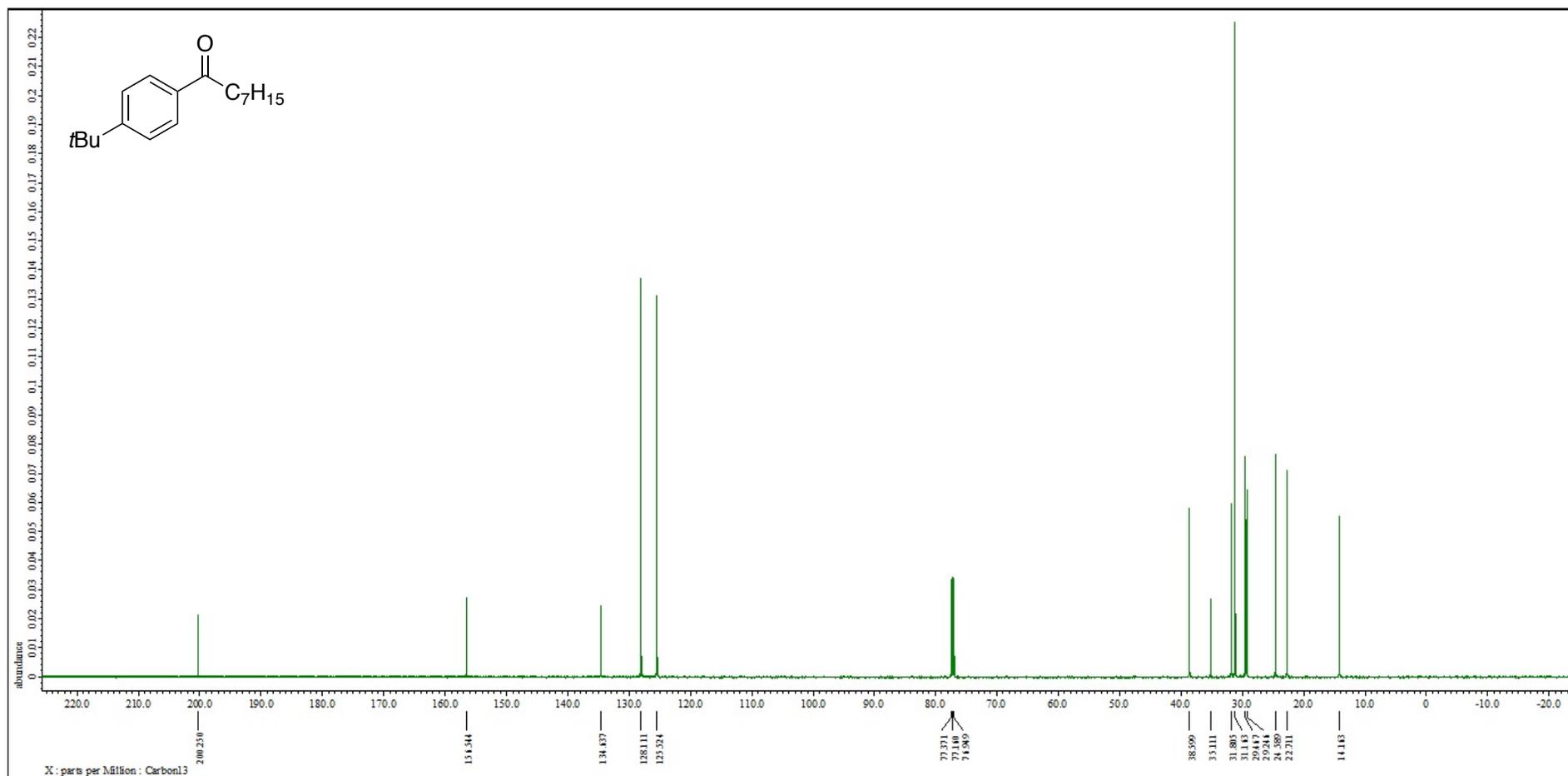


Figure S58. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4b

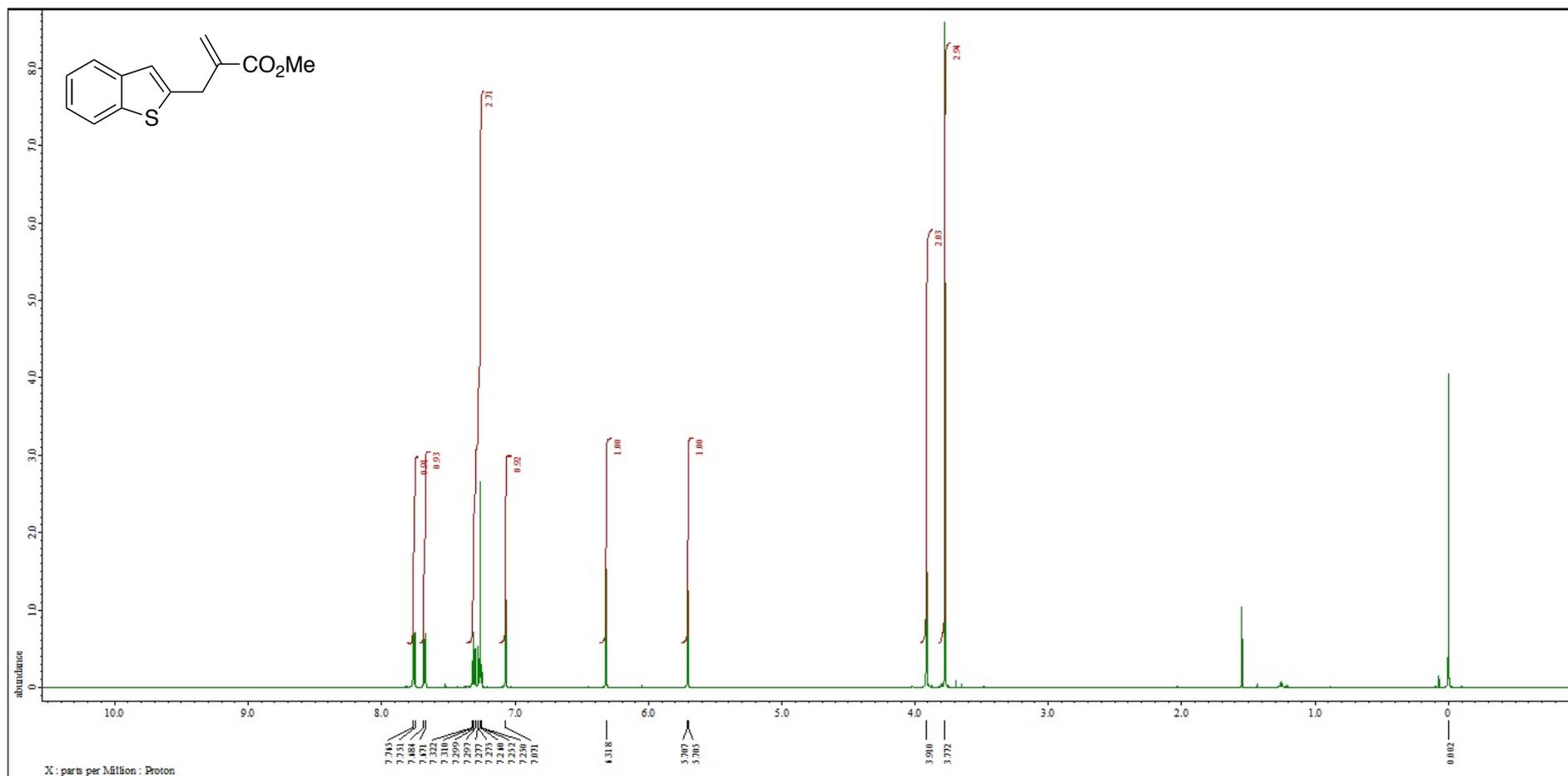


Figure S59. ¹H NMR (600 MHz, CDCl₃) spectrum of **4c**

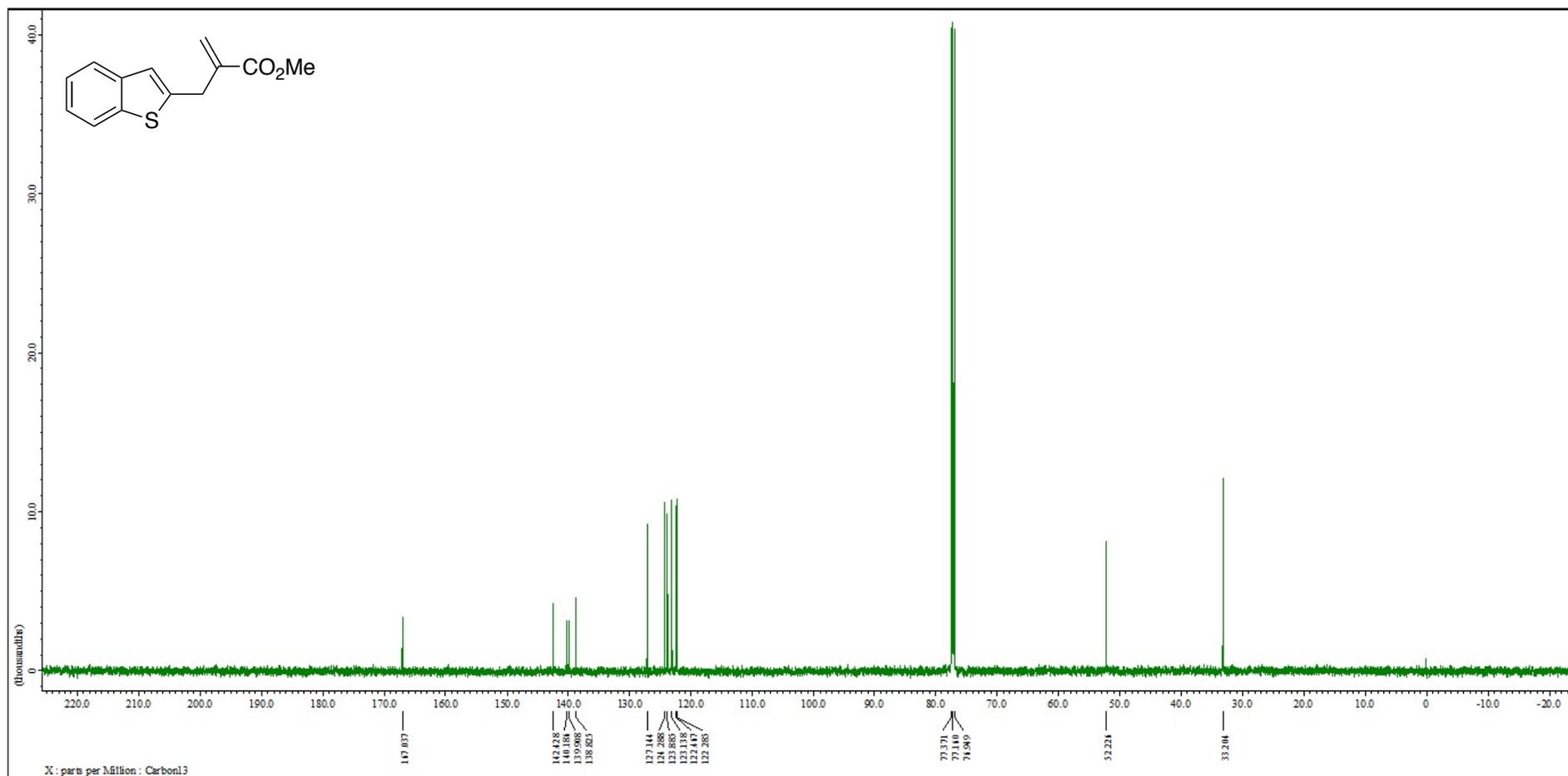


