Supplementary Information

Cuprate Ion-Pair Catalyzed Conjugate Borylation of Vinyl Sulfones in Biphasic System

Siyu Jiang, Yicen Ge,* Ai Zhang, Silong Hu, Tao Jin, Jian Chen, Huangfeng Zhang, Yao Qin, Xiaoyan Ma, Jinghua Tang, Jinyu Liu

College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu, Sichuan 610059, China. Email: geyicen@cdut.edu.cn

*Corresponding Author

Table of Contents

General Information

Commercially Available Reagents and Solvents

Commercially available chemicals, such as vinyl phenyl sulfone, were directly obtained from Merck, Aladdin, and Shanghai Titan Technology. The chemicals were used with-out further purification once delivered, unless otherwise noted. Solvents were purchased from Shanghai Titan Technology as A.R. grade. If an oxygen- and moisture-free system was required, the solvents were distilled in the presence of CaH_2 under N_2 atmosphere. Chiral guanidine phase-transfer catalysts were provided by Dr. Yang Wang from Shenzhen HwaGen Pharmaceutical Co., Ltd.

Glassware and Instruments

For reactions employing oxygen- or moisture-sensitive reagents, the glassware was dried at 110 °C in an oven overnight, or under high vacuum using Edwards oil-sealed rotary pumps. The reactions were carried out with Schlenk equipment. Reagents were injected with microsyringes or pipettes via a rubber septum, or added into the Schlenk reaction bottle under a N_2 counter-flow.

Thin layer chromatography (TLC) was performed on silica HPTLC plates bought from Yantai Jiangyou (8±2 μm ≥ 80%, HSGF254). Detection was carried out by fluorescence under UV light (wavelength, λ = 254 nm), I_2@silica stain, or $KMnO_4$ dip. The corresponding R_f values and eluting solvents used are listed in the experimental section. Column chromatography was performed with silica gel (grain size: 300–400 mesh, General-reagent®, Si60) under a pressure of approximately 1.5 atm. (air pump). The eluting ratios are listed with the respective experiments.

^1H, and $^{13}C\{^1H\}$ nuclear magnetic resonance (NMR) spectra were acquired on Bruker Avance III 400 MHz NMR spectroscopy. Deuterated solvents were used ($CDCl_3$) and the residual solvent peaks might be used as the internal references. Chemical shifts (δ) are reported in parts per million (ppm) related to the residual solvent signals (^1H NMR: C*H*Cl_3, 7.26 ppm; *H*DO, 4.79 ppm; $^{13}C\{^1H\}$ NMR: *C*DCl_3, 77.0 ppm). The following abbreviations are used to indicate the assignment of the signals and their multiplicities in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal; app, apparent. The given coupling constants *J* are listed as an average. All first-order splitting patterns were assigned on the basis of the appearance of the multiplets. Splitting patterns that could not be easily interpreted are designated as multiplets (m) or broad (br). $^{13}C\{^1H\}$ NMR experiments were carried out on a broad band decoupled mode.

GC yields of protoborylation reactions were determined with Fuli GC 9720PLUS system (FID, Zhejiang Fuli Analytical Instruments Inc.) equipped with an AT-SE-30 fused silica capillary column (Length, 30 m; Inner diameter, 0.32 mm; Thin film, 0.25 μm) using biphenyl as an internal standard.

High performance liquid chromatography (HPLC) analysis was performed on a Fuli LC5090 system (UV detector, Zhejiang Fuli Analytical Instruments Inc.) equipped with a Daicel

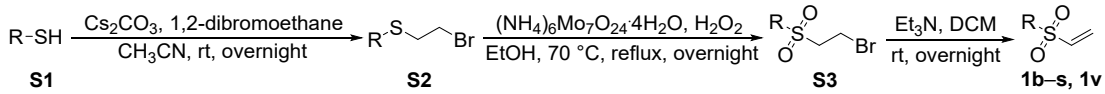
CHIRALPAK® IA (5 μm) column.

IR spectra were obtained by using Tianjin GangDong 650s FTIR spectroscopy. Samples were prepared as thin films on the KBr salt plate.

High-resolution mass spectrometry (HRMS) results were recorded on an Agilent G6546AR Q-TOF (ESI) mass spectrometer and reported in units of mass to charge ratio (m/z).

Preparation and Characterization of Substrates

General Procedure A: Synthesis of Vinyl Sulfones



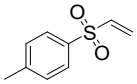
S1 **S2** **S3** **1b–s, 1v**

Vinyl sulfones **1b**–**1s** and **1v** were synthesized with a modified procedure according to the literature.[1] A dry 100 mL Schlenk flask was charged with 9.8 g Cs_2CO_3 (30.0 mmol, 3.0 equiv.). The reaction vessel was purged with nitrogen for 3 times. 30 mL CH_3CN and 2.6 mL 1,2-dibromoethane (30.0 mmol, 3.0 equiv.) were injected with syringe via a rubber septum. Then **S1** (10.0 mmol, 1.0 equiv.) dissolved in minimal amount of CH_3CN was slowly added into the reaction solution dropwise. Next, the reaction mixture was stirred at room temperature overnight. After the reaction was finished, the mixture was filtered and concentrated in vacuum to afford the desired product **S2**. The crude **S2** was directly used in the following step without further purification.

A 100 mL round-bottom flask was charged with **S2**, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.5 mmol, 15 mol%), and 30-50 mL EtOH in sequence, followed by the addition of H_2O_2 (100.0 mmol, 10.0 equiv.). The reaction mixture was allowed to reflux at 70 °C overnight. After the reaction was finished, the solution was concentrated under vacuum and then extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under vacuum to get **S3**. The crude **S3** was directly used in the following step without further purification.

S3 was dissolved with 30 mL DCM, followed by the addition of Et_3N (30.0 mmol, 3.0 equiv.). The mixture was allowed to stir at room temperature overnight. After the reaction was finished, the organic solution was washed with brine and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under vacuum. Further purification of the crude mixture with silica column chromatography gave the desired vinyl sulfones **1b**–**1s** and **1v**.

1-methyl-4-(vinylsulfonyl)benzene 1b



1b was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1549.1 mg (8.5 mmol, 85%) of product as a brown solid powder.

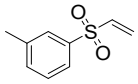
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.64 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.41 (d, *J* = 16.6 Hz, 1H), 5.99 (d, *J* = 9.8 Hz, 1H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm): 143.9, 139.7, 137.1, 130.8, 127.9, 127.1, 22.6.

IR (thin film) ν_{max} (cm^{-1}): 3051, 1385, 1299, 1145, 1086, 988, 815, 740, 677, 554, 506.

HRMS (ESI^+, Q-TOF) calcd for $C_9H_{10}NaO_2S^+$ [M+Na^+]: 205.0294, found 205.0296.

1-methyl-3-(vinylsulfonyl)benzene 1c



1c was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1804.1 mg (9.9 mmol, 99%) of product as a light-yellow oily liquid.

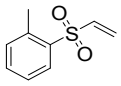
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.74 – 7.64 (m, 2H), 7.48 – 7.37 (m, 2H), 6.65 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.44 (d, *J* = 16.6 Hz, 1H), 6.02 (d, *J* = 9.7 Hz, 1H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.6, 139.3, 138.5, 134.4, 129.2, 128.2, 127.5, 125.0, 21.3.

IR (thin film) ν_{max} (cm^{-1}): 3057, 1382, 1309, 1221, 1141, 1088, 975, 866, 739, 692, 647, 571, 505, 444.

HRMS (ESI, Q-TOF) calcd for $C_9H_{10}NaO_2S^+$ [M+Na$^+$]: 205.0294, found 205.0296.

1-methyl-2-(vinylsulfonyl)benzene 1d



1d was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1494.3 mg (8.2 mmol, 82%) of product as a light-yellow oily liquid.

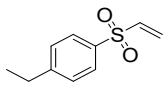
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.45 (d, *J* = 16.6 Hz, 1H), 6.10 (d, *J* = 9.8 Hz, 1H), 2.59 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.2, 137.8, 137.1, 133.8, 132.6, 129.6, 128.0, 126.7, 20.2.

IR (thin film) ν_{max} (cm^{-1}): 3060, 1384, 1309, 1198, 1148, 1060, 977, 807, 742, 644, 571, 513, 460.

HRMS (ESI, Q-TOF) calcd for $C_9H_{10}NaO_2S^+$ [M+Na$^+$]: 205.0294, found 205.0299.

1-ethyl-4-(vinylsulfonyl)benzene 1e



1e was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1491.6 mg (7.6 mmol, 76%) of product as a light-yellow oily liquid.

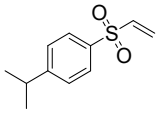
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.64 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.42 (d, *J* = 16.5 Hz, 1H), 6.00 (d, *J* = 9.8 Hz, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 150.8, 138.6, 136.6, 128.8, 128.0, 127.2, 28.9, 15.1.

IR (thin film) ν_{max} (cm^{-1}): 1383, 1310, 1146, 1087, 972, 836, 792, 735, 672, 553, 501.

HRMS (ESI, Q-TOF) calcd for $C_{10}H_{12}NaO_2S^+$ [M+Na$^+$]: 219.0450, found 219.0455.

1-isopropyl-4-(vinylsulfonyl)benzene 1f



1f was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1408.9 mg (6.7 mmol, 67%) of product as a white solid powder.

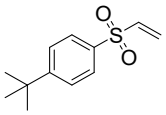
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.84 – 7.72 (m, 2H), 7.43 – 7.35 (m, 2H), 6.65 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.43 (d, *J* = 16.5 Hz, 1H), 6.00 (d, *J* = 9.8 Hz, 1H), 2.99 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 155.4, 139.2, 136.8, 128.7, 127.4, 127.2, 34.2, 23.6.

IR (thin film) ν_{max} (cm^{-1}): 3102, 3053, 2878, 1407, 1313, 1147, 1091, 1056, 975, 840, 782, 724, 669, 610, 563, 508.

HRMS (ESI, Q-TOF) calcd for $C_{11}H_{14}NaO_2S^+$ [M+Na$^+$]: 233.0607, found 233.0612.

1-(tert-butyl)-4-(vinylsulfonyl)benzene 1g



1g was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 448.6 mg (2.0 mmol, 20%) of product as a white solid powder.

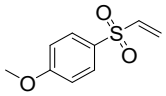
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.86 – 7.74 (m, 2H), 7.59 – 7.50 (m, 2H), 6.65 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.43 (d, *J* = 16.6 Hz, 1H), 6.00 (d, *J* = 9.8 Hz, 1H), 1.34 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 157.6, 139.1, 136.8, 127.8, 127.2, 126.3, 36.2, 31.0.

IR (thin film) ν_{max} (cm^{-1}): 2877, 1393, 1315, 1151, 1108, 1082, 844, 769, 712, 568.

HRMS (ESI, Q-TOF) calcd for $C_{12}H_{16}NaO_2S^+$ [M+Na$^+$]: 247.0763, found 247.0770.

1-methoxy-4-(vinylsulfonyl)benzene 1h



1h was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 931.7 mg (4.7 mmol, 47%) of product as a white solid powder.

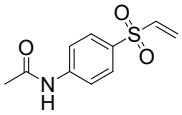
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.86 – 7.77 (m, 2H), 7.05 – 6.96 (m, 2H), 6.63 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.38 (d, *J* = 16.5 Hz, 1H), 5.97 (d, *J* = 9.8 Hz, 1H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 164.1, 138.9, 131.5, 130.1, 125.8, 114.0, 56.1.

IR (thin film) ν_{max} (cm^{-1}): 3058, 1295, 1145, 1089, 1019, 973, 835, 747, 560, 524.

HRMS (ESI, Q-TOF) calcd for $C_9H_{10}NaO_3S^+$ [M+Na$^+$]: 221.0243, found 221.0244.

N-(4-(vinylsulfonyl)phenyl)acetamide 1i



1i was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1036.2 mg (4.6 mmol, 46%) of product as a white solid powder.

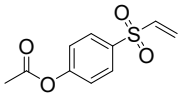
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.09 (s, 1H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 6.64 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.41 (d, *J* = 16.5 Hz, 1H), 6.02 (d, *J* = 9.8 Hz, 1H), 2.20 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 169.2, 143.2, 138.4, 133.9, 129.1, 127.5, 121.0, 24.6.

IR (thin film) ν_{max} (cm^{-1}): 3616, 3269, 3106, 3051, 1398, 1315, 1262, 1143, 1088, 840, 754, 708, 656, 588, 551, 516.

HRMS (ESI, Q-TOF) calcd for $C_{10}H_{11}NNaO_3S^+$ [M+Na$^+$]: 248.0352, found 248.0355.

4-(vinylsulfonyl)phenyl acetate 1j



1j was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 656.1 mg (2.9 mmol, 29%) of product as a colorless oily liquid.

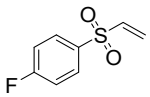
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.97 – 7.87 (m, 2H), 7.33 – 7.26 (m, 2H), 6.65 (dd, *J* = 16.5, 9.7 Hz, 1H), 6.47 (d, *J* = 16.5 Hz, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 169.0, 154.6, 138.3, 136.8, 129.7, 128.0, 122.7, 21.1.

IR (thin film) ν_{max} (cm^{-1}): 3061, 1765, 1374, 1316, 1196, 1146, 1088, 1012, 978, 910, 852, 748, 708, 656, 590, 551, 515.

HRMS (ESI, Q-TOF) calcd for $C_{10}H_{10}NaO_4S^+$ [M+Na$^+$]: 249.0192, found 249.0195.

1-fluoro-4-(vinylsulfonyl)benzene 1k



1k was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 931.0 mg (5.0 mmol, 50%) of product as a white solid powder.

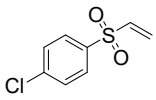
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.95 – 7.87 (m, 2H), 7.26 – 7.20 (m, 2H), 6.65 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.46 (d, *J* = 16.5 Hz, 1H), 6.05 (d, *J* = 9.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 167.9 (d, $J_{C–F}$ = 345.4 Hz), 164.5 (d, $J_{C–F}$ = 345.4 Hz), 138.4, 135.63 (d, $J_{C–F}$ = 3.0 Hz), 135.60 (d, $J_{C–F}$ = 3.0 Hz), 130.8 (d, $J_{C–F}$ = 10.1 Hz), 130.7 (d, $J_{C–F}$ = 10.1 Hz), 127.9, 116.8 (d, $J_{C–F}$ = 23.2 Hz), 116.6 (d, $J_{C–F}$ = 23.2 Hz).

IR (thin film) ν_{max} (cm^{-1}): 3554, 3106, 3065, 1389, 1319, 1236, 1149, 1089, 977, 838, 746, 708, 676 , 610, 553, 507.

HRMS (ESI, Q-TOF) calcd for $C_8H_7FNaO_2S^+$ [M+Na$^+$]: 209.0043, found 209.0043.

1-chloro-4-(vinylsulfonyl)benzene 1l



1l was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1337.5 mg (6.6 mmol, 66%) of product as a light-yellow oily liquid.

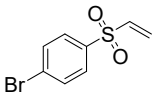
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.83 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.64 (dd, *J* = 16.5, 9.7 Hz, 1H), 6.47 (d, *J* = 16.5 Hz, 1H), 6.07 (d, *J* = 9.7 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.4, 138.2, 138.1, 129.7, 129.4, 128.3.

IR (thin film) ν_{max} (cm^{-1}): 3625, 3094, 3062, 1923, 1390, 1318, 1150, 1090, 1011, 978, 831, 770, 727, 661, 572, 527, 472.

HRMS (ESI, Q-TOF) calcd for $C_8H_7ClNaO_2S^+$ [M+Na$^+$]: 224.9747, found 224.9749.

1-bromo-4-(vinylsulfonyl)benzene 1m



1m was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1359.1 mg (5.5 mmol, 55%) of product as a light-yellow oily liquid.

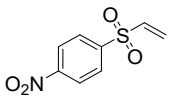
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.78 – 7.73 (m, 2H), 7.72 – 7.66 (m, 2H), 6.64 (dd, *J* = 16.5, 9.7 Hz, 1H), 6.47 (d, *J* = 16.5 Hz, 1H), 6.07 (d, *J* = 9.7 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.6, 138.1, 132.7, 129.5, 129.0, 128.4.

IR (thin film) ν_{max} (cm^{-1}): 3091, 1387, 1318, 1148, 1076, 1008, 977, 827, 762, 719, 656, 565, 518, 413.

HRMS (ESI, Q-TOF) calcd for $C_8H_7BrNaO_2S^+$ [M+Na$^+$]: 268.9242, found 268.9240.

1-nitro-4-(vinylsulfonyl)benzene 1n



1n was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 511.7 mg (2.4 mmol, 24%) of product as a light-yellow solid powder.

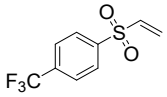
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.47 – 8.33 (m, 2H), 8.16 – 8.04 (m, 2H), 6.68 (dd, *J* = 16.5, 9.3 Hz, 1H), 6.59 (d, *J* = 16.5 Hz, 1H), 6.20 (d, *J* = 9.3 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 150.7, 145.4, 138.3, 131.1, 129.3, 124.5.

IR (thin film) ν_{max} (cm^{-1}): 3112, 3061, 2868, 1941, 1689, 1389, 1351, 1310, 1154, 1093, 997, 958, 855, 761, 715, 662, 571, 522, 456, 416.

HRMS (ESI, Q-TOF) calcd for $C_8H_7NNaO_4S^+$ [M+Na$^+$]: 235.9988, found 235.9994.

1-(trifluoromethyl)-4-(vinylsulfonyl)benzene 1o



1o was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1346.4 mg (5.7 mmol, 57%) of product as a white solid powder.

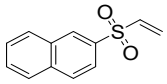
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.03 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 6.67 (dd, *J* = 16.5, 9.6 Hz, 1H), 6.54 (d, *J* = 16.5 Hz, 1H), 6.14 (d, *J* = 9.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 143.2, 137.7, 135.3 (q, $J_{C–F}$ = 33.3 Hz), 129.4, 128.5, 126.5 (q, $J_{C–F}$ = 4.0 Hz), 123.1 (q, $J_{C–F}$ = 274.2 Hz).

IR (thin film) ν_{max} (cm^{-1}): 3108, 3059, 1324, 1151, 1014, 977, 843, 793, 747, 702, 656, 597, 516.424.

HRMS (ESI, Q-TOF) calcd for $C_9H_7F_3NaO_2S^+$ [M+Na$^+$]: 259.0011, found 259.0013.

2-(vinylsulfonyl)naphthalene 1p



1p was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 261.9 mg (1.2 mmol, 12%) of product as a white solid powder.

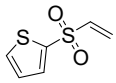
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.50 (d, *J* = 1.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.82 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.65 (dddd, *J* = 18.3, 8.1, 6.9, 1.4 Hz, 2H), 6.72 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.52 (d, *J* = 16.5 Hz, 1H), 6.07 (d, *J* = 9.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.5, 136.3, 135.2, 132.7, 129.68, 129.66, 129.4, 129.3, 128.0, 127.8, 127.7, 122.6.

IR (thin film) ν_{max} (cm^{-1}): 3678, 3617, 3048, 1382, 1307, 1129, 1071, 988, 909, 860, 821, 754, 733, 677, 553, 483.

HRMS (ESI, Q-TOF) calcd for $C_{12}H_{10}NaO_2S^+$ [M+Na$^+$]: 241.0294, found 241.0298.

2-(vinylsulfonyl)thiophene 1q



1q was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 1341.6 mg (7.7 mmol, 77%) of product as a light-yellow solid powder.

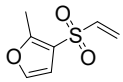
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.74 – 7.66 (m, 2H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.75 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.45 (dd, *J* = 16.4, 0.6 Hz, 1H), 6.03 (dd, *J* = 9.8, 0.6 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.0, 139.3, 135.8, 134.1, 128.1, 127.3.

IR (thin film) ν_{max} (cm^{-1}): 3101, 3053, 1394, 1310, 1228, 1139, 1015, 972, 858, 747, 674, 640, 569, 510.

HRMS (ESI, Q-TOF) calcd for $C_6H_6NaO_2S_2^+$ [M+Na$^+$]: 196.9701, found 196.9706.

2-methyl-3-(vinylsulfonyl)furan 1r



1r was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 103.3 mg (0.6 mmol, 6%) of product as a light-yellow oily liquid.

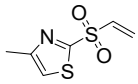
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.31 (d, *J* = 2.1 Hz, 1H), 6.67 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 6.38 (d, *J* = 16.5 Hz, 1H), 6.00 (d, *J* = 9.9 Hz, 1H), 2.53 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.1, 141.7, 138.8, 127.3, 121.4, 110.6, 12.8.

IR (thin film) ν_{max} (cm^{-1}): 1387, 1313, 1217, 1132, 1089, 971, 852, 742, 656, 563, 514.

HRMS (ESI, Q-TOF) calcd for $C_7H_8NaO_3S^+$ [M+Na$^+$]: 195.0086, found 195.0088.

4-methyl-2-(vinylsulfonyl)thiazole 1s



1s was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 321.7 mg (1.7 mmol, 17%) of product as a light-yellow solid powder.

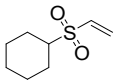
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.30 (q, *J* = 1.0 Hz, 1H), 6.87 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.64 (dd, *J* = 16.5, 0.7 Hz, 1H), 6.24 (dd, *J* = 9.7, 0.7 Hz, 1H), 2.53 (d, *J* = 1.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 164.2, 156.4, 136.3, 132.4, 121.4, 17.1.

IR (thin film) ν_{max} (cm^{-1}): 2329, 1326, 1144, 507.

HRMS (ESI, Q-TOF) calcd for $C_6H_7NNaO_2S_2^+$ [M+Na$^+$]: 211.9810, found 211.9818.

(vinylsulfonyl)cyclohexane 1v



1v was synthesized following the general synthetic procedure A. Purification by column chromatography (PE/EA = 10:1–3, column size 254 × 32 mm) yielded a total of 975.8 mg (5.6 mmol, 56%) of product as a light-yellow solid powder.

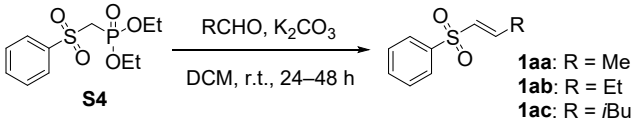
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 6.56 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.40 (d, *J* = 16.6 Hz, 1H), 6.18 (d, *J* = 9.8 Hz, 1H), 2.78 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.14 (dt, *J* = 11.4, 2.1 Hz, 2H), 1.90 (dt, *J* = 12.7, 3.1 Hz, 2H), 1.73 – 1.67 (m, 1H), 1.43 (qd, *J* = 12.4, 3.4 Hz, 2H), 1.30 – 1.17 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 134.2, 131.3, 61.8, 25.2, 25.1, 25.0.

IR (thin film) ν_{max} (cm^{-1}): 2860, 2261, 1384, 1304, 1265, 1128, 1019, 857, 795, 724, 650.

HRMS (ESI, Q-TOF) calcd for $C_8H_{14}NaO_2S^+$ [M+Na$^+$]: 197.0607, found 197.0611.

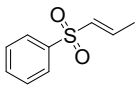
General Procedure B: Synthesis of Vinyl Sulfones



Vinyl sulfones **1aa**–**1ac** was synthesized with a modified procedure according to the literature.[2]

A dry 100 mL Schlenk flask was charged with 2.9 g **S4** (10.0 mmol, 1.0 equiv.) under N_2 atmosphere, followed by the addition of 50 mL DCM and sealing with a rubber septum. After **S4** was fully dissolved, 2.1 g K_2CO_3 (15.0 mmol, 1.5 equiv.) was added into the reaction vessel under a N_2 counter-flow. Next, 15.0 mmol aldehyde (1.5 equiv.) was injected dropwise via syringe. Then the reaction mixture was stirred at room temperature for 24–48 h. After the reaction was finished, to the mixture was added 20 mL satd. aqueous solution of NH_4Cl, followed by extraction with DCM (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under vacuum. Further purification of the residual with silica column chromatography gave the desired vinyl sulfones **1aa**–**1ac**.

(E)-(prop-1-en-1-ylsulfonyl)benzene 1aa



1aa was synthesized following the general synthetic procedure B. Purification by column chromatography (PE/EA = 12:1–2, column size 254 × 32 mm) yielded a total of 1457.9 mg (8.0 mmol, 80%) of product as a colorless oily liquid.

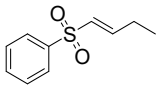
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.88 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.54 (dd, *J* = 8.3, 6.8 Hz, 2H), 6.99 (dq, *J* = 14.1, 6.9 Hz, 1H), 6.35 (dd, *J* = 15.0, 1.7 Hz, 1H), 1.93 (dd, *J* = 6.9, 1.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.5, 140.5, 133.2, 131.6, 129.1, 127.4, 17.2.

IR (thin film) ν_{max} (cm^{-1}): 3027, 1296, 1144, 1083, 955, 812, 751, 717, 685, 594, 544.

HRMS (ESI, Q-TOF) calcd for $C_9H_{10}NaO_2S^+$ [M+Na$^+$]: 205.0294, found 205.0297.

(E)-(but-1-en-1-ylsulfonyl)benzene 1ab



1ab was synthesized following the general synthetic procedure B. Purification by column chromatography (PE/EA = 30:1–6, column size 254 × 32 mm) yielded a total of 1491.6 mg (7.6 mmol, 76%) of product as a light-yellow oily liquid.

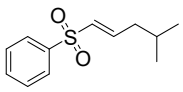
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.90 – 7.84 (m, 2H), 7.64 – 7.58 (m, 1H), 7.56 – 7.51 (m, 2H), 7.05 (dt, *J* = 15.1, 6.1 Hz, 1H), 6.30 (dt, *J* = 15.1, 1.8 Hz, 1H), 2.32 – 2.23 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 148.5, 140.7, 133.2, 129.6, 129.2, 127.5, 24.7, 11.6.

IR (thin film) ν_{max} (cm^{-1}): 3057, 1310, 1216, 1146, 1085, 969, 833, 754, 690, 595, 551.

HRMS (ESI, Q-TOF) calcd for $C_{10}H_{12}NaO_2S^+$ [M+Na$^+$]: 219.0450, found 219.0449.

(E)-((4-methylpent-1-en-1-yl)sulfonyl)benzene 1ac



1ac was synthesized following the general synthetic procedure B. Purification by column

chromatography (PE/EA = 30:1–6, column size 254 × 32 mm) yielded a total of 1974.0 mg (8.8 mmol, 88%) of product as a yellow oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.90 – 7.84 (m, 2H), 7.64 – 7.57 (m, 1H), 7.57 – 7.49 (m, 2H), 6.96 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.31 (dt, *J* = 15.0, 1.5 Hz, 1H), 2.12 (td, *J* = 7.2, 1.4 Hz, 2H), 1.79 (dp, *J* = 13.4, 6.7 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 6H).

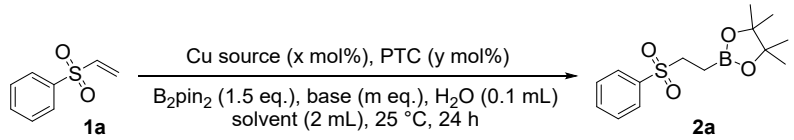
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 146.1, 140.7, 133.2, 131.2, 129.2, 127.5, 40.5, 27.7, 22.2.

IR (thin film) ν_{max} (cm^{-1}): 3621, 3057, 1310, 1147, 1086, 977, 841, 799, 753, 716, 689, 597, 552.

HRMS (ESI, Q-TOF) calcd for $C_{12}H_{16}NaO_2S^+$ [M+Na^+]: 247.0763, found 247.0760.

Miscellaneous Optimization of Reaction Conditions

Table S1 Optimization of the conjugate borylation reactions[a]



1a **2a**

entry	Cu source (x)[b]	PTC (y)	solvent	base (m)	yield (%)[c]
1	CH_3COOCu (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	n.r.
2	CuCl (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	7
3	CuCl (0.1)	TBAC (0.1)	DCM	K_2CO_3 (3.0)	<5
3[d]	CuCl (0.1)	TBAC (0.1)	DCM	K_2CO_3 (3.0)	8
4	CuBr (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	9
5	$Cu(MeCN)_4PF_6$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	<5
6	$Cu(MeCN)_4PF_6$ (0.1)	TBAC (0.1)	DCM	K_2CO_3 (3.0)	<5
7[d]	$Cu(MeCN)_4PF_6$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	<5
8[d]	$Cu(MeCN)_4PF_6$ (0.1)	TBAC (0.1)	DCM	K_2CO_3 (3.0)	<5
9	$CuCl_2·5H_2O$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	20
10	$CuBr_2$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	17
11	$Cu(NO_3)_2·3H_2O$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	22
12	$Cu(OAc)_2$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	18
13	$Cu(OTf)_2$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	n.r.
14	$CuSO_4·5H_2O$ (0.1)	TBAI (0.1)	DCM	K_2CO_3 (3.0)	28
15	$CuSO_4·5H_2O$ (0.1)	TBAF (0.1)	DCM	K_2CO_3 (3.0)	13
16	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	DCM	K_2CO_3 (3.0)	34
17	$CuSO_4·5H_2O$ (0.1)	TBAB (0.1)	DCM	K_2CO_3 (3.0)	27
18	$CuSO_4·5H_2O$ (0.1)	DTAC (0.1)	DCM	K_2CO_3 (3.0)	11
19	$CuSO_4·5H_2O$ (0.1)	CTAC (0.1)	DCM	K_2CO_3 (3.0)	9
20	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (3.0)	70
21	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	Tol	K_2CO_3 (3.0)	9
22	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	Et_2O	K_2CO_3 (3.0)	<5
23	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	octane	K_2CO_3 (3.0)	73
24	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	$CHCl_3$	K_2CO_3 (3.0)	n.r.
25	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (1.0)	n.r.
26	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (2.0)	62
27	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (4.0)	31
28	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	KOH (3.0)	n.r.
29	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_3PO_4 (3.0)	33
30	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	KF (3.0)	39
31	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	KOAc (3.0)	18
32	$CuSO·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	Na_2CO_3 (3.0)	62
33	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	Li_2CO_3 (3.0)	n.r.
34	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	Cs_2CO_3 (3.0)	60
35[e]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (3.0)	33
31[f]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (3.0)	<5
32[g]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (3.0)	49
33[h]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.1)	*n*-Hex	K_2CO_3 (3.0)	66
34	$CuSO_4·5H_2O$ (0.1)	TBAC (0.25)	*n*-Hex	K_2CO_3 (3.0)	85
35	$CuSO_4·5H_2O$ (0.1)	TBAC (0.5)	*n*-Hex	K_2CO_3 (3.0)	65
36[i]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.25)	*n*-Hex	K_2CO_3 (3.0)	58
37[j]	$CuSO_4·5H_2O$ (0.1)	TBAC (0.25)	*n*-Hex	K_2CO_3 (3.0)	84
38	$CuSO_4·5H_2O$ (0.25)	TBAC (0.25)	*n*-Hex	K_2CO_3 (3.0)	92
39[k]	CuCl (5)	TBAI (5)	DCM	K_2CO_3 (3.0)	95
40	CuCl (5)	TBAC (5)	DCM	K_2CO_3 (3.0)	97
41	$CuSO_4·5H_2O$ (5)	TBAI (5)	DCM	K_2CO_3 (3.0)	88
42	$CuSO_4·5H_2O$ (5)	TBAC (5)	DCM	K_2CO_3 (3.0)	88
43	–	–	*n*-Hex	K_2CO_3 (3.0)	n.r.
44	–	TBAC (0.25)	*n*-Hex	K_2CO_3 (3.0)	n.r.

45	$CuSO_4·5H_2O$ (0.25)	–	*n*-Hex	K_2CO_3 (3.0)	8
46	$CuSO_4·5H_2O$ (0.25)	SDBS (0.25)	*n*-Hex	K_2CO_3 (3.0)	6

[a] Reagents and conditions: **1a** (0.2 mmol), B_2pin_2 (0.3 mmol), Cu source (0.2-0.5 μmol), PTC (0.2–1.0 μmol), base (0.2-0.8 mmol), H_2O (0.1 mL), solvent (2 mL), 25 °C, 24 h, air. TBAI (tetrabutylammonium iodide), TBAF (tetrabutylammonium fluoride), TBAC (tetrabutylammonium chloride), TBAB (tetrabutylammonium bromide), DTAC (dodecyltrimethylammonium chloride), CTAC (hexadecyltrimethylammonium chloride), SDBS (sodium dodecyl benzene sulfonate).

[b] For tests with <1 mol% catalyst loading, the copper sources were pre-dispersed and added as a solution, most Cu(I) salts in DMF, $Cu(MeCN)_4PF_6$ in DCM, Cu(II) in H_2O.

[c] Calibrated GC yields of **2a** using biphenyl as an internal standard.

[d] 48 h was used.

[e] 0.05 mL H_2O was used.

[f] 0.2 mL H_2O was used.

[g] 1.0 equiv. B_2pin_2 was used.

[h] 2.0 equiv. B_2pin_2 was used.

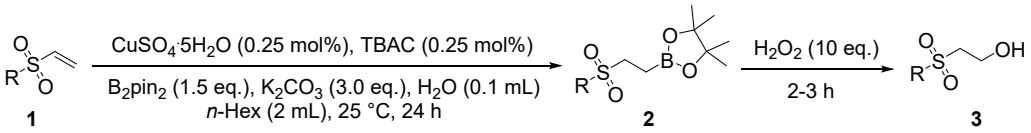
[i] 12 h was used.

[j] 36 h was used.

[k] In our preliminary investigations, we found that Cu(I) precursors would demonstrate good catalytic performance in a homogeneous system, especially with the assistance of ligands. This observation is also consistent with the literatures published. However, in the current biphasic system, due to the challenge of mass transfer across phases, the catalytic activity between Cu(I) and Cu(II) became quite different with the presence of PTC. In general, the efficiency of Cu(I) salts was much lower than Cu(II). From Table S1, it can be found that no matter what kind of PTC was used, the cuprous salts gave miserable results at a catalyst loading of 0.1 mol% after 24 h, with most substrate **1a** unreacted, whereas the cupric salt such as $CuSO_4·5H_2O$ could offer **2a** with improved yields around 30%. Even if the reaction time was lengthened to 48 h, the yields could not be improved. On the contrary, when a greatly enhanced catalyst loading of 5 mol% was employed, all reactions could be finished almost quantitively. However, it is noteworthy that the generation of metallic Cu(0) species were clearly observed in some reaction vessels. Therefore, we believed that the superior performance of Cu(II) in these cases would be attributed to the following two reasons. First, Cu(II) was initially dissolved in the basic aqueous phase, which was later reduced by the reductive B species transferred from the organic phase. The process was slow and stepwise, under the control of PTC, by which only a low concentration of highly reactive cuprate ion-pair existed in the system. Normally, for reactions with >1 mol% Cu(II), the blue color of aqueous phase would fade after 5–10 min stirring at room temperature in air, and the mixture became brownish or grey. However, for most covalent Cu(I) salts, such as CuCl and CuI, they could neither be easily dissolved in DCM nor H_2O. This would be difficult for PTC to form true catalytic species and thus caused an induction period, if any. A special was shown in the case of $Cu(MeCN)_4PF_6$, which has good solubility in both organic solvents and the aqueous solution, still giving no desired product. Second, the over-reduction of Cu(I) to Cu(0) existed. If the catalytic Cu(I) species was generated too fast and failed to enroll in the catalytic cycles, the deactivation would also be an important issue to undermine the reaction efficiency. Cu(II) salts, which have a higher oxidation state, would probably avoid such side reactions much better, compared with Cu(I) salts. Specifically, no much Cu(0) was observed in the reaction of entry 42, Table S1, when TBAC was used. In the other three reaction with 5 mol% Cu, metallic Cu(0) was observed either on the side or the bottom of reaction vials.

Preparation and Characterization of *β*-Sulfonyl Alcohols

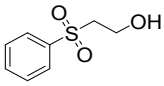
General procedure: Conjugate Borylation of Vinyl Sulfones Followed by Oxidation



1 **2** **3**

To a 4 mL vial were added 82.9 mg K_2CO_3 (0.6 mmol, 3.0 equiv.) and 76.2 mg B_2pin_2 (0.3 mmol, 1.5 equiv.), followed by quick addition of 2 mL *n*-hexane and 0.1 mL H_2O. Then 10 μL aqueous solution of $CuSO_4·5H_2O$ (0.125 mg, 0.25 mol%) and 10 μL aqueous solution of TBAC (0.14 mg, 0.25 mol%) were added in sequence. The mixture was stirred at 25 °C for 1 min, before 0.2 mmol **1** (1.0 equiv.) was added. Next, the reaction was allowed to stir at 25 °C for 24 h. Due to the instability of some *β*-sulfonylboronates, the borylation product **2** was directly transformed into the corresponding *β*-sulfonyl alcohol via oxidation by H_2O_2. When the reaction was finished, 2 mmol H_2O_2 (30w% aq., 10.0 equiv.) was added dropwise into the vial. After 2-3 h, the resulting mixture was quenched with 1 mL saturated brine, while the aqueous phase was extracted twice with 2 mL EA. The combined organic phases were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography to give the desired *β*-sulfonyl alcohol **3**.

2-(phenylsulfonyl)ethan-1-ol 3a



3a was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 31.3 mg (0.17 mmol, 84%) of product as a light-yellow oily liquid.

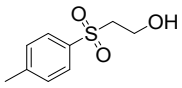
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.03 – 7.83 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 3.99 (t, *J* = 5.4 Hz, 2H), 3.41 – 3.30 (m, 2H), 2.87 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.9, 134.0, 129.4, 127.9, 58.2, 56.2.

IR (thin film) ν_{max} (cm^{-1}): 2924, 1398, 1290, 1141, 1082, 800, 734, 689, 569, 529.

HRMS (ESI, Q-TOF) calcd for $C_8H_{10}NaO_3S^+$ [M+Na^+]: 209.0243, found 209.0246.

2-tosylethan-1-ol 3b



3b was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 35.2 mg (0.18 mmol, 88%) of product as a grey oily liquid.

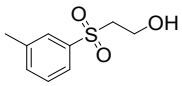
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 3.98 (t, *J* = 5.3 Hz, 2H), 3.36 – 3.28 (t, 2H), 2.83 (s, 1H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 145.2, 137.1, 131.2, 128.5, 59.1, 56.4, 20.2.

IR (thin film) ν_{max} (cm^{-1}): 1399, 1289, 1141, 1052, 815, 727, 660, 565, 518.

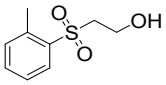
HRMS (ESI, Q-TOF) calcd for $C_9H_{12}NaO_3S^+$ [M+Na$^+$]: 223.0399, found 223.0402.

2-(m-tolylsulfonyl)ethan-1-ol 3c



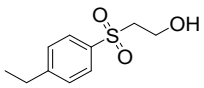
3c was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 27.2 mg (0.14 mmol, 68%) of product as a colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.77 – 7.67 (m, 2H), 7.53 – 7.42 (m, 2H), 3.98 (q, *J* = 4.8 Hz, 2H), 3.41 – 3.27 (m, 2H), 2.85 (s, 1H), 2.45 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.3, 138.7, 135.0, 130.7, 128.2, 125.6, 58.2, 56.3, 21.3.
IR (thin film) ν_{max} (cm^{-1}): 1294, 1228, 1137, 1052, 867, 792, 725, 687, 593, 540, 491.
HRMS (ESI, Q-TOF) calcd for $C_9H_{12}NaO_3S^+$ [M+Na$^+$]: 223.0399, found 223.0405.

2-(o-tolylsulfonyl)ethan-1-ol 3d



3d was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 29.6 mg (0.15 mmol, 74%) of product as a colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 – 7.32 (m, 2H), 4.00 (t, *J* = 5.6 Hz, 2H), 3.42 – 3.33 (m, 2H), 2.86 (s, 1H), 2.69 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 137.9, 136.8, 134.1, 132.4, 130.0, 126.8, 57.3, 56.3, 21.2.
IR (thin film) ν_{max} (cm^{-1}): 1743, 1290, 1145, 1052, 730, 600.
HRMS (ESI, Q-TOF) calcd for $C_9H_{12}NaO_3S^+$ [M+Na$^+$]: 223.0399, found 223.0404.

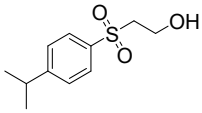
2-((4-ethylphenyl)sulfonyl)ethan-1-ol 3e



3e was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 36.9 mg (0.17 mmol, 86%) of product as a colorless oily liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.83 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 3.99 (q, *J* = 5.7 Hz, 2H), 3.41 – 3.24 (m, 2H), 2.83 (t, *J* = 6.4 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 151.3, 136.0, 129.0, 128.1, 58.2, 56.4, 28.9, 15.1.

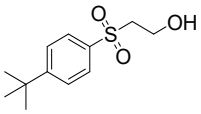
IR (thin film) ν_{max} (cm^{-1}): 3367, 2967, 1407, 1295, 1142, 1053, 837, 798, 717, 655, 570, 526.
HRMS (ESI, Q-TOF) calcd for $C_{10}H_{14}NaO_3S^+$ [M+Na^+]: 237.0556, found 237.0559.

2-((4-isopropylphenyl)sulfonyl)ethan-1-ol 3f



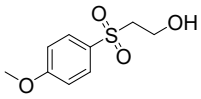
3f was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 35.2 mg (0.15 mmol, 77%) of product as a light-yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.89 – 7.79 (m, 2H), 7.48 – 7.39 (m, 2H), 3.98 (t, *J* = 5.2 Hz, 2H), 3.38 – 3.30 (m, 2H), 3.01 (h, *J* = 6.9 Hz, 1H), 2.91 (s, 1H), 1.27 (d, *J* = 7.0 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 156.5, 137.7, 128.9, 127.6, 58.2, 56.4, 34.7, 23.6.
IR (thin film) ν_{max} (cm^{-1}): 3746, 2368, 1408, 1304, 1142, 1087, 1052, 838, 780, 706, 647, 576.
HRMS (ESI, Q-TOF) calcd for $C_{11}H_{16}NaO_3S^+$ [M+Na^+]: 251.0712, found 251.0715.

2-((4-(tert-butyl)phenyl)sulfonyl)ethan-1-ol 3g



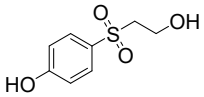
3g was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC in DCM followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 46.5 mg (0.19 mmol, 96%) of product as a light-yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.84 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 3.99 (t, *J* = 5.4 Hz, 2H), 3.41 – 3.27 (m, 2H), 1.35 (s, 9H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 158.6, 135.8, 128.6, 126.5, 58.2, 56.4, 35.3, 31.4.
IR (thin film) ν_{max} (cm^{-1}): 2092, 1398, 1286, 1146, 1106, 1051, 799, 701, 572, 520.
HRMS (ESI, Q-TOF) calcd for $C_{12}H_{18}NaO_3S^+$ [M+Na^+]: 265.0869, found 265.0878.

2-((4-methoxyphenyl)sulfonyl)ethan-1-ol 3h



3h was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 31.6 mg (0.15 mmol, 73%) of product as a white solid powder.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.87 – 7.78 (m, 2H), 7.05 – 6.98 (m, 2H), 3.95 (t, *J* = 5.5 Hz, 2H), 3.87 (s, 3H), 3.34 – 3.27 (m, 2H), 2.92 (s, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 164.5, 130.3, 130.1, 114.6, 58.4, 56.3, 55.7.
IR (thin film) ν_{max} (cm^{-1}): 2053, 1499, 1271, 1140, 1022, 837, 734, 569, 532.
HRMS (ESI, Q-TOF) calcd for $C_9H_{12}NaO_4S^+$ [M+Na^+]: 239.0349, found 239.0360.

4-((2-hydroxyethyl)sulfonyl)phenol 3j



3j was obtained as the hydrolyzation product of ester **1j** following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 39.2 mg (0.19 mmol, 97%) of product as a colorless oily liquid.

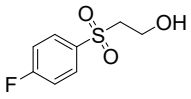
^{1}H NMR (400 MHz, DMSO) δ_H (ppm) 10.59 (s, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.85 (t, *J* = 5.5 Hz, 1H), 3.63 (q, *J* = 6.2 Hz, 2H), 3.41 – 3.29 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, DMSO) δ_C (ppm) 162.7, 129.6, 115.7, 58.0, 55.1.

IR (thin film) ν_{max} (cm^{-1}): 2128, 1289, 1140, 995, 638.

HRMS (ESI, Q-TOF) calcd for $C_8H_{10}NaO_4S^+$ [M+Na$^+$]: 225.0192, found 225.0194.

2-((4-fluorophenyl)sulfonyl)ethan-1-ol 3k



3k was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 39.2 mg (0.19 mmol, 96%) of product as a colorless oily liquid.

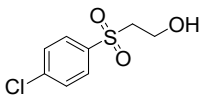
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.98 – 7.92 (m, 2H), 7.30 – 7.20 (m, 2H), 4.00 (q, *J* = 5.6 Hz, 2H), 3.38 – 3.30 (m, 2H), 2.80 (t, *J* = 6.1 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 167.2 (d, $J_{C–F}$ = 258.6 Hz), 164.7 (d, $J_{C–F}$ = 258.6 Hz), 135.11 (d, $J_{C–F}$ = 3.0 Hz), 135.08 (d, $J_{C–F}$ = 3.0 Hz), 130.9 (d, $J_{C–F}$ = 10.1 Hz), 130.8 (d, $J_{C–F}$ = 10.1 Hz), 116.9 (d, $J_{C–F}$ = 22.2 Hz), 116.6 (d, $J_{C–F}$ = 22.2 Hz), 58.4, 56.2.

IR (thin film) ν_{max} (cm^{-1}): 2063, 1288, 1236, 1143, 1057, 840, 733, 563, 521.

HRMS (ESI, Q-TOF) calcd for $C_8H_9FNaO_3S^+$ [M+Na$^+$]: 227.0149, found 227.0149.

2-((4-chlorophenyl)sulfonyl)ethan-1-ol 3l



3l was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 41.9 mg (0.19 mmol, 95%) of product as a light-yellow oily liquid.

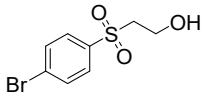
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.91 – 7.83 (m, 2H), 7.60 – 7.52 (m, 2H), 4.07 – 3.97 (m, 2H), 3.39 – 3.32 (m, 2H), 2.69 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 140.9, 137.4, 130.7, 129.5, 58.3, 56.7.

IR (thin film) ν_{max} (cm^{-1}): 2363, 1395, 1309, 1144, 1087, 1013, 800, 760, 716, 619, 528, 467.

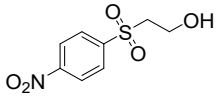
HRMS (ESI, Q-TOF) calcd for $C_8H_9ClNaO_3S^+$ [M+Na$^+$]: 242.9853, found 242.9855.

2-((4-bromophenyl)sulfonyl)ethan-1-ol 3m



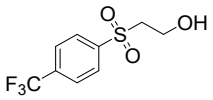
3m was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 47.7 mg (0.18 mmol, 90%) of product as a white solid powder.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.82 – 7.75 (m, 2H), 7.75 – 7.69 (m, 2H), 3.99 (q, *J* = 5.9 Hz, 2H), 3.40 – 3.29 (m, 2H), 2.77 (t, *J* = 6.2 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.0, 132.7, 129.5, 129.4, 56.2.
IR (thin film) ν_{max} (cm^{-1}): 2293, 1390, 1309, 1144, 1064, 1010, 825, 750, 711, 609, 562, 413.
HRMS (ESI, Q-TOF) calcd for $C_8H_9BrNaO_3S^+$ [M+Na$^+$]: 286.9348, found 286.9348.