Figure S60. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4c

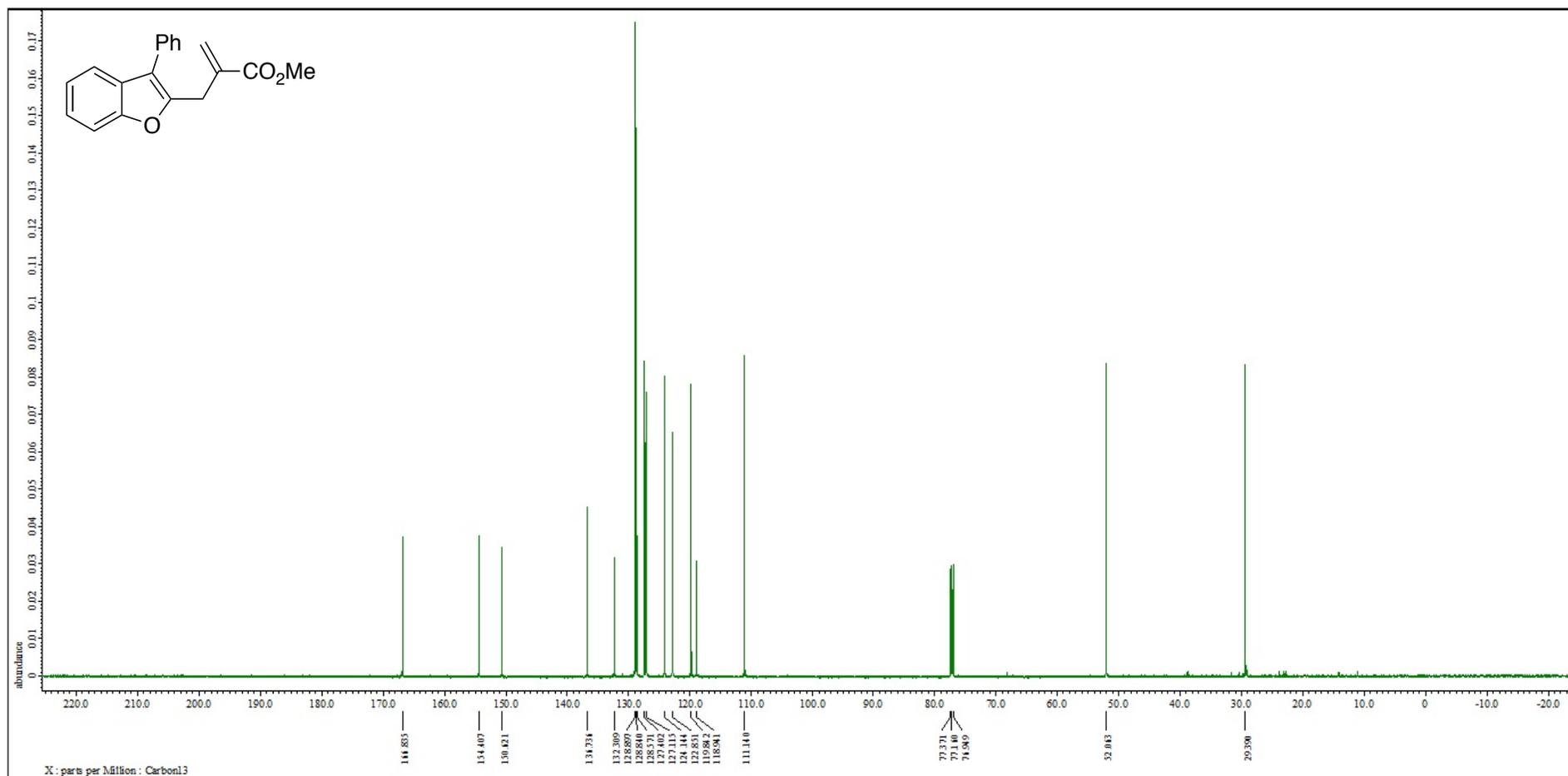


Figure S62. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4d

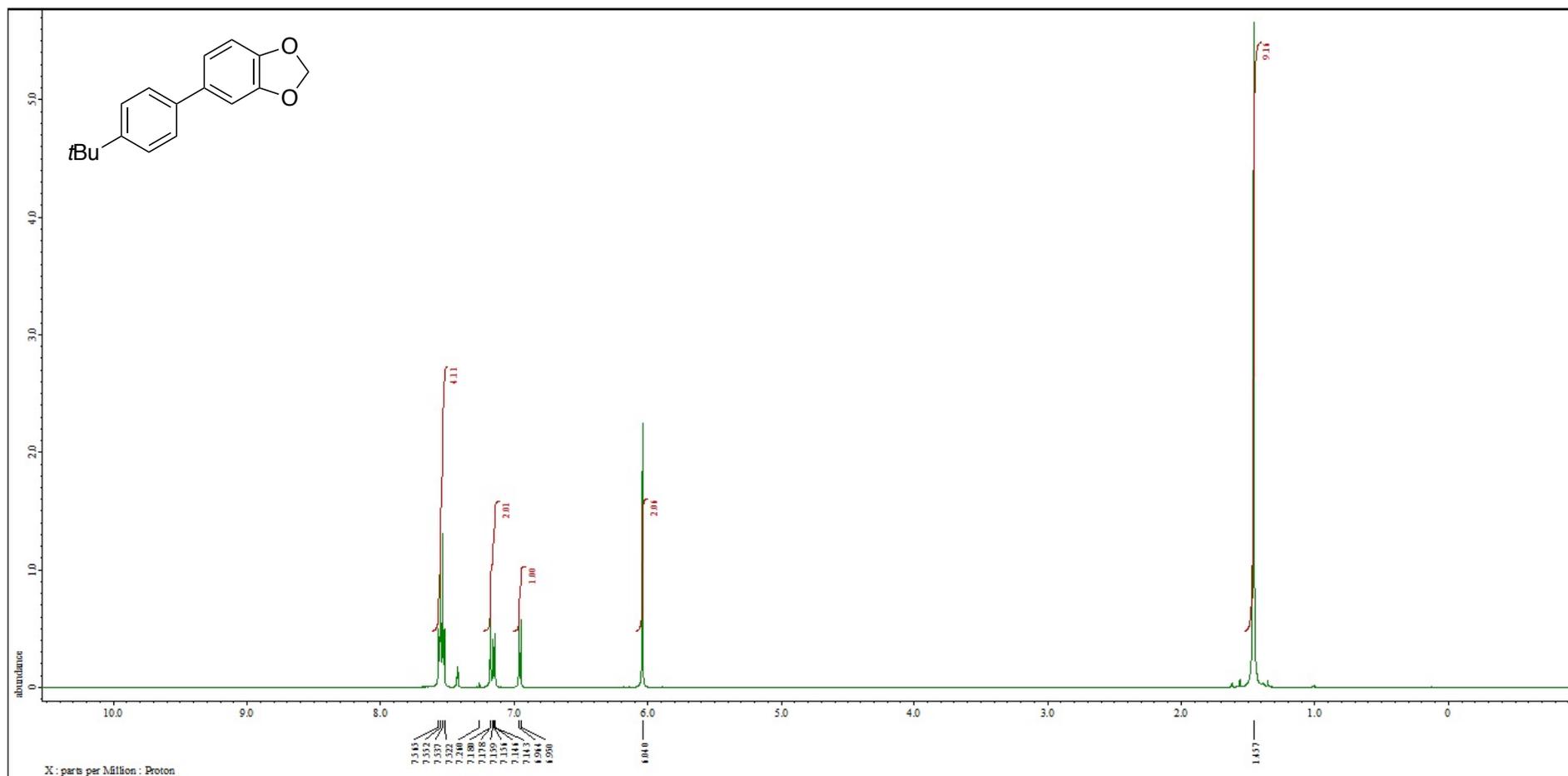