2-((4-nitrophenyl)sulfonyl)ethan-1-ol 3n



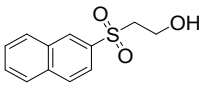
3n was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC in DCM followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 33.3 mg (0.14 mmol, 72%) of product as a white solid powder.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.46 – 8.40 (m, 2H), 8.19 – 8.13 (m, 2H), 4.08 (q, *J* = 5.2 Hz, 2H), 3.45 – 3.39 (m, 2H), 2.37 (s, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 151.5, 145.0, 133.9, 125.0, 59.5, 57.1.
IR (thin film) ν_{max} (cm^{-1}): 3525, 3107, 2360, 1940, 1397, 1349, 1285, 1182, 1137, 1082, 1024, 800, 736, 703, 551, 430.
HRMS (ESI, Q-TOF) calcd for $C_8H_9NNaO_5S^+$ [M+Na$^+$]: 254.0094, found 254.0097.

2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-ol 3o



3o was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 44.2 mg (0.17 mmol, 87%) of product as a white solid powder.
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.08 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 4.04 (q, *J* = 5.6 Hz, 2H), 3.44 – 3.35 (m, 2H), 2.66 (t, *J* = 6.1 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 142.7, 135.7 (q, $J_{C–F}$ = 33.3 Hz), 128.7, 126.6 (q, $J_{C–F}$ = 4.0 Hz), 123.0 (q, $J_{C–F}$ = 274.7 Hz) 58.3, 56.2.
IR (thin film) ν_{max} (cm^{-1}): 3057, 1322, 1267, 1143, 1059, 1013, 843, 738, 605, 517, 422.
HRMS (ESI, Q-TOF) calcd for $C_9H_9F_3NaO_3S^+$ [M+Na$^+$]: 277.0117, found 277.0121.

2-(naphthalen-2-ylsulfonyl)ethan-1-ol 3p



3p was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4 \cdot 5H_2O$ and 1 mol% TBAC in DCM followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 40.2 mg (0.17 mmol, 85%) of product as a white solid powder.

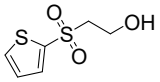
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.51 (d, *J* = 2.3 Hz, 1H), 8.06 – 7.97 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.67 (dddd, *J* = 19.1, 8.1, 6.9, 1.4 Hz, 2H), 4.07 – 3.97 (m, 2H), 3.46 – 3.39 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 135.7, 135.4, 132.1, 129.9, 129.8, 129.5, 129.4, 128.0, 127.9, 122.4, 58.3, 56.4.

IR (thin film) ν_{max} (cm^{-1}): 3554, 3056, 1398, 1349, 1296, 1212, 1129, 1040, 914, 859, 819, 752, 717, 653, 555, 484.

HRMS (ESI, Q-TOF) calcd for $C_{12}H_{12}NaO_3S^+$ [M+Na$^+$]: 259.0399, found 259.0406.

2-(thiophen-2-ylsulfonyl)ethan-1-ol 3q



3q was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 34.2 mg (0.18 mmol, 89%) of product as a colorless oily liquid.

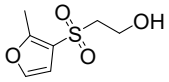
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.79 – 7.69 (m, 2H), 7.18 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.03 (q, *J* = 4.8 Hz, 2H), 3.50 – 3.41 (m, 2H), 2.81 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.8, 134.5, 134.4, 128.1, 59.7, 56.5.

IR (thin film) ν_{max} (cm^{-1}): 3392, 3100, 1308, 1231, 1137, 1057, 1020, 855, 727, 662, 588, 536.

HRMS (ESI, Q-TOF) calcd for $C_6H_8NaO_3S_2^+$ [M+Na$^+$]: 214.9807, found 214.9810.

2-((2-methylfuran-3-yl)sulfonyl)ethan-1-ol 3r



3r was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 34.2 mg (0.18 mmol, 89%) of product as a colorless oily liquid.

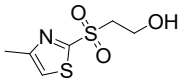
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.35 (d, *J* = 2.1 Hz, 1H), 6.61 (d, *J* = 2.1 Hz, 1H), 4.09 – 3.98 (t, 2H), 3.39 – 3.29 (m, 2H), 2.75 (s, 1H), 2.59 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 159.1, 142.1, 120.2, 110.5, 59.8, 56.8, 13.8.

IR (thin film) ν_{max} (cm^{-1}): 1389, 1301, 1223, 1128, 1092, 1037, 948, 889, 800, 732, 658, 616, 560, 468.

HRMS (ESI, Q-TOF) calcd for $C_7H_{10}NaO_4S^+$ [M+Na$^+$]: 213.0192, found 213.0195.

2-((4-methylthiazol-2-yl)sulfonyl)ethan-1-ol 3s



3s was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4 \cdot 5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 11.6 mg (0.06 mmol, 28%) of product as a colorless oily liquid.

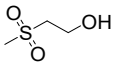
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.33 (q, *J* = 0.9 Hz, 1H), 4.15 (q, *J* = 4.6 Hz, 2H), 3.67 – 3.59 (m, 2H), 3.22 (s, 1H), 2.55 (d, *J* = 1.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 164.1, 156.1, 121.2, 64.0, 54.6, 17.2.

IR (thin film) ν_{max} (cm^{-1}): 3102, 2254, 1730, 1318, 1261, 1120, 1071, 1024, 863, 798, 719, 535, 455.

HRMS (ESI, Q-TOF) calcd for $C_6H_9NNaO_3S_2^+$ [M+Na$^+$]: 229.9916, found 229.9919.

2-(methylsulfonyl)ethan-1-ol 3t



3t was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 18.6 mg (0.15 mmol, 75%) of product as a colorless oily liquid.

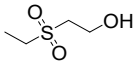
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 4.12 (q, *J* = 4.4 Hz, 2H), 3.28 – 3.21 (m, 2H), 3.03 (s, 3H), 2.70 (d, *J* = 5.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 56.8, 56.5, 42.7.

IR (thin film) ν_{max} (cm^{-1}): 2068, 1276, 1126, 1024, 971, 800.

HRMS (ESI, Q-TOF) calcd for $C_3H_8NaO_3S^+$ [M+Na$^+$]: 147.0086, found 147.0086.

2-(ethylsulfonyl)ethan-1-ol 3u



3u was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size 254 × 17 mm) yielded a total of 22.4 mg (0.16 mmol, 81%) of product as a colorless oily liquid.

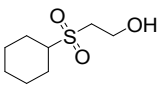
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 4.09 (t, *J* = 5.2 Hz, 2H), 3.22 – 3.16 (m, 2H), 3.11 (q, *J* = 7.5 Hz, 2H), 2.93 (s, 1H), 1.39 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 56.2, 54.0, 48.9, 6.4.

IR (thin film) ν_{max} (cm^{-1}): 2073, 1401, 1276, 1124, 1051, 792, 731, 496.

HRMS (ESI, Q-TOF) calcd for $C_4H_{10}NaO_3S^+$ [M+Na$^+$]: 161.0243, found 161.0245.

2-(cyclohexylsulfonyl)ethan-1-ol 3v



3v was synthesized following the general procedure of conjugate borylation of vinyl sulfones followed by oxidation. Purification by column chromatography (PE/EA = 10:1–5, column size

254 × 17 mm) yielded a total of 29.6 mg (0.15 mmol, 77%) of product as a light-yellow oily liquid.

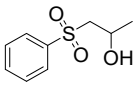
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 4.18 – 3.98 (m, 2H), 3.22 – 3.06 (m, 2H), 2.95 (ddt, *J* = 16.1, 12.6, 6.3 Hz, 2H), 2.16 (dd, *J* = 13.0, 2.0 Hz, 2H), 1.92 (dt, *J* = 11.8, 2.8 Hz, 2H), 1.72 (dt, *J* = 13.8, 3.3 Hz, 1H), 1.52 (qd, *J* = 12.4, 3.5 Hz, 2H), 1.35 – 1.17 (m, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 62.1, 56.0, 51.5, 25.0, 25.0, 24.8.

IR (thin film) ν_{max} (cm^{-1}): 3555, 3295, 2860, 1396, 1264, 1121, 1059, 799, 706, 604.

HRMS (ESI, Q-TOF) calcd for $C_8H_{16}NaO_3S^+$ [M+Na$^+$]: 215.0712, found 215.0711.

1-(phenylsulfonyl)propan-2-ol 3aa



3aa was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 12:1–8, column size 254 × 17 mm) yielded a total of 36.4 mg (0.18 mmol, 91%) of product as a colorless oily liquid.

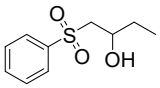
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.97 – 7.88 (m, 2H), 7.73 – 7.64 (m, 1H), 7.63 – 7.54 (m, 2H), 4.39 – 4.26 (m, 1H), 3.44 (s, 1H), 3.28 – 3.12 (m, 2H), 1.24 (d, *J* = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.1, 133.1, 128.5, 126.9, 62.3, 61.3.

IR (thin film) ν_{max} (cm^{-1}): 3608, 3064, 2922, 1701, 1393, 1296, 1144, 1081, 940, 840, 789, 748, 688, 576, 533.

HRMS (ESI, Q-TOF) calcd for $C_9H_{12}NaO_3S^+$ [M+Na$^+$]: 223.0399, found 223.0397.

1-(phenylsulfonyl)butan-2-ol 3ab



3ab was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4{\cdot}5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–4, column size 254 × 17 mm) yielded a total of 46.5 mg (0.20 mmol, 98%) of product as a light-yellow oily liquid.

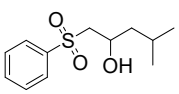
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.96 – 7.87 (m, 2H), 7.71 – 7.62 (m, 1H), 7.57 (tt, *J* = 6.5, 1.5 Hz, 2H), 4.12 – 4.00 (m, 1H), 3.38 (s, 1H), 3.26 – 3.13 (m, 2H), 1.63 – 1.39 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.1, 134.0, 129.4, 127.8, 67.0, 61.8, 29.4, 9.2.

IR (thin film) ν_{max} (cm^{-1}): 3506, 3065, 2931, 1395, 1298, 1145, 1084, 980, 896, 748, 689, 598, 539.

HRMS (ESI, Q-TOF) calcd for $C_{10}H_{14}NaO_3S^+$ [M+Na$^+$]: 237.0556, found 237.0552.

4-methyl-1-(phenylsulfonyl)pentan-2-ol 3ac



3ac was synthesized following the general procedure of conjugate borylation of vinyl sulfones with 1 mol% $CuSO_4 \cdot 5H_2O$ and 1 mol% TBAC followed by oxidation. Purification by column chromatography (PE/EA = 10:1–2, column size 254 × 17 mm) yielded a total of 43.1 mg (0.18 mmol, 89%) of product as a colorless oily liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.98 – 7.86 (m, 2H), 7.73 – 7.64 (m, 1H), 7.63 – 7.54 (m, 2H), 4.24 (tdt, *J* = 8.7, 4.6, 2.2 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.25 – 3.10 (m, 2H), 1.74 (ddq, *J* = 13.1, 8.6, 6.6 Hz, 1H), 1.51 (ddd, *J* = 14.6, 8.8, 5.7 Hz, 1H), 1.16 (ddd, *J* = 13.4, 8.4, 4.7 Hz, 1H), 0.85 (dd, *J* = 13.1, 6.6 Hz, 6H).

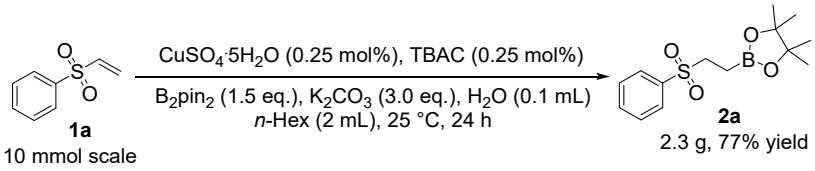
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 139.2, 134.0, 129.4, 127.8, 64.2, 62.6, 45.3, 24.1, 22.9, 21.8.

IR (thin film) ν_{max} (cm^{-1}): 3507, 3064, 1393, 1300, 1144, 1084, 1023, 843, 747, 689, 603, 542.

HRMS (ESI, Q-TOF) calcd for $C_{12}H_{18}NaO_3S^+$ [M+Na$^+$]: 265.0869, found 265.0864.

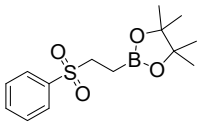
Scale-up Reaction & Derivatization

Gram-scale Reaction



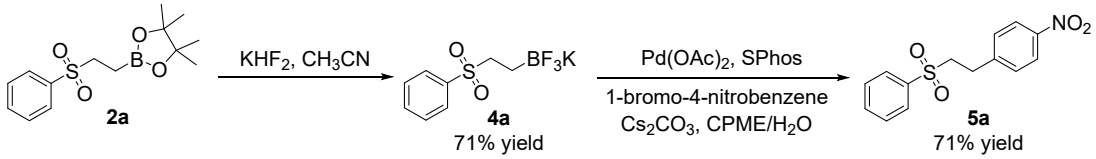
To a 250 mL round-bottom flask were added 4.1 g K_2CO_3 (30.0 mmol, 3.0 equiv.), 3.8 g B_2pin_2 (15.0 mmol, 1.5 equiv.), 6.2 mg $CuSO_4·5H_2O$ (0.25 mol%), and 7.0 mg TBAC (0.25 mol%), followed by the addition of 100 mL *n*-Hex and 5 mL H_2O. stirring firstly for 1 min. The mixture was stirred at 25 °C for 1 min, before 10.0 mmol **1a** (1.0 equiv.) was added. Next, the reaction was allowed to stir at 25 °C for 24 h. After the reaction was finished, the resulting mixture was quenched with 50 mL saturated brine. The aqueous phase was extracted twice with 100 mL EA. The combined organic phases were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The residual was further purified by column chromatography to give the desired *β*-sulfonylboronate **2a** (2.3 g, 7.7 mmol, 77% yield).

4,4,5,5-tetramethyl-2-(2-(phenylsulfonyl)ethyl)-1,3,2-dioxaborolane 2a



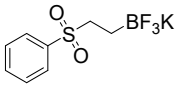
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 7.94 – 7.84 (m, 2H), 7.67 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 3.21 – 3.11 (m, 2H), 1.21 (s, 12H), 1.17 (d, *J* = 8.3 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 138.60, 133.50, 129.14, 128.29, 83.84, 51.98, 24.73. (Due to quadrupolar relaxation, the carbon attached to the boron atom was not detected.)
IR (thin film) ν_{max} (cm^{-1}): 3618, 3060, 2935, 1371, 1315, 1273, 1145, 1088, 1023, 967, 916, 882, 845, 793, 736, 692, 624, 536.
HRMS (ESI, Q-TOF) calcd for $C_{14}H_{21}BNaO_4S^+$ [M+Na$^+$]: 319.1146, found 319.1149.

Derivatization: Suzuki-Miyaura Cross-Coupling



4a and **5a** were synthesized with a modified procedure according to the literatures.[3] 59.2 mg *β*-sulfonylboronate **2a** (0.2 mmol, 1.0 equiv.) was dissolved in 1 mL MeCN, followed by dropwise addition of 0.2 mL saturated aqueous solution of KHF_2 (1.02 mmol, 5.1 equiv.). The mixture was stirred at room temperature for 3 h, then concentrated and azeotroped with MeOH. The residual was placed under vacuum for 3 h, and recrystallized with hot acetone and Et_2O. The resulting precipitate was collected and dried under vacuum to give the desired potassium trifluoroborate **4a** as a white solid (39.2 mg, 0.14 mmol, 71% yield).

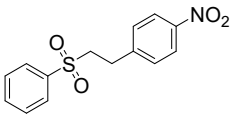
difluoro(2-(phenylsulfonyl)ethyl)borane potassium fluoride 4a



^{1}H NMR (400 MHz, D_2O) δ_H (ppm) 7.88 (ddd, *J* = 8.6, 4.0, 1.4 Hz, 2H), 7.80 – 7.71 (m, 1H), 7.69 – 7.60 (m, 2H), 3.29 – 3.07 (m, 2H), 0.78 – 0.22 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, D_2O) δ_C (ppm) 139.2, 136.9, 132.1, 132.0, 130.4, 130.2, 55.8.
IR (thin film) ν_{max} (cm^{-1}): 1259, 1211, 1142, 1054, 971, 853, 791, 754, 686, 578, 521.
HRMS (ESI, Q-TOF) calcd for $C_8H_9BF_3O_2S^-$ [M^-]: 237.0374, found 237.0372.

To a 10 mL Schlenk tube were added 4.5 mg $Pd(OAc)_2$ (0.02 mmol, 10 mol%), 16.4 mg SPhos (0.04 mmol, 20 mol%), 40.4 mg 1-bromo-4-nitrobenzene (0.2 mmol, 1.0 equiv.), 66.3 mg **4a** (0.24 mmol, 1.2 equiv.), and 195.5 mg Cs_2CO_3 (0.6 mmol, 3.0 equiv.). The reaction vessel was purged with N_2 for three times, followed by the addition of 1 mL CPME and 140 μL H_2O. The reaction mixture was stirred at room temperature for 10 min and then heated to 95 °C for 20 h with vigorous stirring. When finished, the reaction was cooled to room temperature and quenched with 1 mL H_2O. After extraction with 10 mL EA for 4 times, the combined organic phases were washed with brine, dried over Na_2SO_4 anhydrous, and concentrated. The residual was further purified by column chromatography (PE/EA=10:1-3, column size 254 × 17 mm) to give the desired arylated sulfone **5a** as a yellow solid (41.4 mg, 0.14 mmol, 71% yield).

nitro-4-(2-(phenylsulfonyl)ethyl)benzene 5a



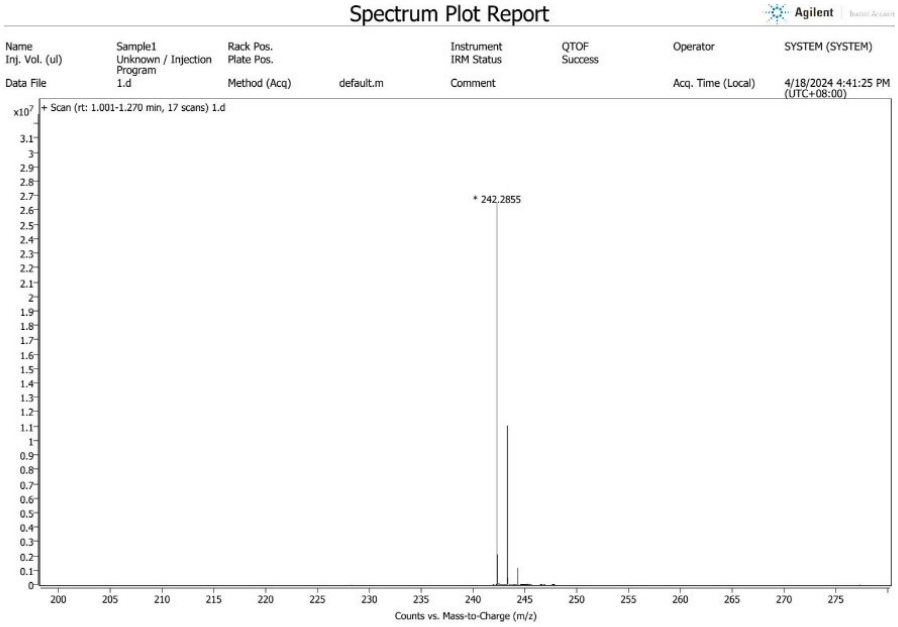
^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm) 8.19 – 8.06 (m, 2H), 7.93 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.74 – 7.64 (m, 1H), 7.58 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.34 – 7.28 (m, 2H), 3.45 – 3.33 (m, 2H), 3.25 – 3.13 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ_C (ppm) 147.0, 145.0, 138.7, 134.1, 129.5, 129.3, 128.1, 124.0, 56.6, 28.5.
IR (thin film) ν_{max} (cm^{-1}): 2289, 1742, 1511, 1341, 1294, 1143, 1084, 849, 746, 687, 535.
HRMS (ESI, Q-TOF) calcd for $C_{14}H_{13}NNaO_4S^+$ [M+Na^+]: 314.0457, found 314.0454.

Mechanistic Investigations

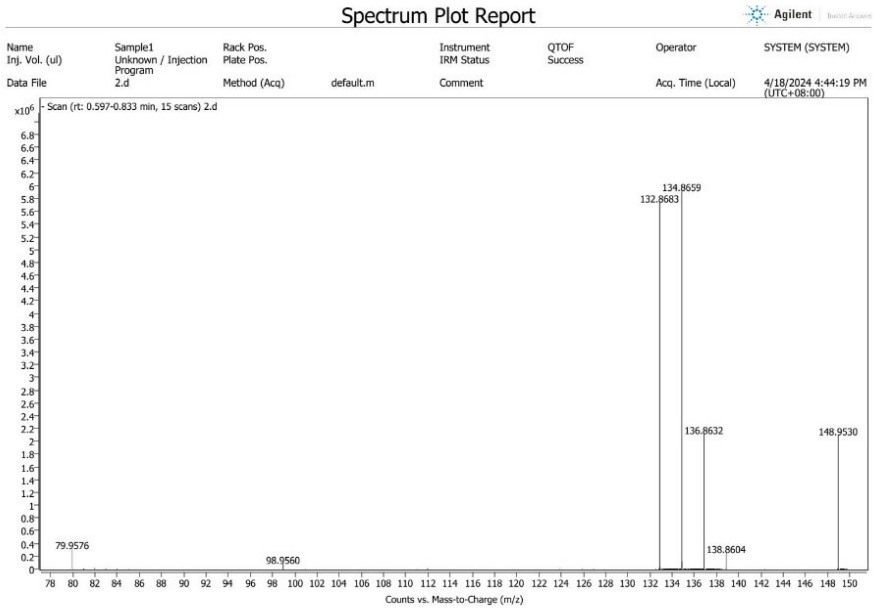
Synthesis of TBA($CuCl_2$) complex

To a 50 mL dry Schlenk flask were added 99.0 mg CuCl (1.0 mmol, 1.0 equiv.) and 278.0 mg TBAC (1.0 equiv.). The reaction vessel was purged with N_2 for three times, followed by the addition of freshly-distilled 20 mL DCM. The solution was stirred overnight at room temperature until the copper salt was completely dissolved. The mixture was later concentrated under vacuum without further purification to give 325.6 mg TBA($CuCl_2$) (0.86 mmol, 86% yield) as a greenish yellow solid.

1) **HRMS** (ESI$^+$, Q-TOF) calcd for TBA^+ [M^+]: 242.2842, found 242.2855.



2) **HRMS** (ESI$^-$, Q-TOF) calcd for ($^{63}Cu^{35}Cl_2$)$^-$ [M^-]: 132.8678, found 132.8683.



Detection of Intermediates in the Reaction

Sample I:

To a 4 mL vial were added 82.9 mg K_2CO_3 (0.6 mmol, 3.0 equiv.), 76.2 mg B_2pin_2 (0.3 mmol, 1.5 equiv.), 5.0 mg $CuSO_4 \cdot 5H_2O$ (0.02 mmol, 10 mol%), and 5.6 mg TBAC (0.02 mmol, 10 mol%), followed by the addition of 2 mL *n*-hexane and 0.1 mL H_2O. The resulting mixture was stirred at 25 °C for 1 h. Then HRMS analysis of the above organic phase was performed.

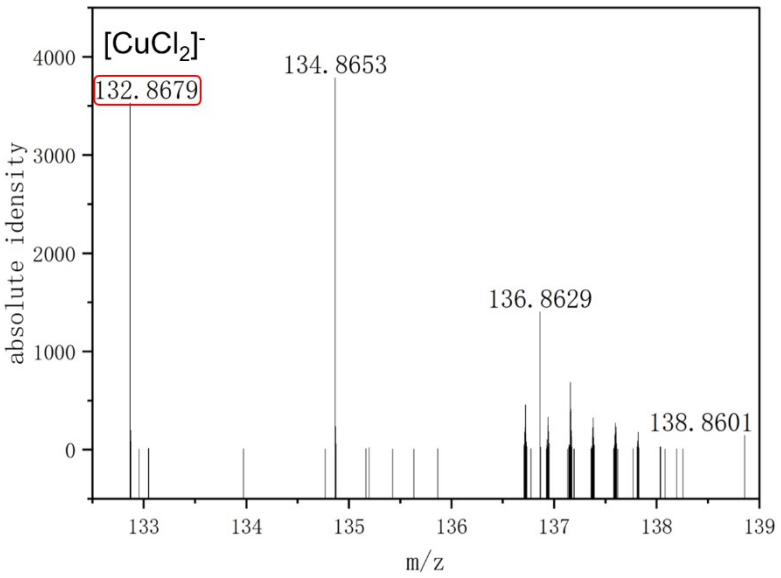
sample I:

$CuSO_4 \cdot 5H_2O$/TBAC (10 mol%)
B_2pin_2 (1.5 eq.), K_2CO_3 (3.0 eq.)
H_2O (0.1 mL), *n*-hexane (2 mL)
25 °C, 1 h, in the absence of **1a**

HRMS analysis detected:

Cl–Cu⁻–Cl

m/z calcd. for $[^{63}Cu^{35}Cl_2]^-$: 132.8678
found: 132.8679



Sample II:

To a 4 mL vial were added 82.9 mg K_2CO_3 (0.6 mmol, 3.0 equiv.), 76.2 mg B_2pin_2 (0.3 mmol, 1.5 equiv.), and 75.4 mg TBA($CuCl_2$) (0.2 mmol, 1.0 equiv.), followed by the addition of 2 mL *n*-hexane and 0.1 mL H_2O. The resulting mixture was stirred at 25 °C for 19 h. Then HRMS analysis of the above organic phase was performed.

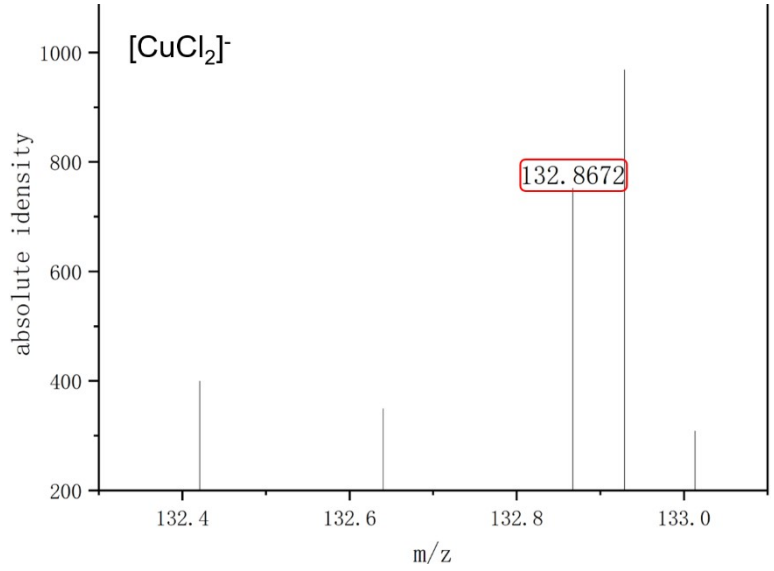
sample II:

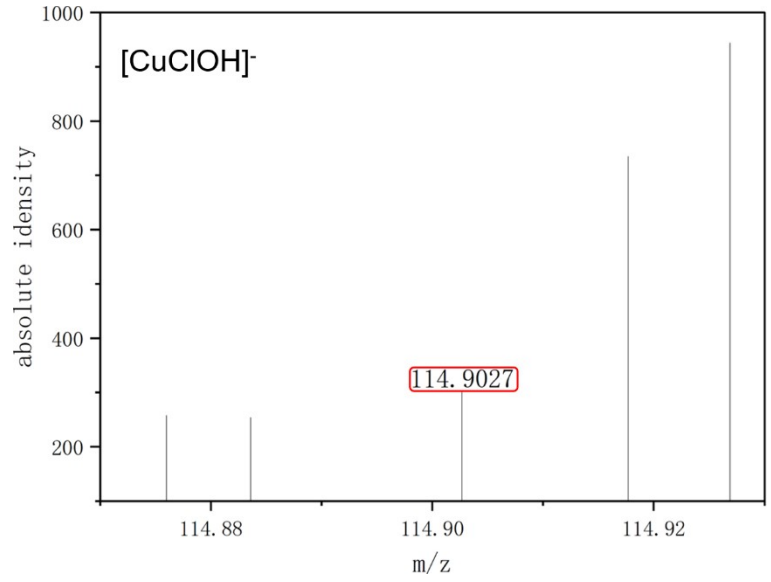
TBA($CuCl_2$) (1.0 eq.)
B_2pin_2 (1.5 eq.), K_2CO_3 (3.0 eq.)
H_2O (0.1 mL), *n*-Hex (2 mL)
25 °C, 19 h, in the absence of **1a**

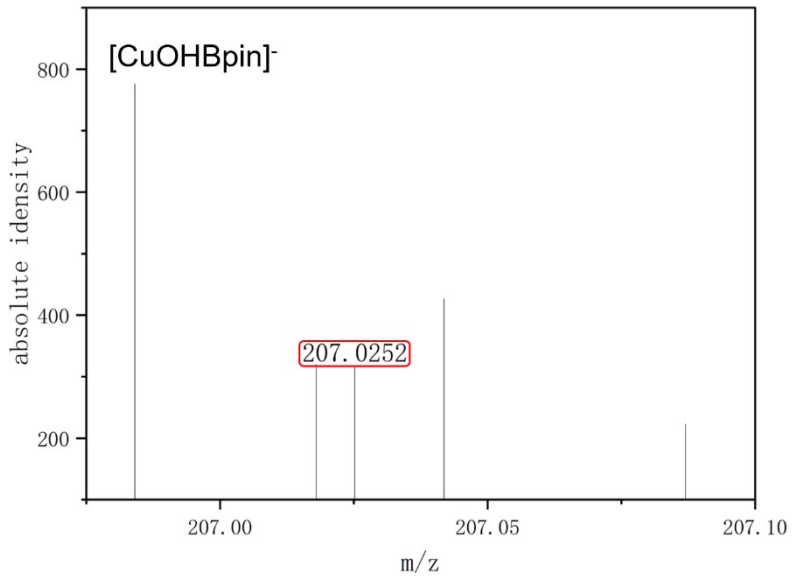
HRMS analysis detected:

Cl–Cu⁻–Cl Cl–Cu⁻–OH HO–Cu⁻–Bpin

m/z calcd. for $[^{63}Cu^{35}Cl_2]^-$: 132.8678
found: 132.8672
calcd. for $[^{63}Cu^{35}Cl(OH)]^-$: 114.9017
found: 114.9027
calcd. for $[^{63}Cu(OH)Bpin]^-$: 207.0259
found: 207.0252

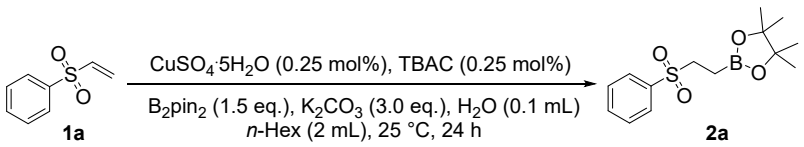

[CuCl2]-
absolute idensity
1000
800
600
400
200
132.8672
132.4
132.6
132.8
133.0
m/z


[CuClOH]-
absolute idensity
1000
800
600
400
200
114.9027
114.88
114.90
114.92
m/z


[CuOHBpin]-
absolute idensity
800
600
400
200
207.0252
207.00
207.05
207.10
m/z

Control Experiments

Table S2 Control experiments of borylation with varied reaction conditions[a]



1a **2a**

Entry	Variation from Standard Condition	Yield (%)[b]
1	without H_2O[c]	<5
2	without K_2CO_3	15
3	with 2 equiv. TEMPO	39
4	with 2 equiv. BHT	75
5	with 1 equiv. NaCl (s)	49
6	TBA($CuCl_2$) complex as catalyst	88
7	with 0.1 mL MeOH as proton source instead	none[d]

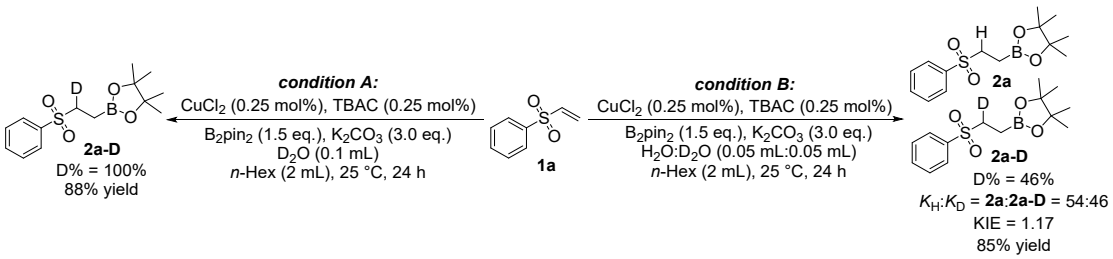
[a] Reagents and conditions: **1a** (0.2 mmol), B_2pin_2 (0.3 mmol), $CuSO_4 \cdot 5H_2O$ (0.5 μmol), TBAC (0.5 μmol), K_2CO_3 (0.6 mmol), H_2O (0.1 mL), *n*-Hex (2 mL), 25 °C, 24 h, air.

[b] Calibrated GC yields of **2a** using biphenyl as an internal standard.

[c] $CuSO_4$ anhydrous was also used.

[d] Almost fully conversion of **1a** and B_2pin_2 were observed. The product of MeO^- conjugate addition was isolated.

Deuterium Labeling Experiments



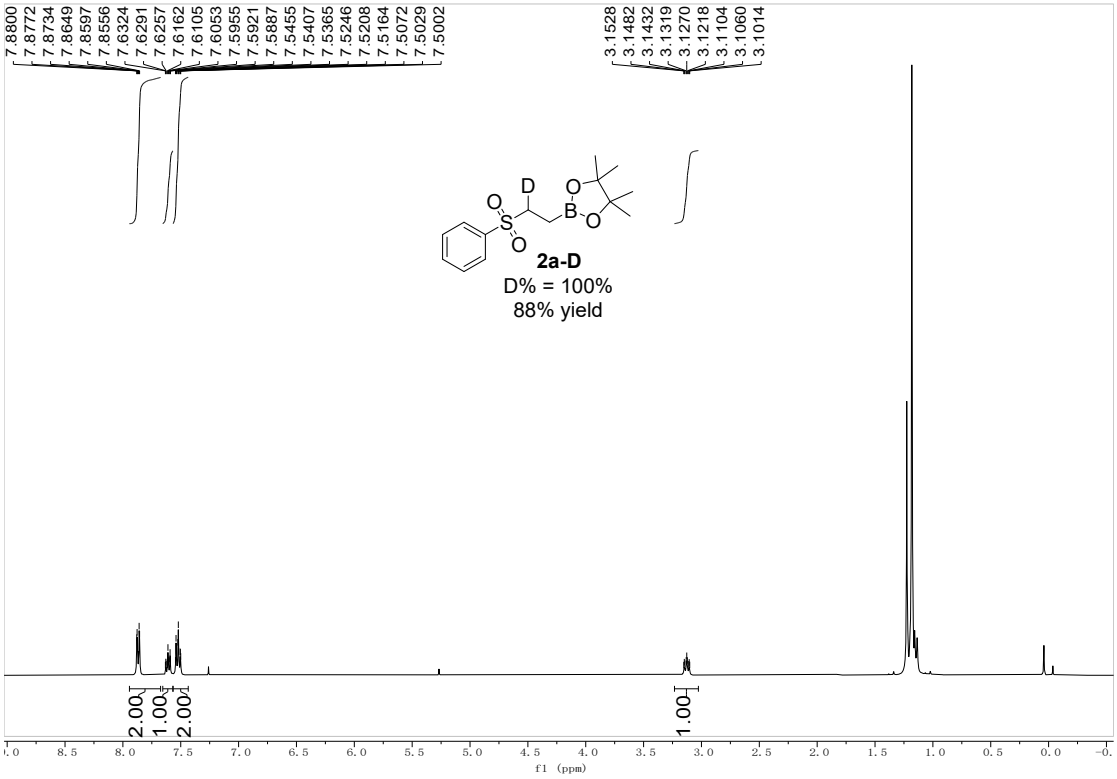
Condition A: To a 4 mL vial were added 82.9 mg K_2CO_3 (0.6 mmol, 3.0 equiv.) and 76.2 mg B_2pin_2 (0.3 mmol, 1.5 equiv.), followed by quick addition of 2 mL *n*-hexane and 0.1 mL D_2O. Then 10 μL solution of $CuSO_4·5H_2O$ (0.125 mg, 0.25 mol%) in D_2O and 10 μL solution of TBAC (0.14 mg, 0.25 mol%) in D_2O were added in sequence. The mixture was stirred at 25 °C for 1 min, before 33.6 mg **1a** (0.2 mmol, 1.0 equiv.) was added. Next, the reaction was allowed to stir at 25 °C for 24 h.

Condition B: To a 4 mL vial were added 82.9 mg K_2CO_3 (0.6 mmol, 3.0 equiv.) and 76.2 mg B_2pin_2 (0.3 mmol, 1.5 equiv.), followed by quick addition of 2 mL *n*-hexane, 0.05 mL H_2O, and 0.05 mL D_2O. Then 10 μL solution of $CuSO_4·5H_2O$ (0.125 mg, 0.25 mol%, D_2O:H_2O = 1:1) and 10 μL solution of TBAC (0.14 mg, 0.25 mol%, D_2O:H_2O = 1:1) were added in sequence. The mixture was stirred at 25 °C for 1 min, before 33.6 mg **1a** (0.2 mmol, 1.0 equiv.) was added. Next, the reaction was allowed to stir at 25 °C for 24 h.

For both **Condition A** and **Condition B**, when the reaction was finished, the resulting mixture was later quenched with 1 mL saturated brine, while the aqueous phase was extracted twice with 2 mL EA. The combined organic phases were dried over Na_2SO_4 anhydrous, filtered, and concentrated. The position of deuterium atom on **2a-D** and deuteration rate were determined by ^{1}H NMR. According to the results of borylation under **Condition B**, the KIE value (K_H:K_D) is 1.17, which indicates that the protonation is not the rate-determine step.

The yields of borylation product were acquired by further oxidization to its corresponding alcohol and purification by column chromatography, 88% and 85%, respectively. As the boronate was oxidized under the basic condition where the *α*-D would be replaced, the KIE value were not determined with **3a-D**.

a) **Condition A**



b) **Condition B**

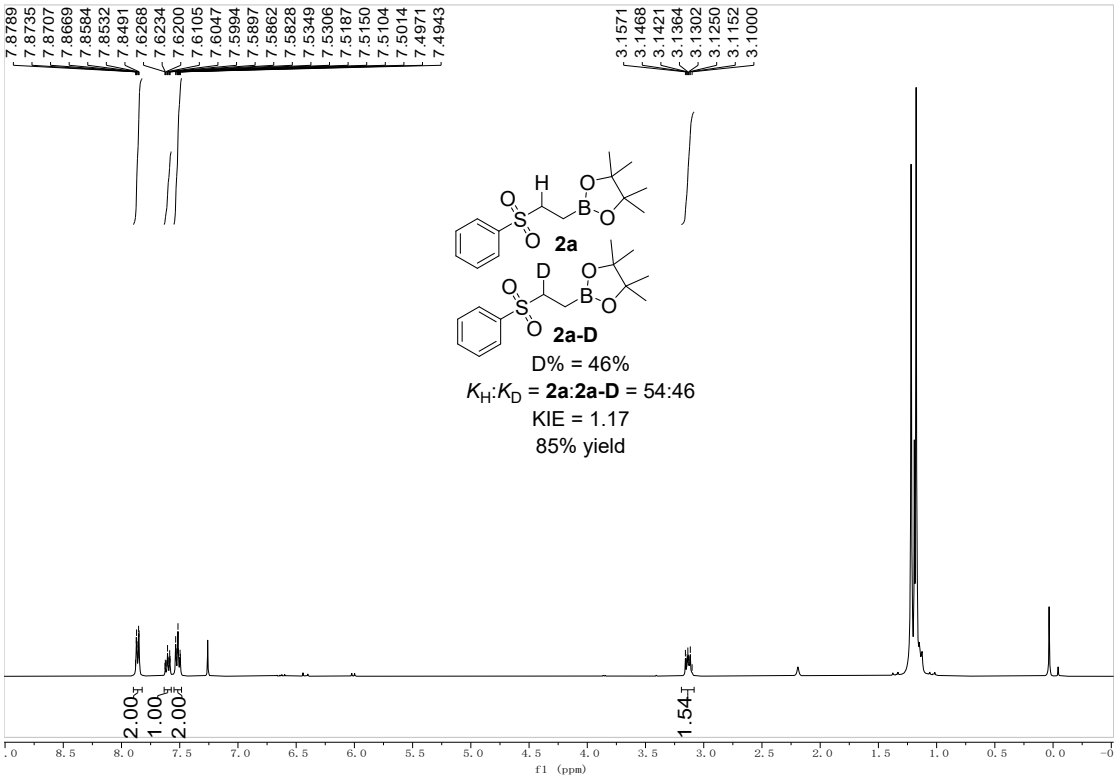
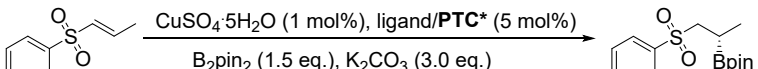
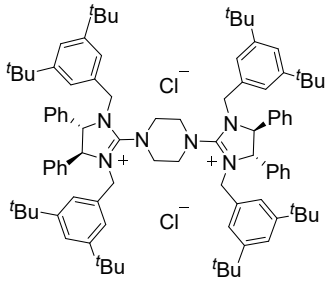


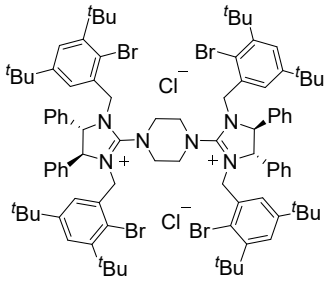
Figure S1 ^{1}H NMR spectra of protoborylation reaction mixtures in deuterium labelling experiments: a) **Condition A**; b) **Condition B**.

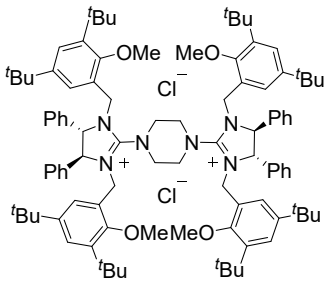
Enantioselective Conjugate Borylation of Vinyl Sulfone with Chiral Phosphine Ligands or Phase Transfer Catalysts

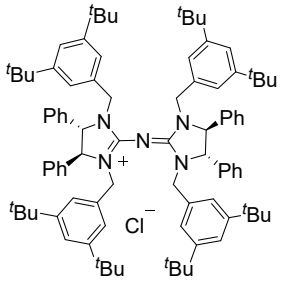
Table S3 Enantioselective conjugate borylation with chiral phosphine ligands or phase transfer catalysts[a]

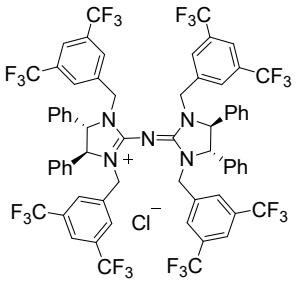


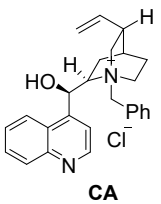

BG-1

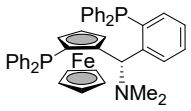

BG-2


BG-3


PN-1


PN-2


CA


(*S*,*S*)-Taniaphos


(*S*,*R*)-Josiphos

entry	ligand/**PTC***	solvent	yield (%)[b]	ee (%)[c]
1	**BG-1**	*n*-Hex	>99	8
2	**BG-1**	Tol	93	4
3	**BG-1**	DCM	>99	35
4	**BG-2**	DCM	>99	15
5	**BG-3**	DCM	85	13
6	**PN-1**	DCM	91	4
7	**PN-2**	DCM	71	15
8	**CA**	DCM	69	-12
9	(*S*,*S*)-Taniaphos	DCM	76	-9
10	(*S*,*S*)-Taniaphos	*n*-Hex	8	–
11	(*S*,*R*)-Josiphos	DCM	>99	-10
12	(*S*,*R*)-Josiphos	*n*-Hex	<5	–

[a] Reagents and conditions: **1aa** (0.2 mmol), B_2pin_2 (0.3 mmol), $CuSO_4 \cdot 5H_2O$ (2 μmol), **PTC*** (0.01 mmol), K_2CO_3 (0.6 mmol), H_2O (0.1 mL), solvent (2 mL), 25 °C, 24 h, air.

[b] GC yields via area normalization.

[c] Determined by HPLC of the corresponding alcohol on a chiral stationary phase.

Assignment of Stereochemistry

The absolute configuration of the major enantiomer in **3aa** was assigned as *S*, according to the results of HPLC analysis and literature.[4] Due to the established retention of configuration at the boron-bound stereocenters after oxidation of boronates, the absolute configuration of the major enantiomer in **2aa** was also determined as *S*.

References

[1] B. Niu, B. G. Blackburn, K. Sachidanandan, M. V. Cooke and S. Laulhe, *Green Chemistry*. **2021**, *23*, 9454–9459.

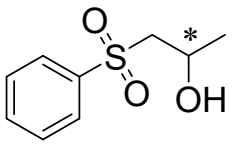
[2] P. Mauleon, I. Alonso, M. R. Rivero and J. C. Carretero, *Journal of Organic Chemistry*. **2007**, *72*, 9924-9935.

[3] J. He, H. Jiang, R. Takise, R. Y. Zhu, G. Chen, H. X. Dai, T. G. M. Dhar, J. Shi, H. Zhang, P. T. W. Cheng and J. Q. Yu, *Angewandte Chemie International Edition*. **2015**, *55*, 785–789.

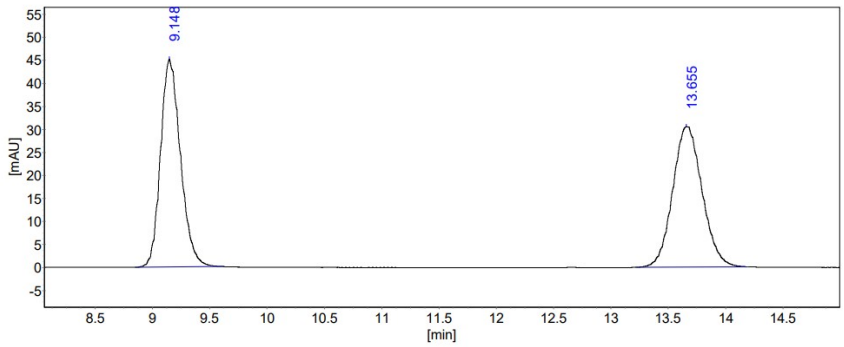
[4] A. L. Moure, R. G. Arrayas and J. C. Carretero, *Chem Commun (Camb)*. **2011**, *47*, 6701–6703.