Figure S63. ¹H NMR (600 MHz, CDCl₃) spectrum of 4e

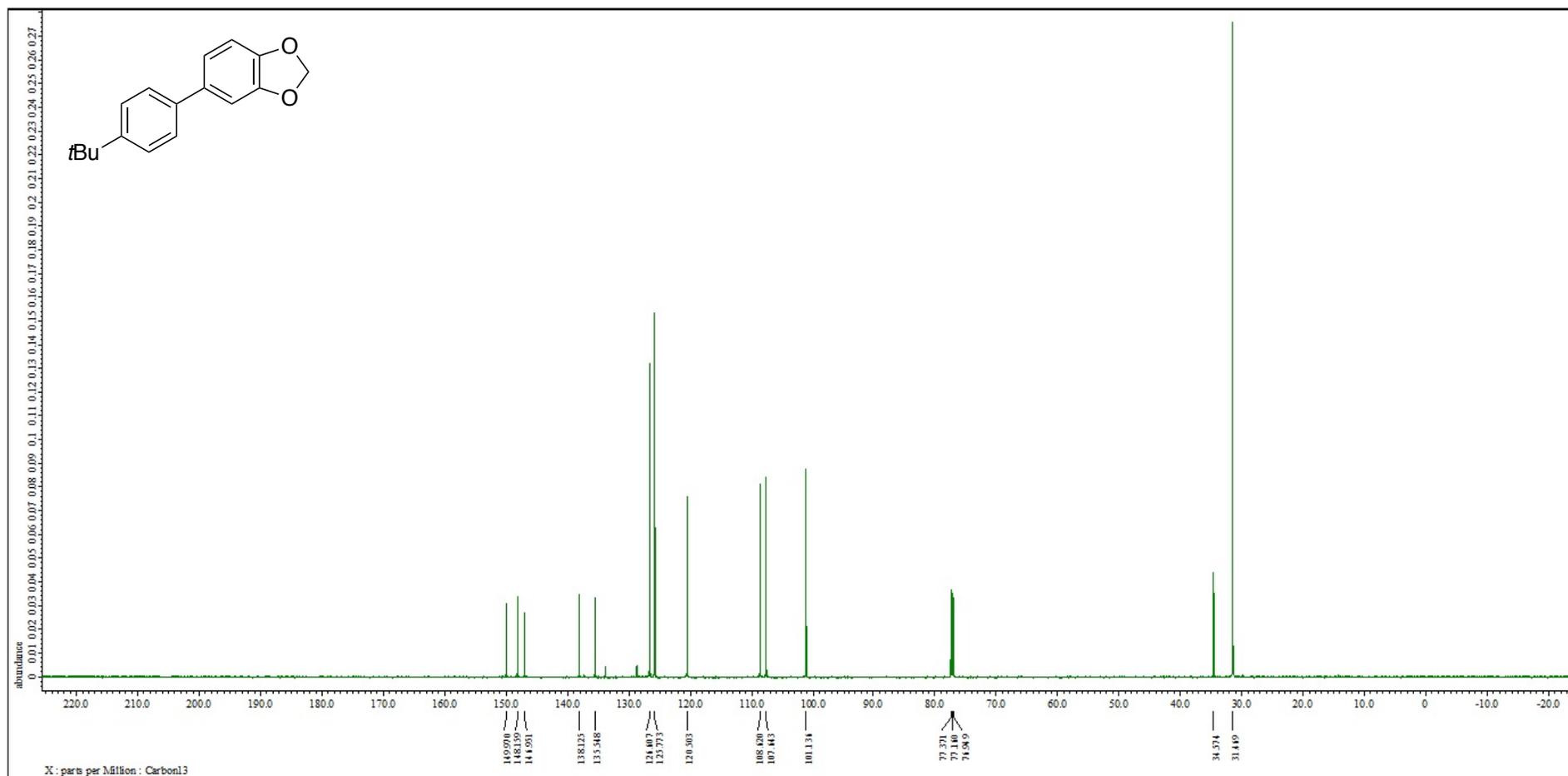


Figure S64. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 4e

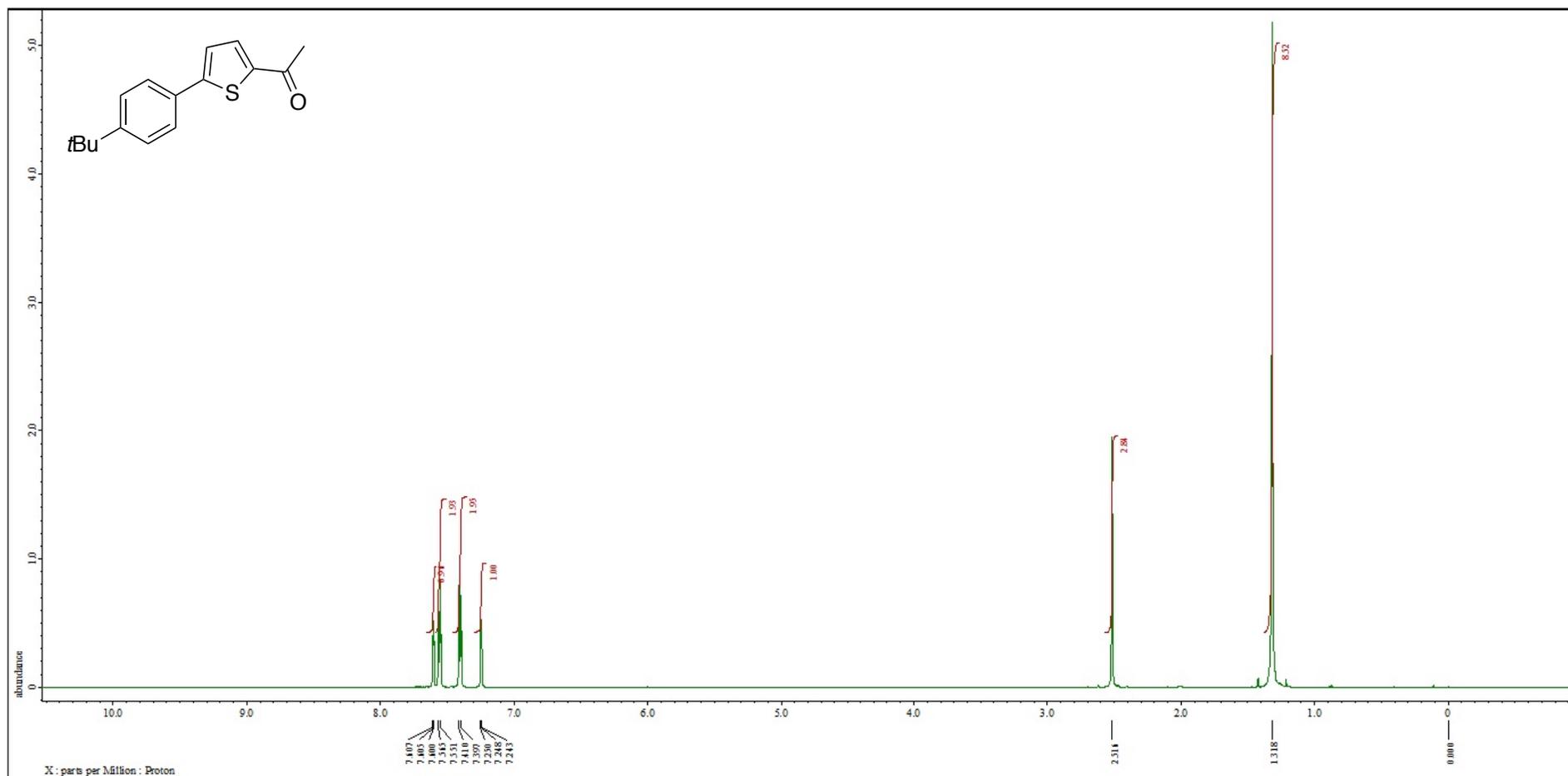