HPLC traces

Column: CHIRALPAK® IA, 5 µm
Eluant: *n*-hexane:*i*-PrOH = 70:30
Flow Rate: 1.0 mL·min^{-1}
Λ = 254 nm
Retention Times: 9.2 min (*S*), 13.8 min (*R*)



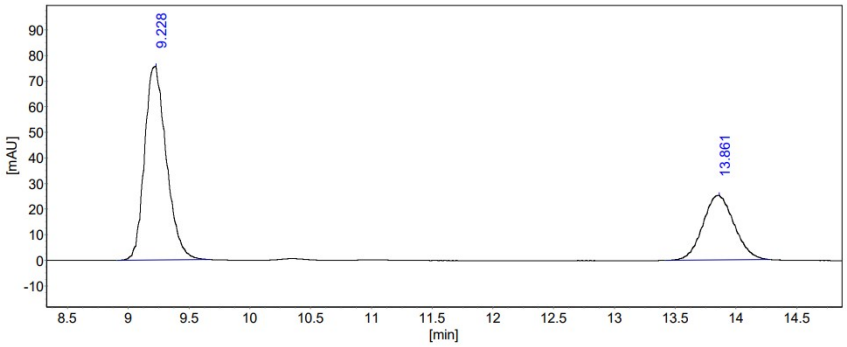
Racemic:



Analysis Results

No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		9.148	45217.6	545423.1	49.9942	49.9942	+ BB
2		13.655	30523.4	545548.9	50.0058	50.0058	+ BB
	Total:		**75741.0**	**1090972.1**	**100.0000**	**100.0000**	

Chiral: 35.2% ee

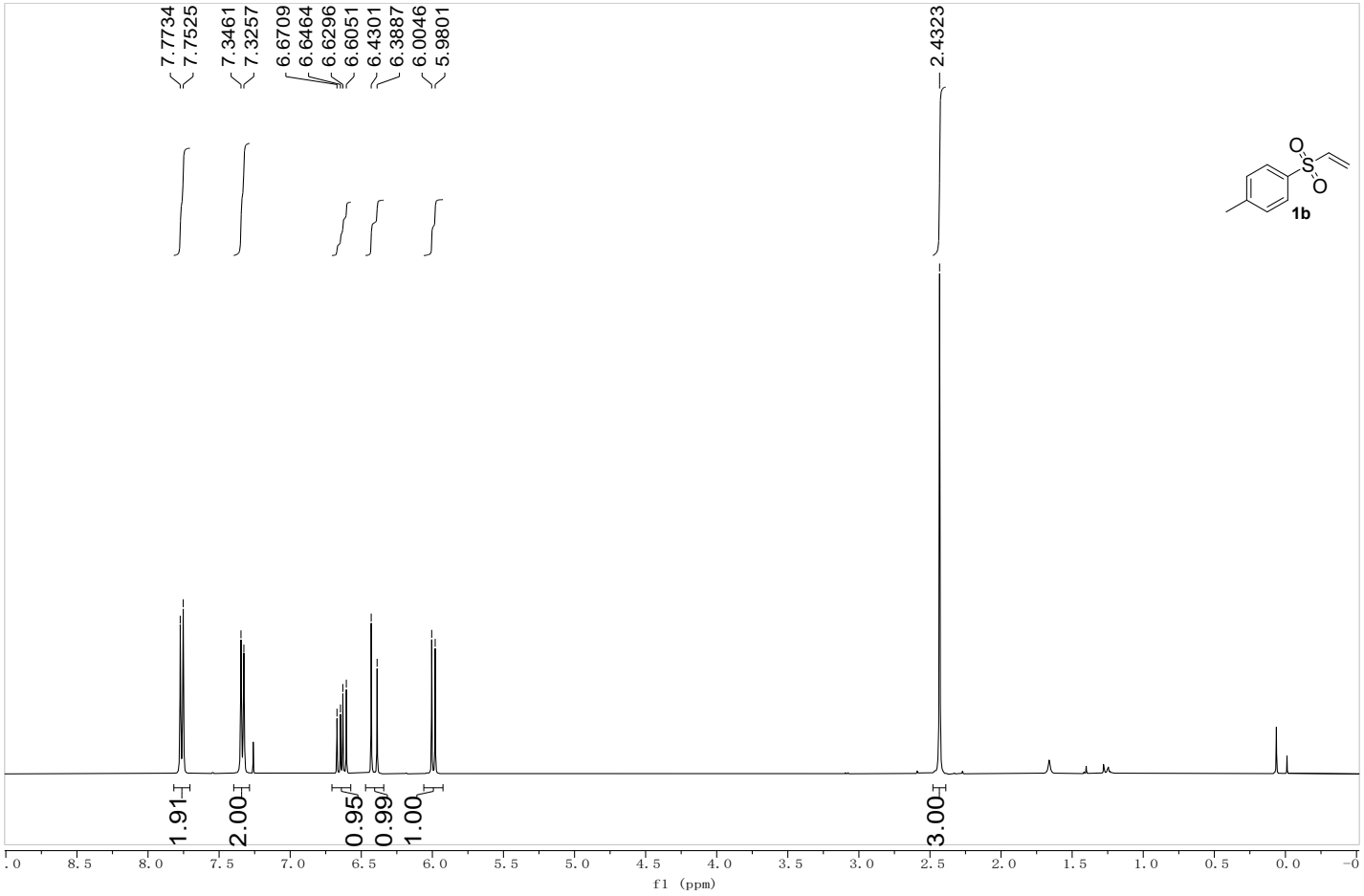


Analysis Results

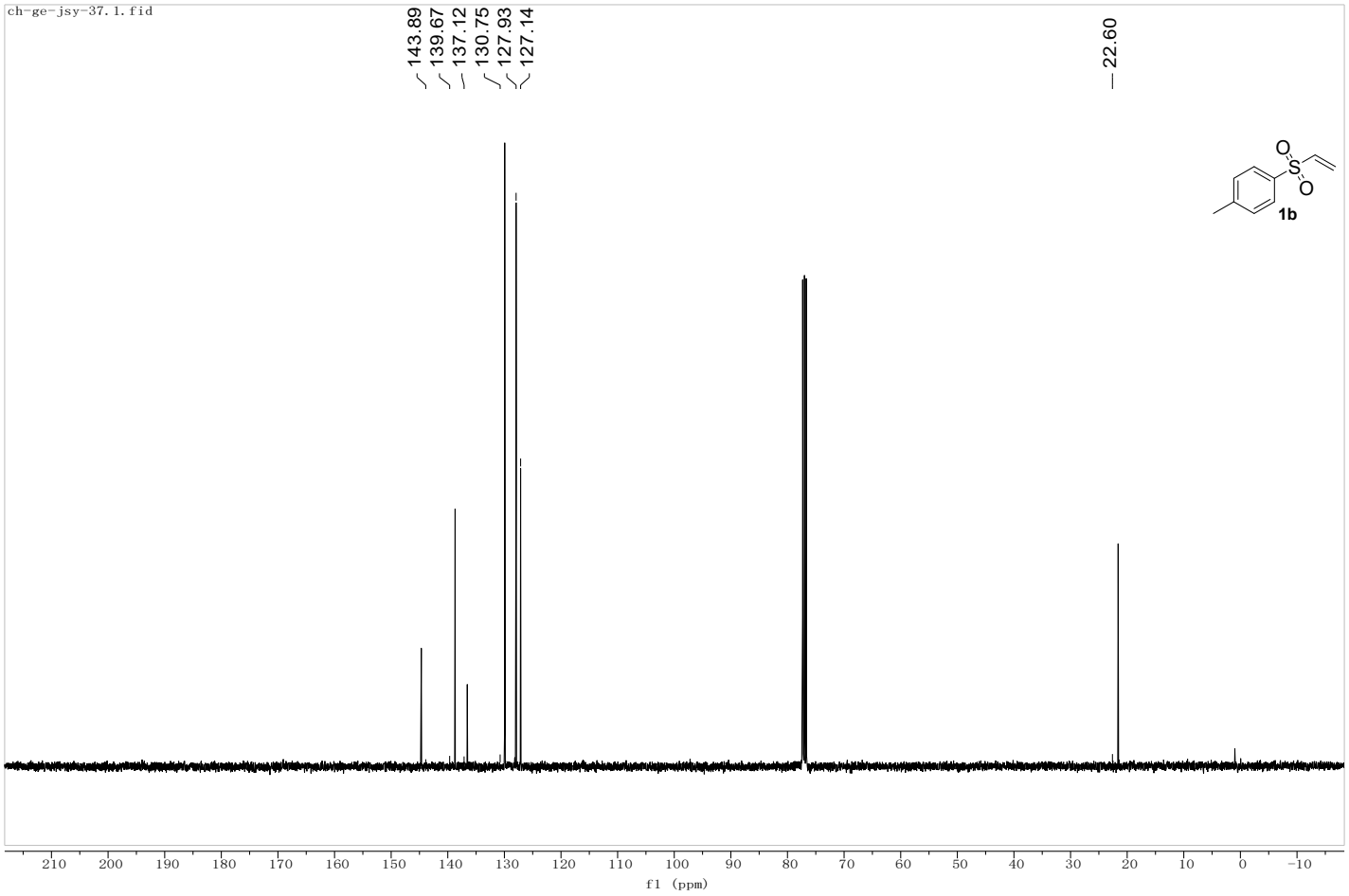
No.	Compound	R.Time	Height	Area	Area%	Conc.	Type
1		9.228	75729.0	944706.0	67.6016	67.6016	+ BB
2		13.861	25321.1	452755.5	32.3984	32.3984	+ BB
	Total:		**101050.1**	**1397461.5**	**100.0000**	**100.0000**	

NMR Spectra

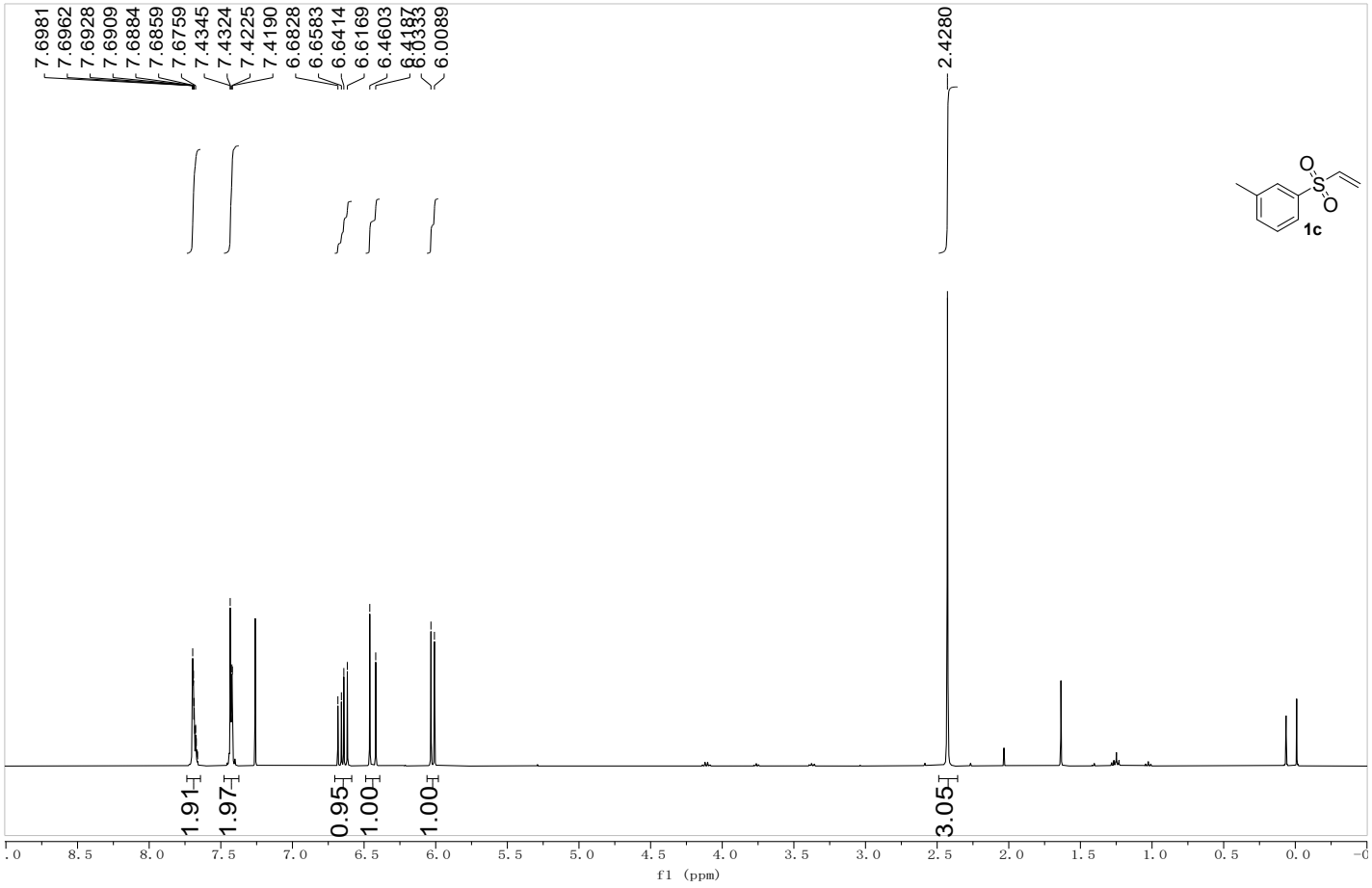
1b ^{1}H NMR (400 MHz, $CDCl_3$)



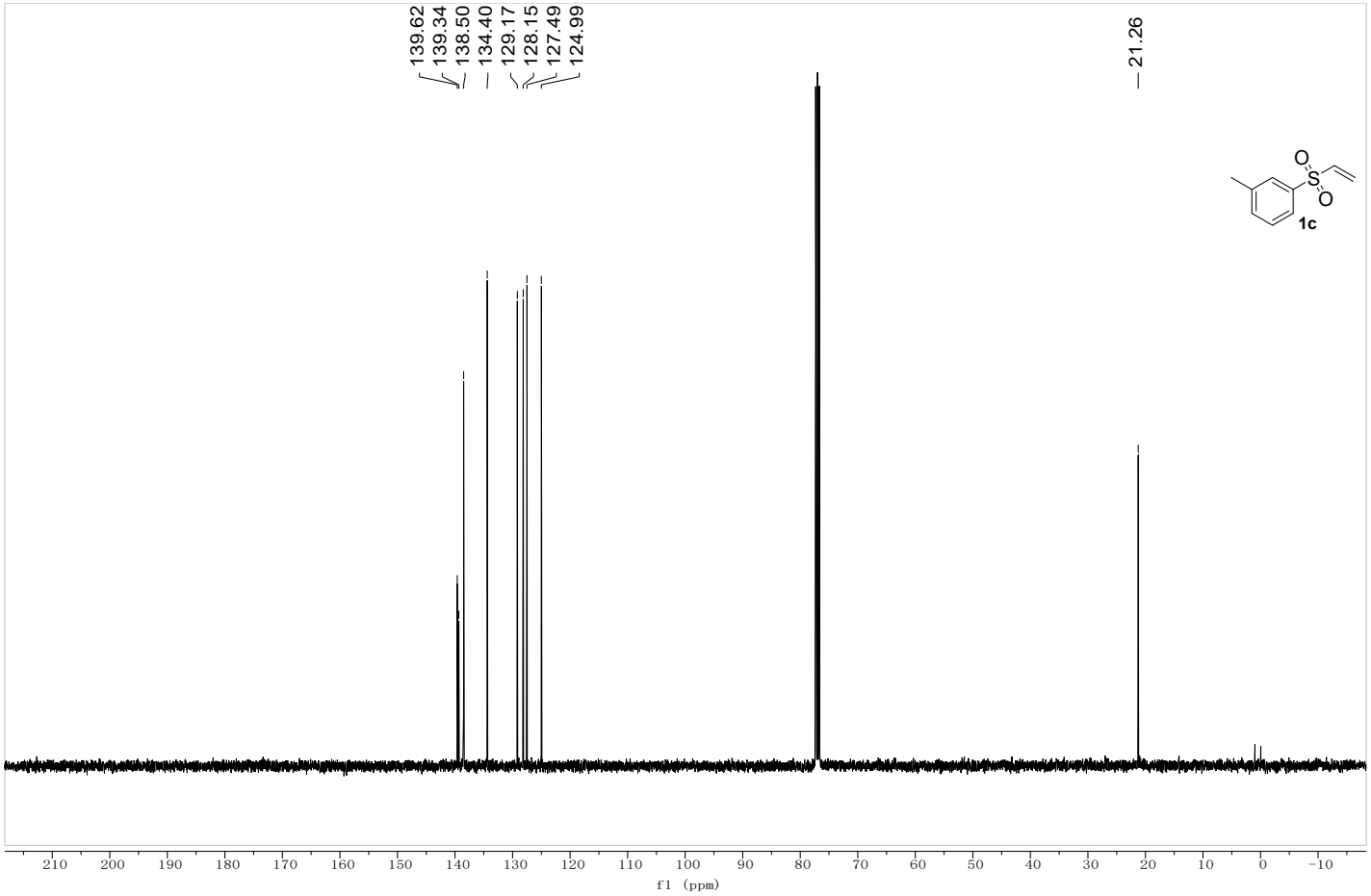
1b $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



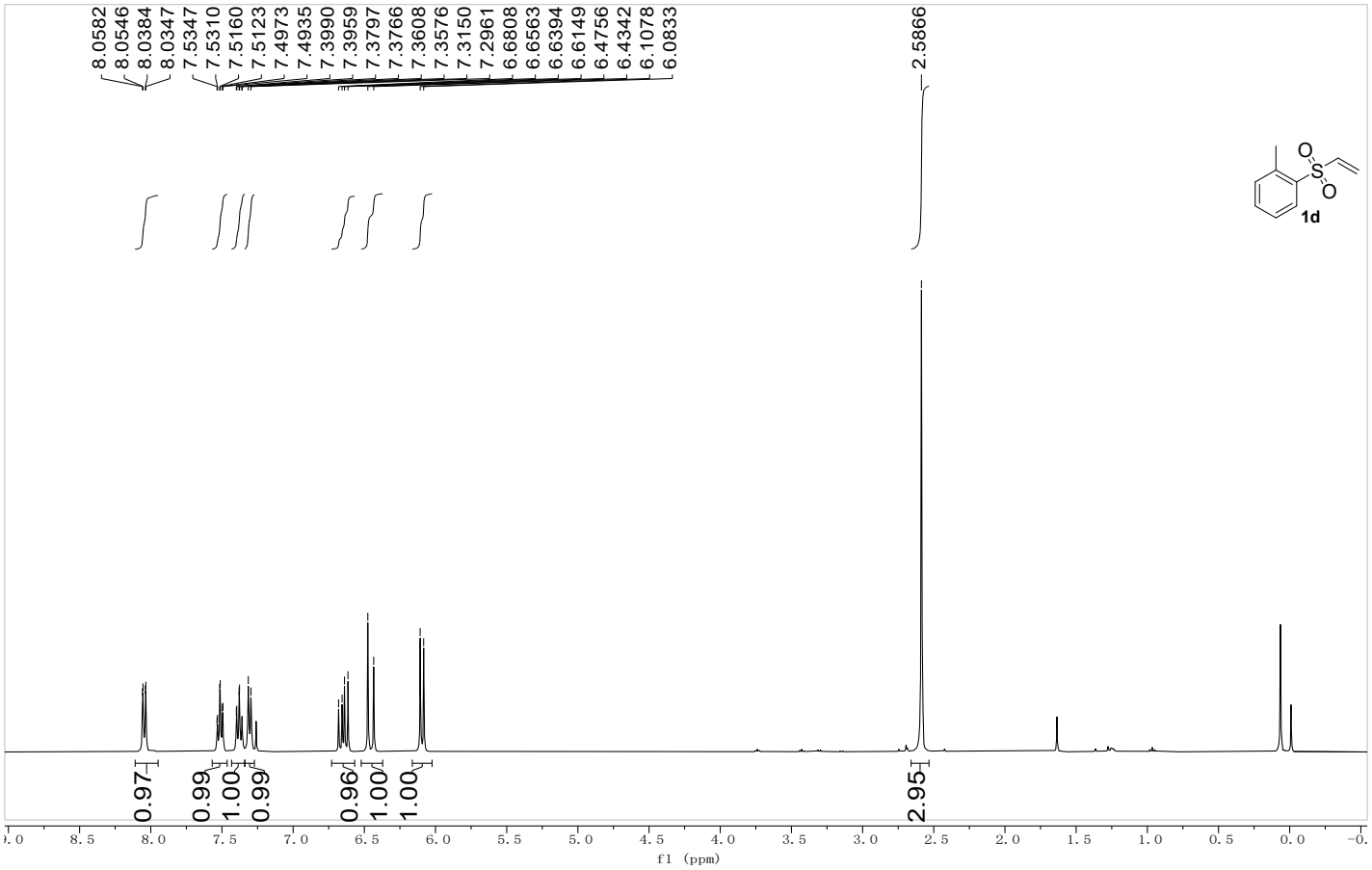
1c ^{1}H NMR (400 MHz, $CDCl_3$)



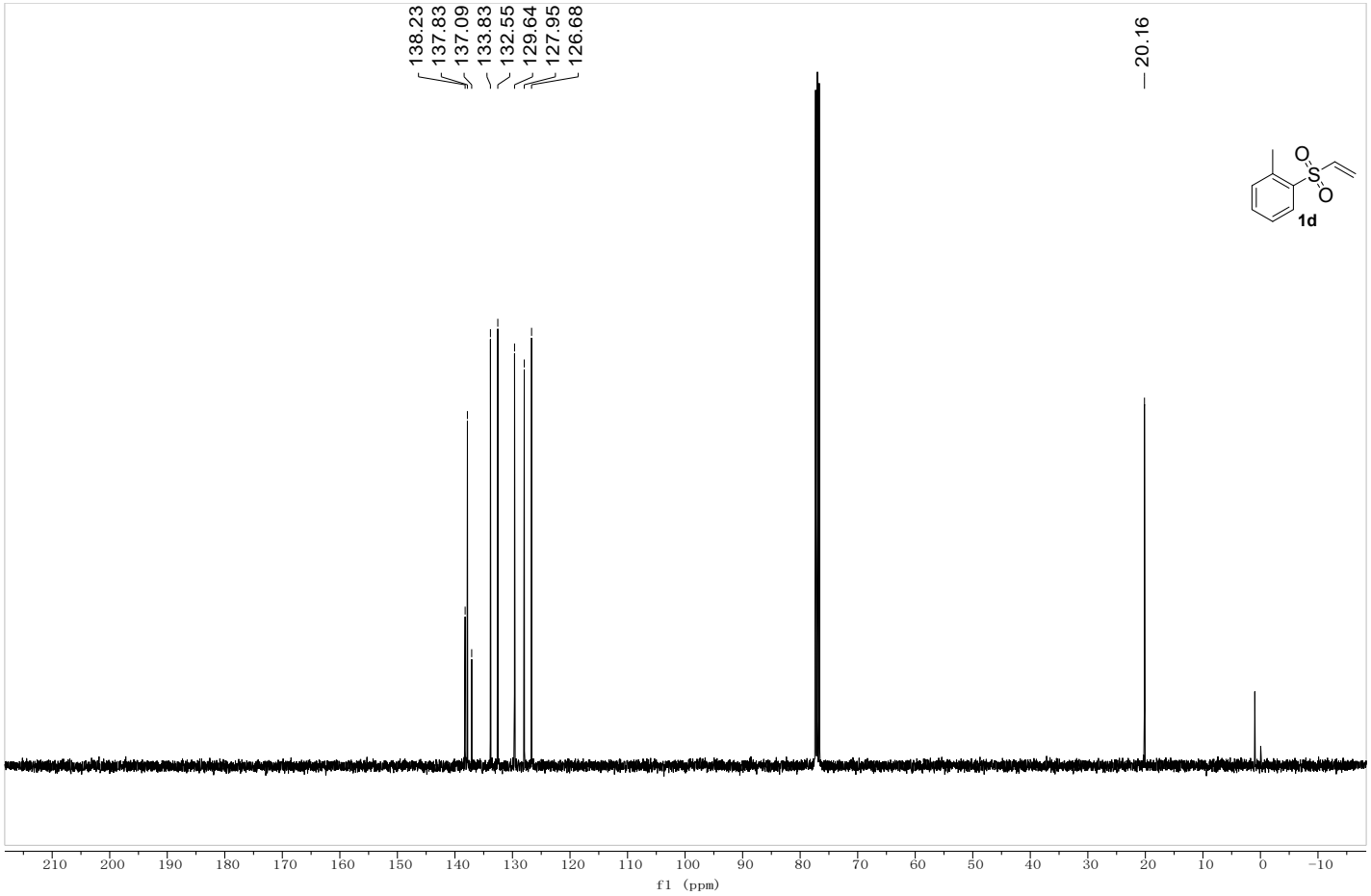
1c $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



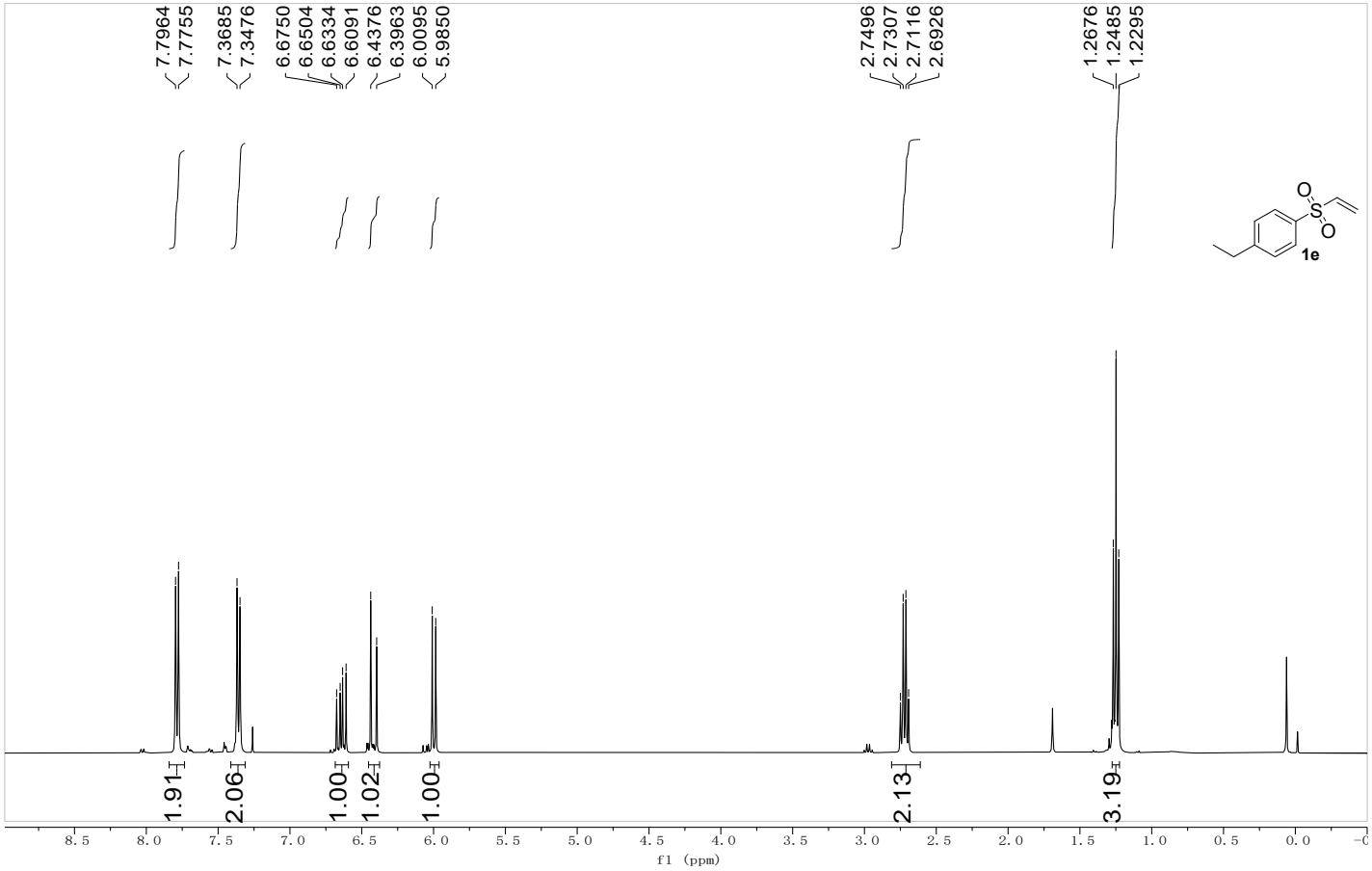
1d ^{1}H NMR (400 MHz, $CDCl_3$)



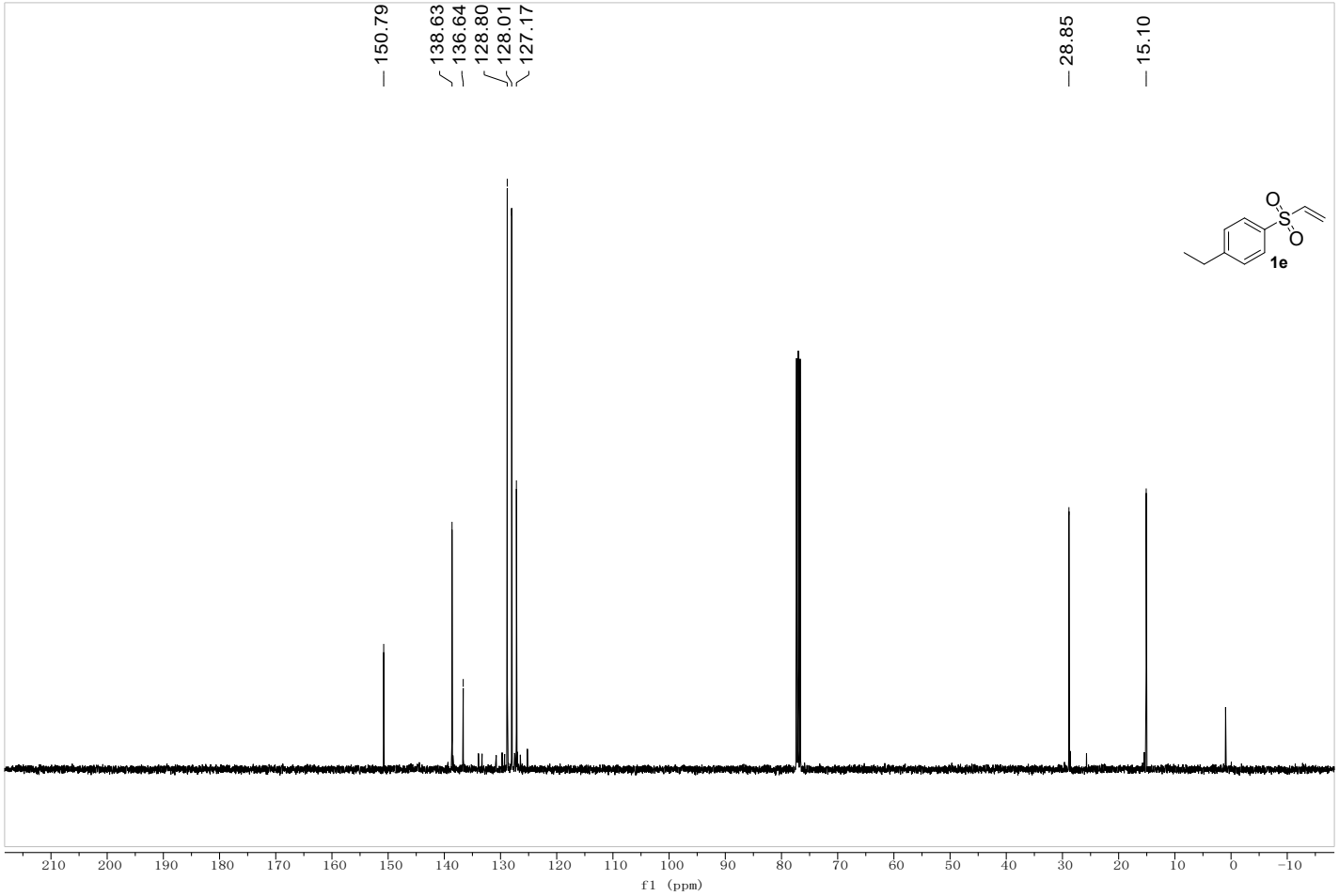
1d $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



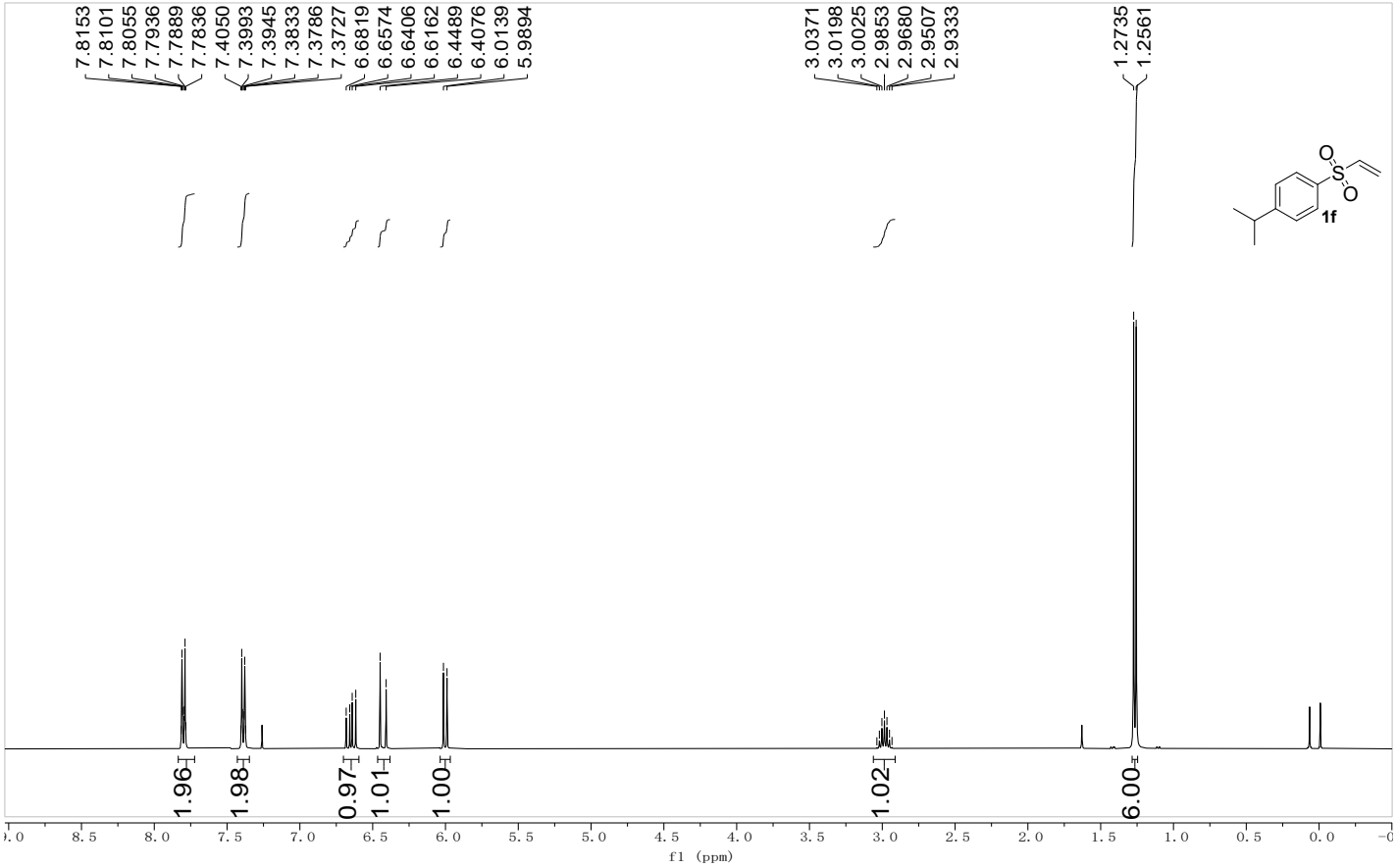
1e ^{1}H NMR (400 MHz, $CDCl_3$)



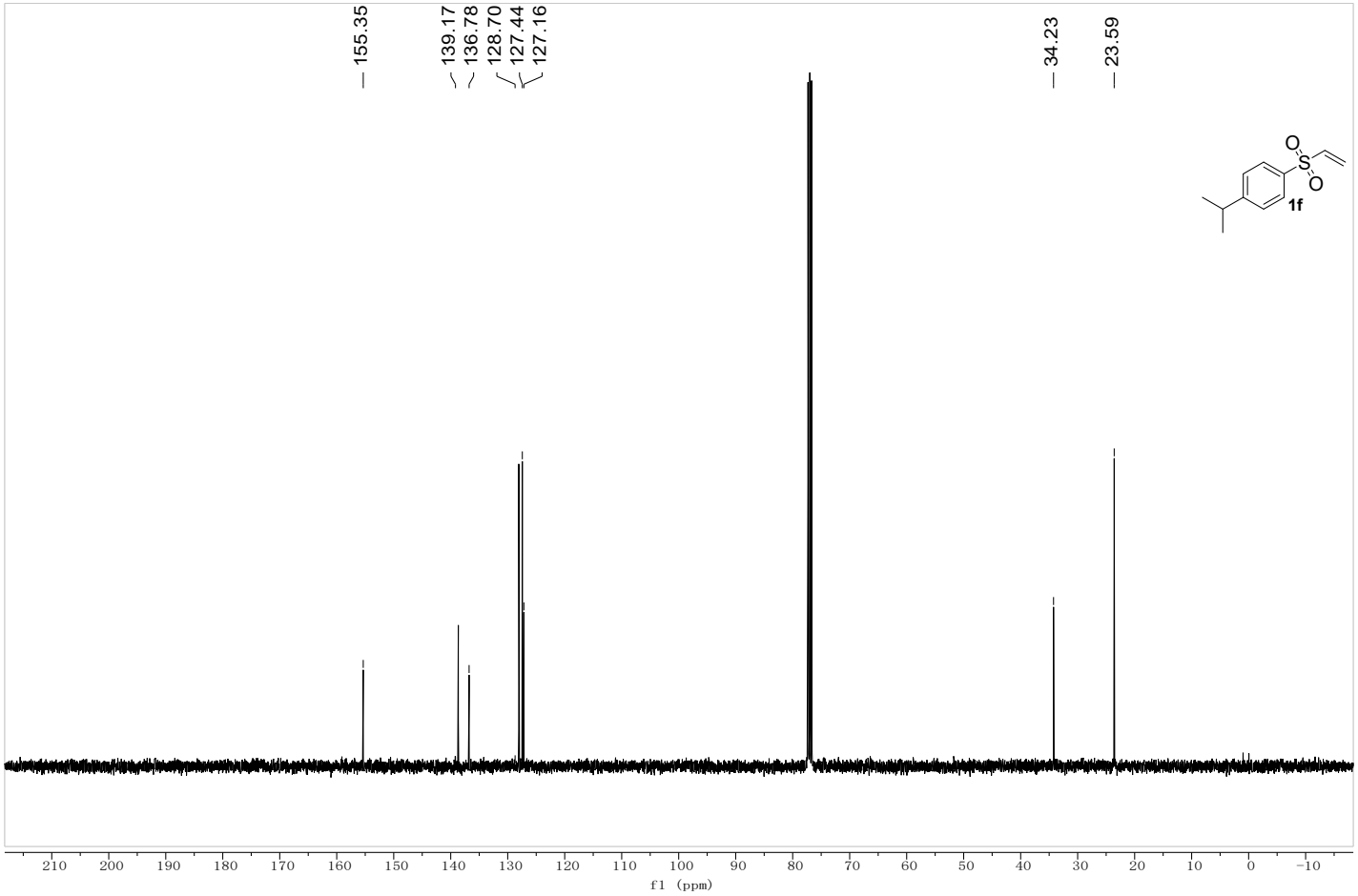
1e $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



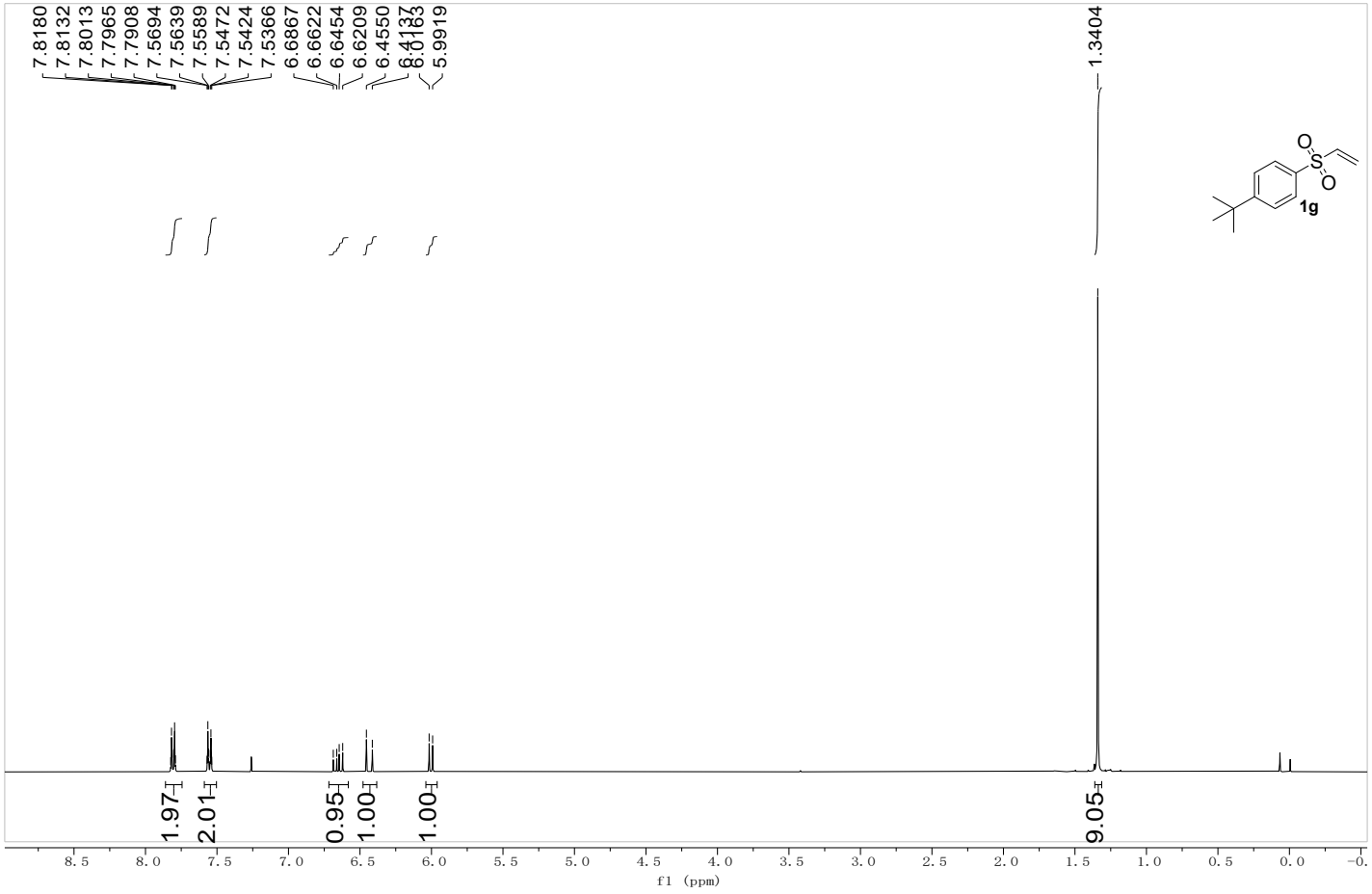
1f ^{1}H NMR (400 MHz, $CDCl_3$)



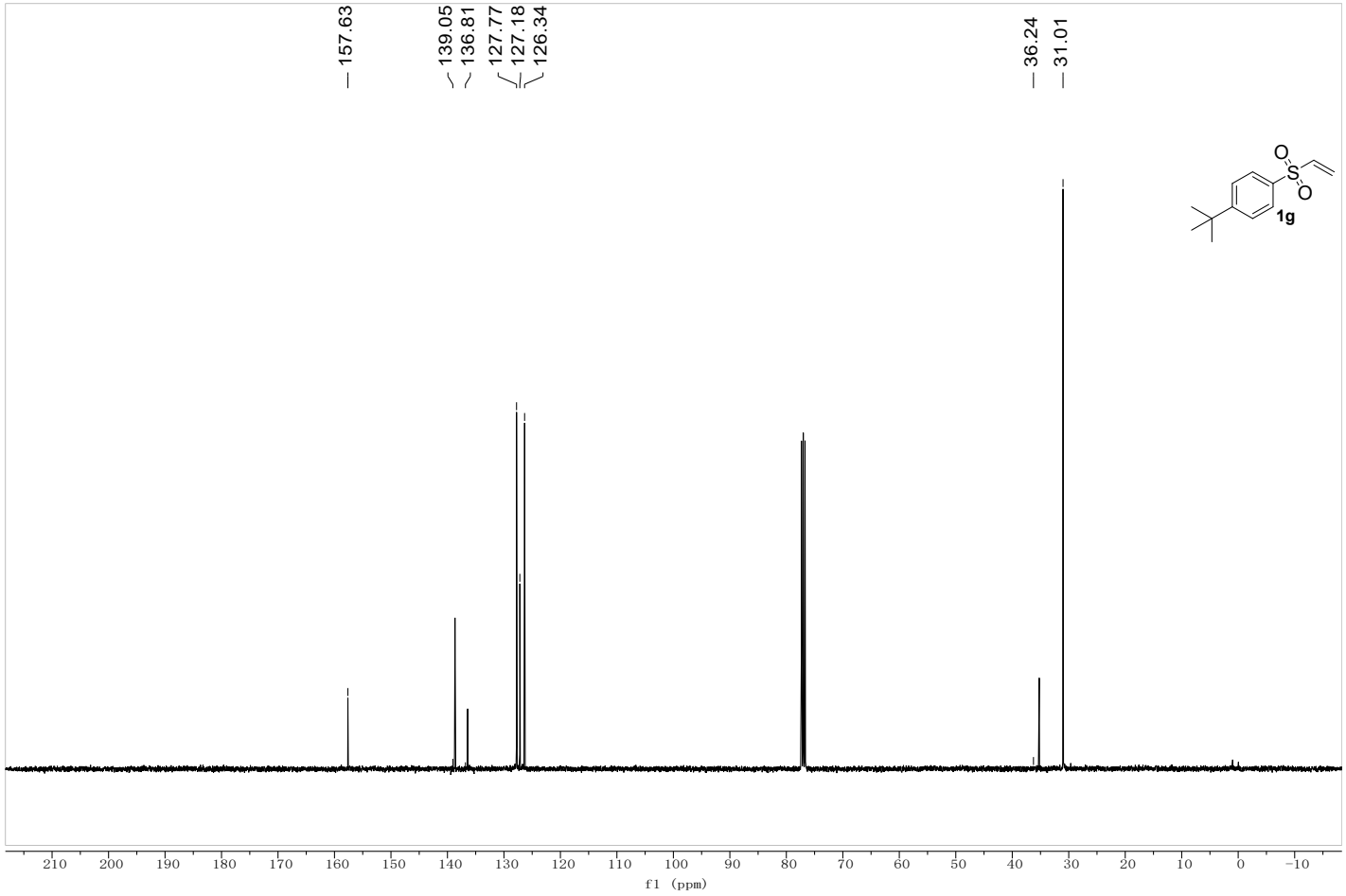
1f $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