Figure S65. ¹H NMR (600 MHz, CDCl₃) spectrum of **4f**

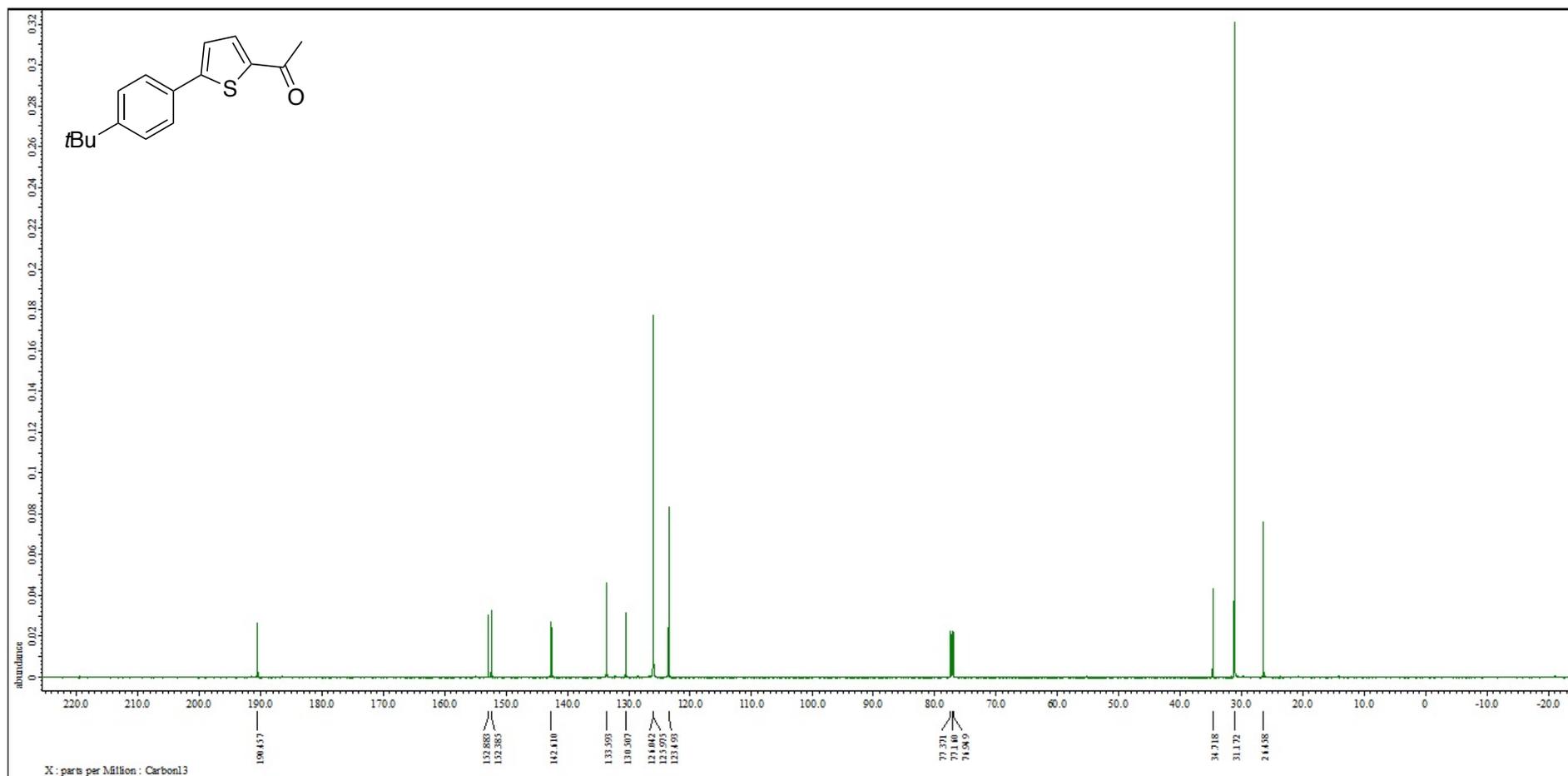


Figure S66. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4f

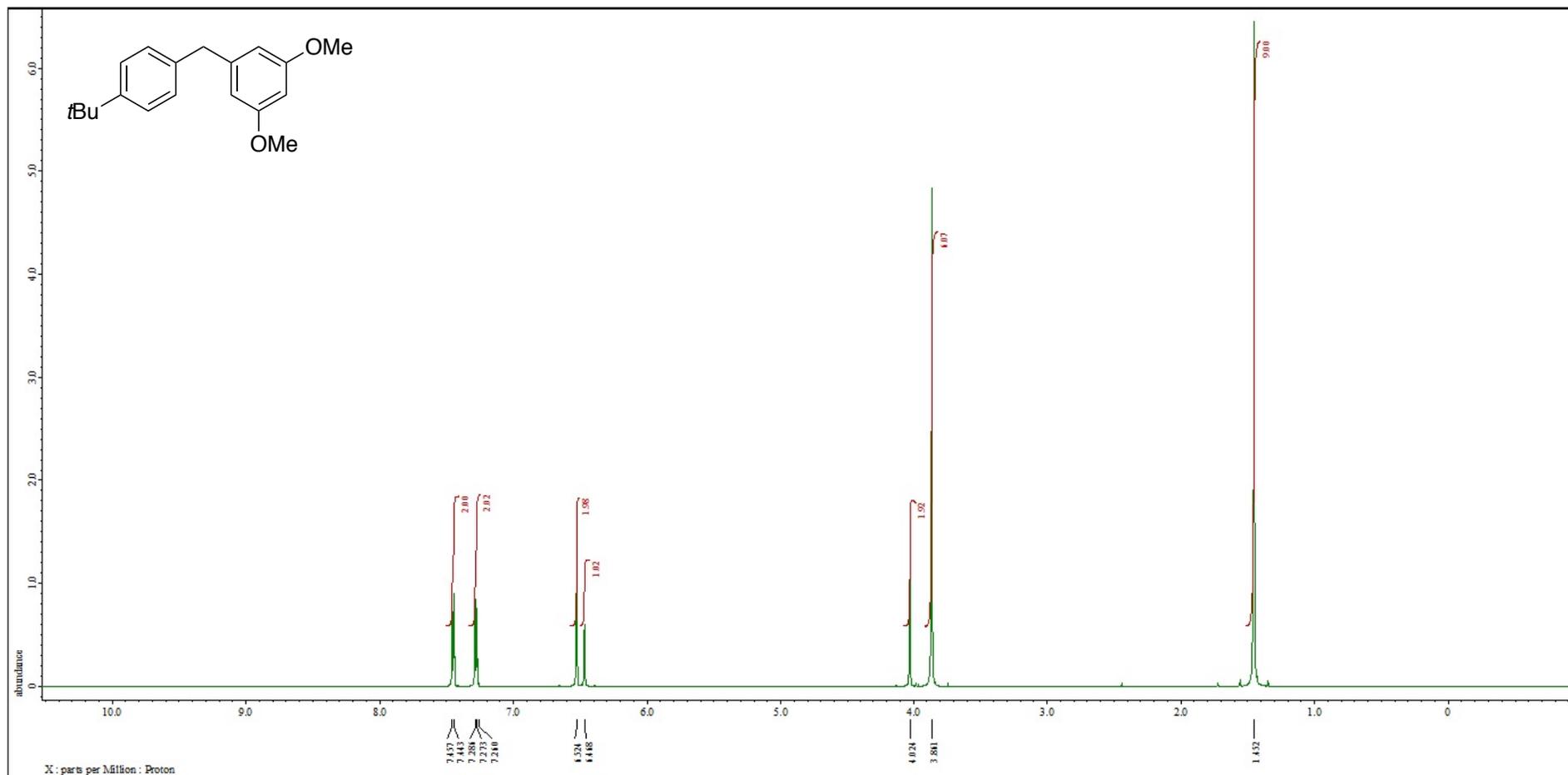


Figure S67. ¹H NMR (600 MHz, CDCl₃) spectrum of **4g**

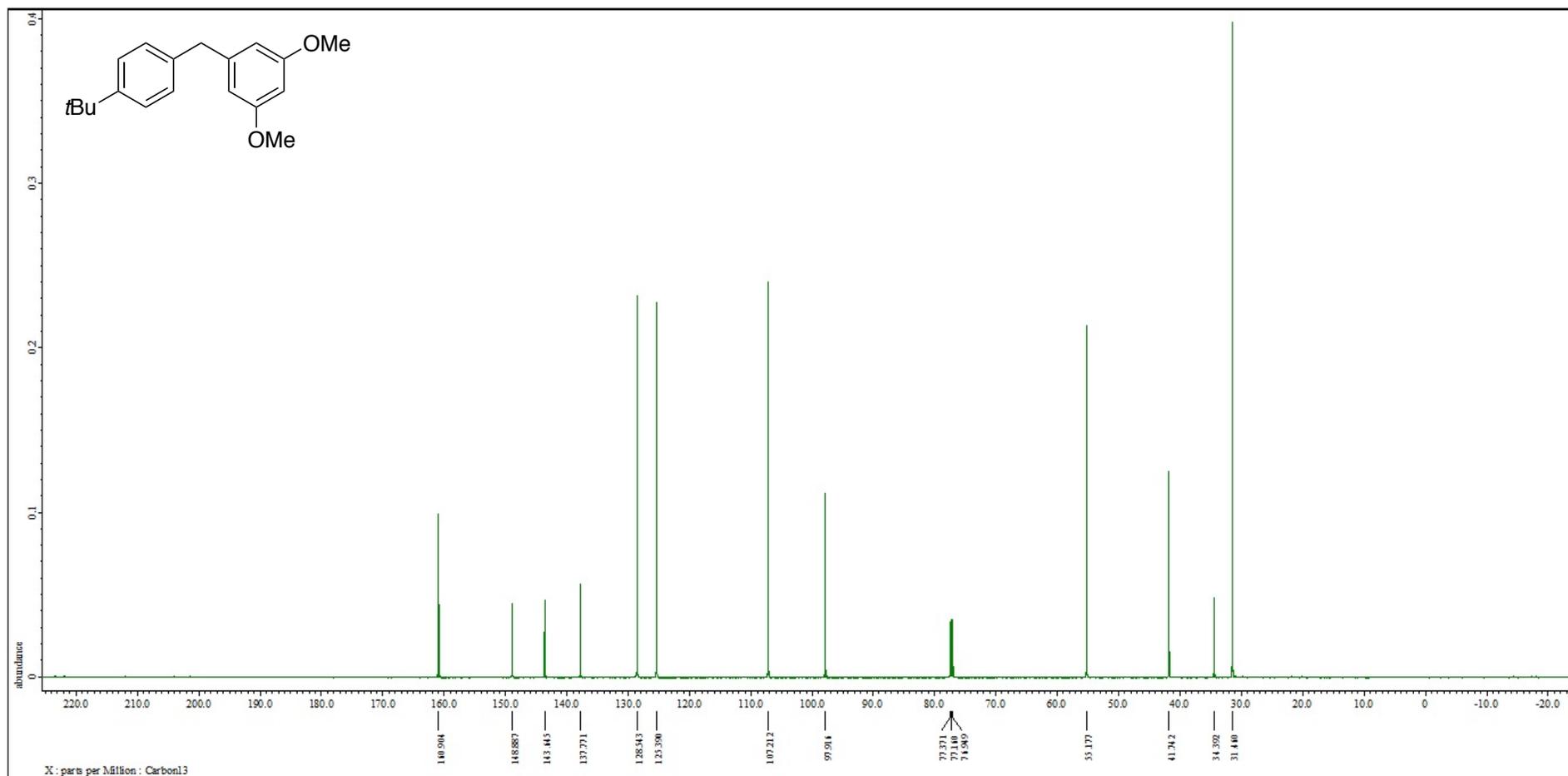


Figure S68. ¹³C NMR (151 MHz, CDCl₃) spectrum of **4g**

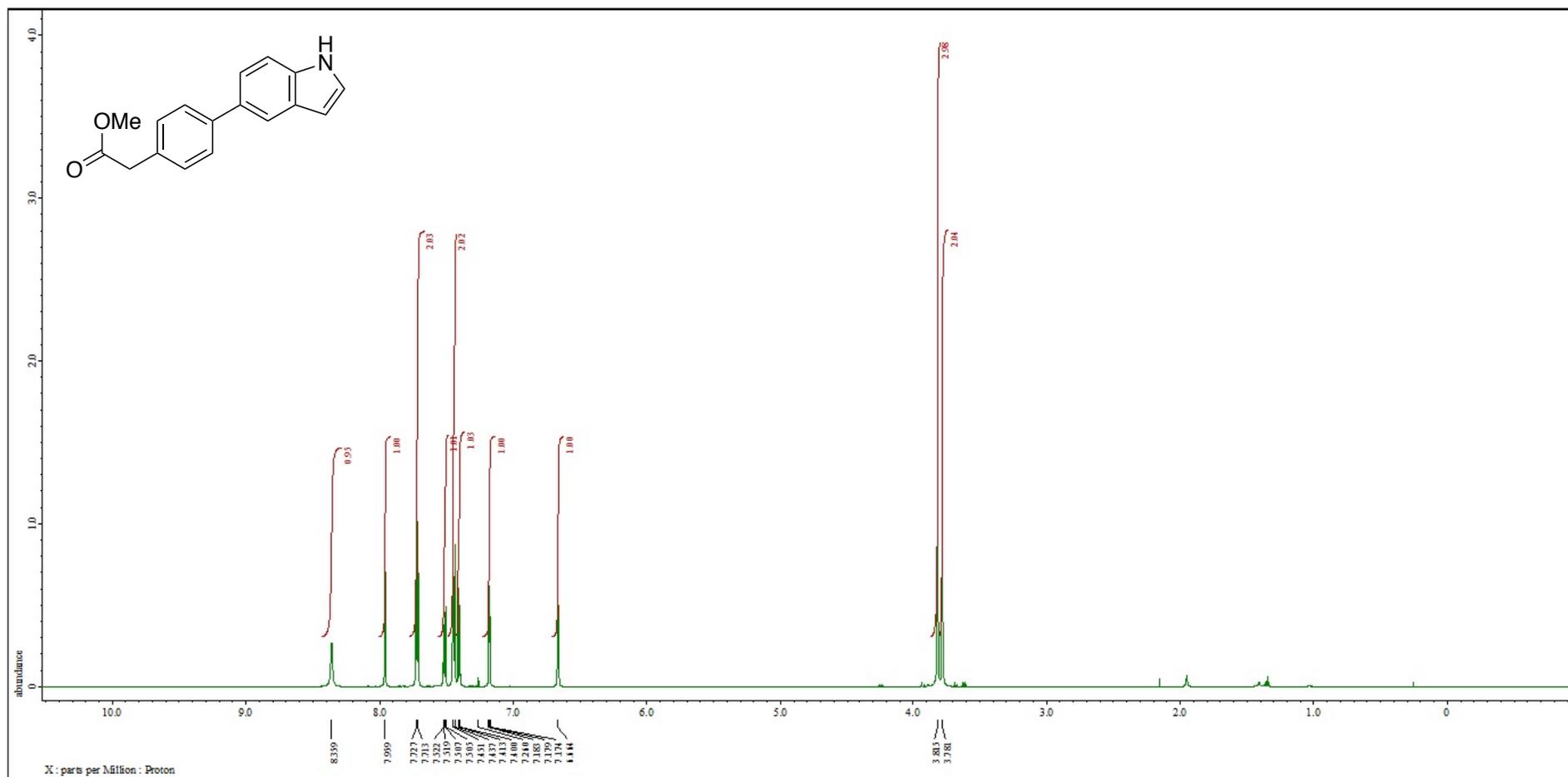


Figure S69. ¹H NMR (600 MHz, CDCl₃) spectrum of **4h**

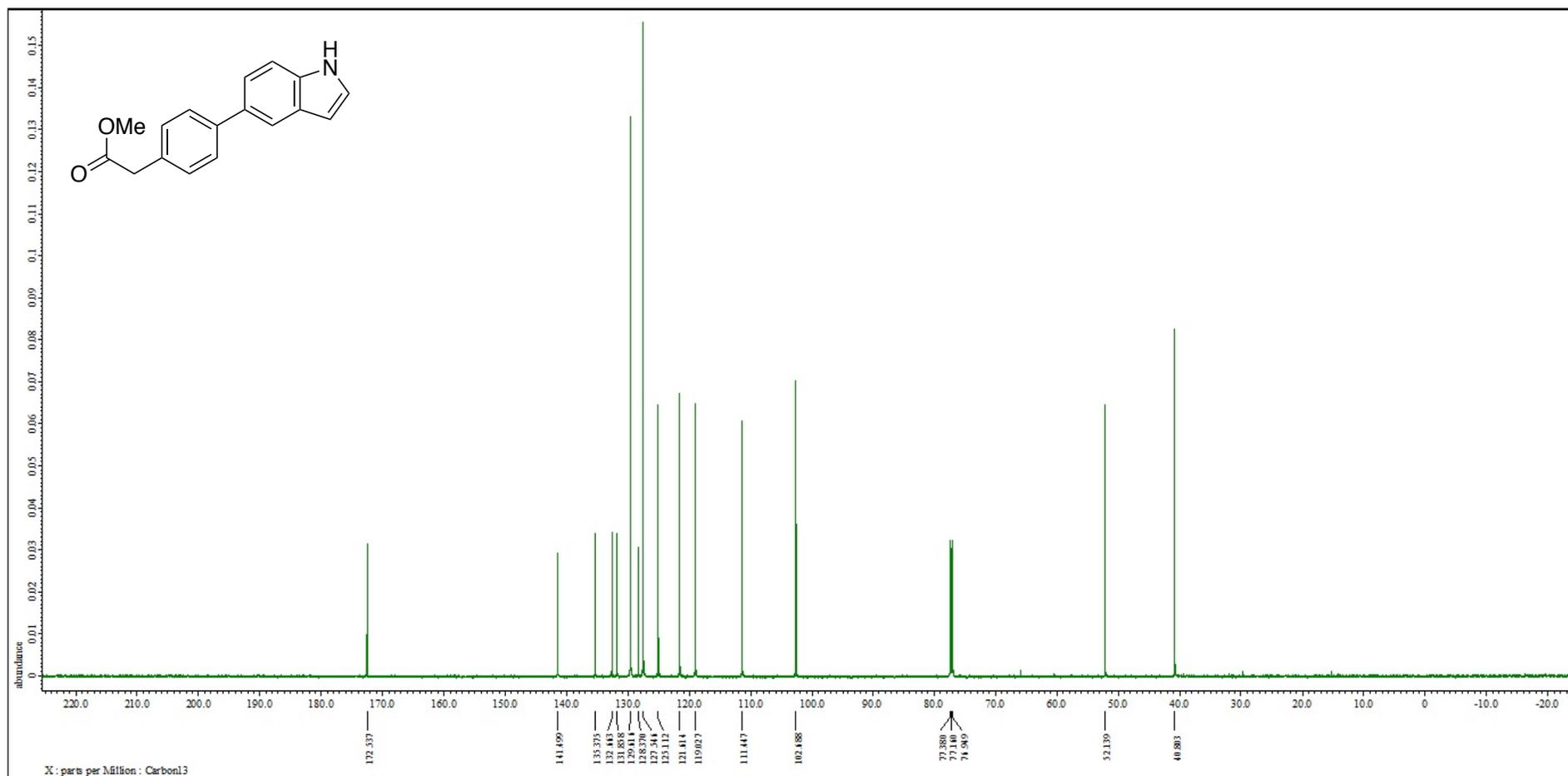