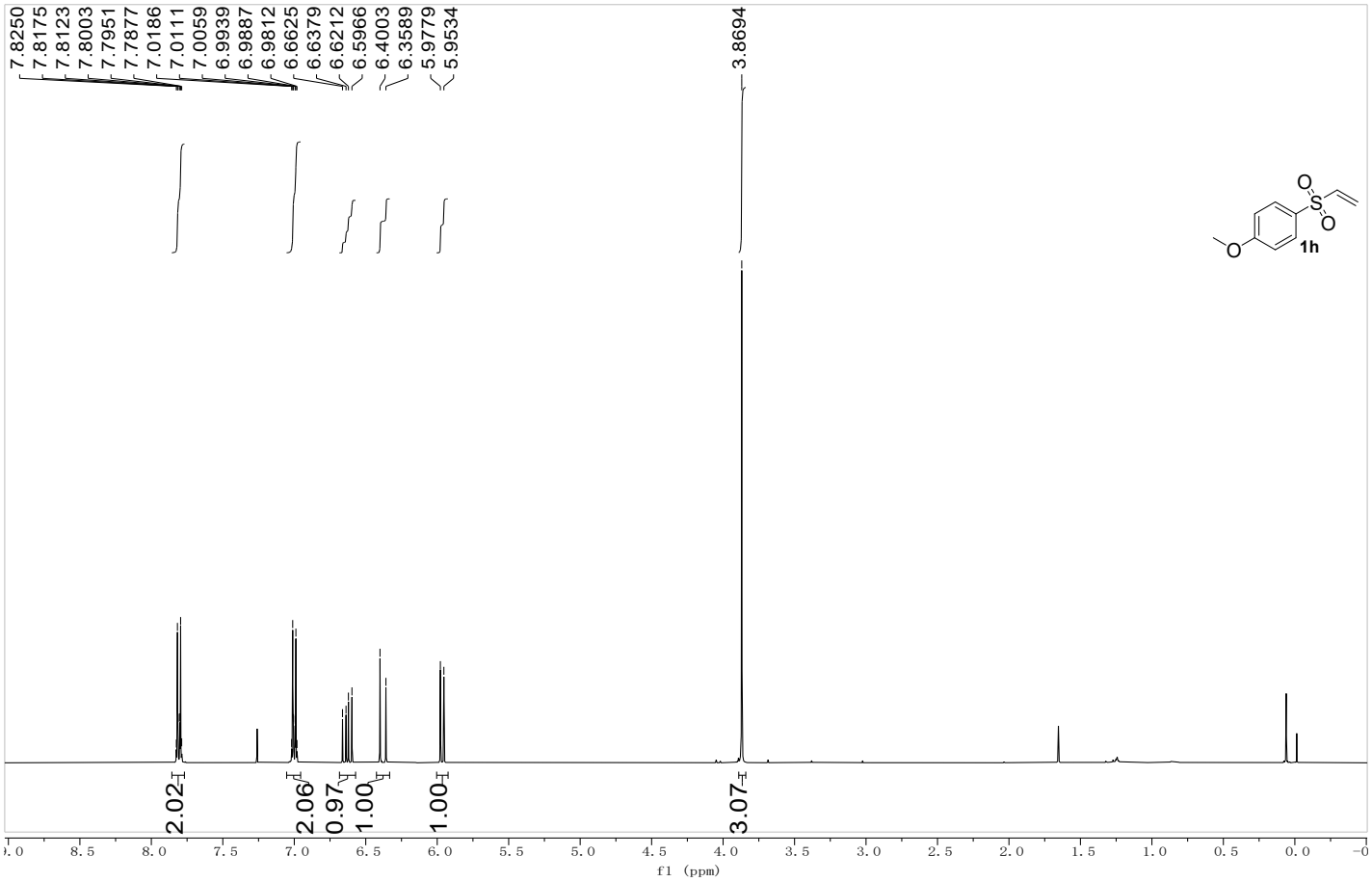
1g ^{1}H NMR (400 MHz, $CDCl_3$)



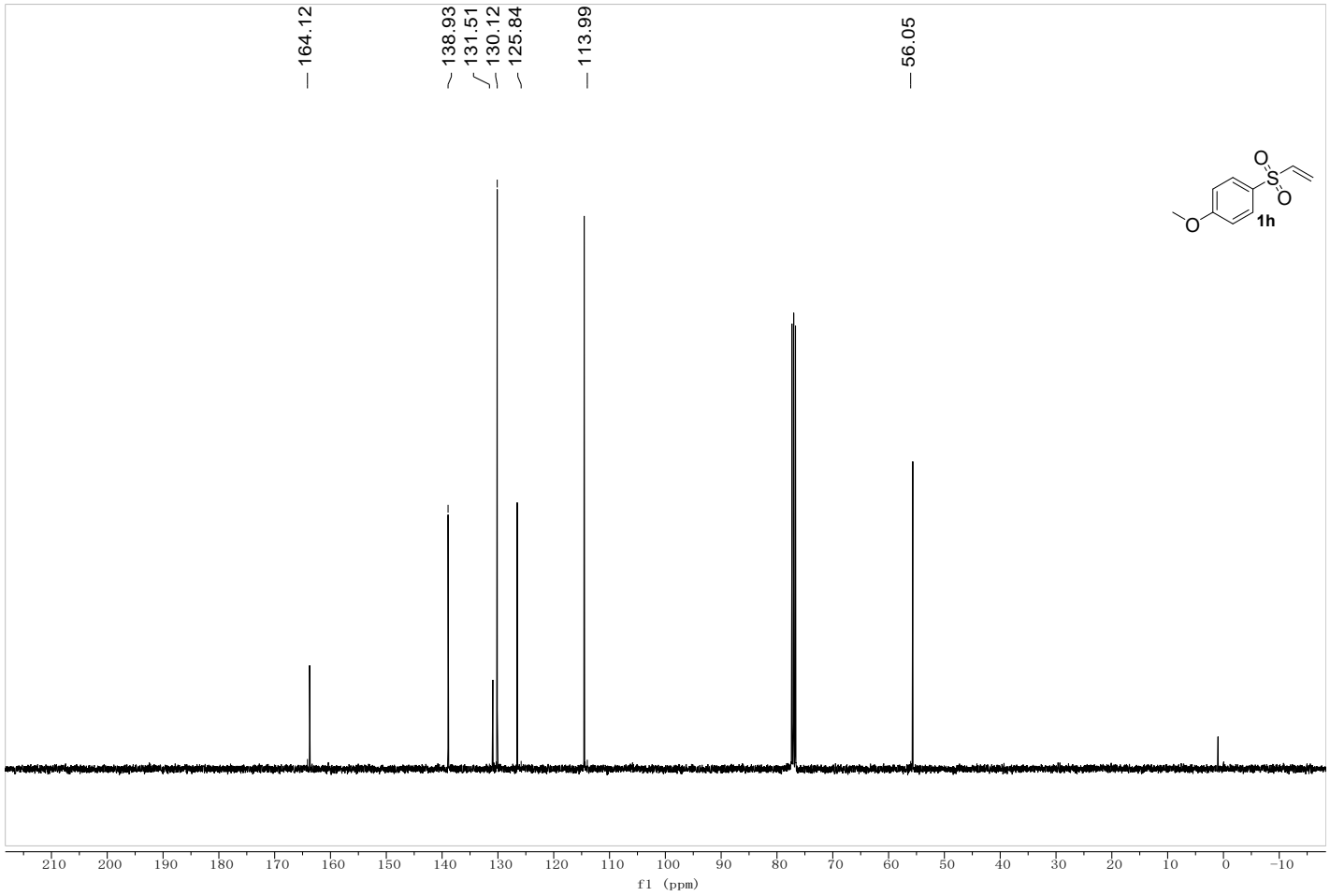
1g $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



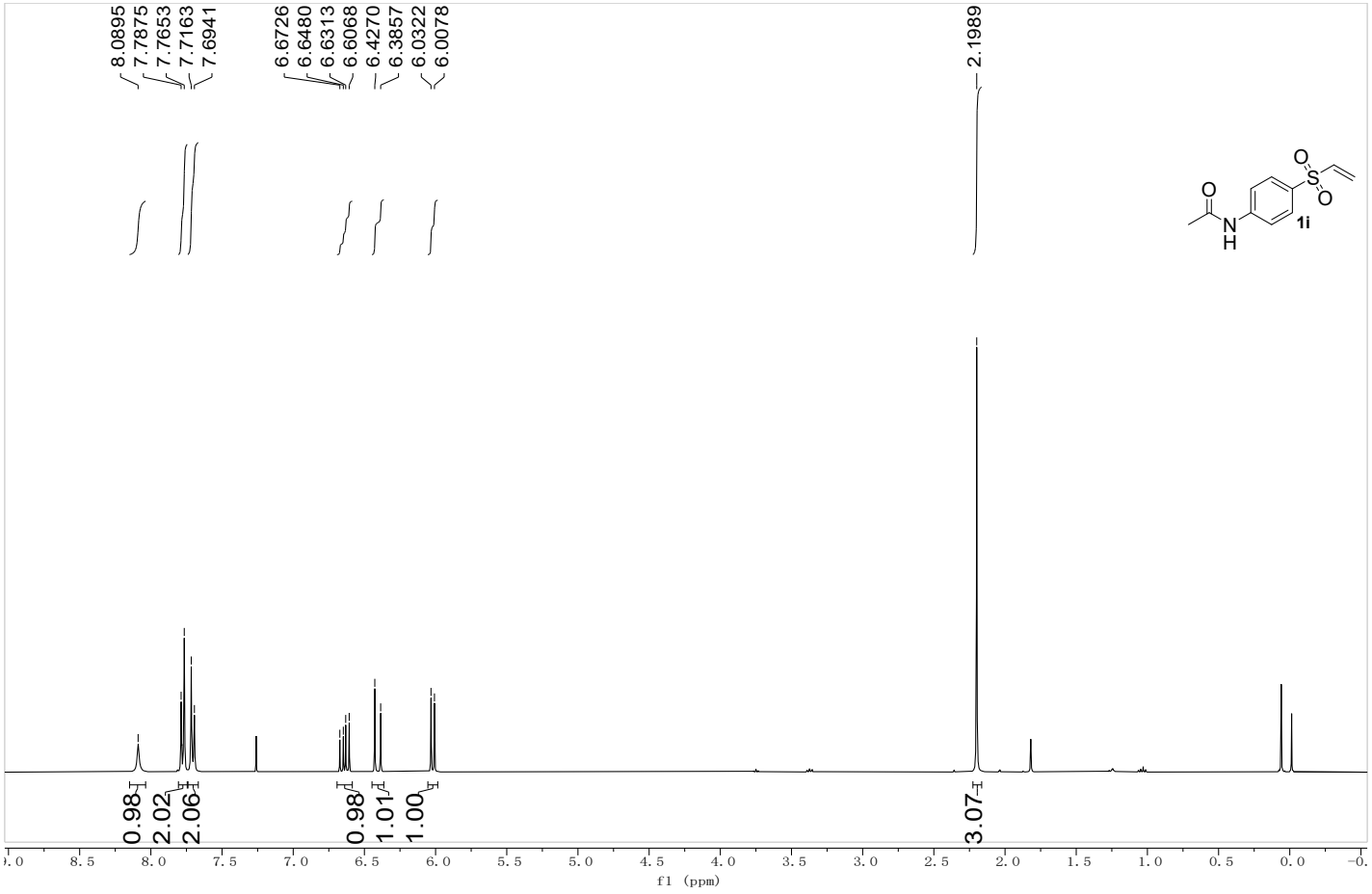
1h ^{1}H NMR (400 MHz, $CDCl_3$)



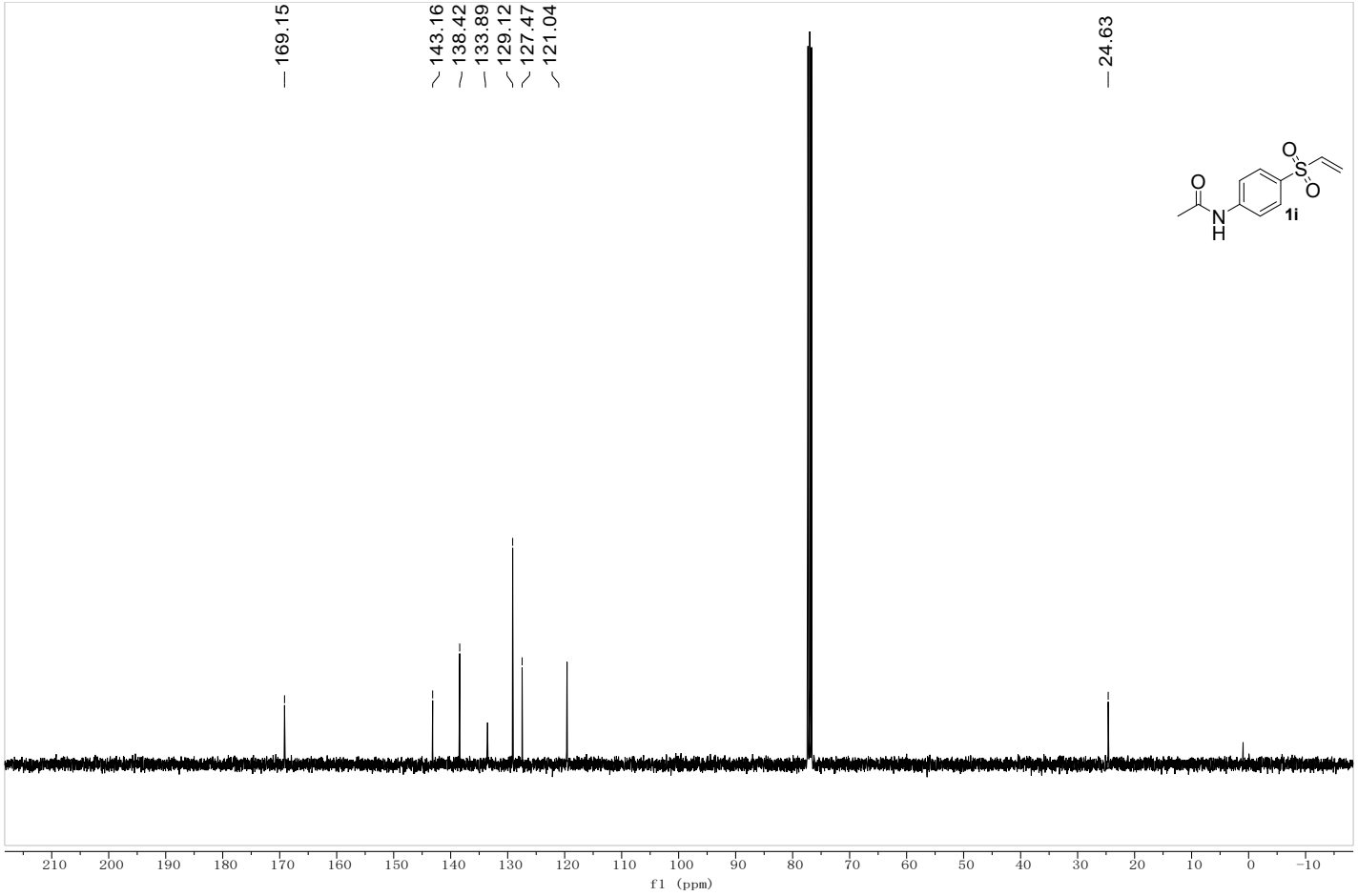
1h $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



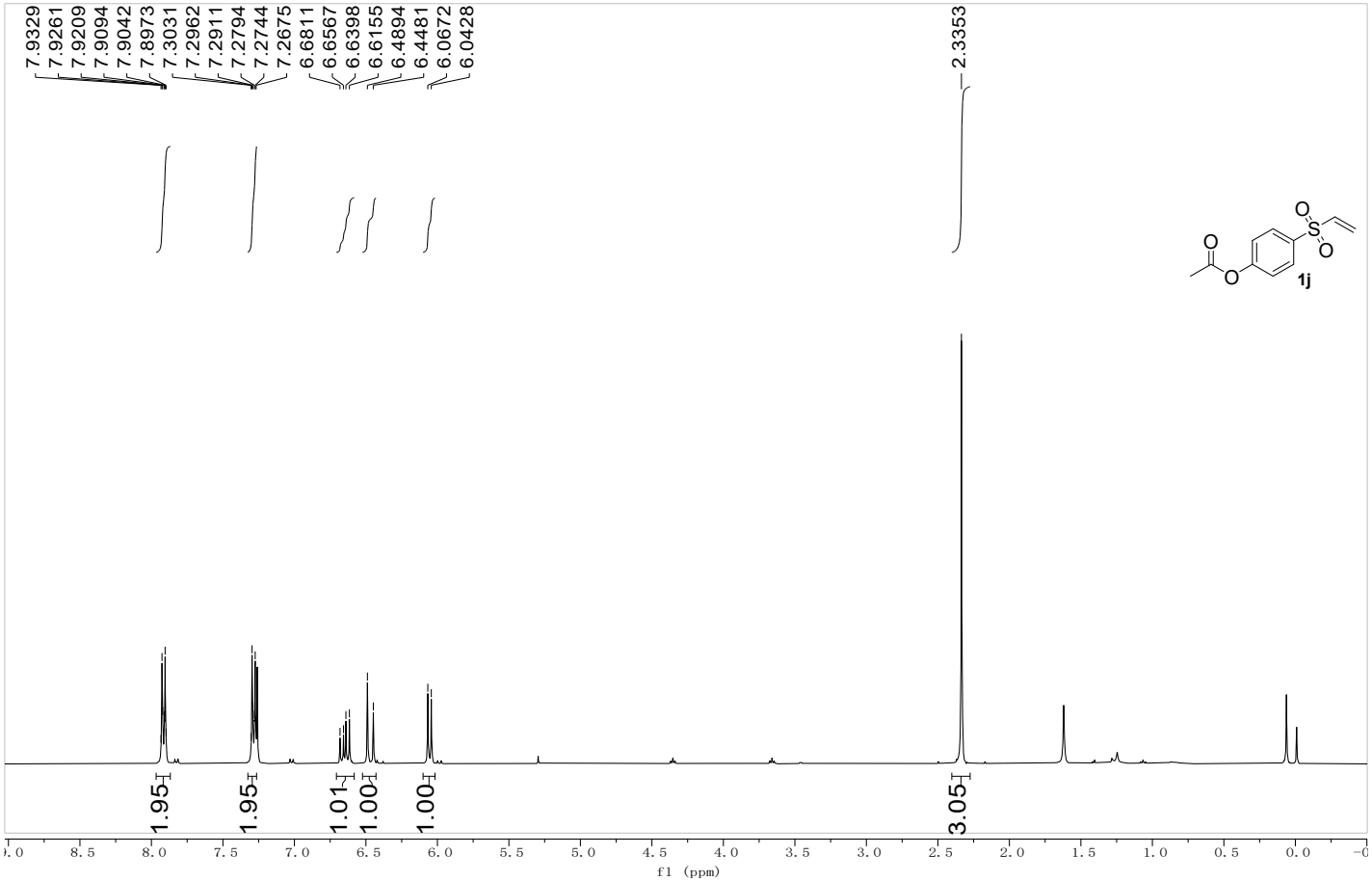
1i ^{1}H NMR (400 MHz, $CDCl_3$)



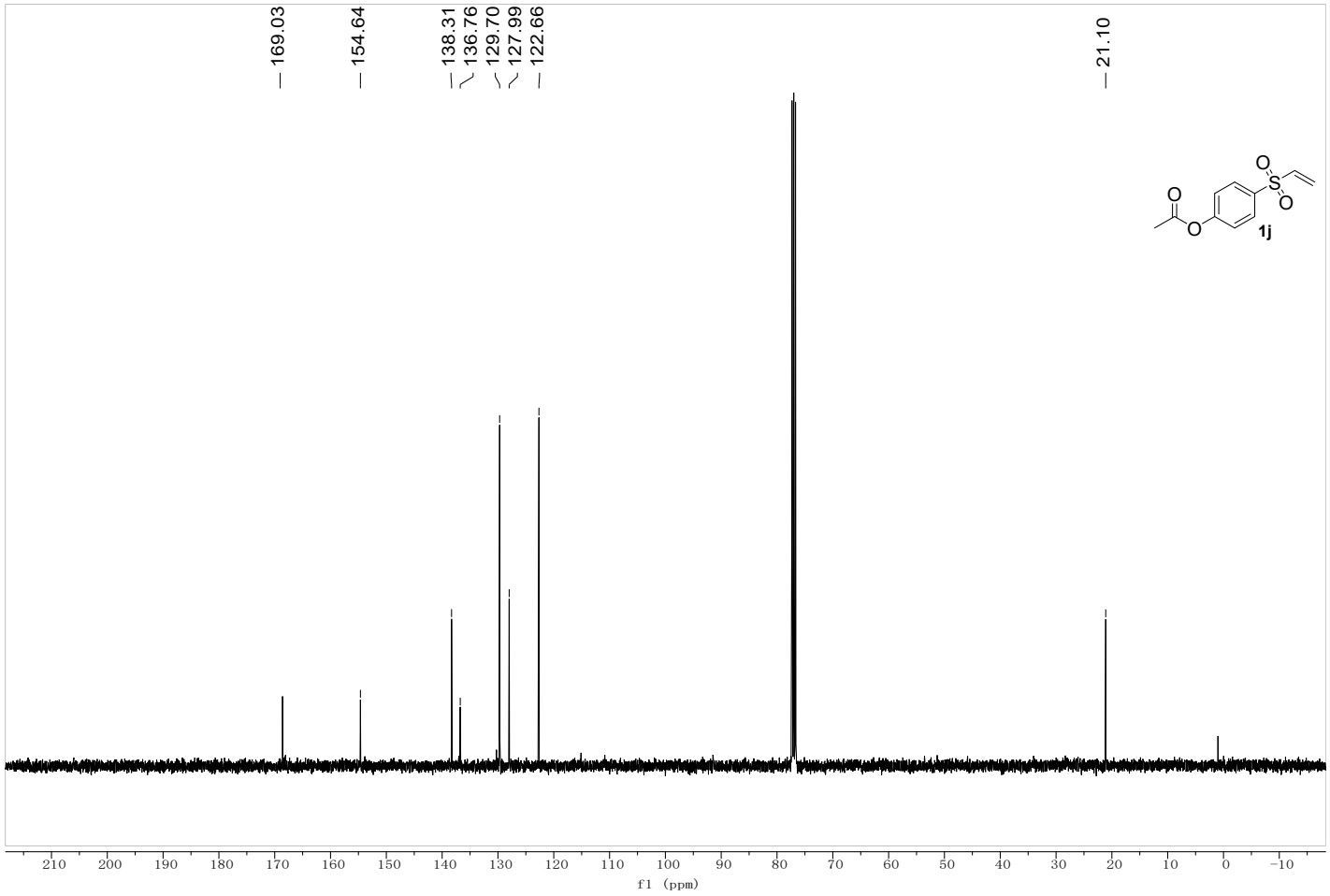
1i $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



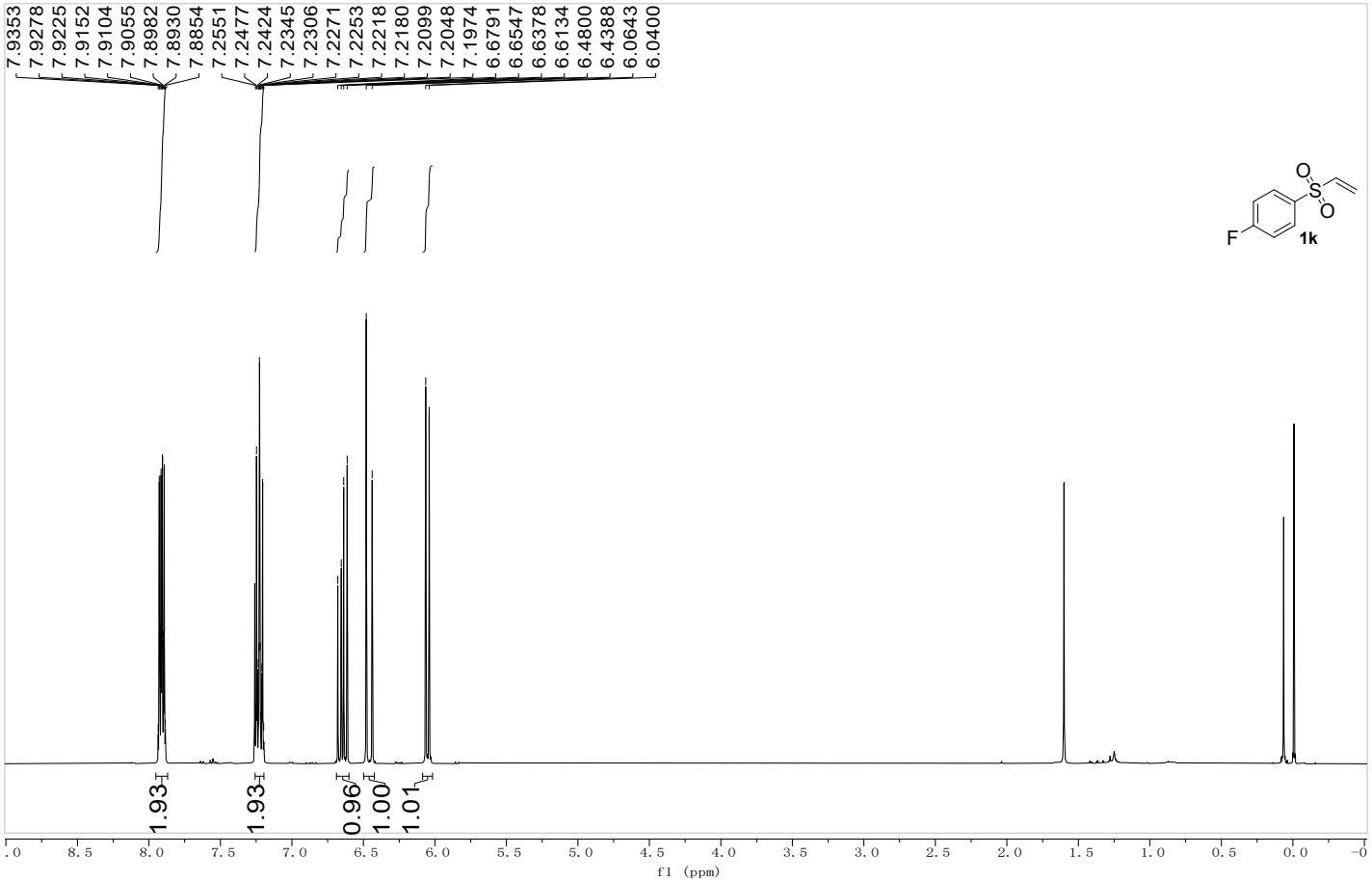
1j ^{1}H NMR (400 MHz, $CDCl_3$)



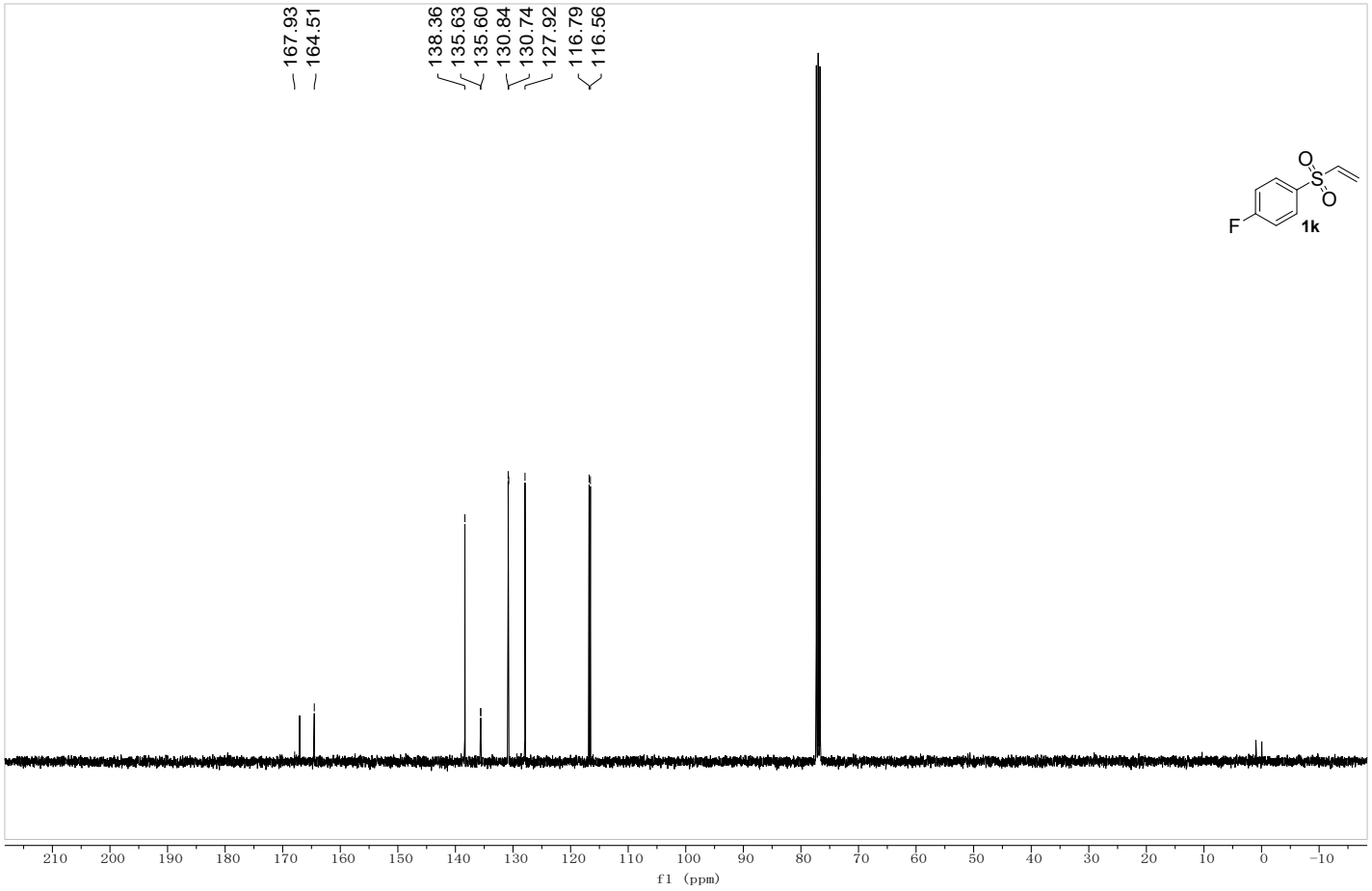
1j $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



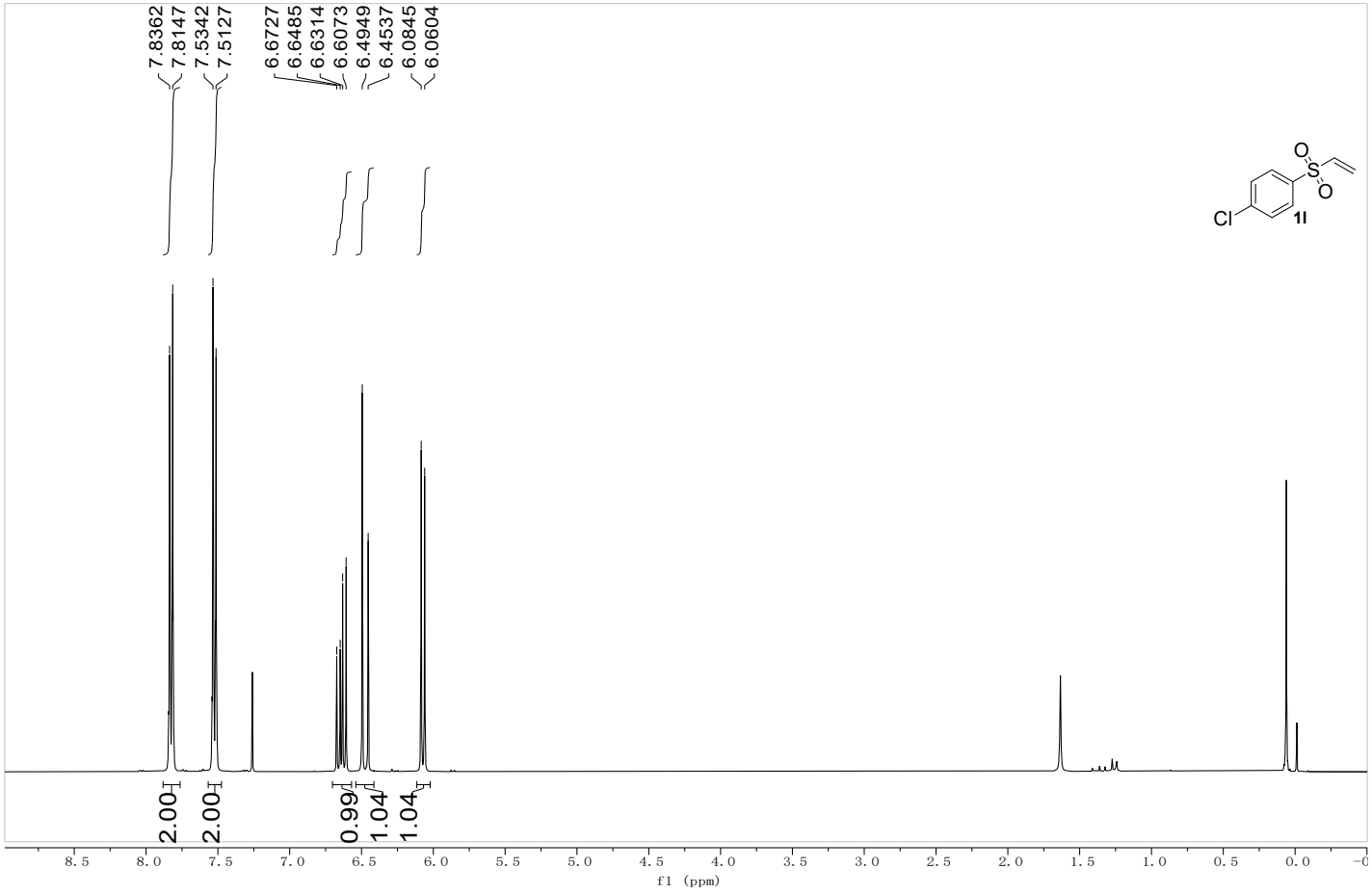
1k ^{1}H NMR (400 MHz, $CDCl_3$)



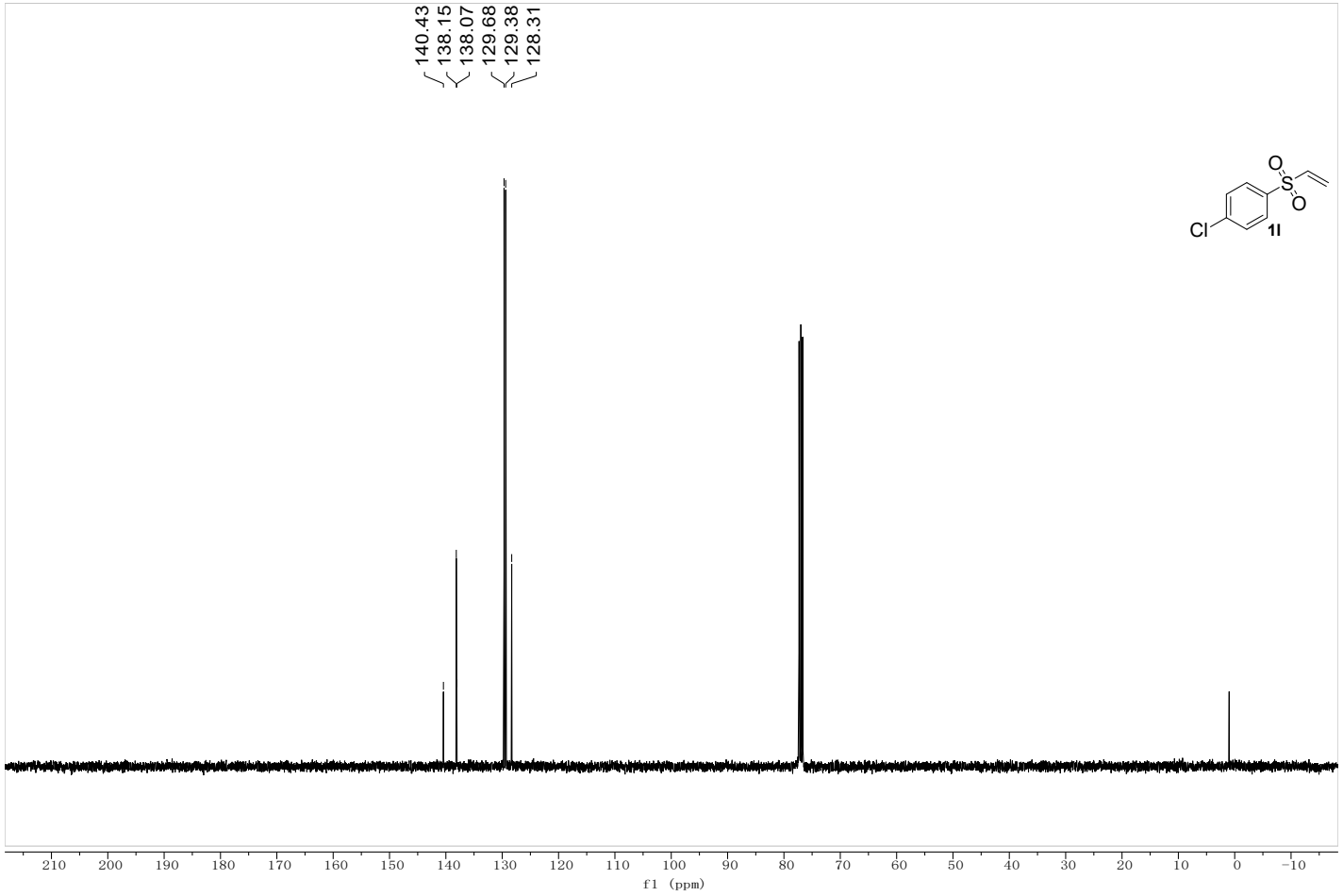
1k $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



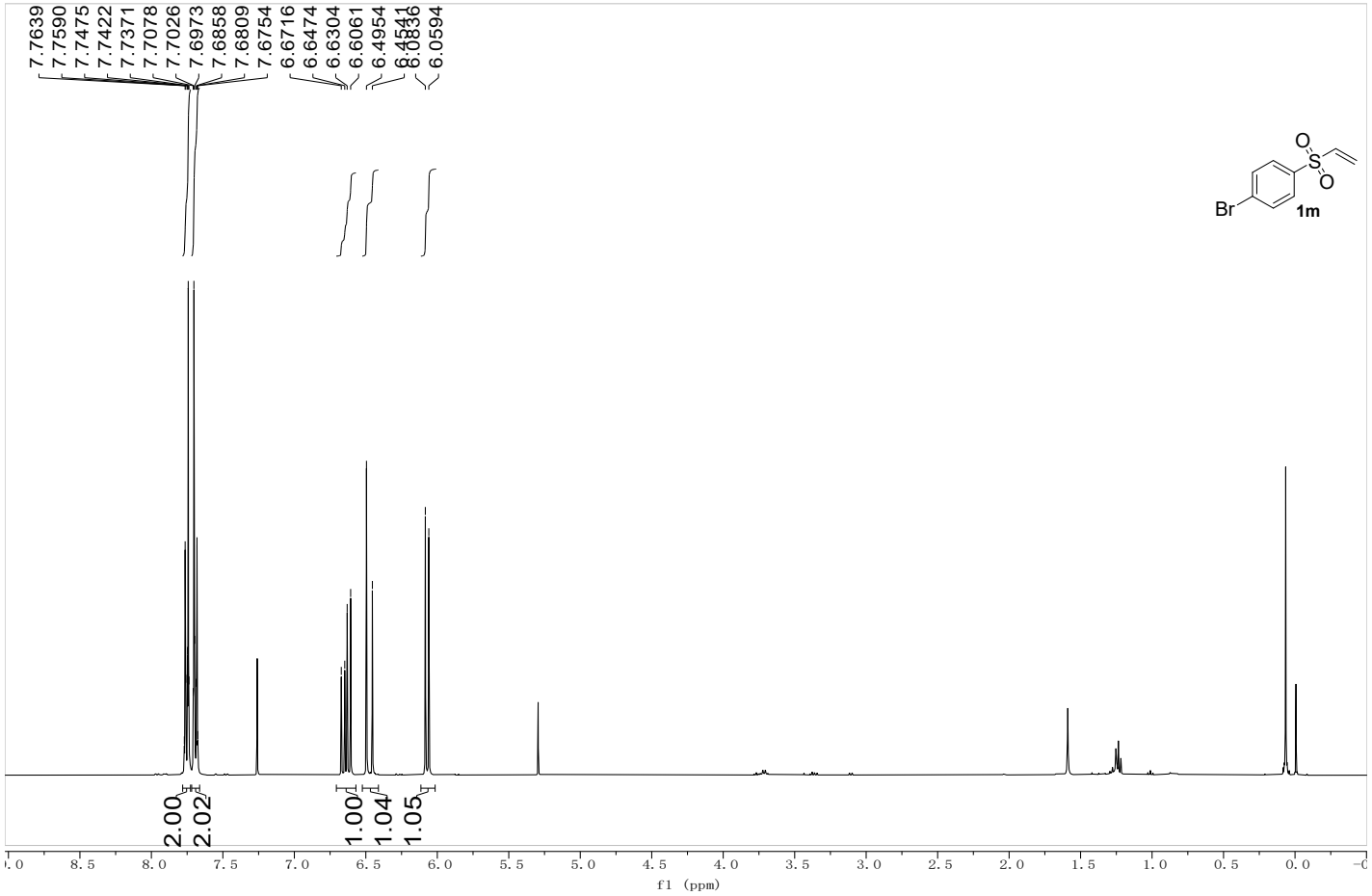
1l ^{1}H NMR (400 MHz, $CDCl_3$)



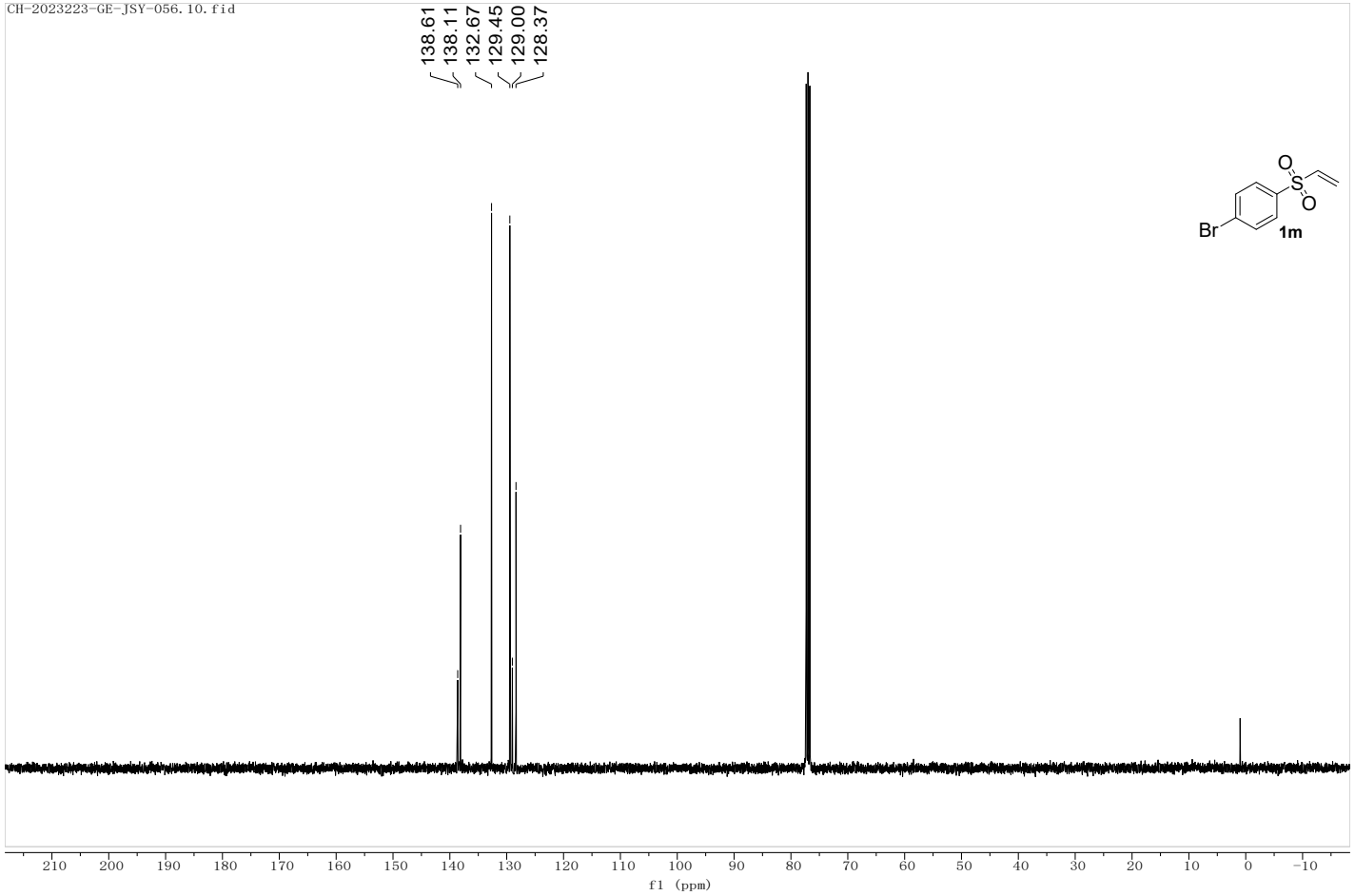
1l $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