Figure S70. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 4h

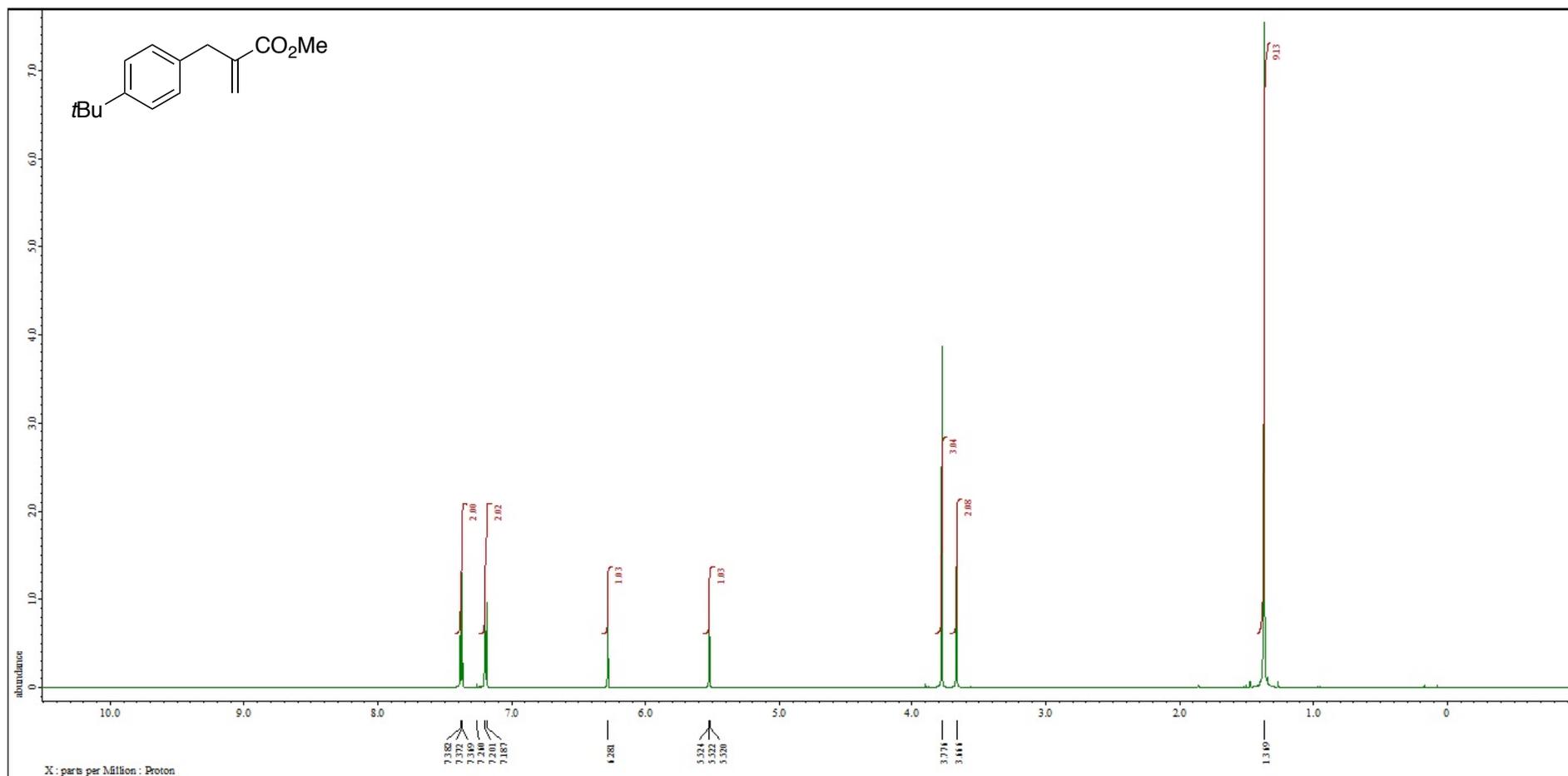


Figure S71. ¹H NMR (600 MHz, CDCl₃) spectrum of **4i**

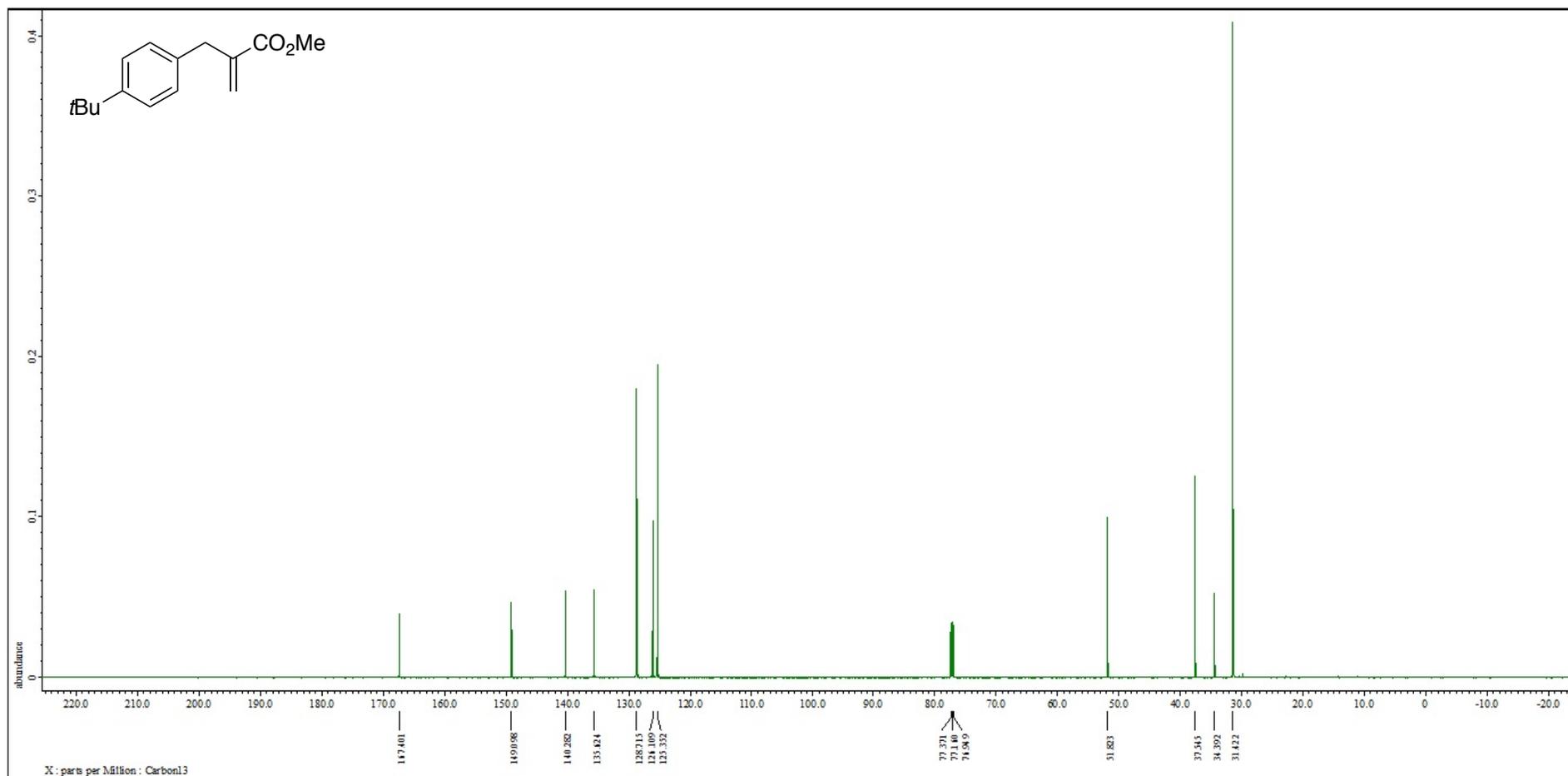