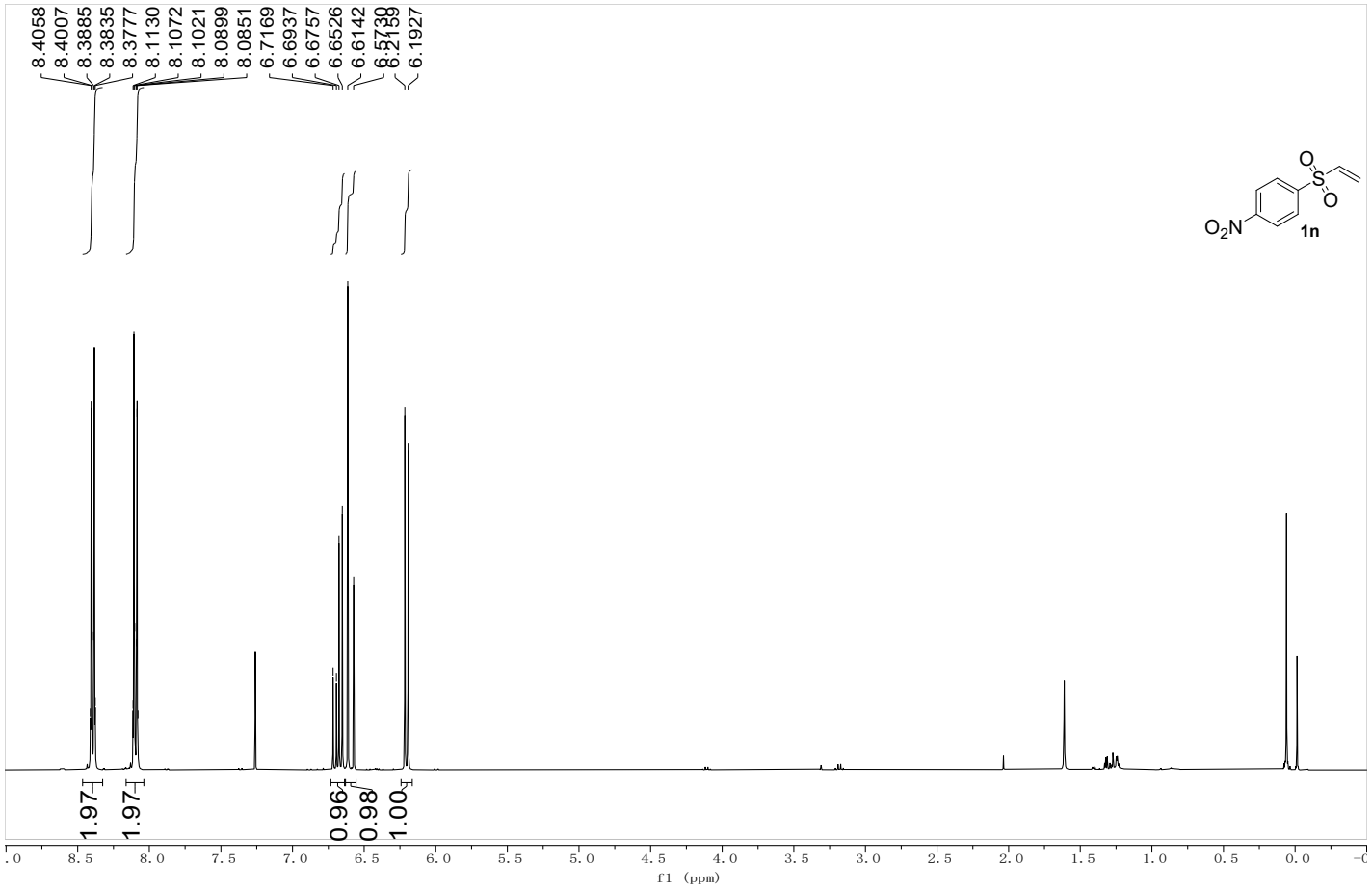
1m ^{1}H NMR (400 MHz, $CDCl_3$)



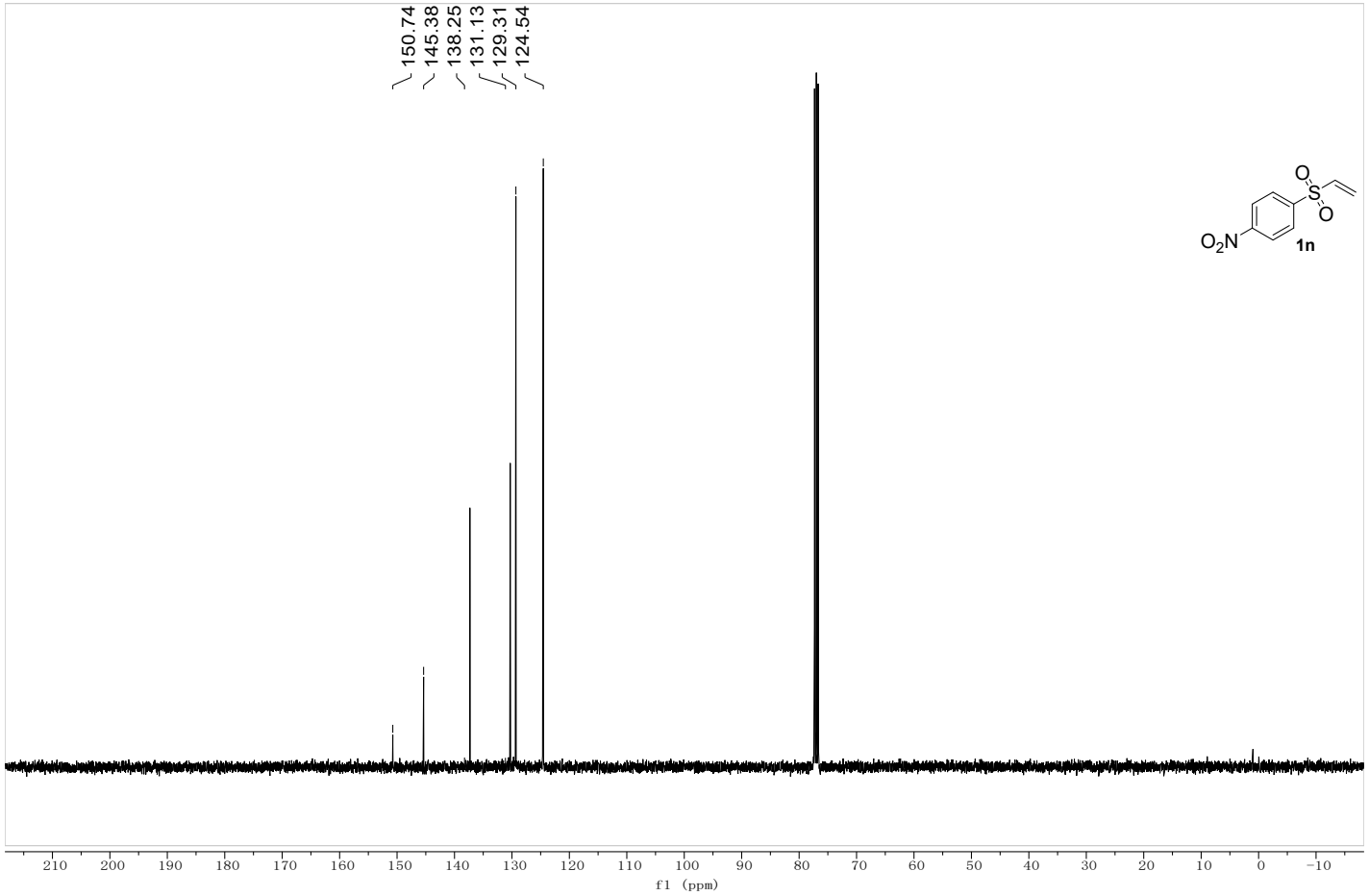
1m $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



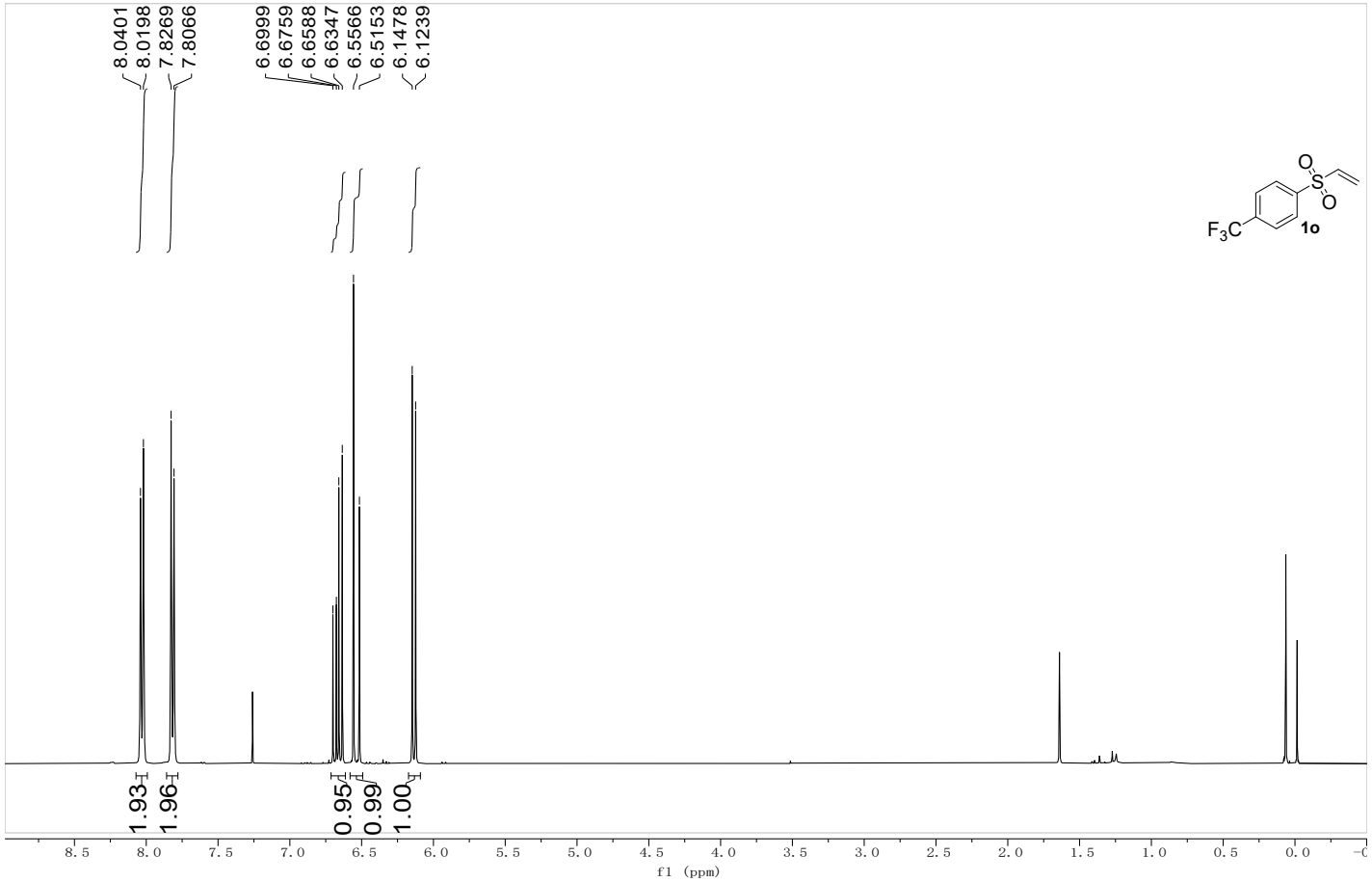
1n ^{1}H NMR (400 MHz, $CDCl_3$)



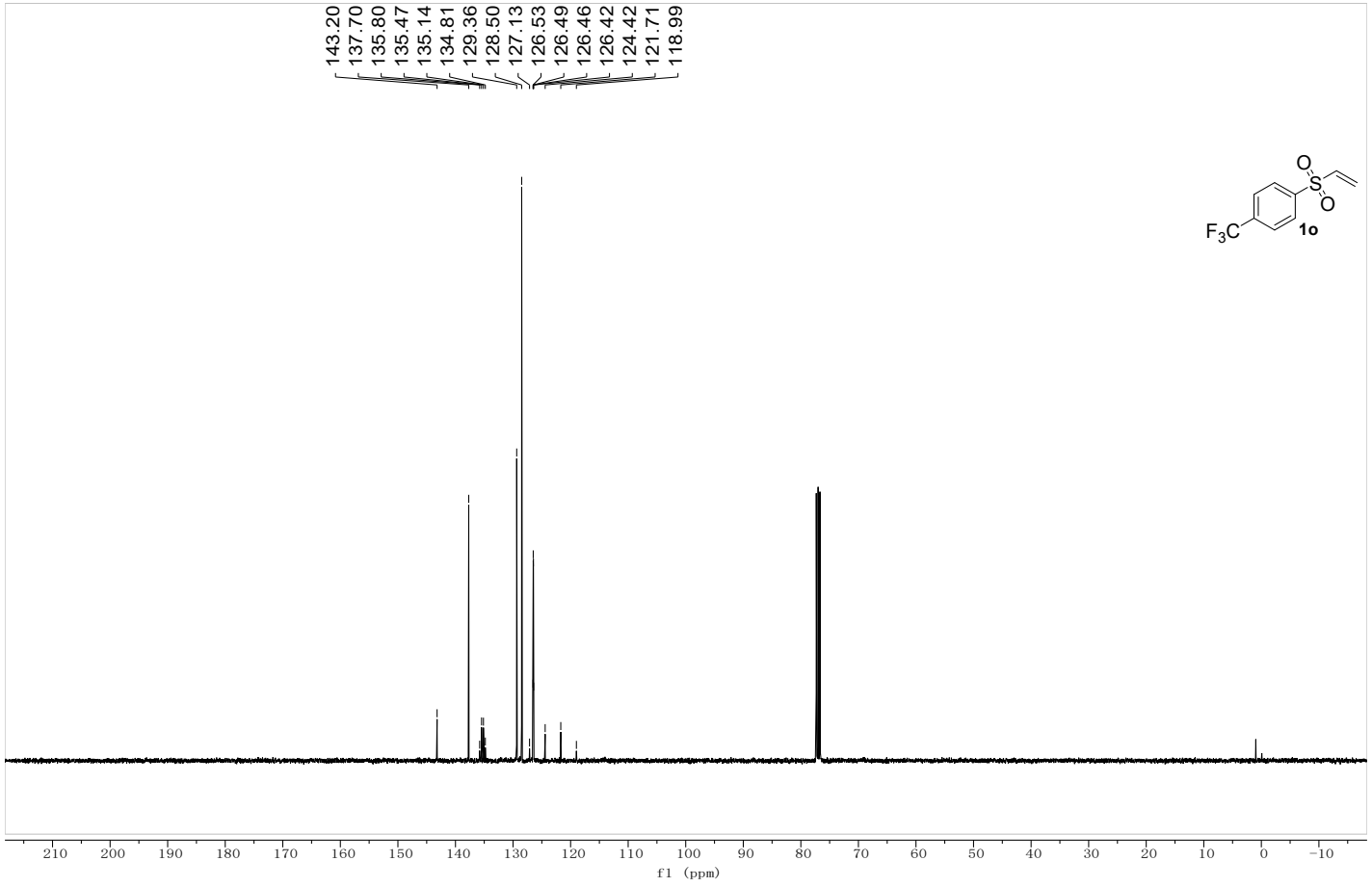
1n $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



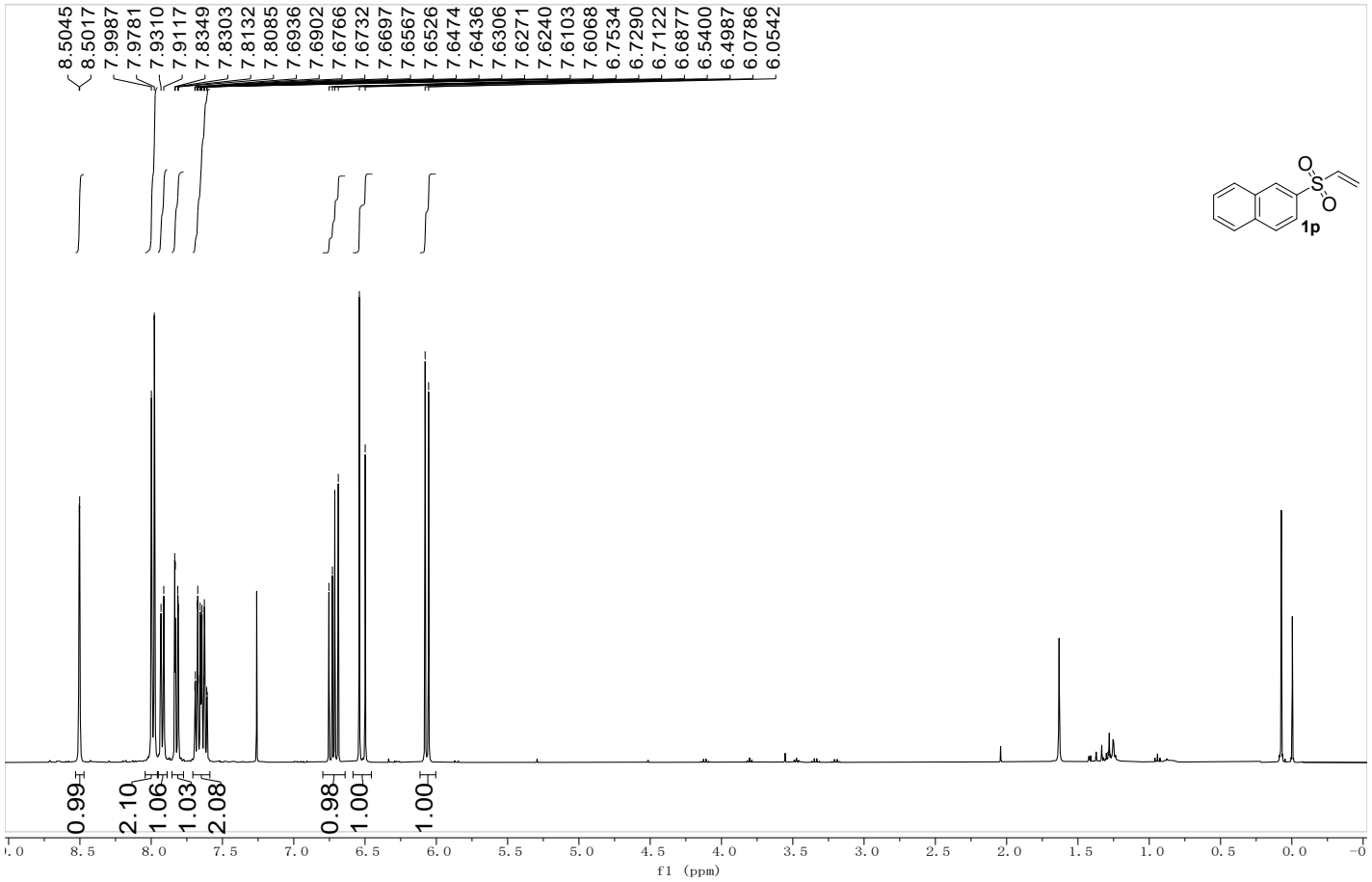
1o ^{1}H NMR (400 MHz, $CDCl_3$)



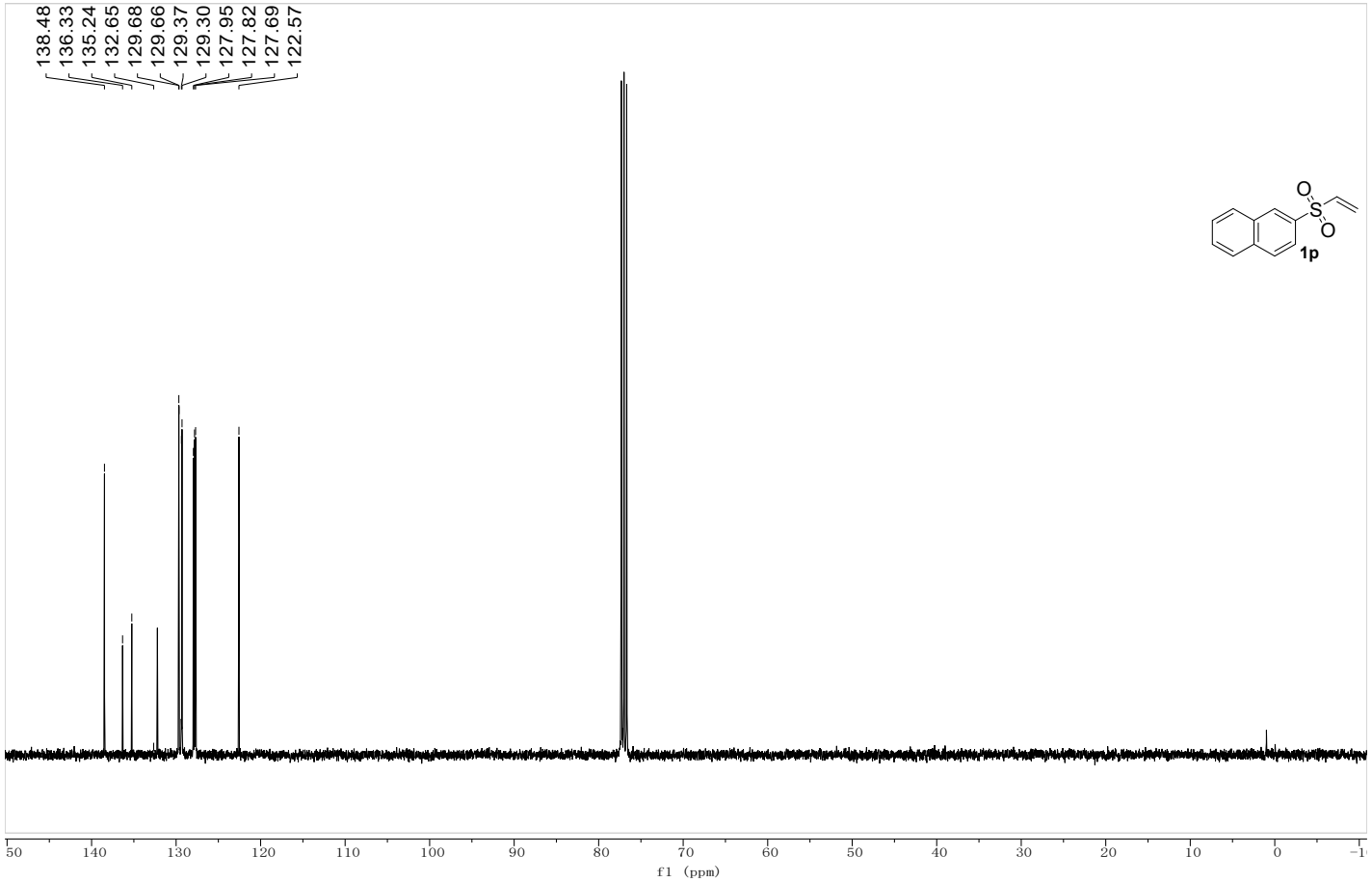
1o $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



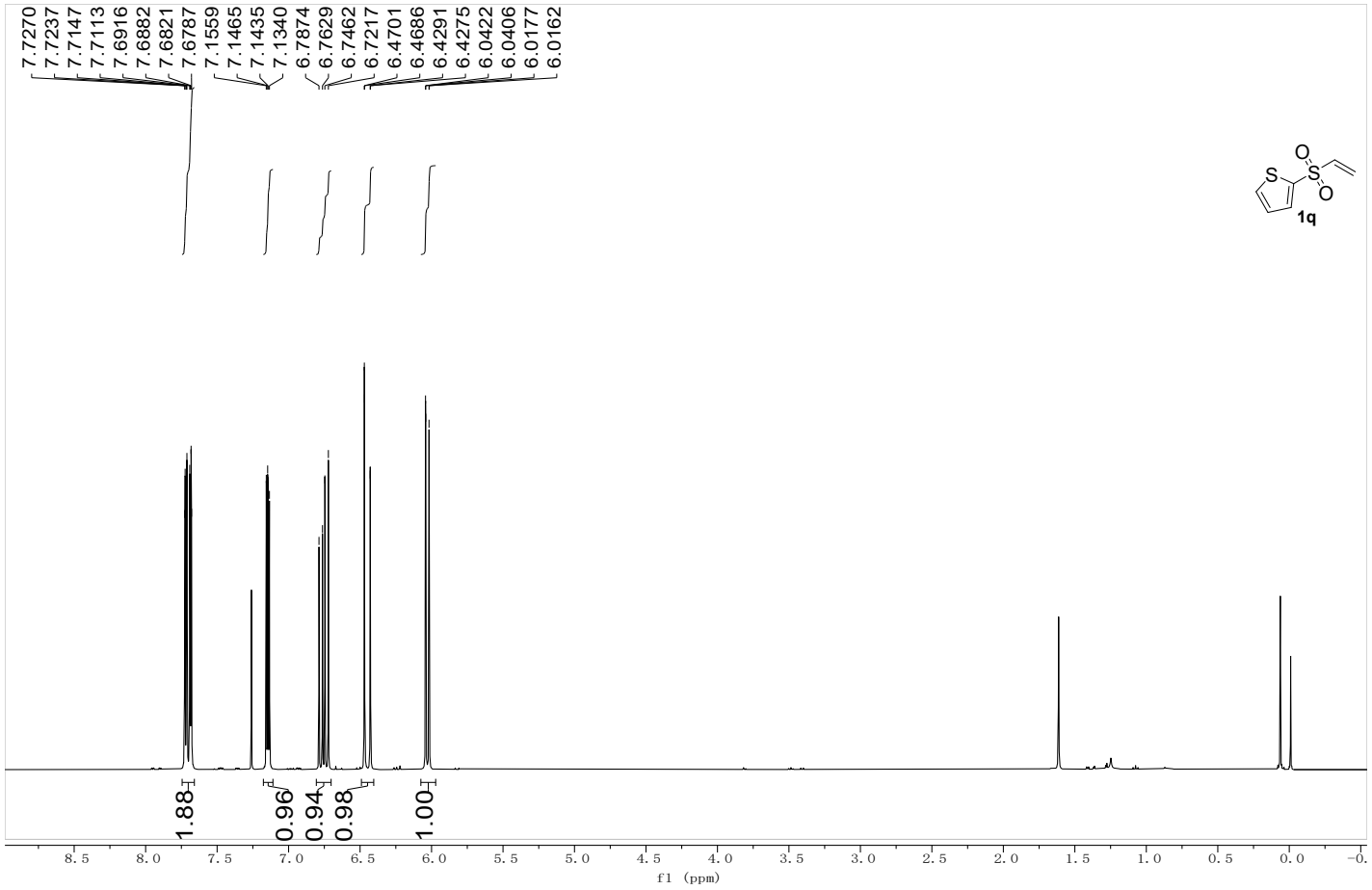
1p ^{1}H NMR (400 MHz, $CDCl_3$)



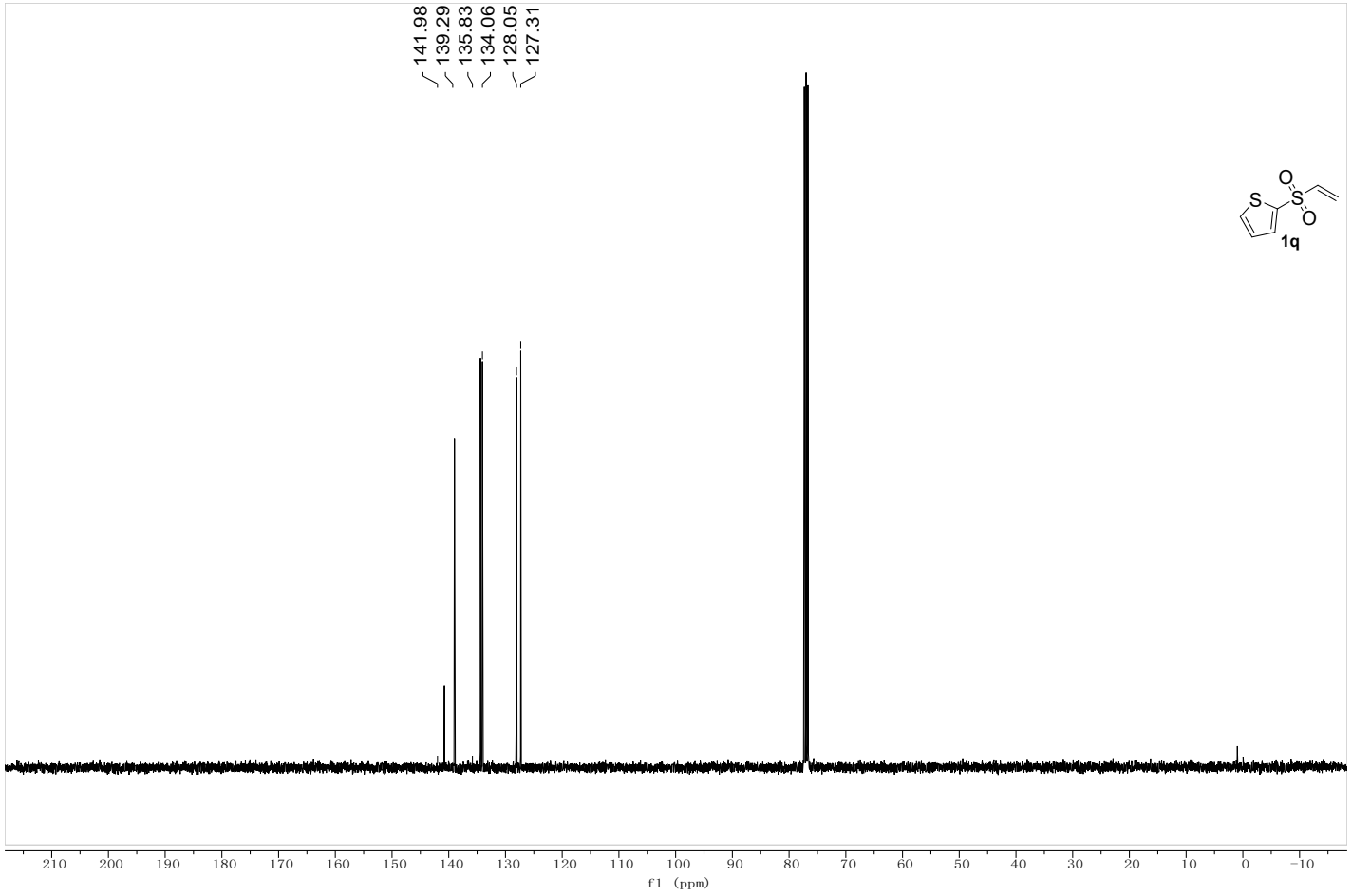
1p $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



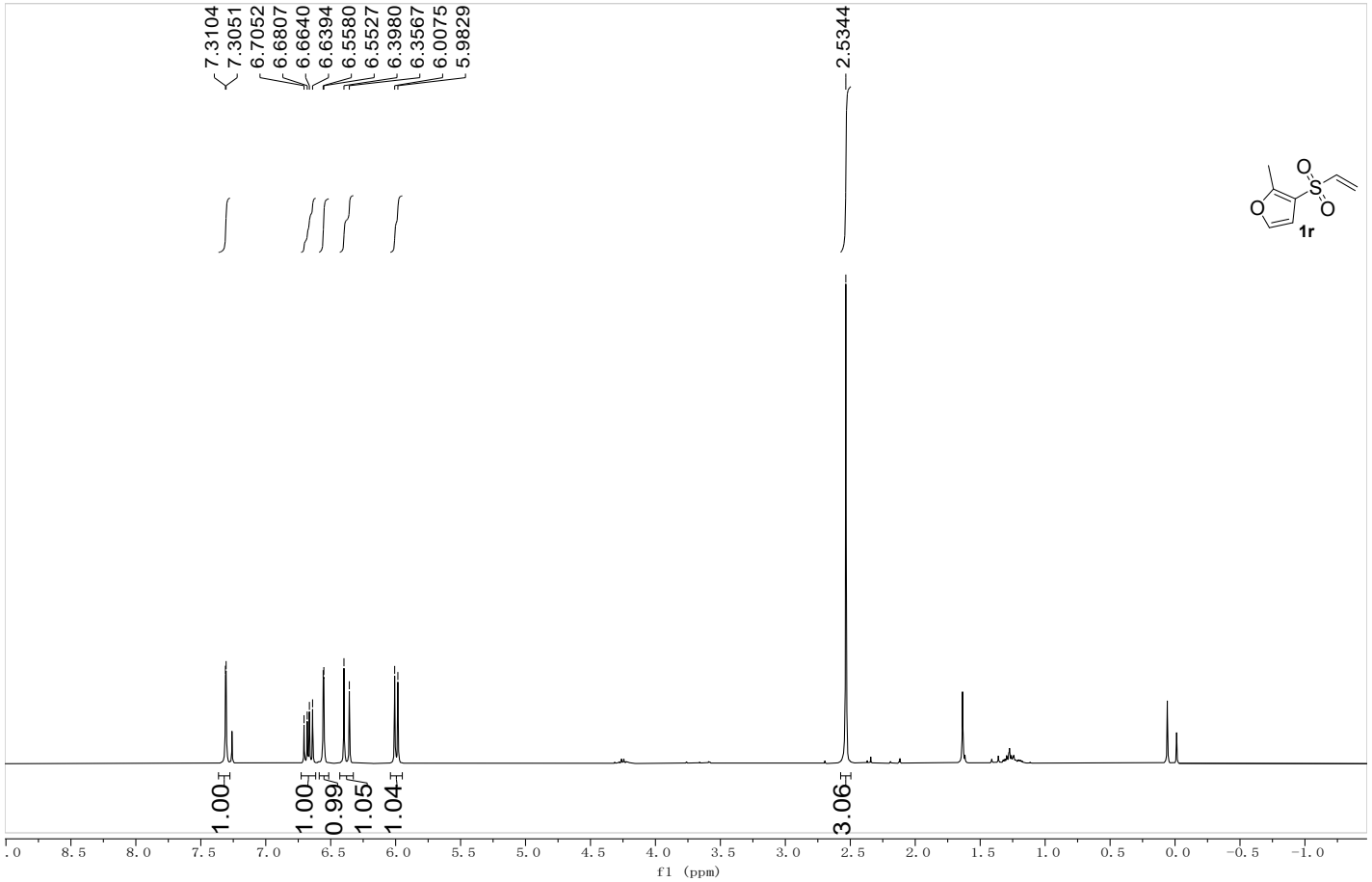
1q ^{1}H NMR (400 MHz, $CDCl_3$)



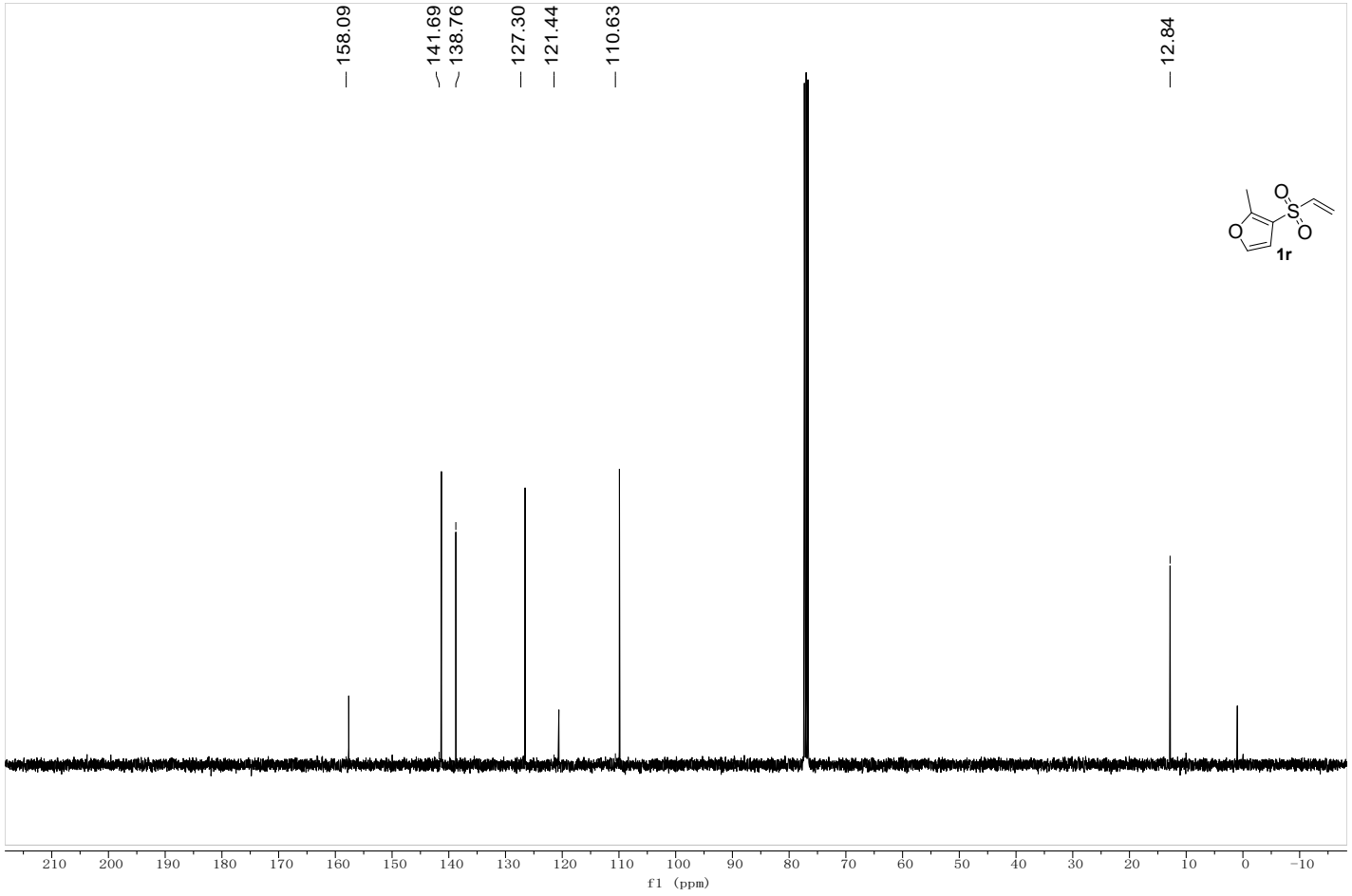
1q $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



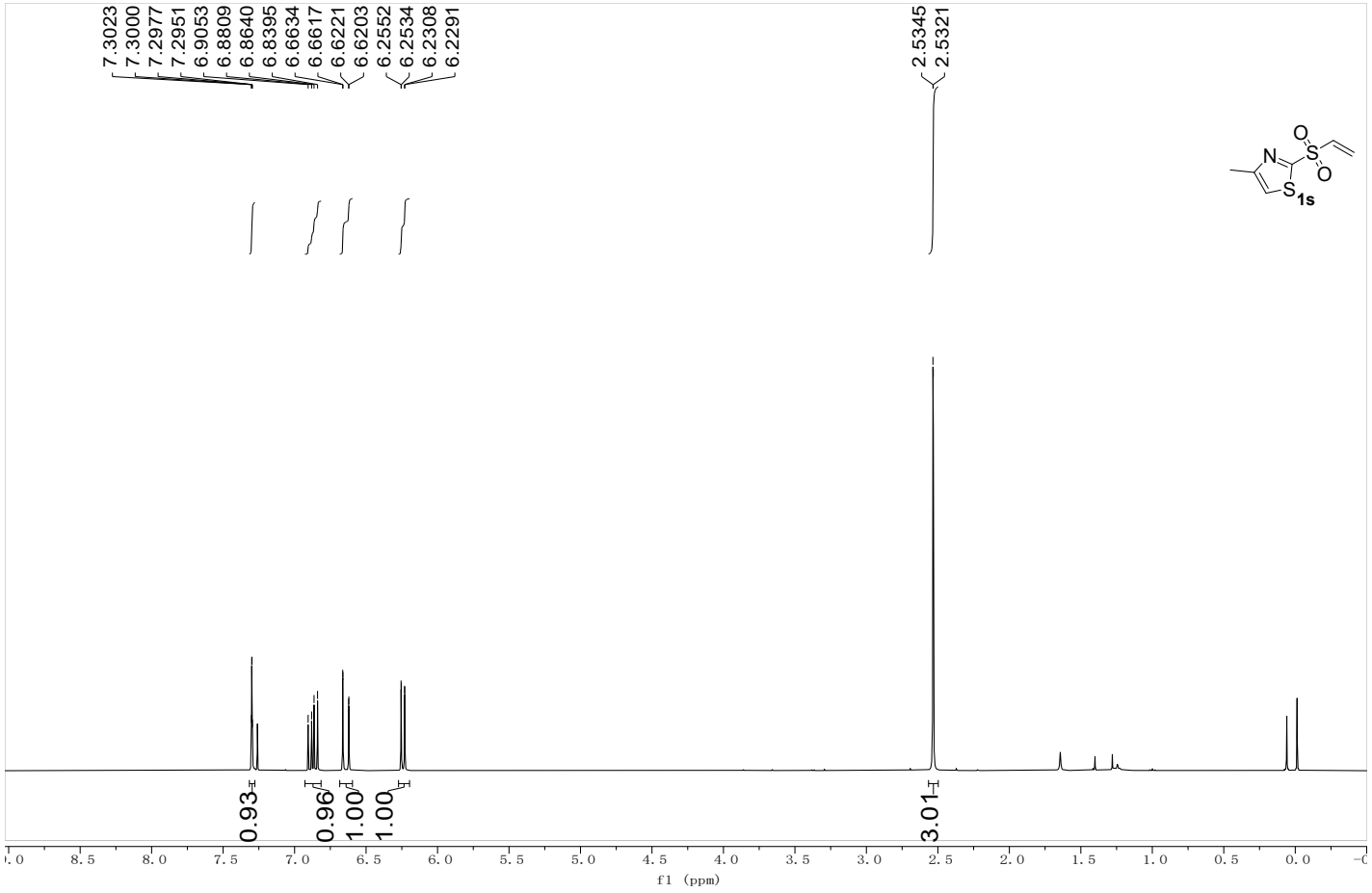
1r ^{1}H NMR (400 MHz, $CDCl_3$)



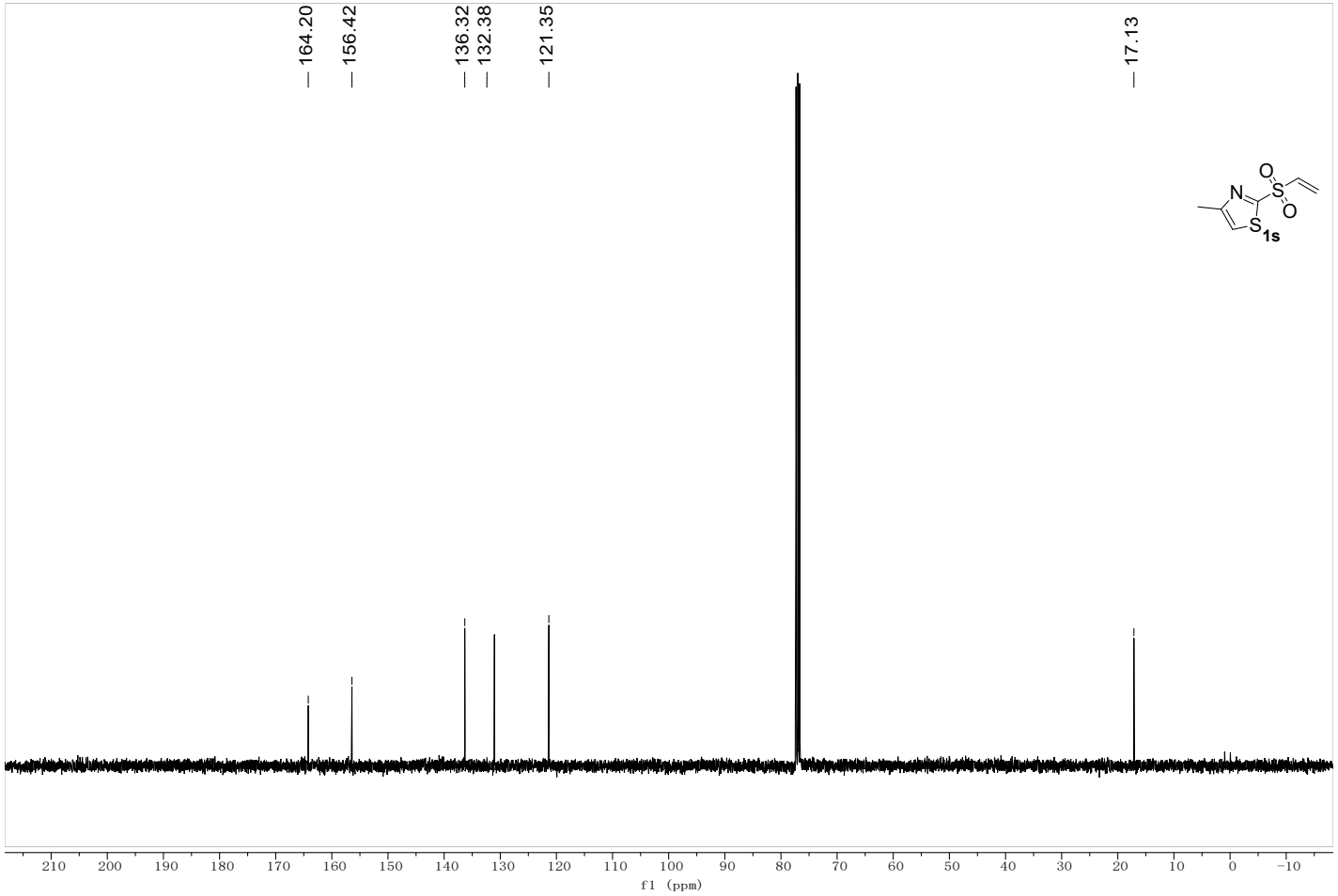
1r $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



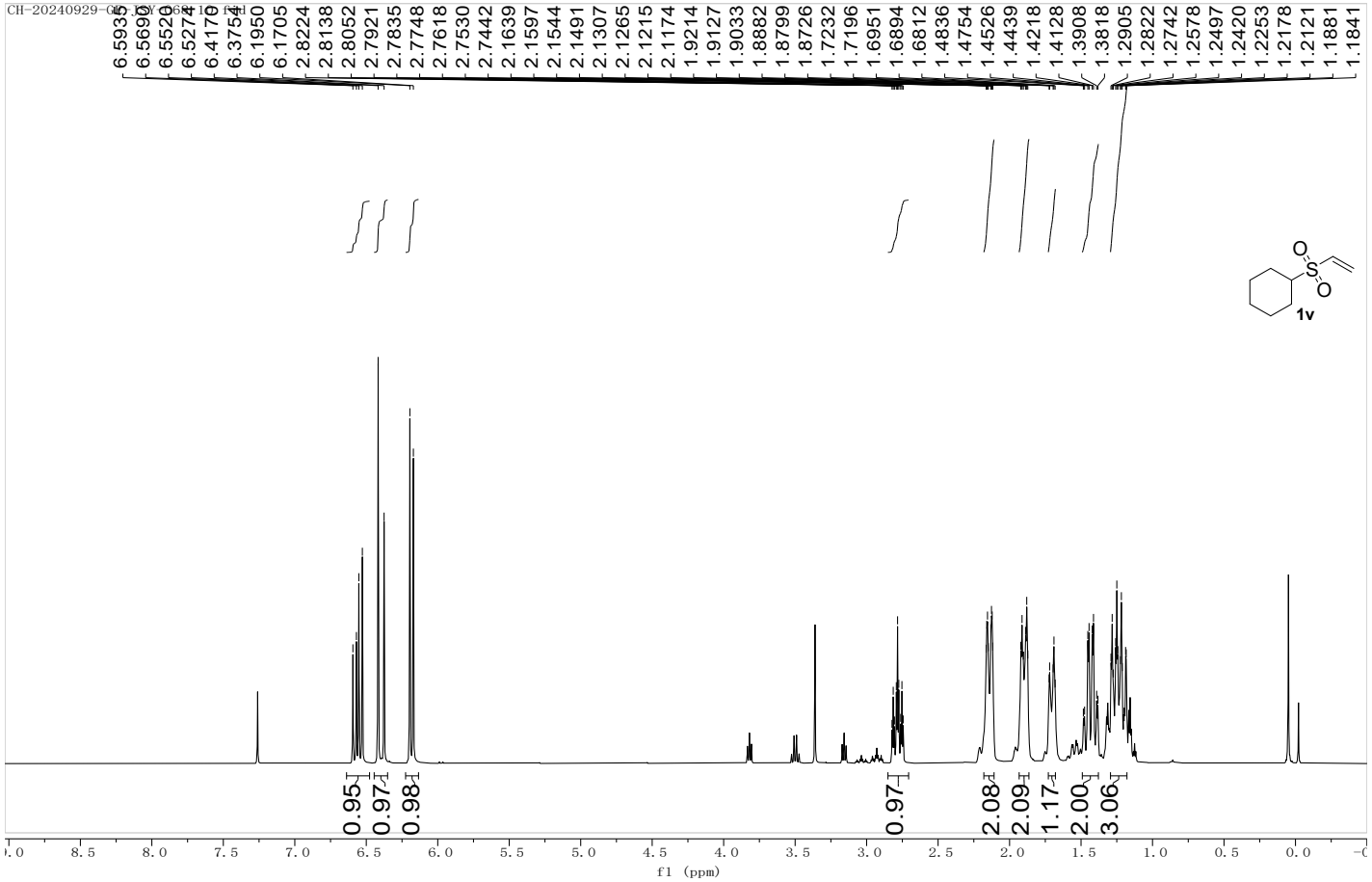
1s ^{1}H NMR (400 MHz, $CDCl_3$)