Figure S72. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4i

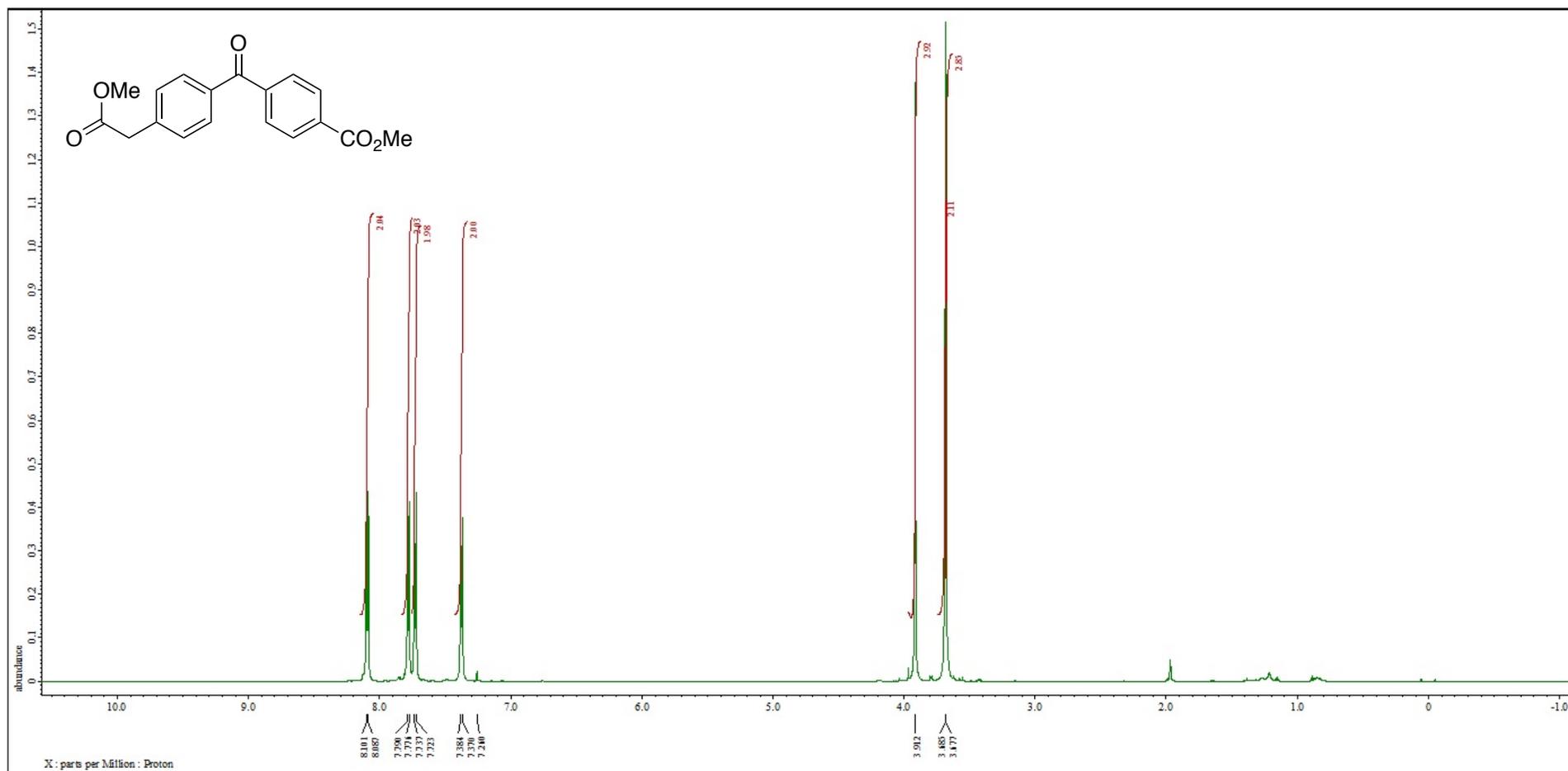


Figure S73. ¹H NMR (600 MHz, CDCl₃) spectrum of **4j**

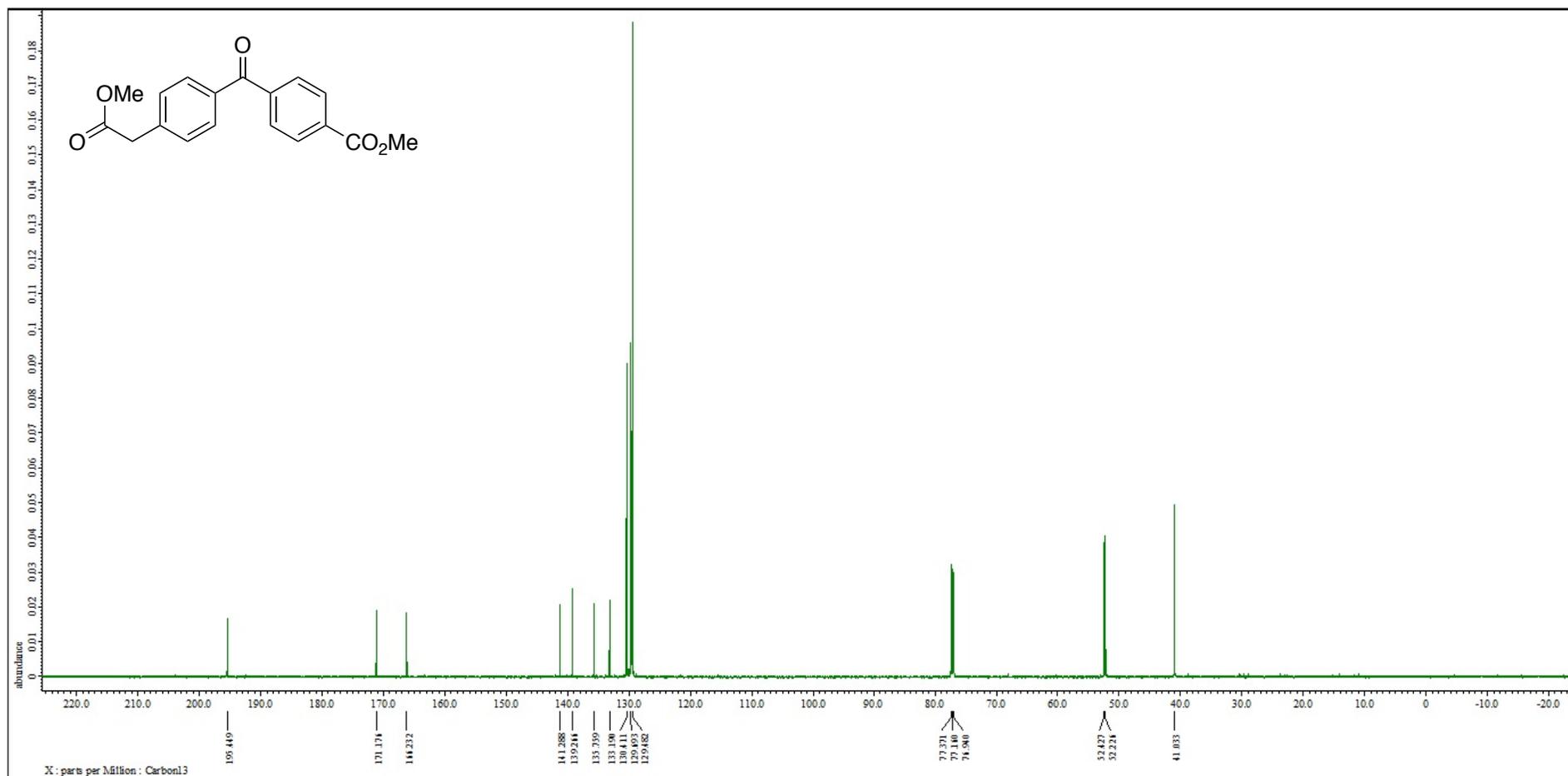