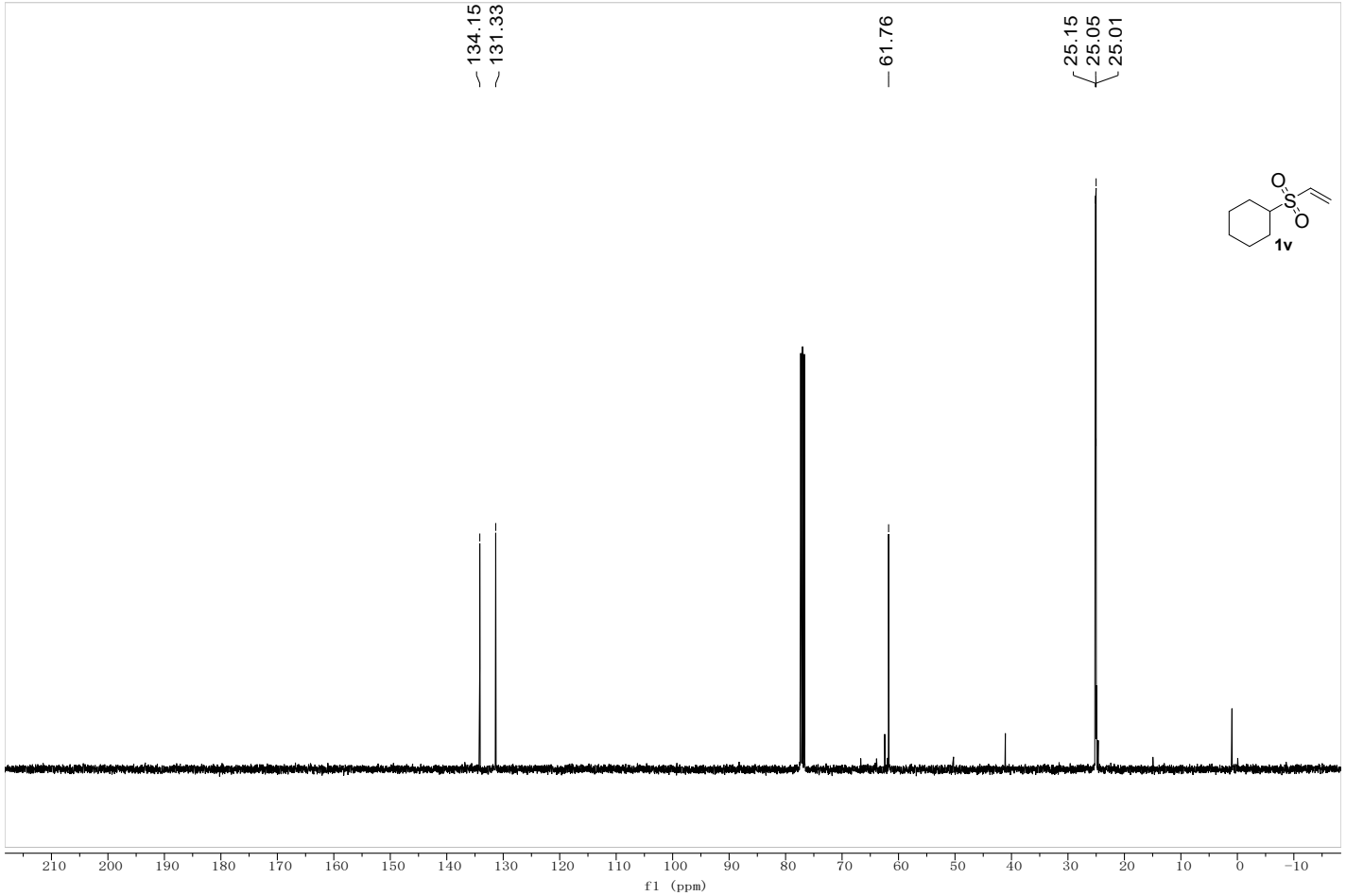
1s $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



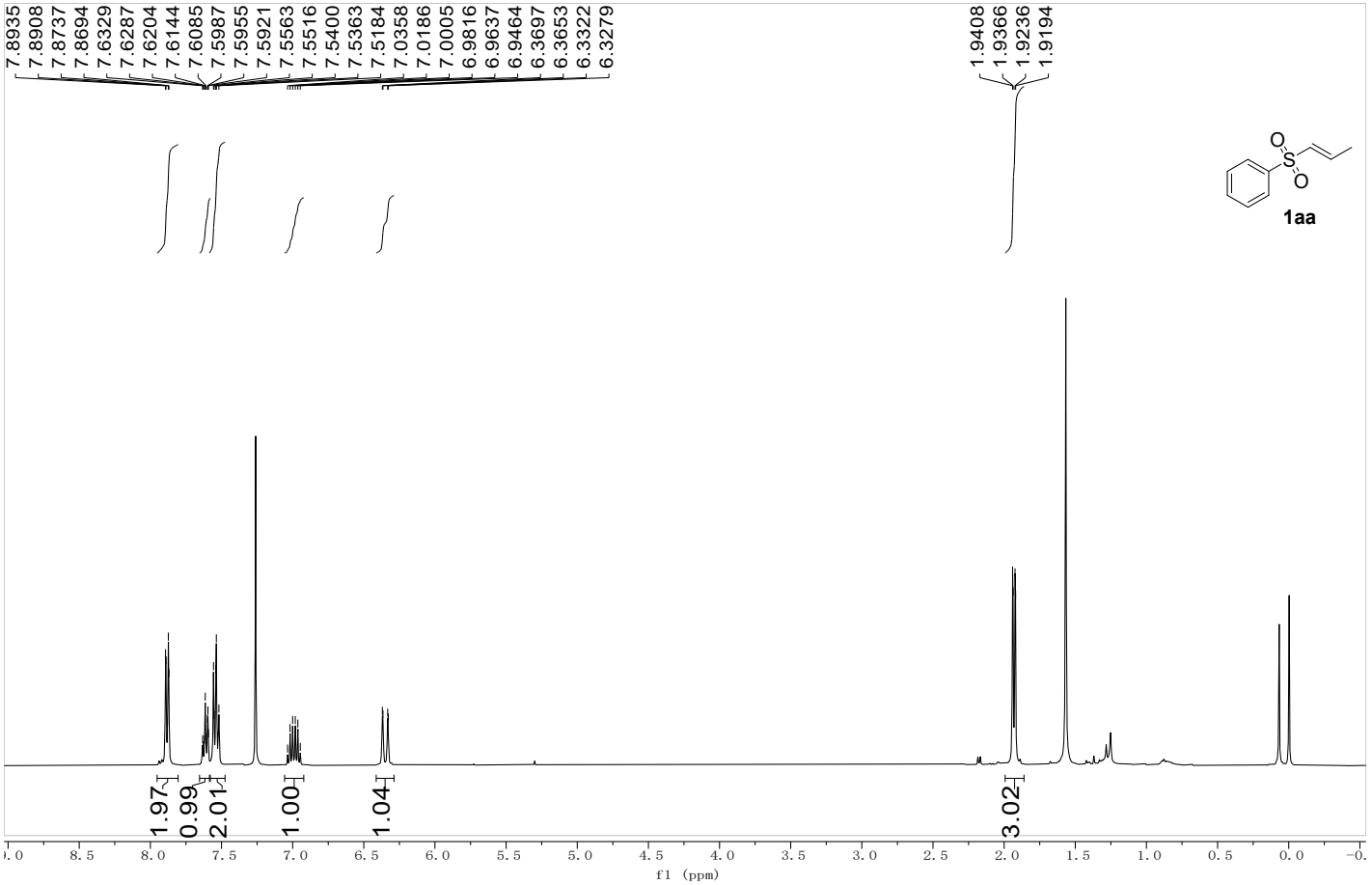
1v ^{1}H NMR (400 MHz, $CDCl_3$)



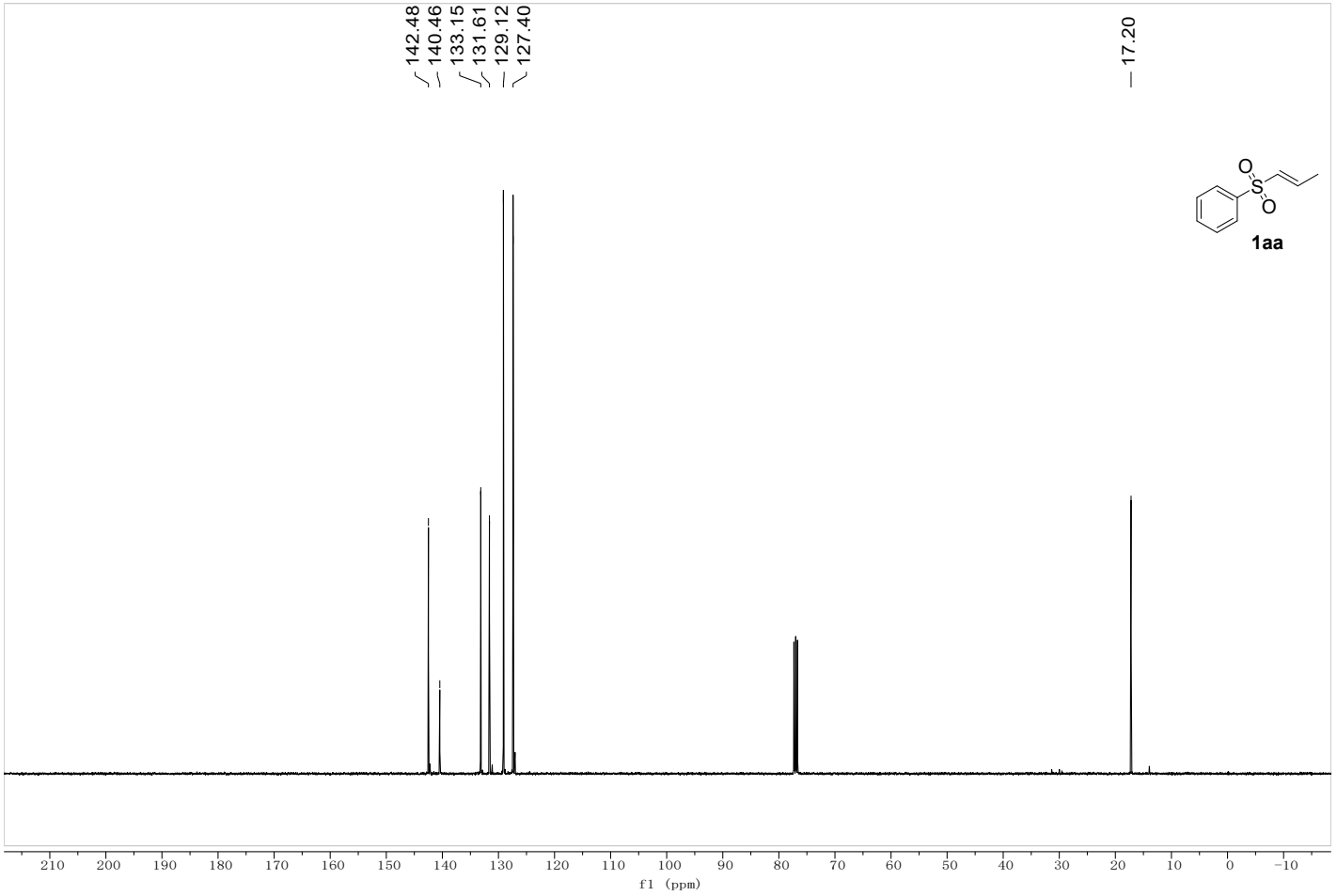
1v $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



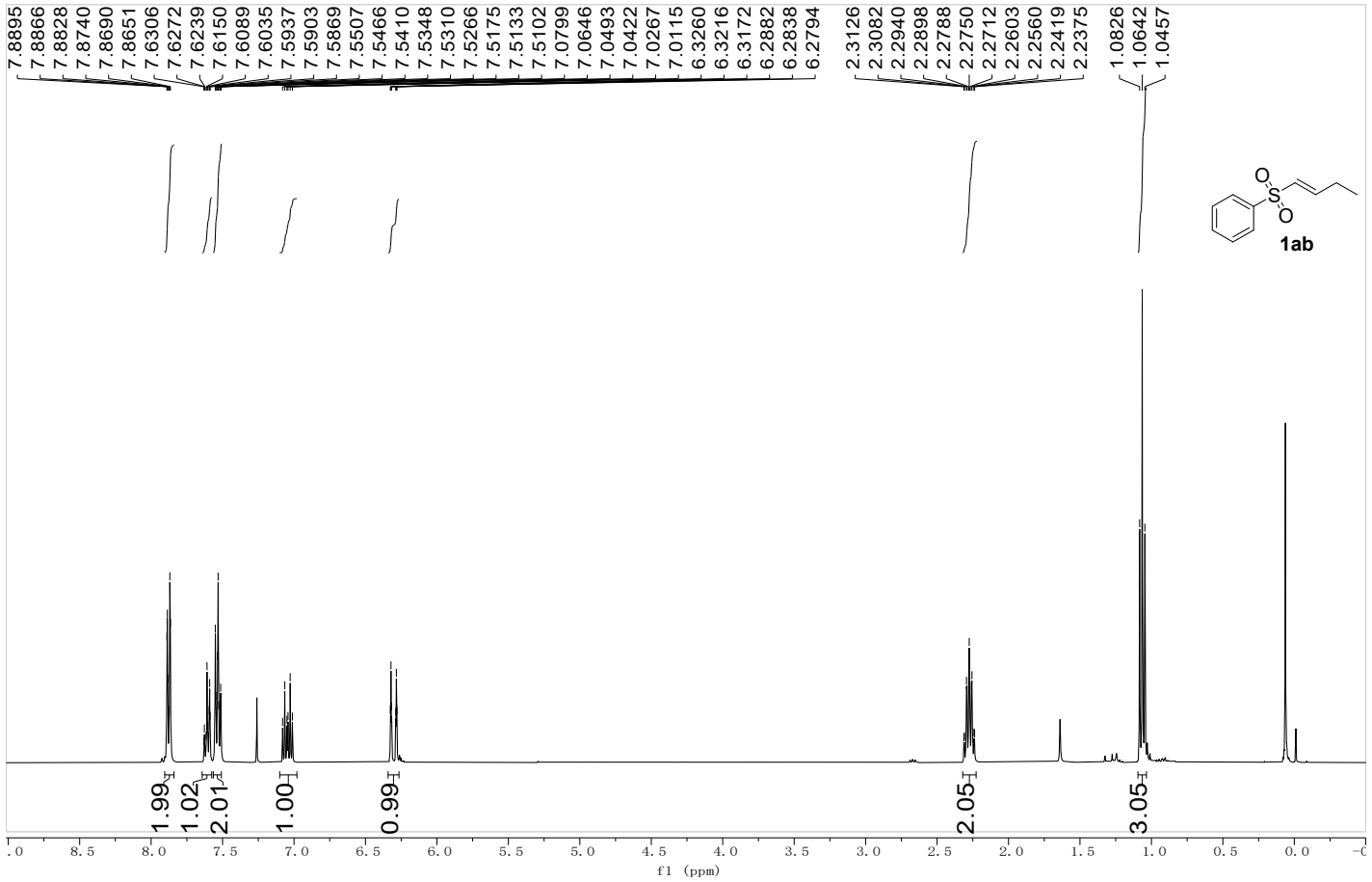
1aa ^{1}H NMR (400 MHz, $CDCl_3$)



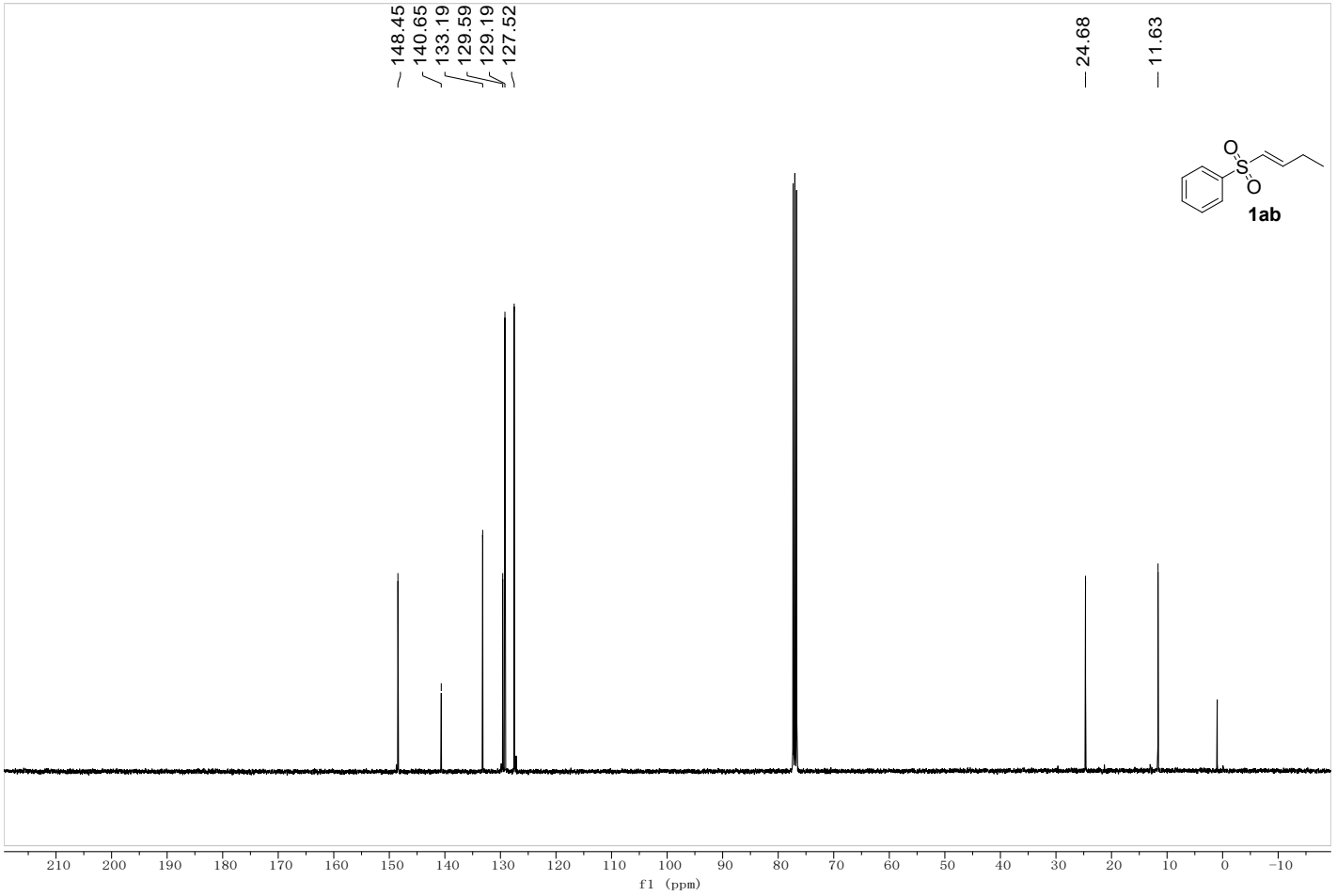
1aa $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



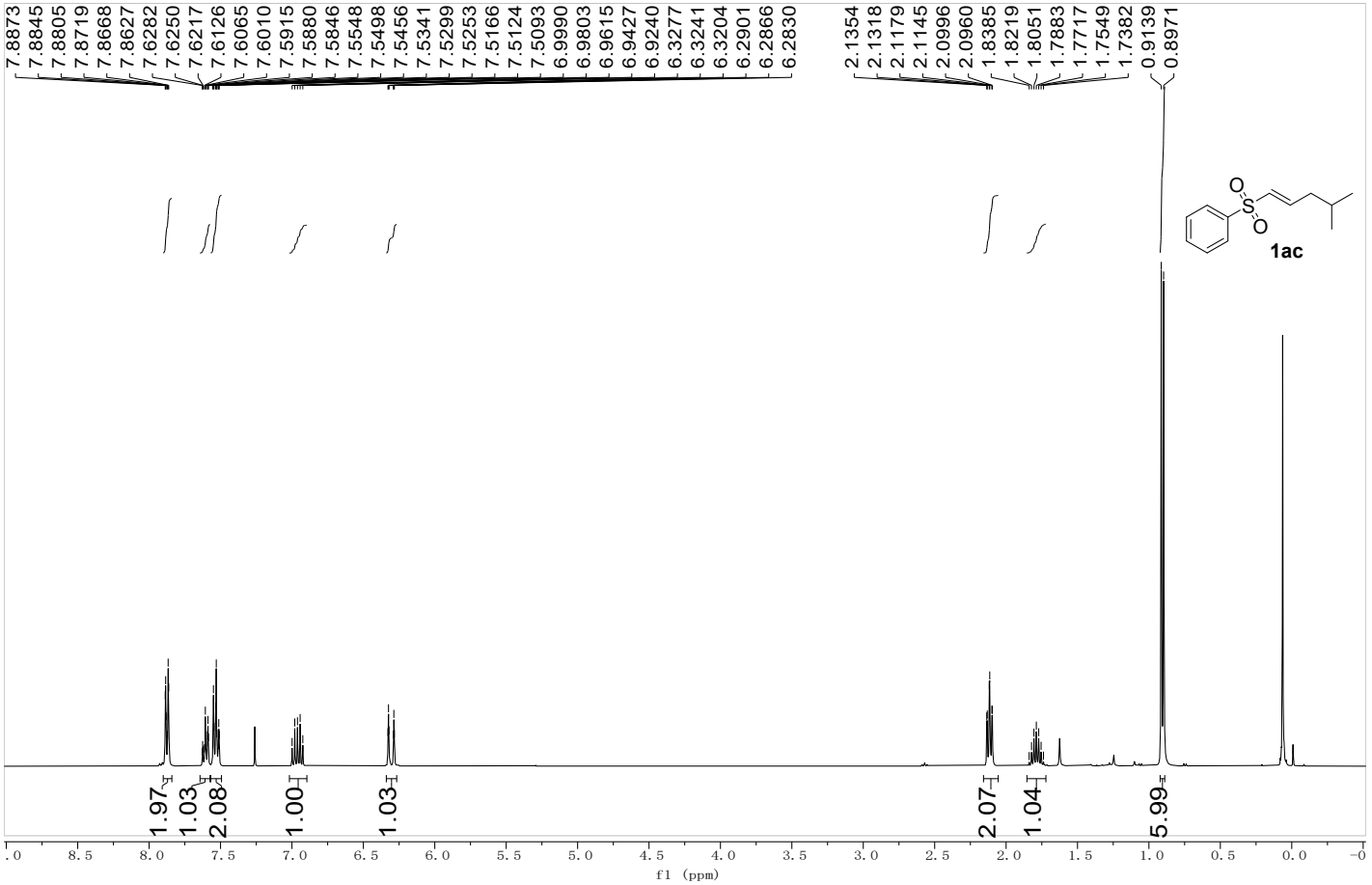
1ab ^{1}H NMR (400 MHz, $CDCl_3$)



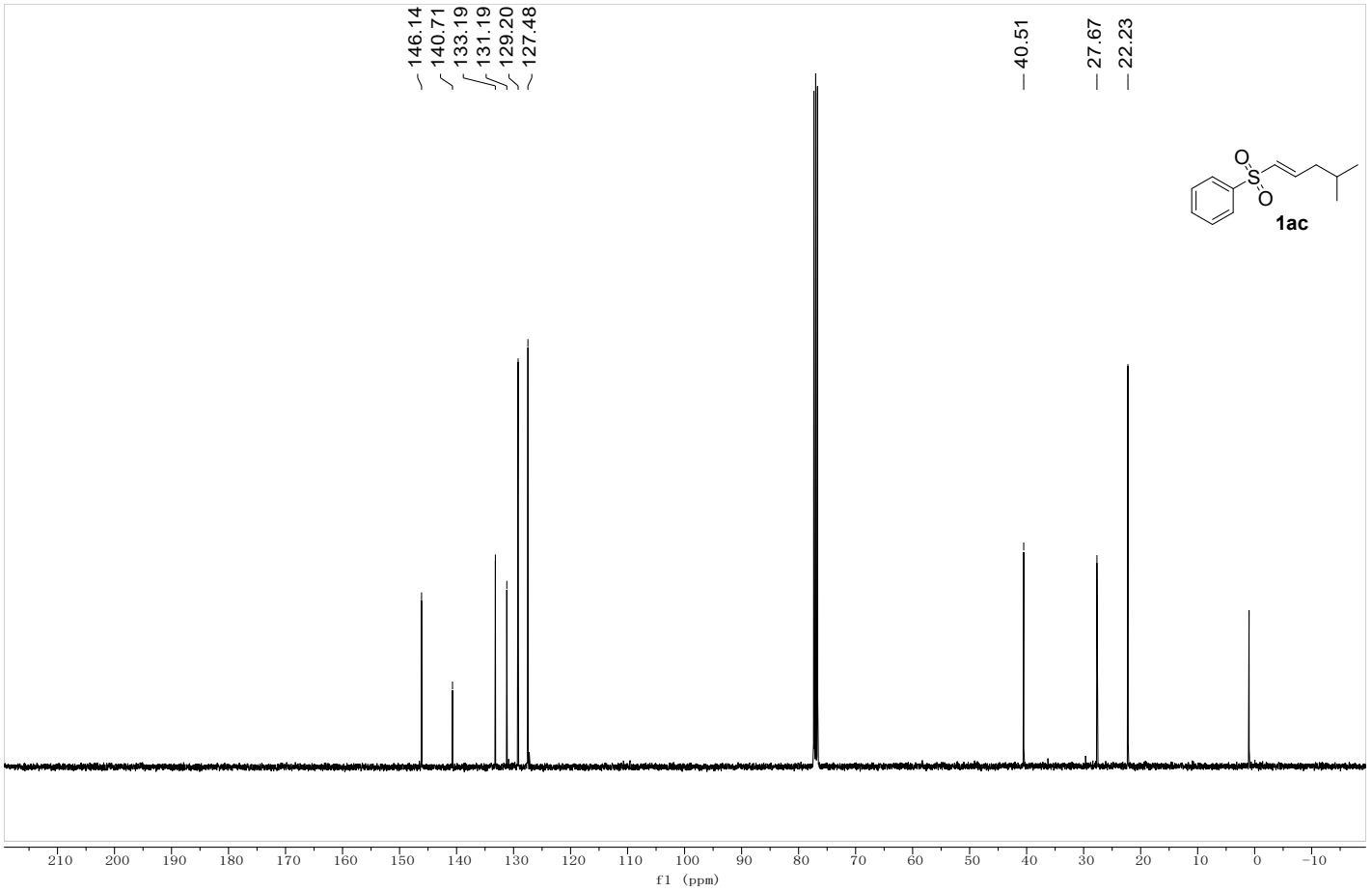
1ab $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



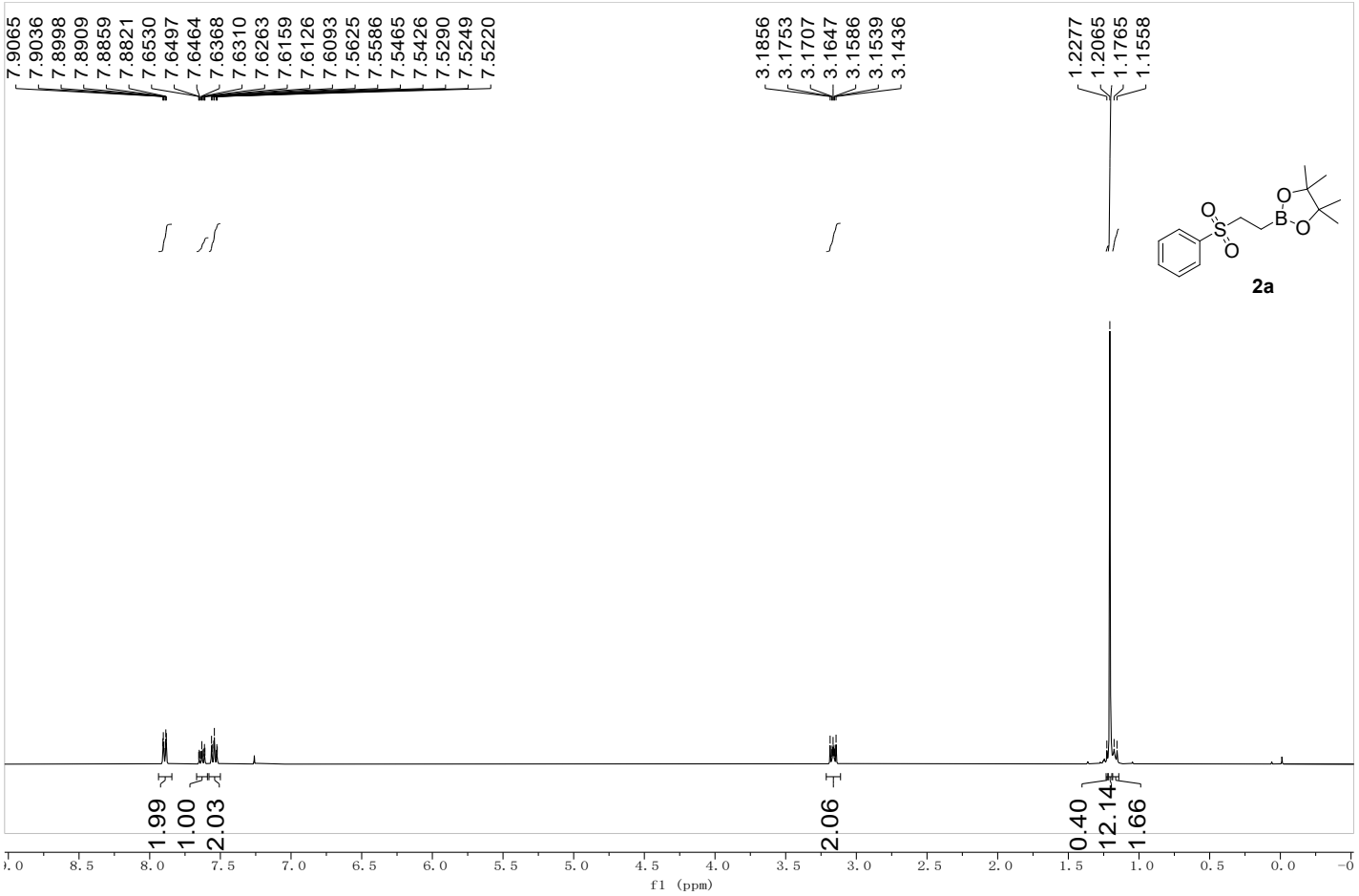
1ac ^{1}H NMR (400 MHz, $CDCl_3$)



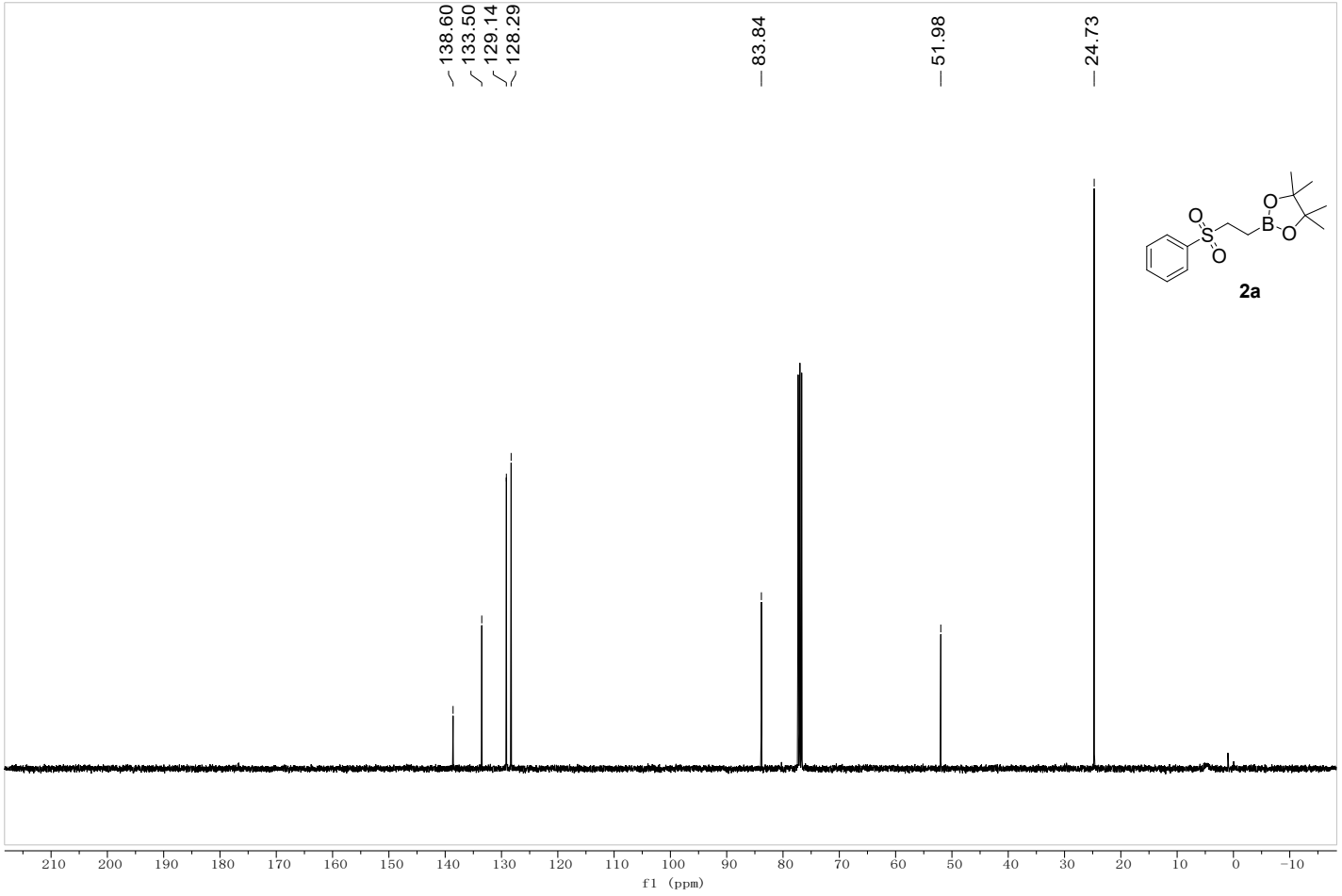
1ac $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



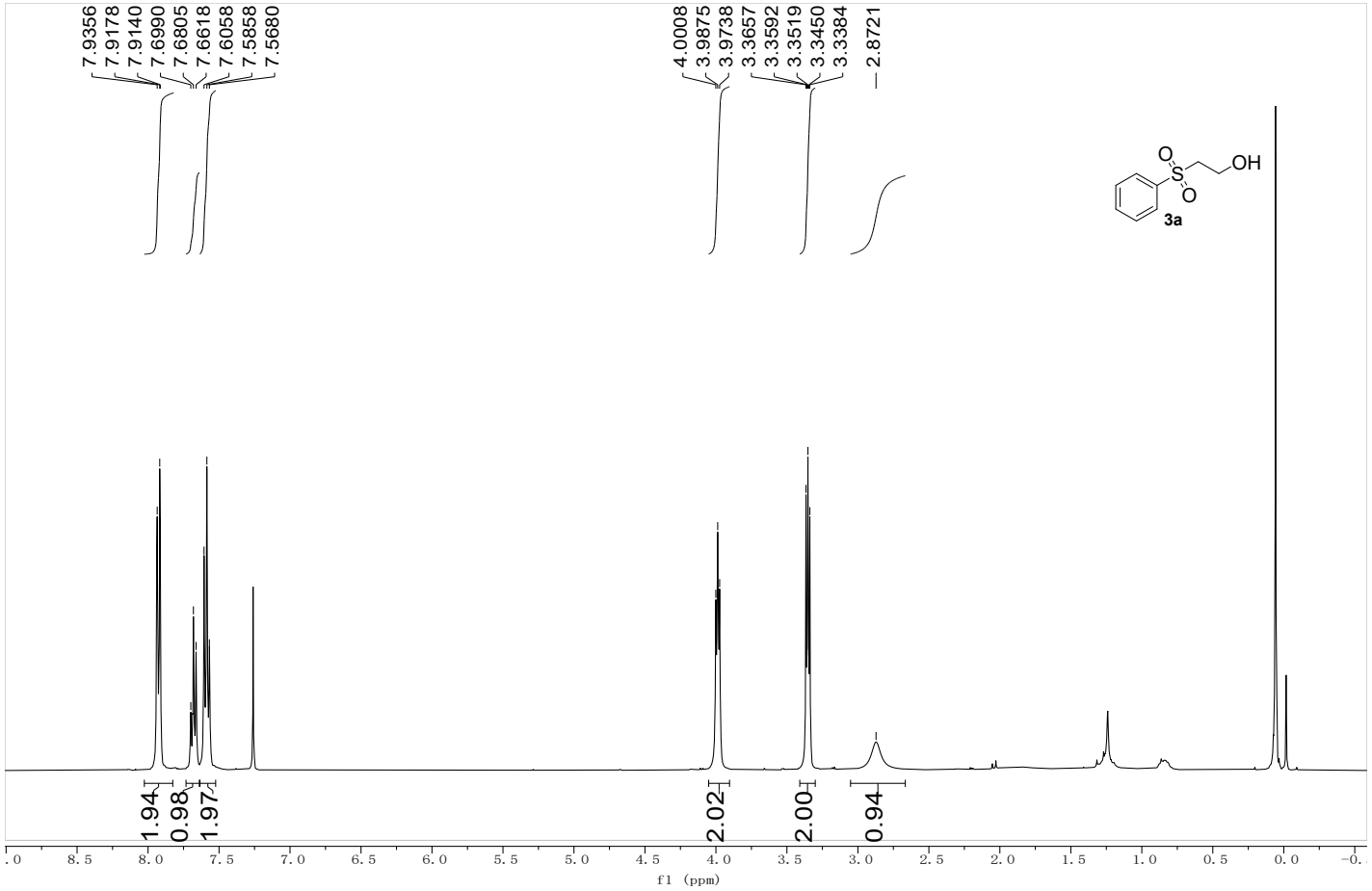
2a ^{1}H NMR (400 MHz, $CDCl_3$)



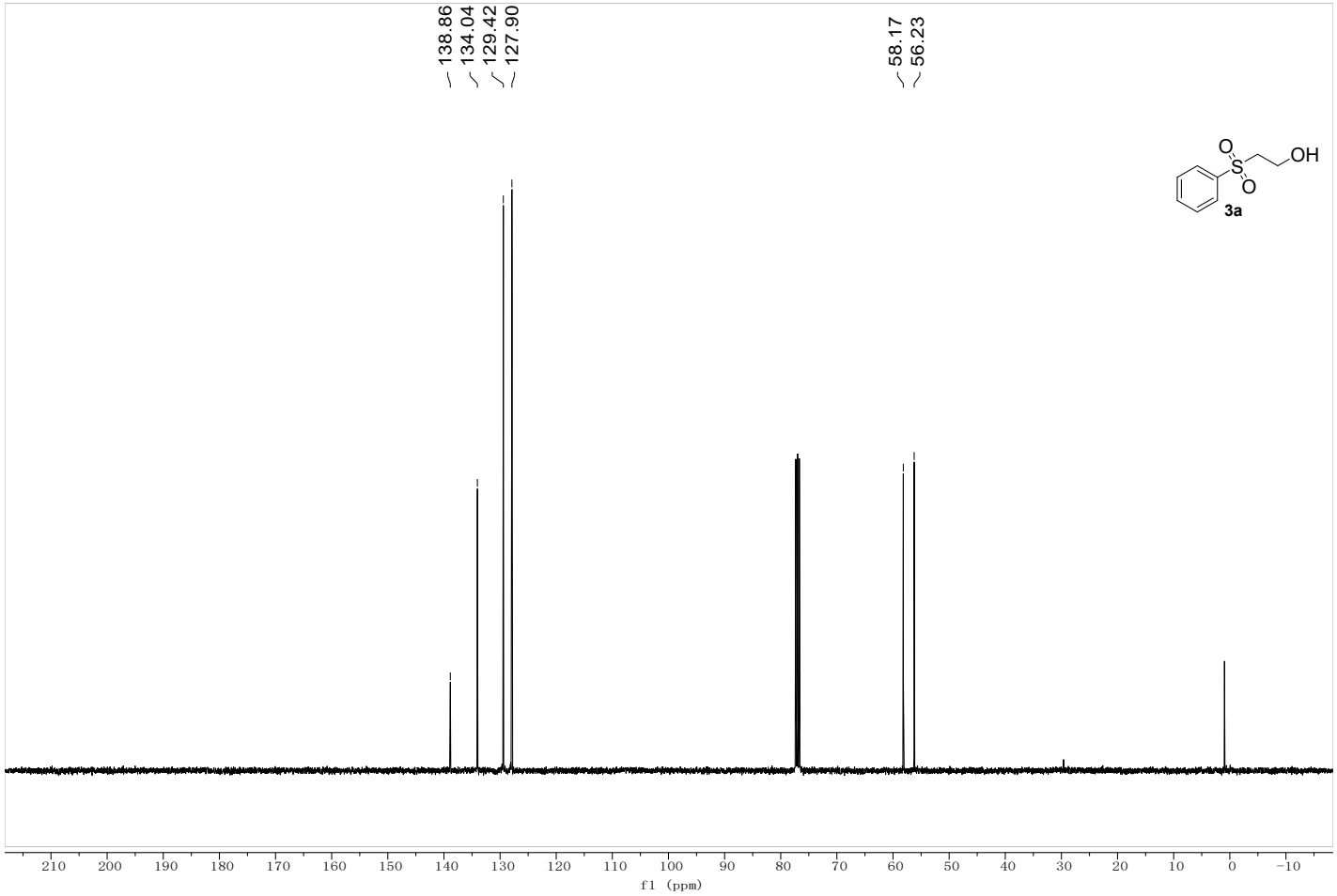
2a $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



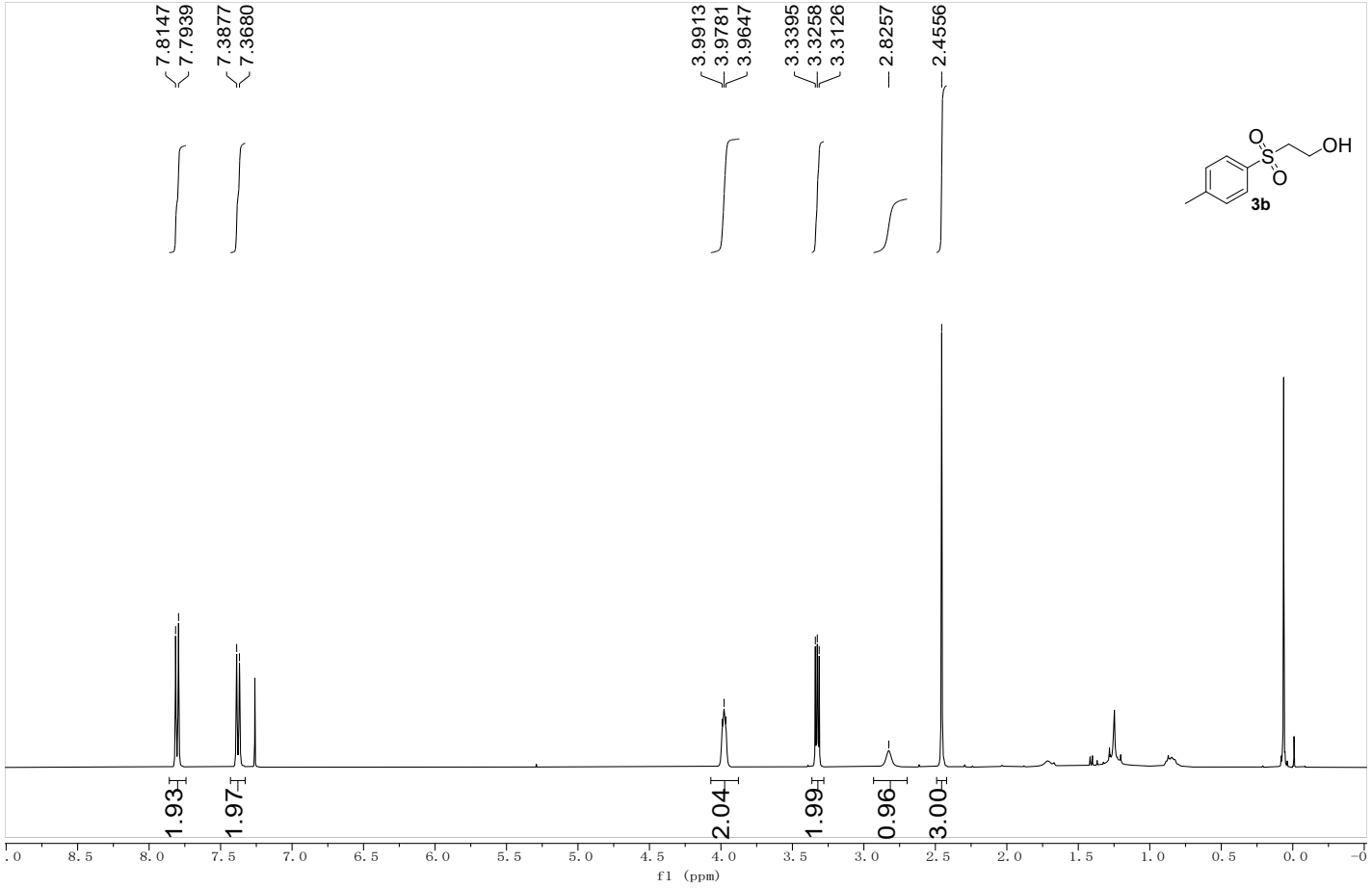
3a ^{1}H NMR (400 MHz, $CDCl_3$)



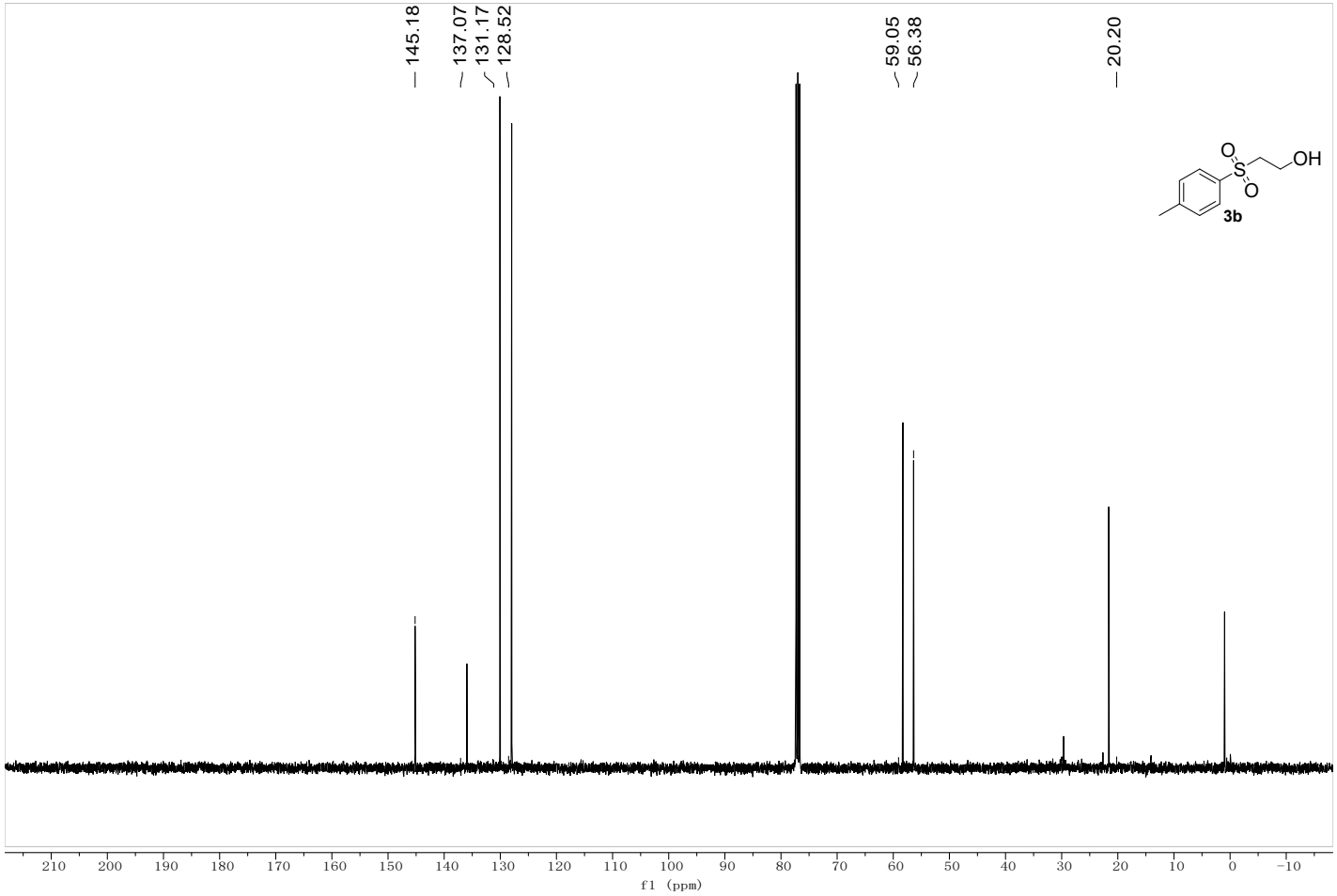
3a $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$)



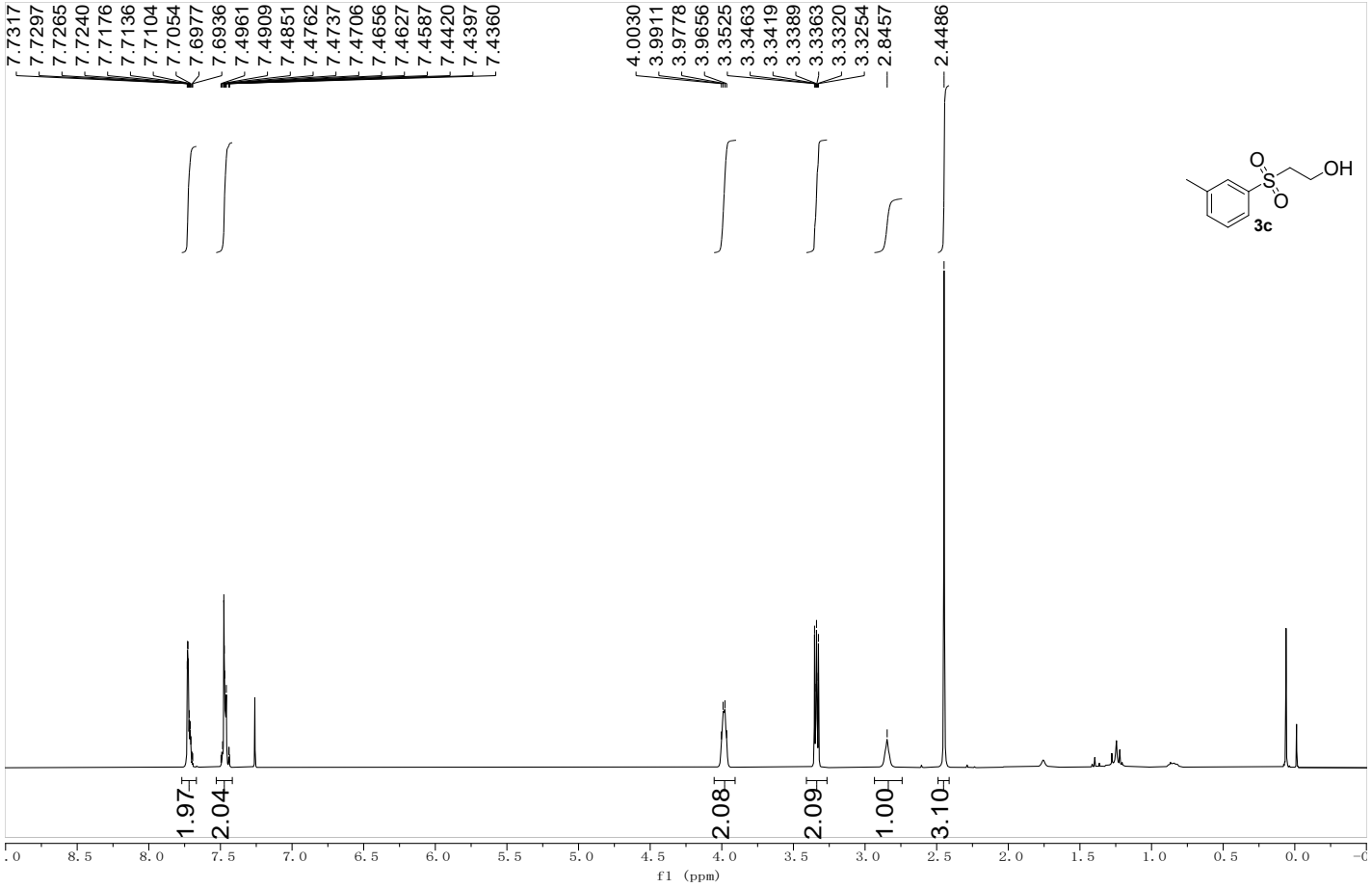
3b ^{1}H NMR (400 MHz, $CDCl_3$)



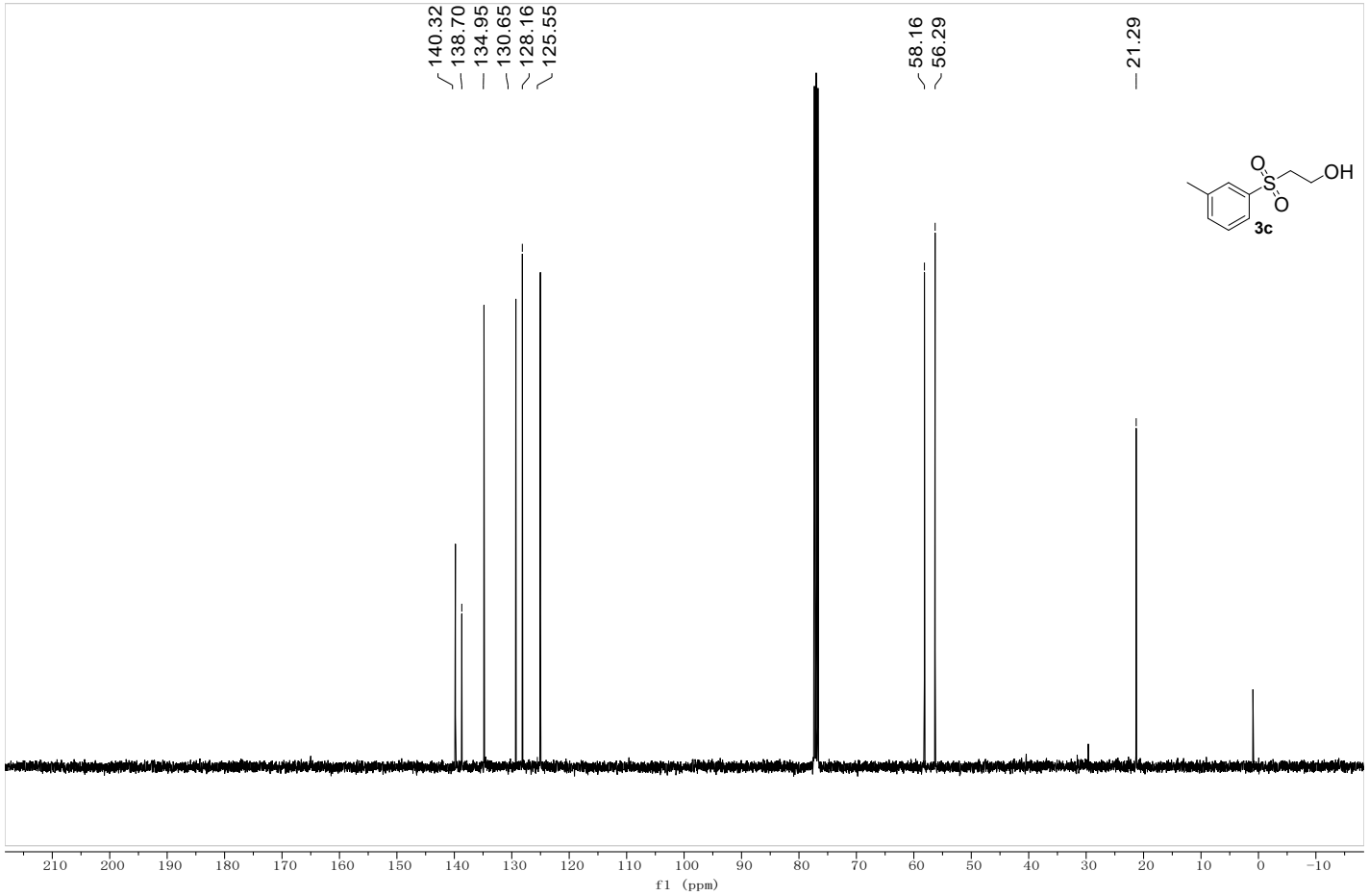
3b $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



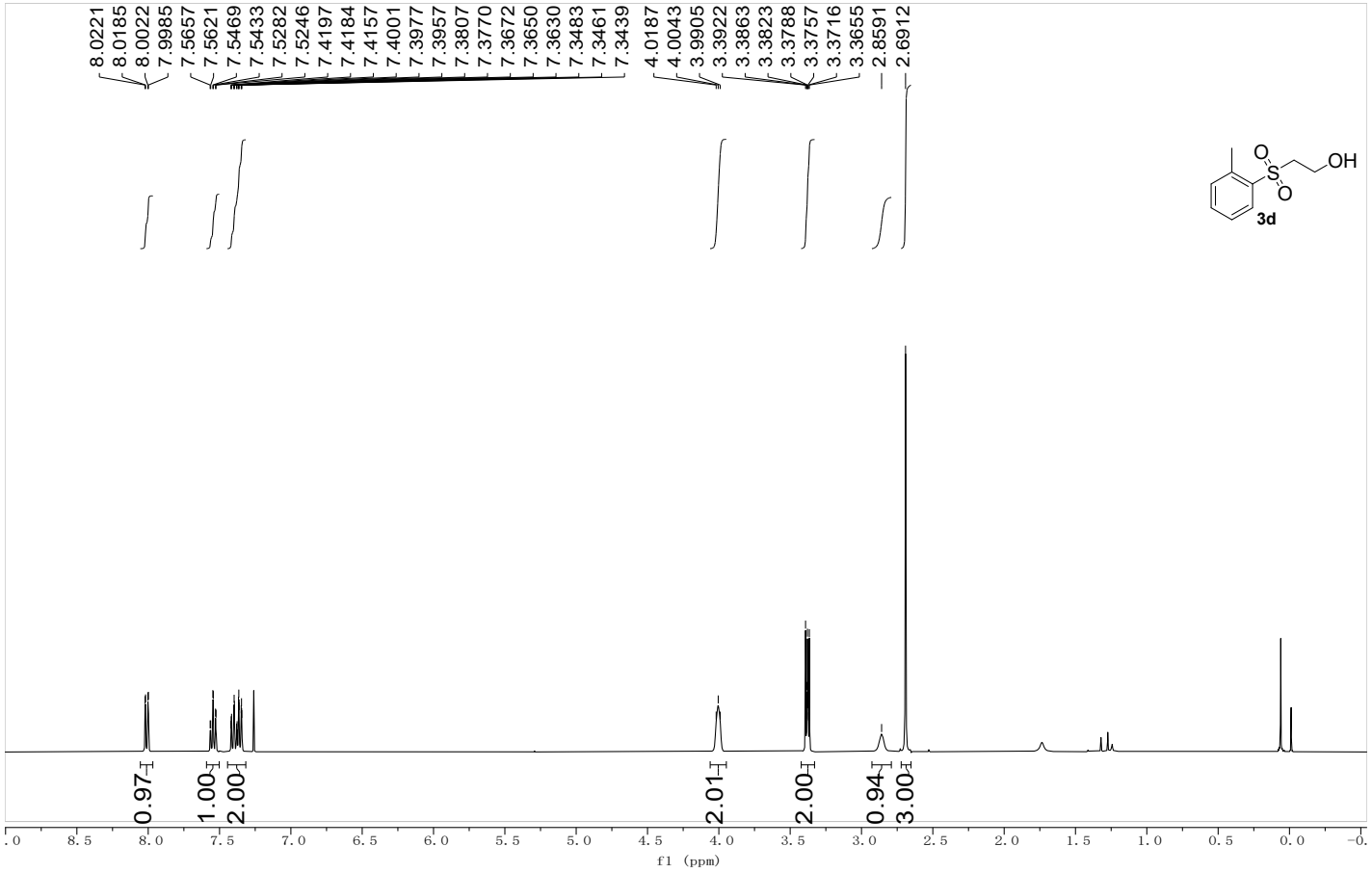
3c ^{1}H NMR (400 MHz, $CDCl_3$)



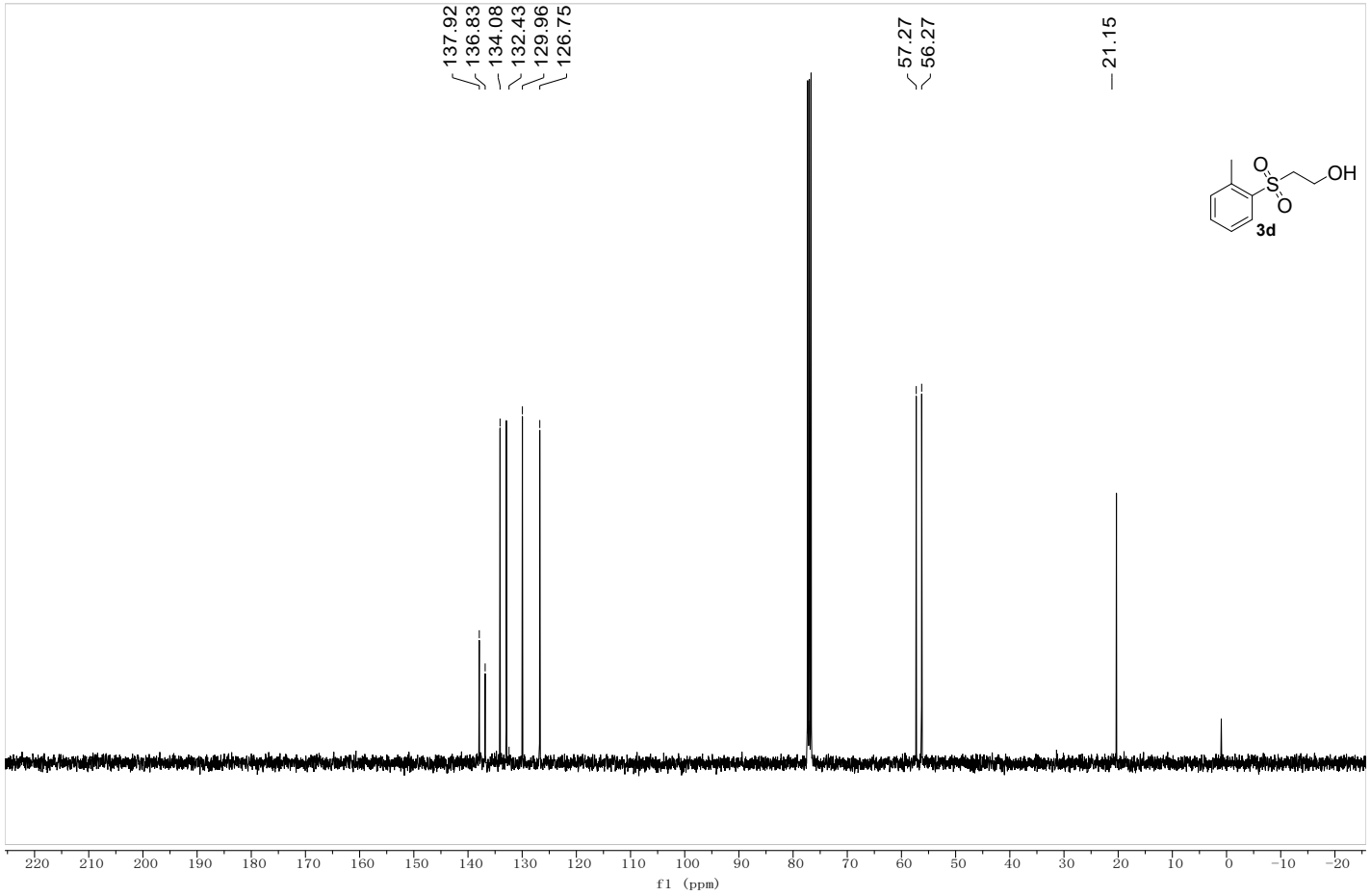
3c $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



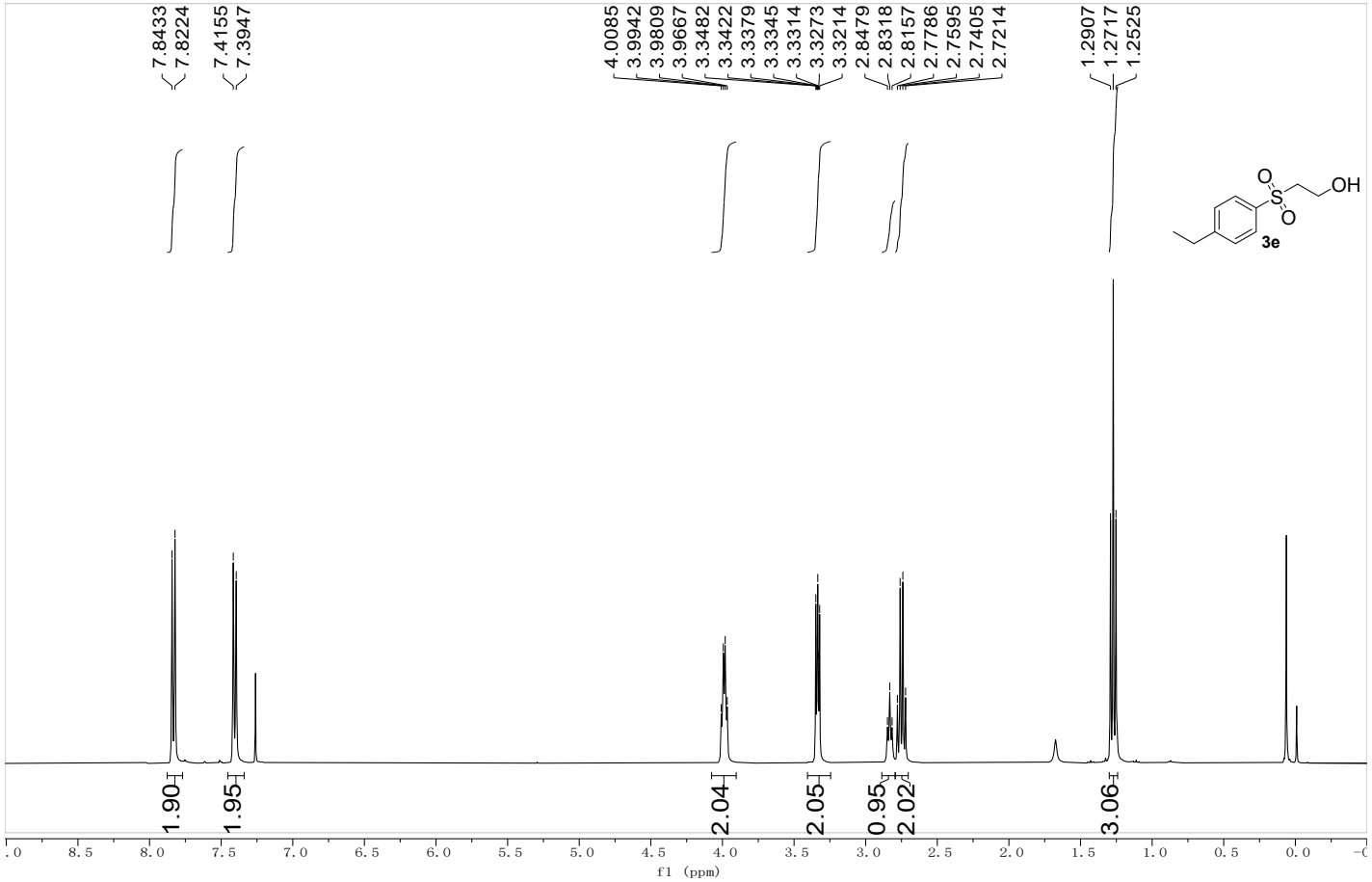
3d ^{1}H NMR (400 MHz, $CDCl_3$)



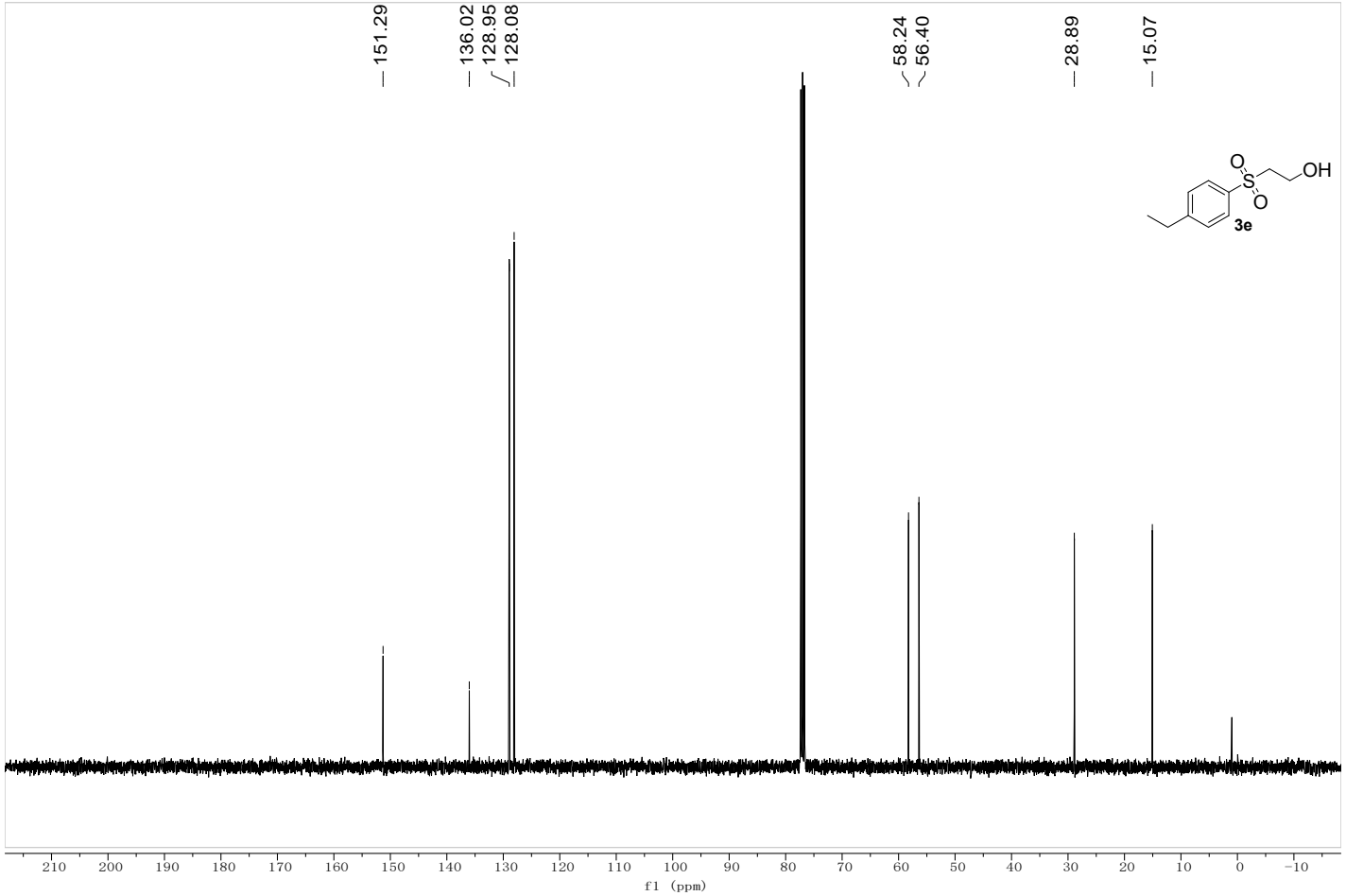
3d $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



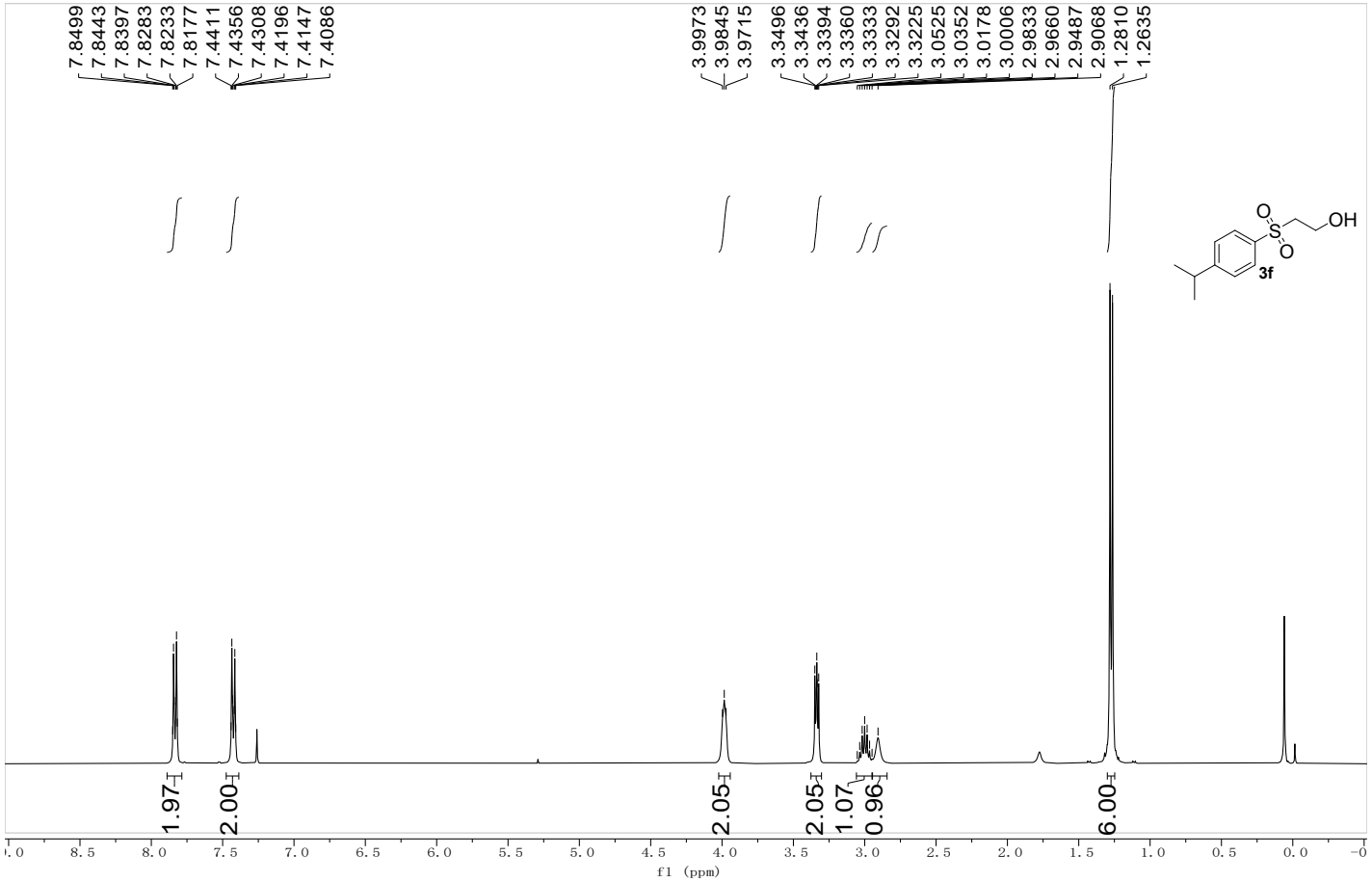
3e ^{1}H NMR (400 MHz, $CDCl_3$)



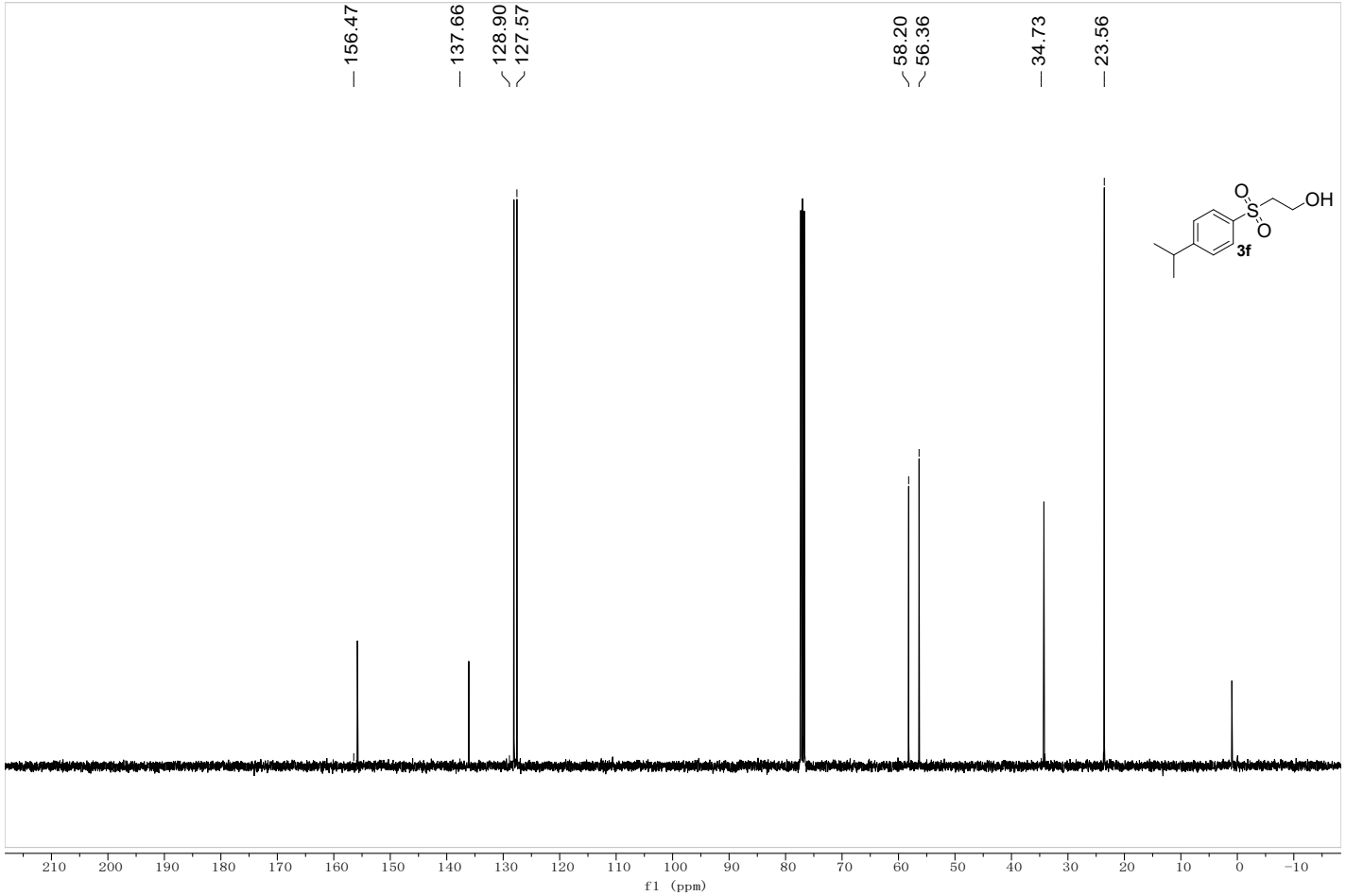
3e $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



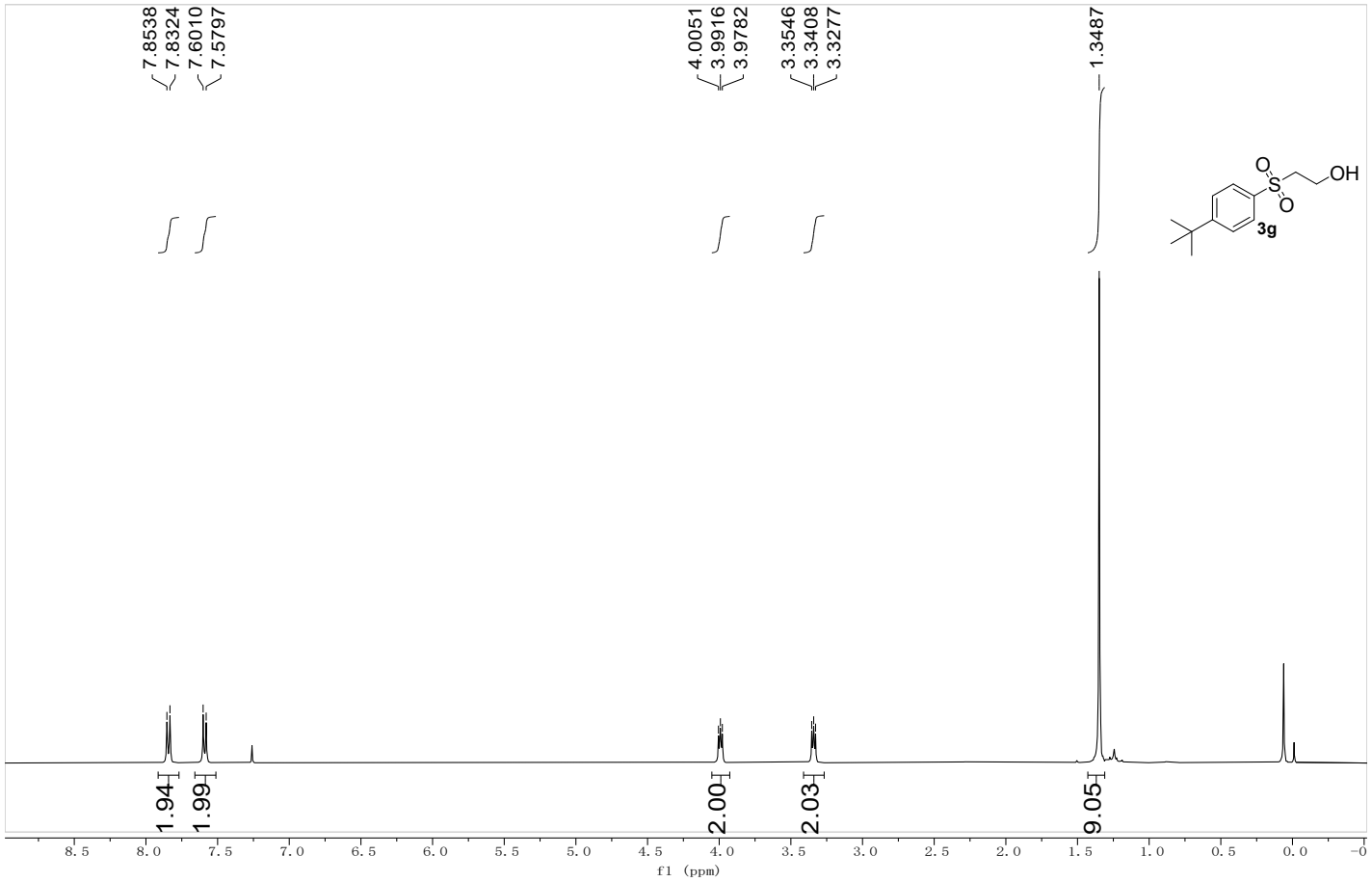
3f ^{1}H NMR (400 MHz, $CDCl_3$)



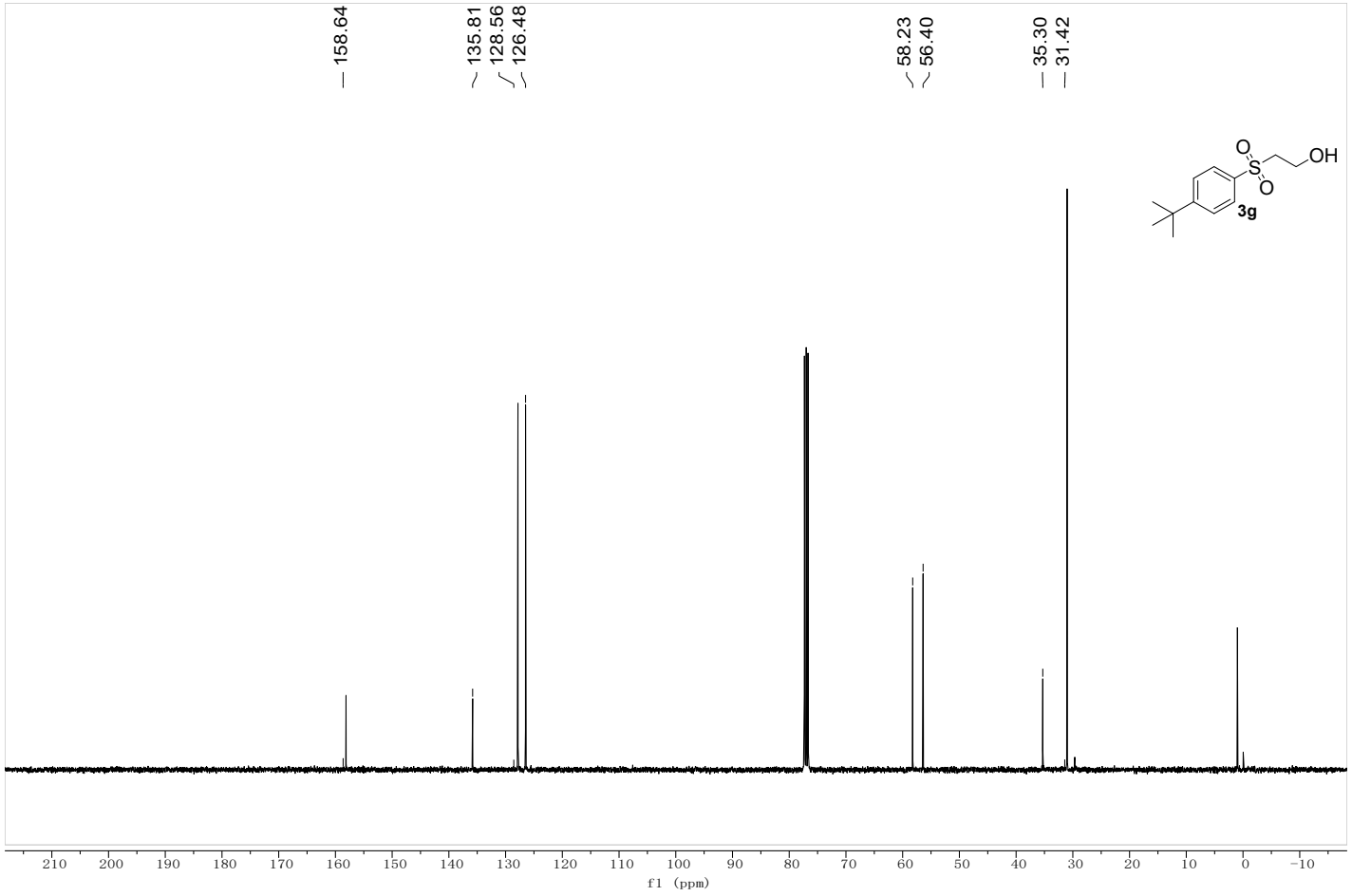
3f $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



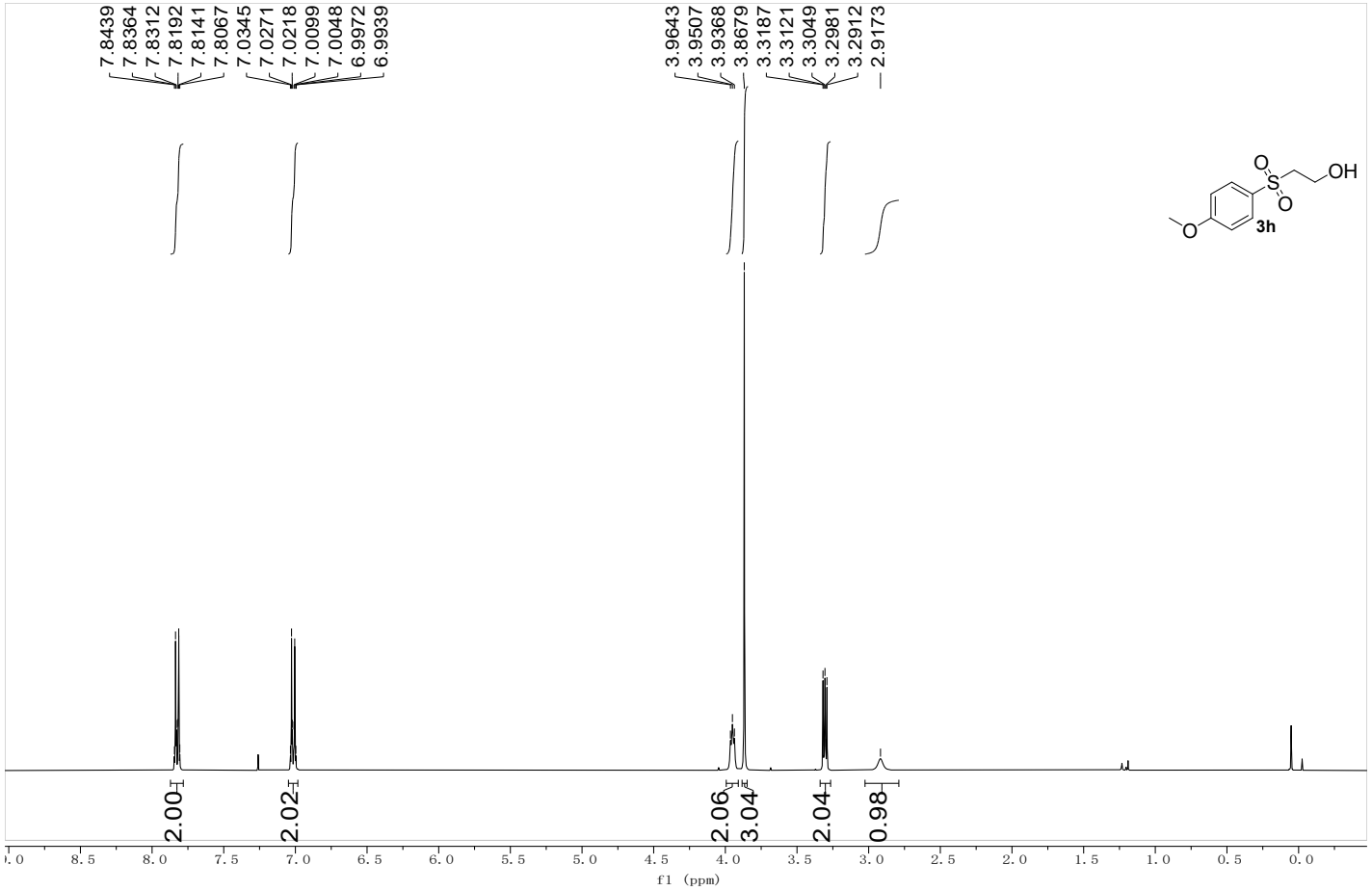
3g ^{1}H NMR (400 MHz, $CDCl_3$)



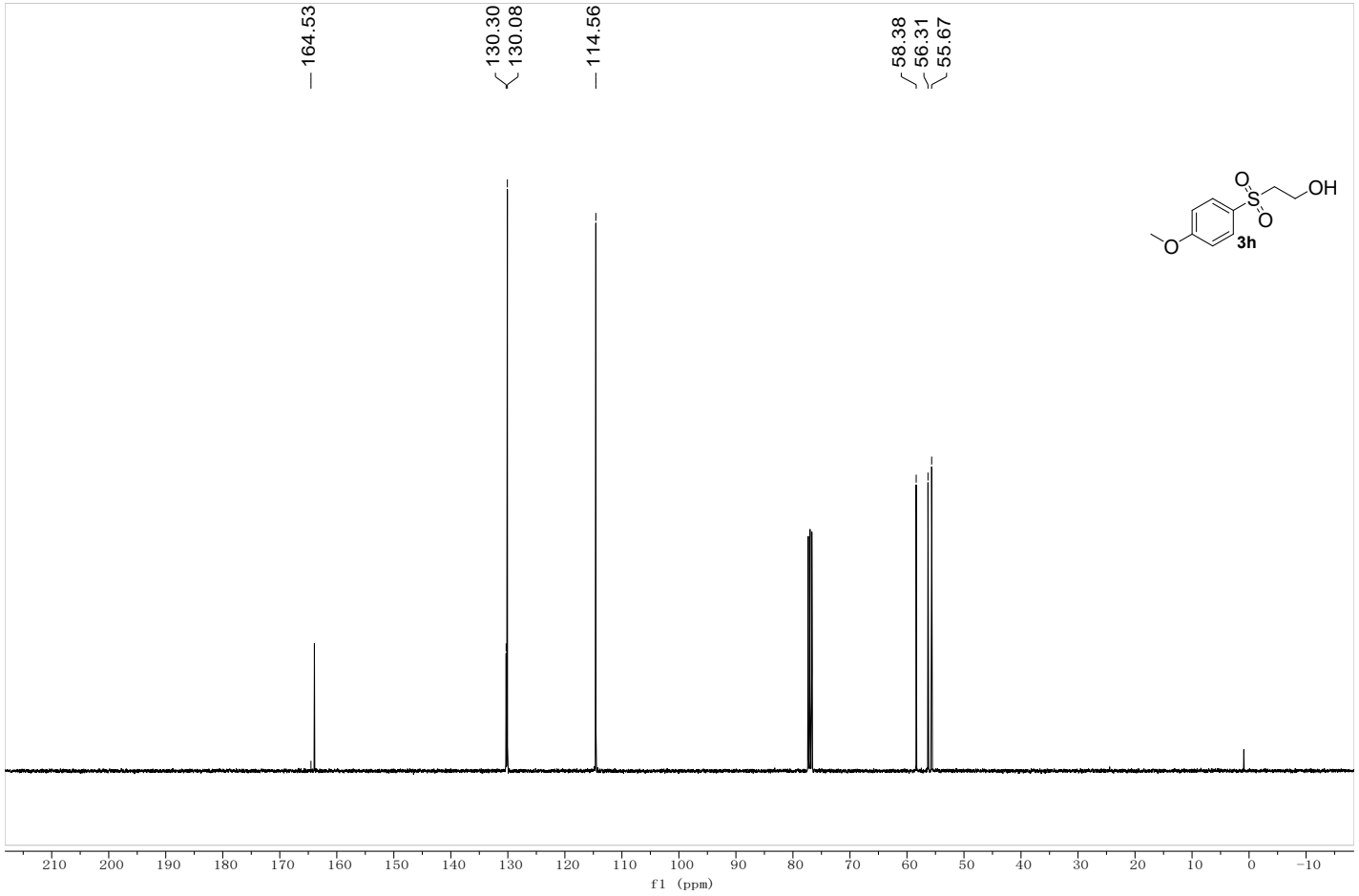
3g $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