Figure S74. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 4j

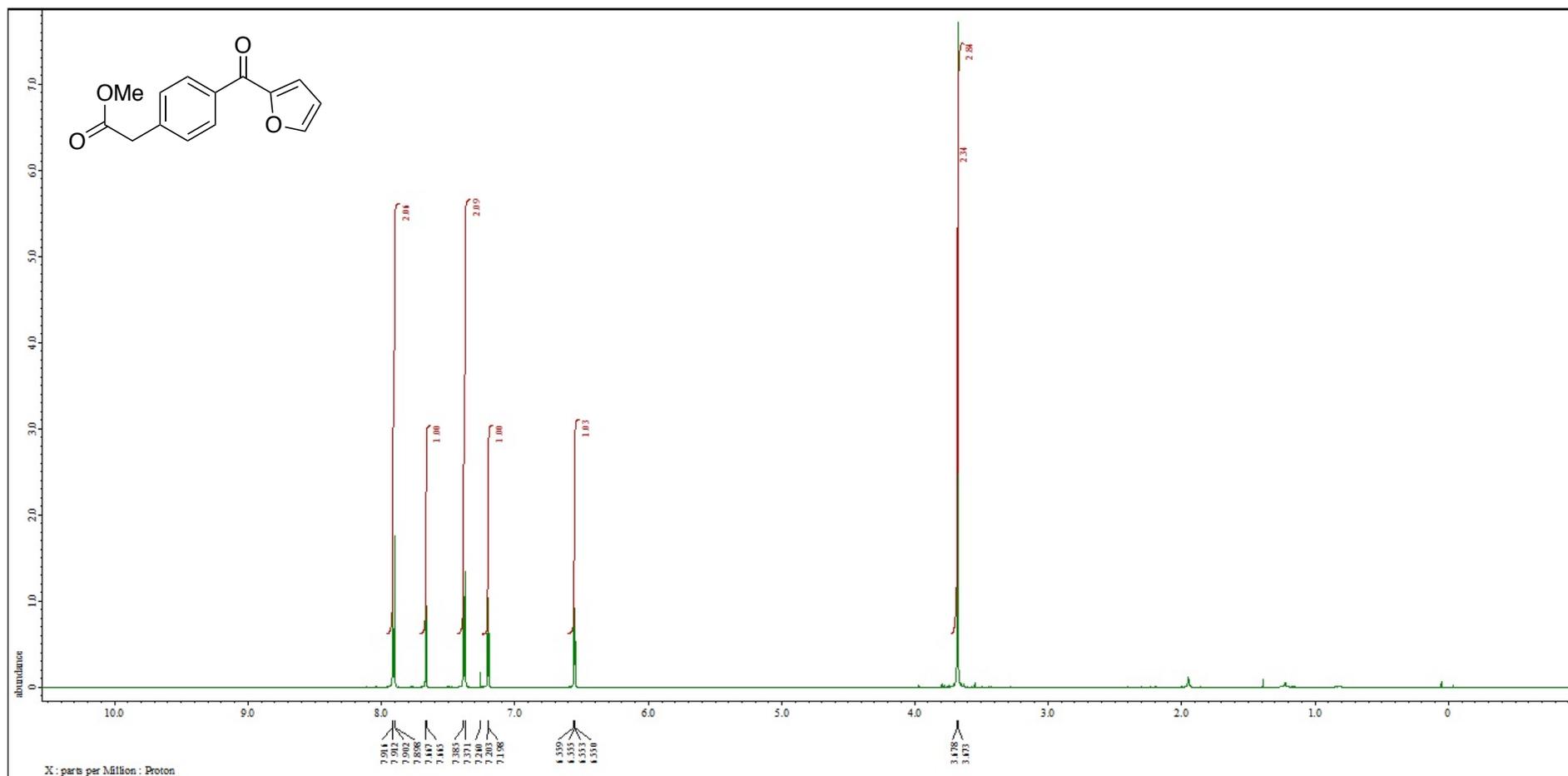


Figure S75. ¹H NMR (600 MHz, CDCl₃) spectrum of 4k

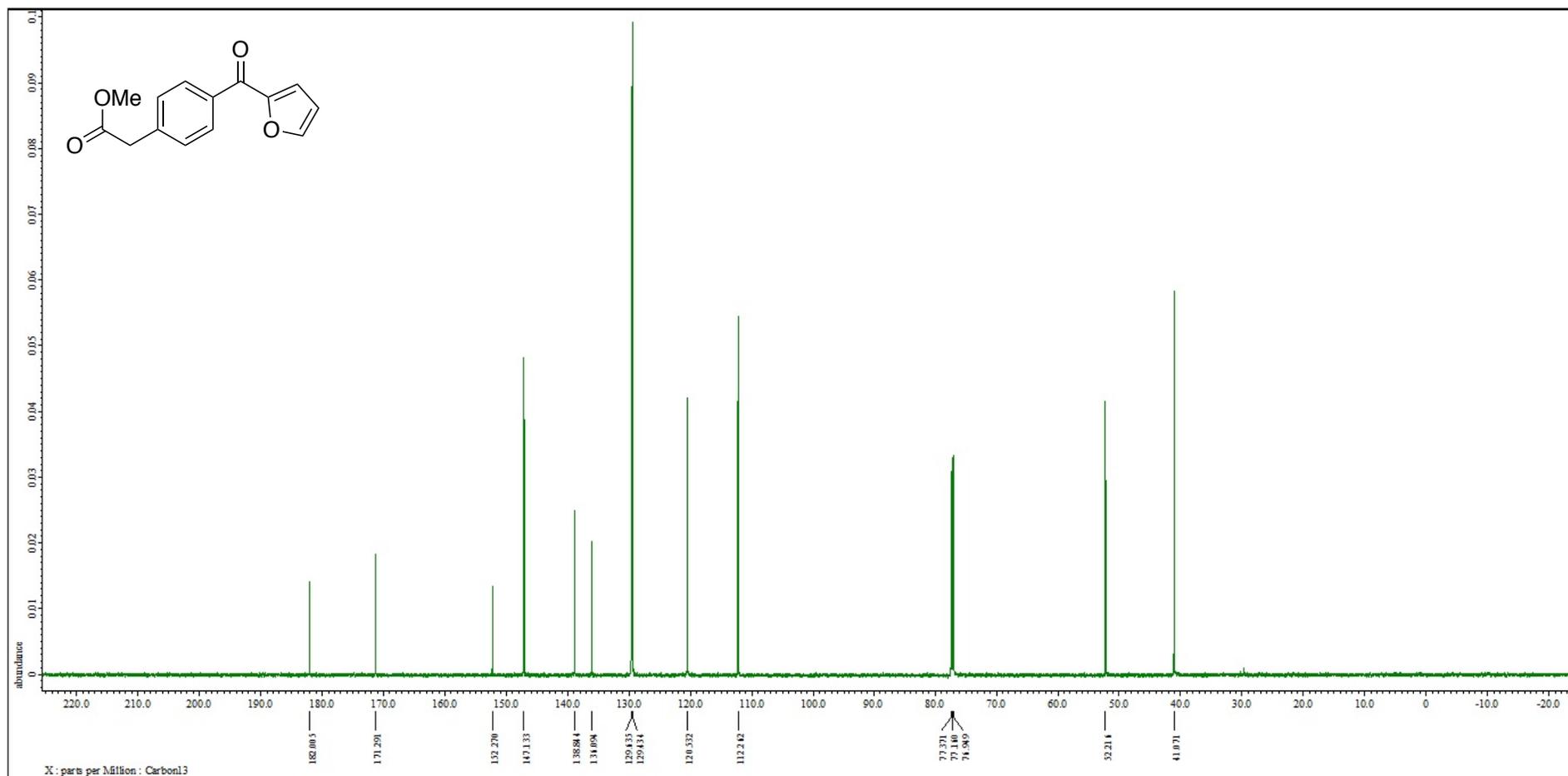


Figure S76. ^{13}C NMR (151 MHz, CDCl_3) spectrum of 4k