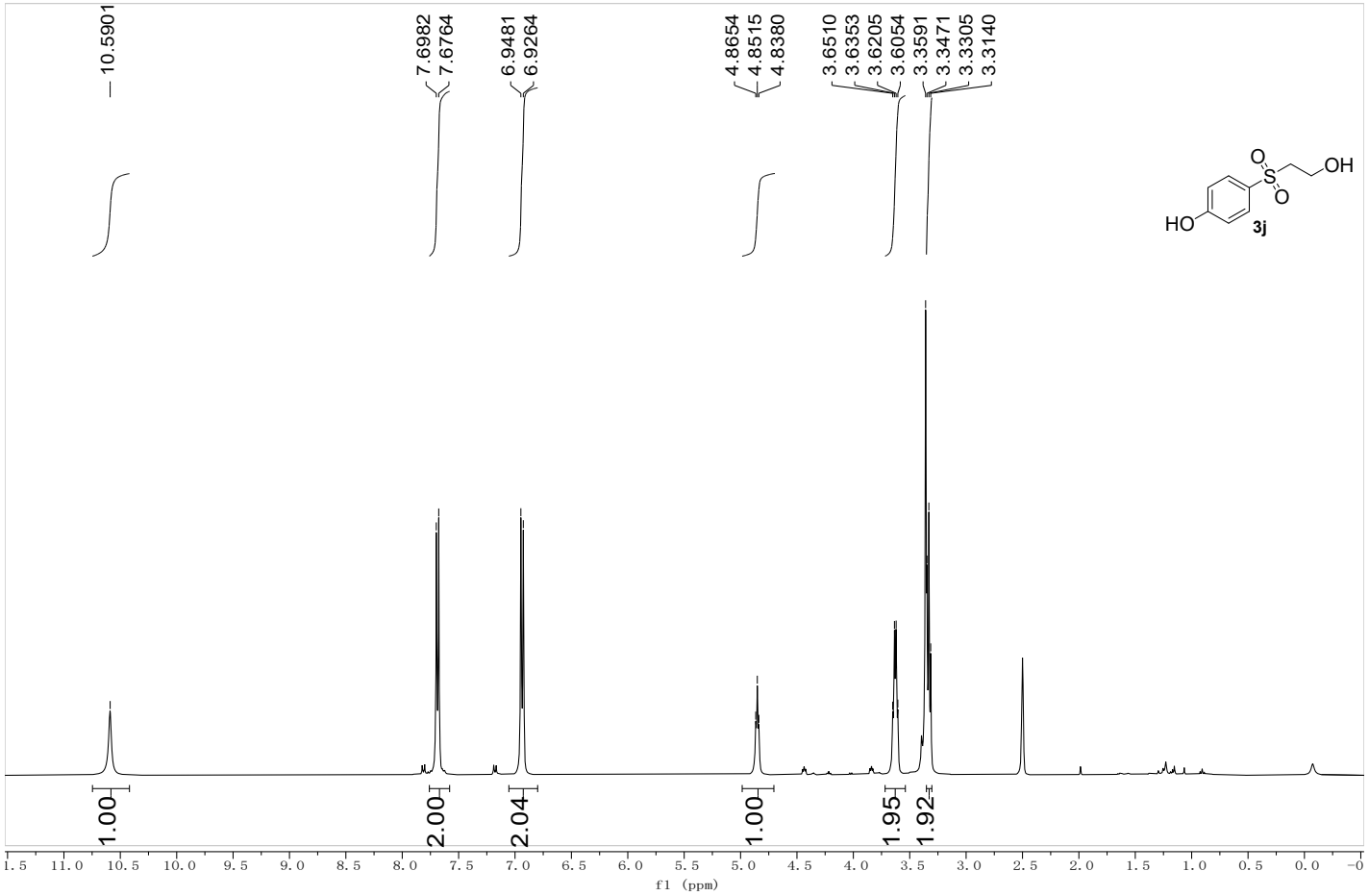
3h ^{1}H NMR (400 MHz, $CDCl_3$)



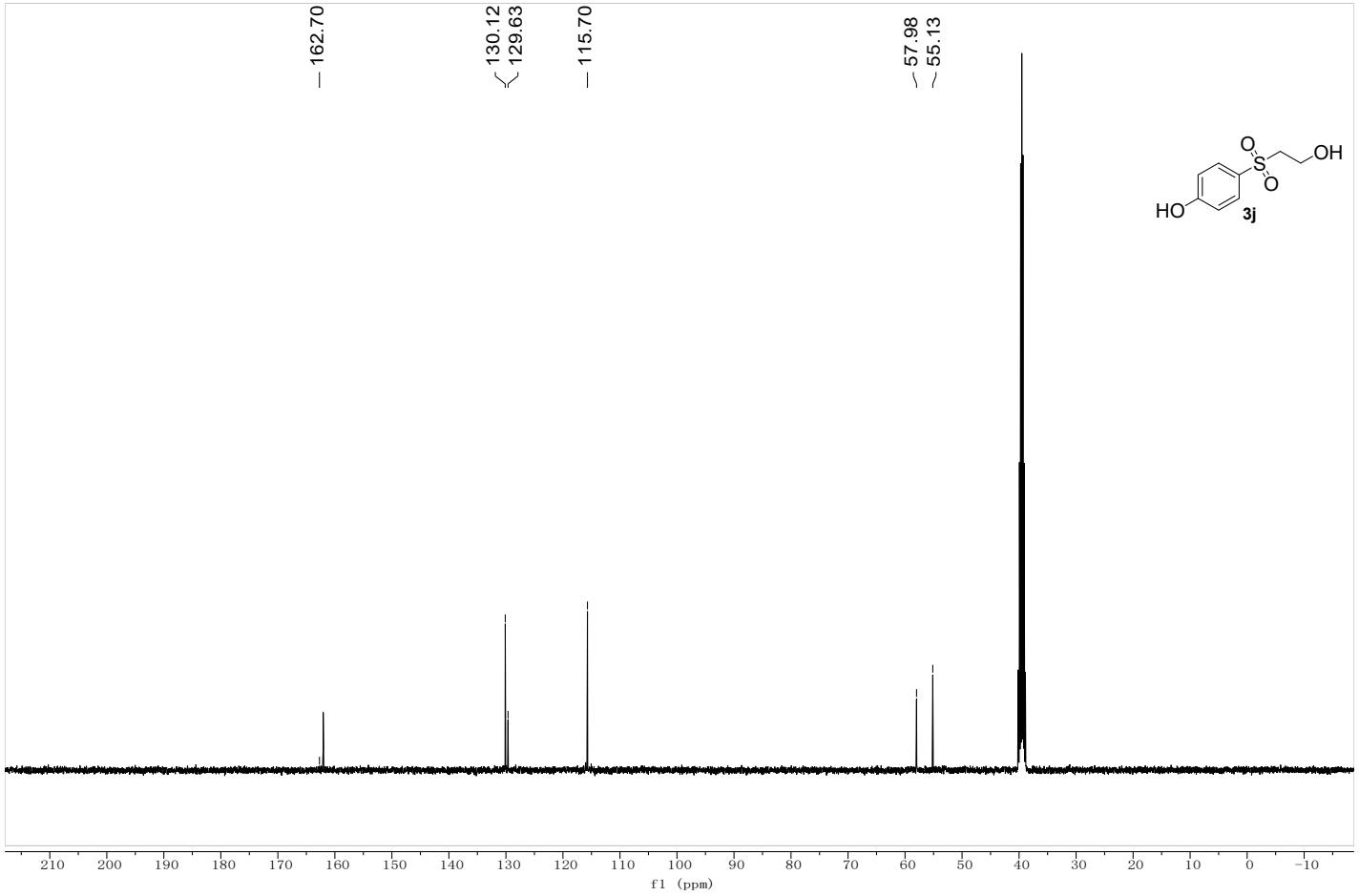
3h $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



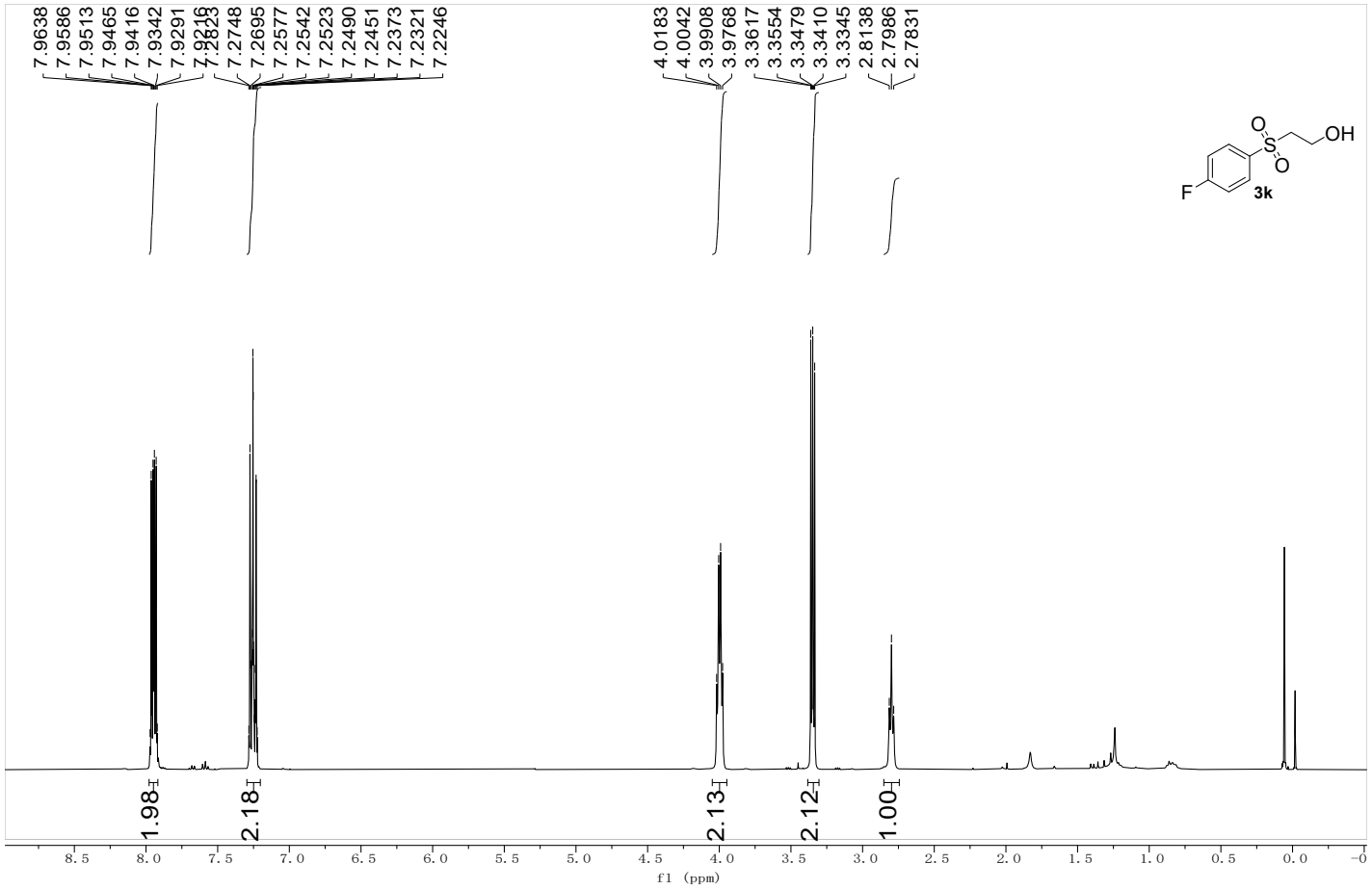
3j ^{1}H NMR (400 MHz, DMSO)



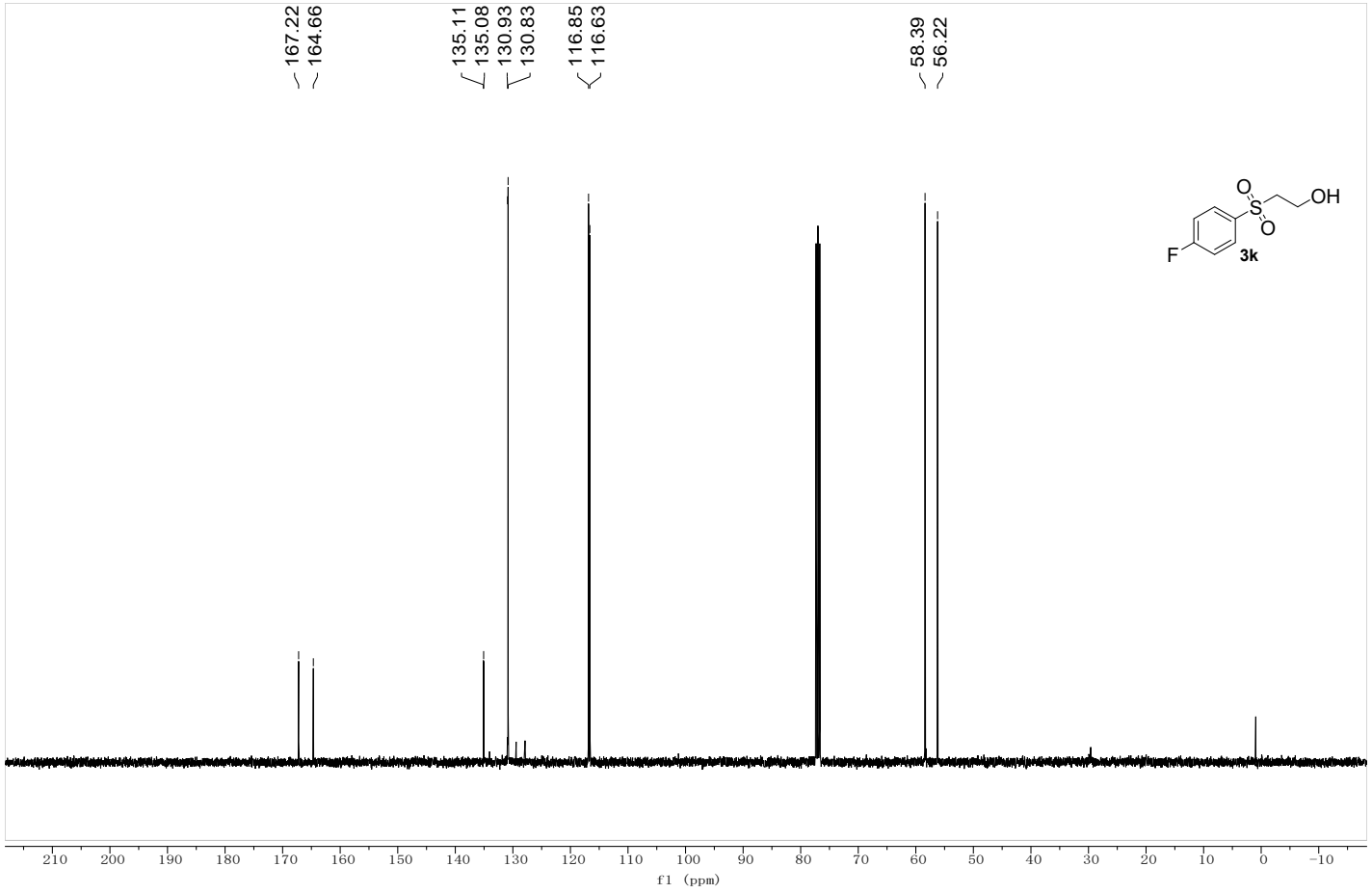
3j $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO)



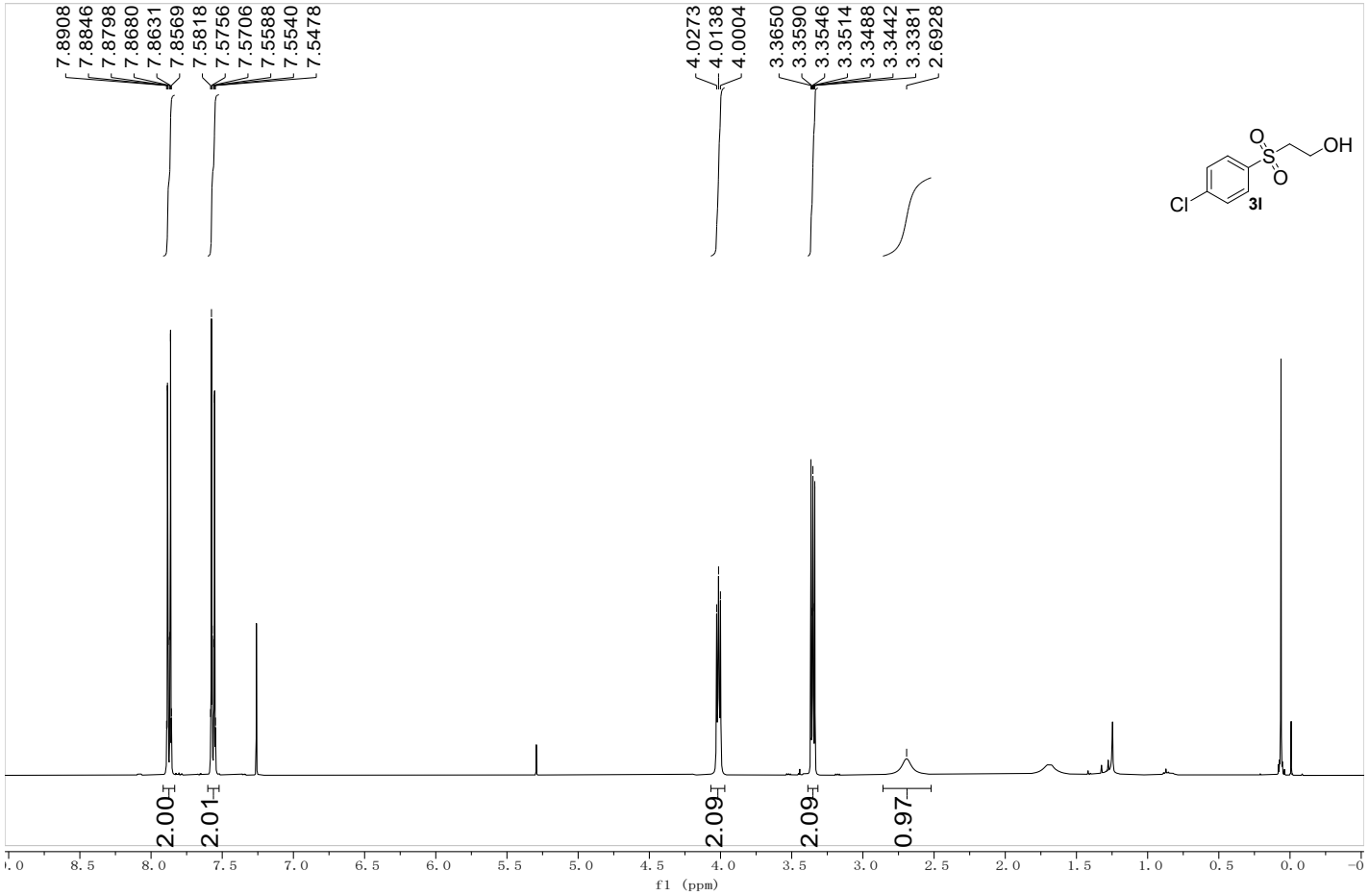
3k ^{1}H NMR (400 MHz, $CDCl_3$)



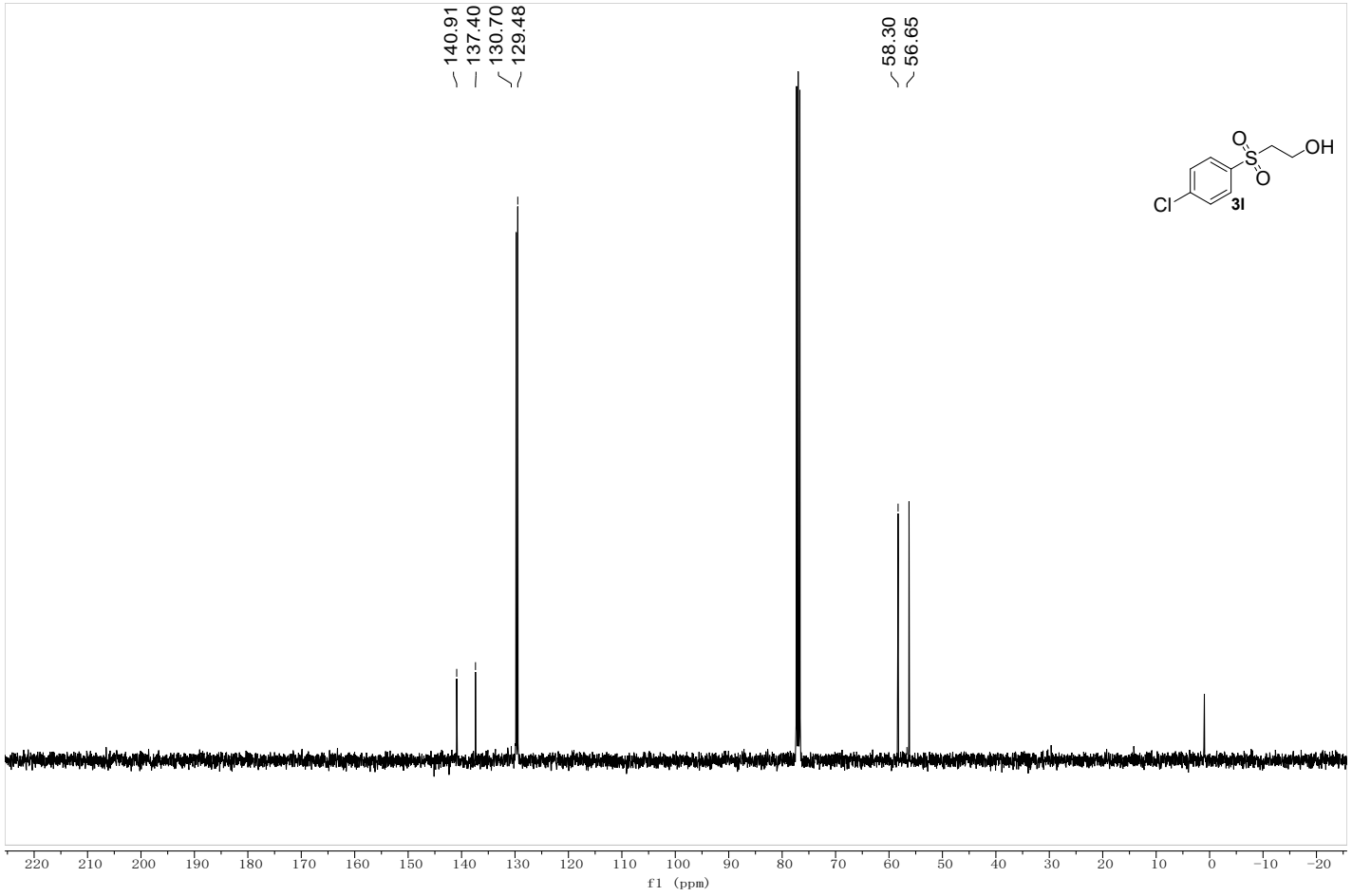
3k $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



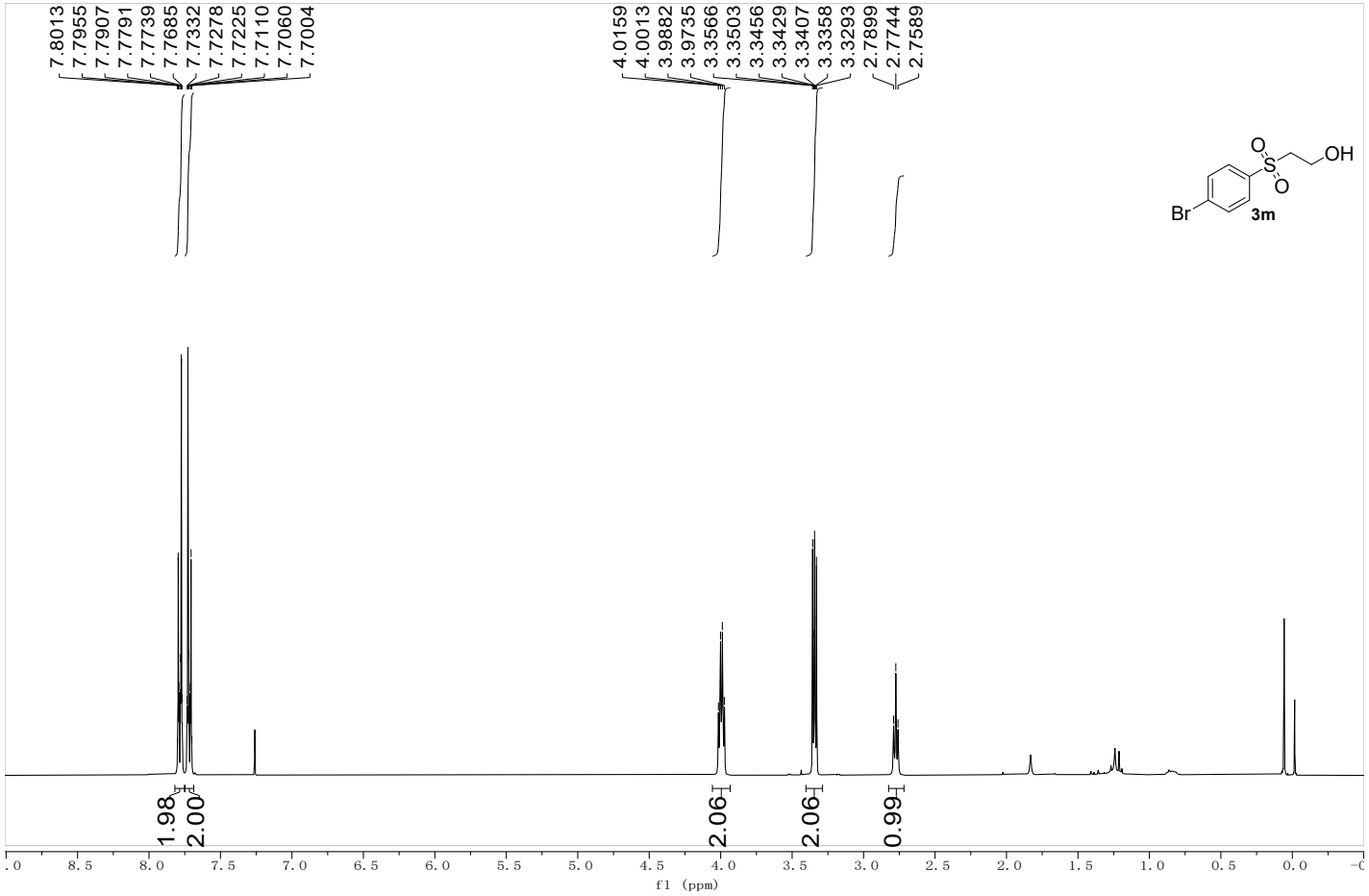
3l ^{1}H NMR (400 MHz, $CDCl_3$)



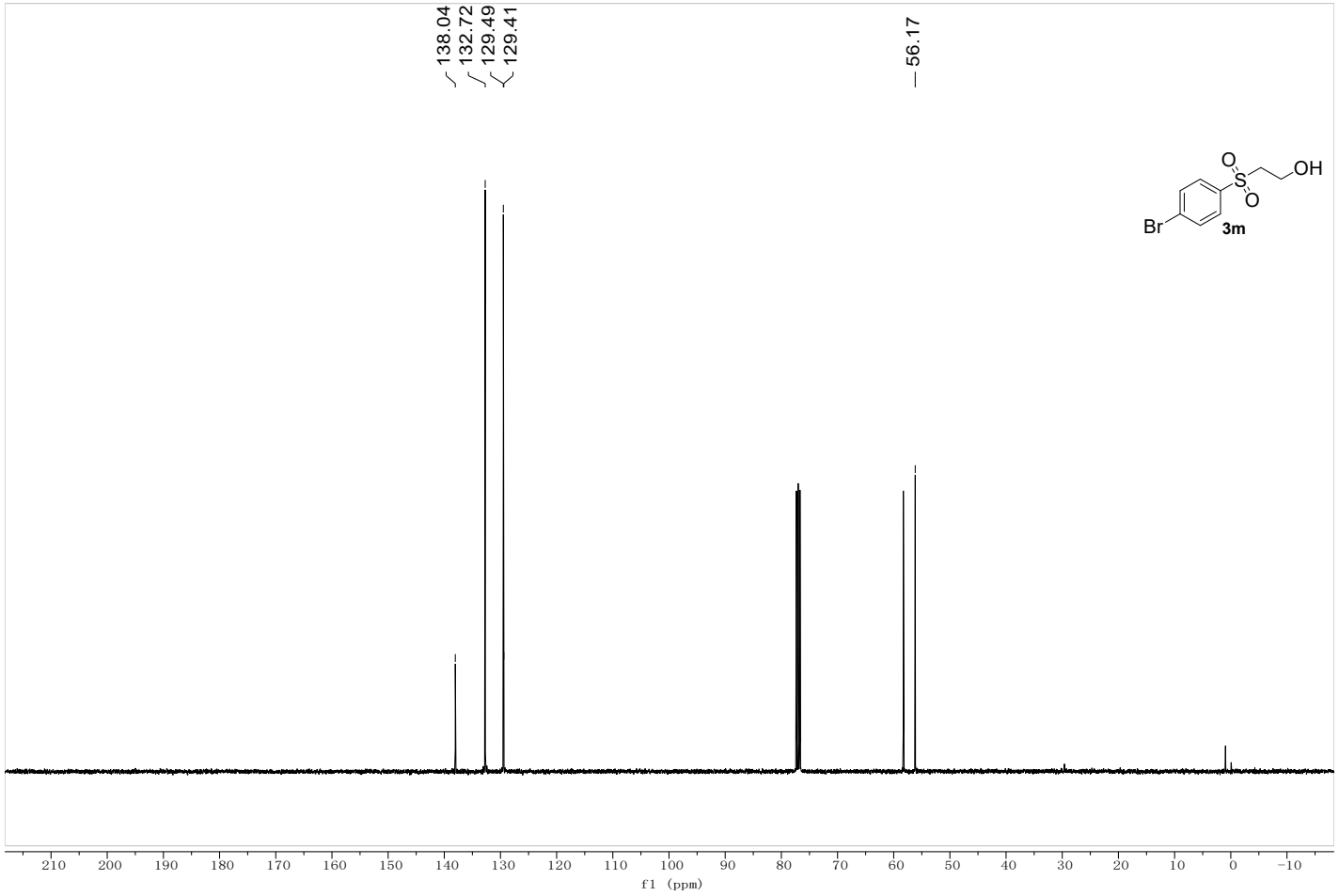
3l $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



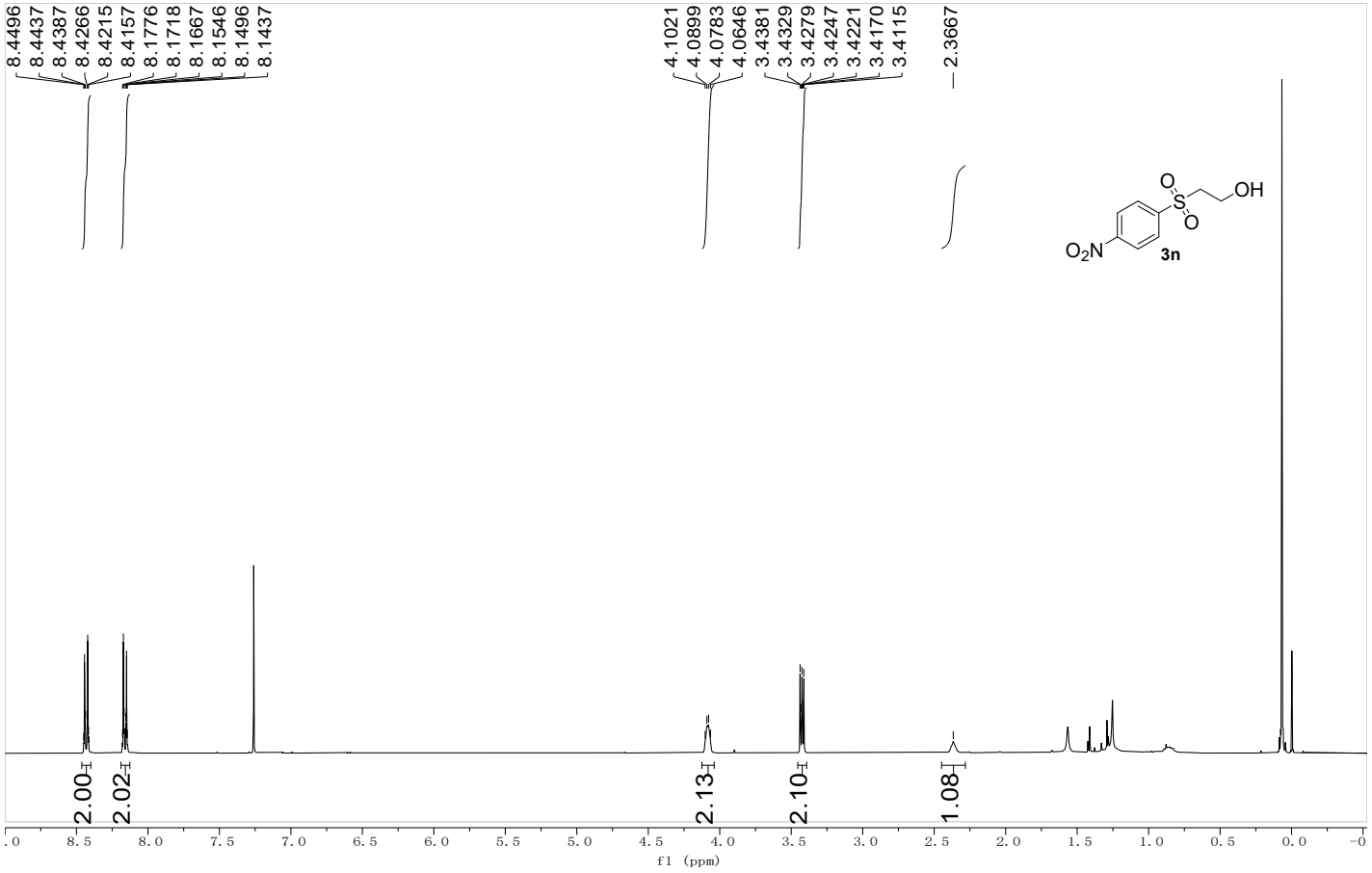
3m ^{1}H NMR (400 MHz, $CDCl_3$)



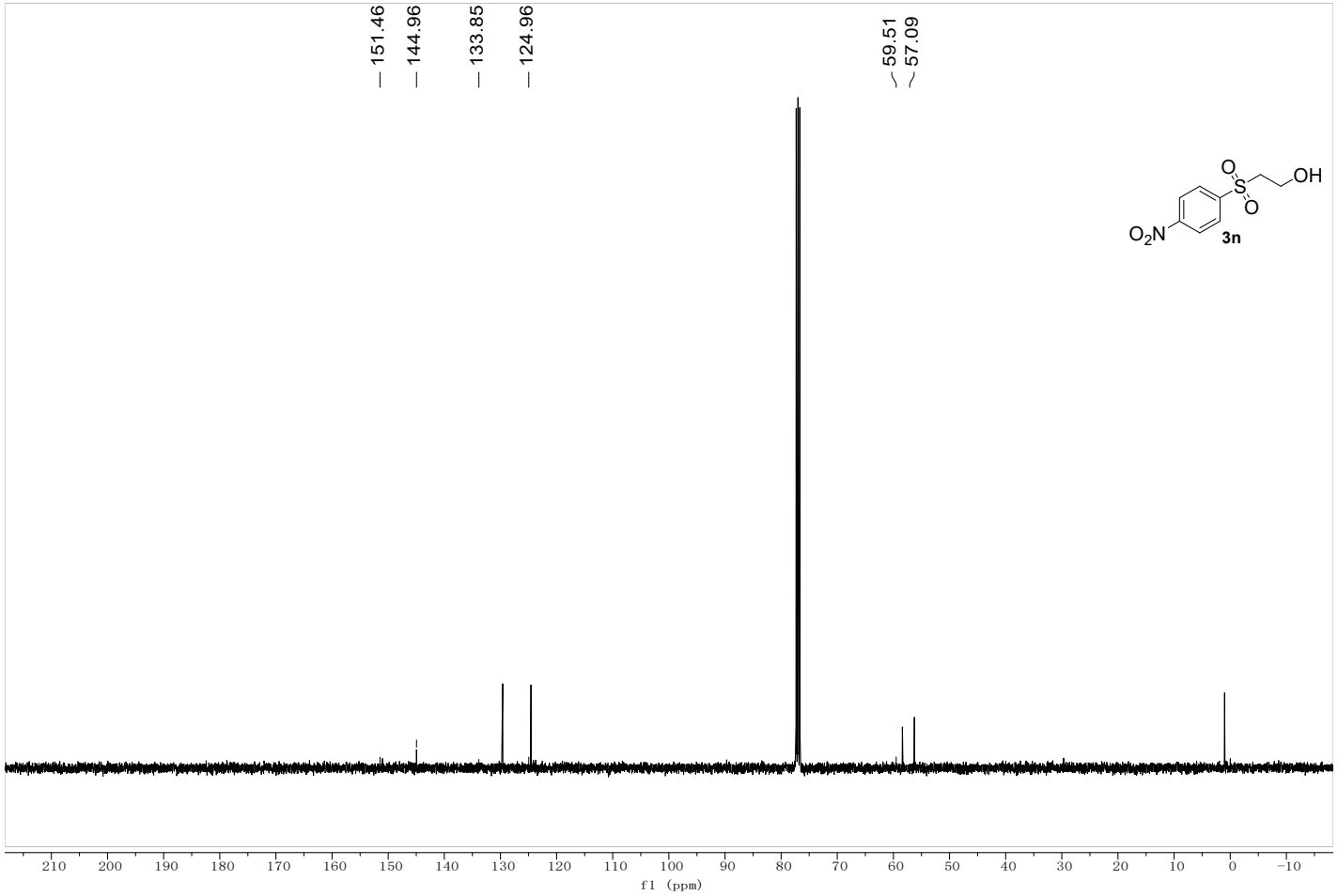
3m $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



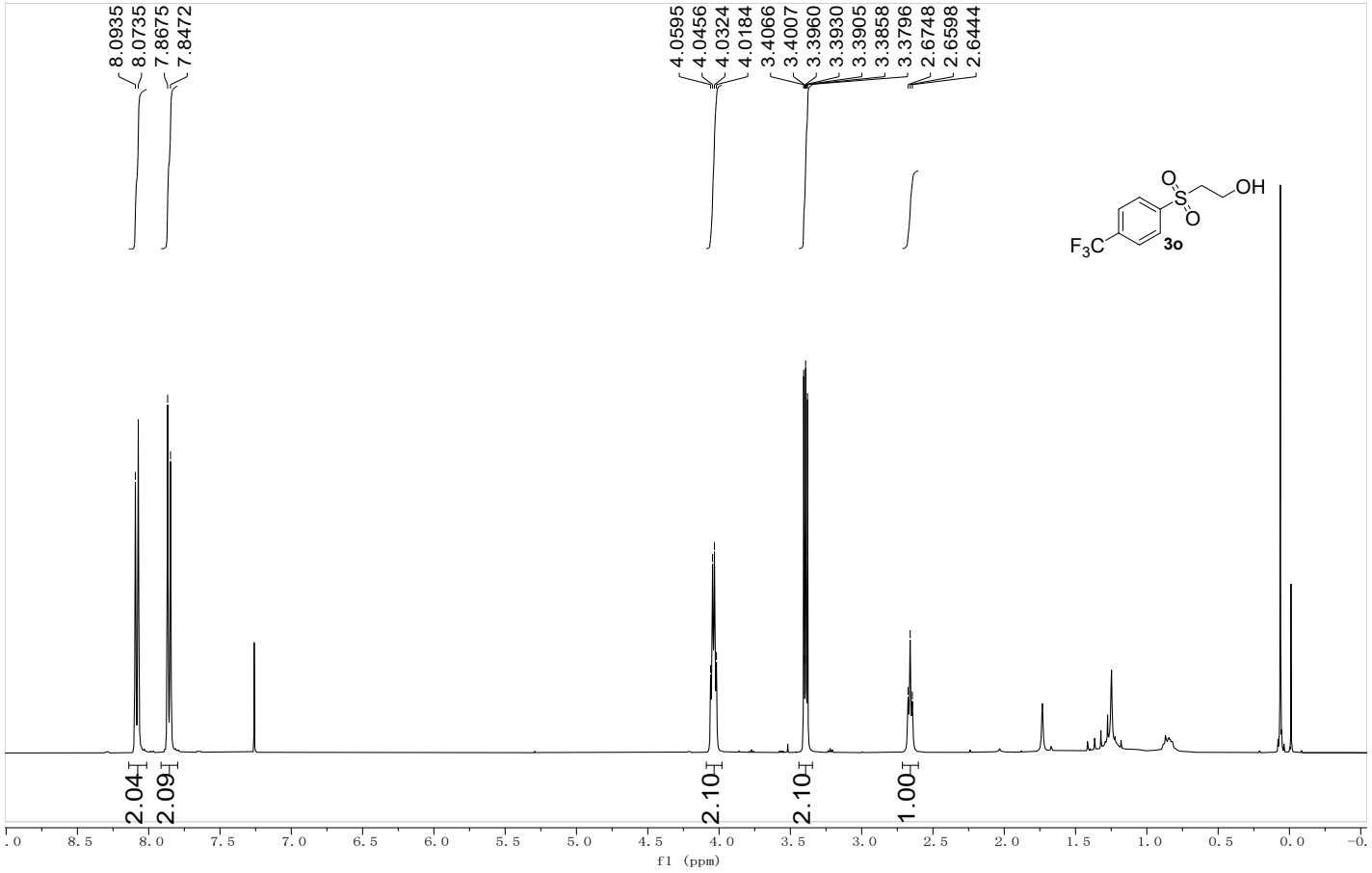
3n ^{1}H NMR (400 MHz, $CDCl_3$)



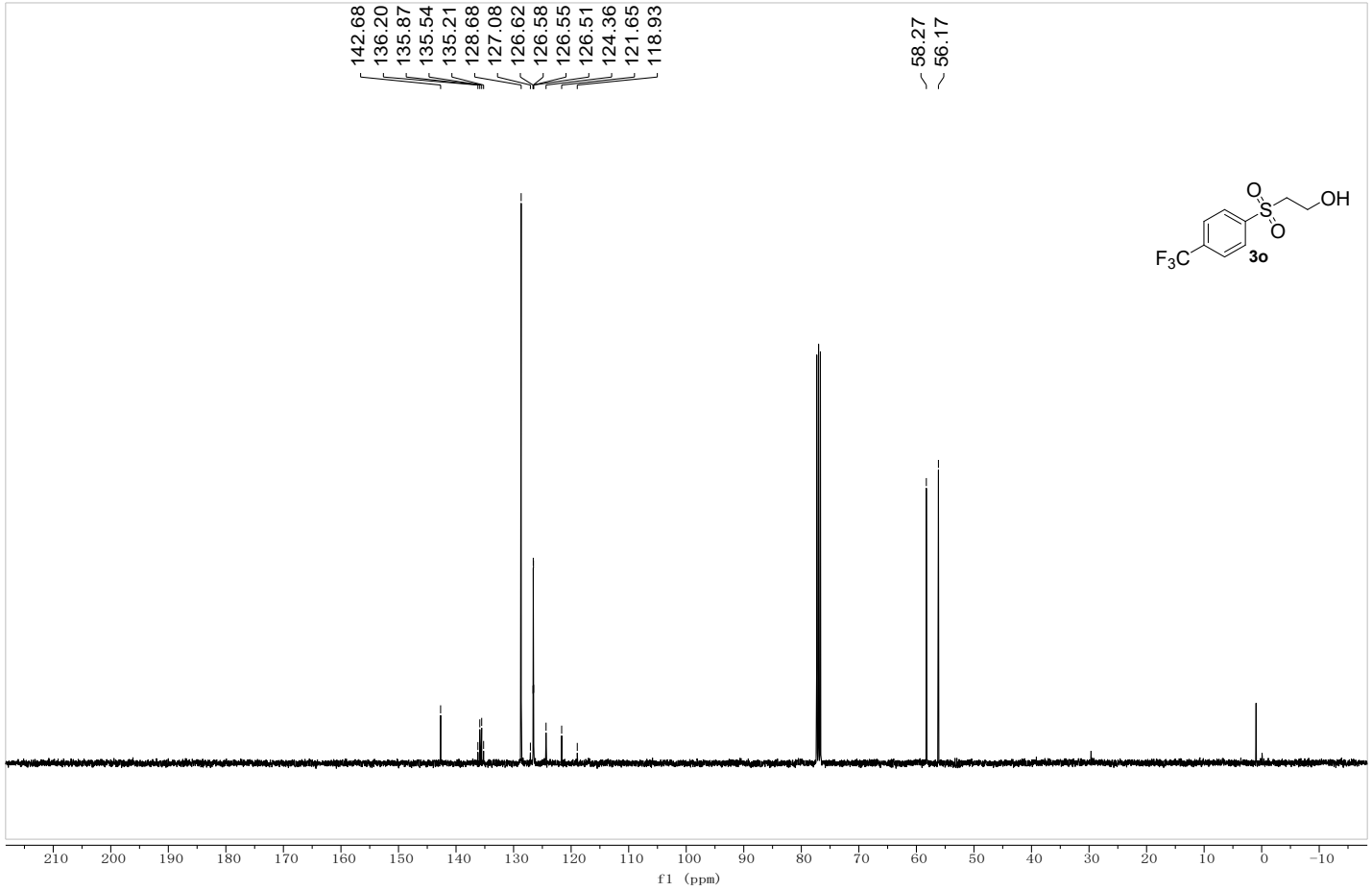
3n $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



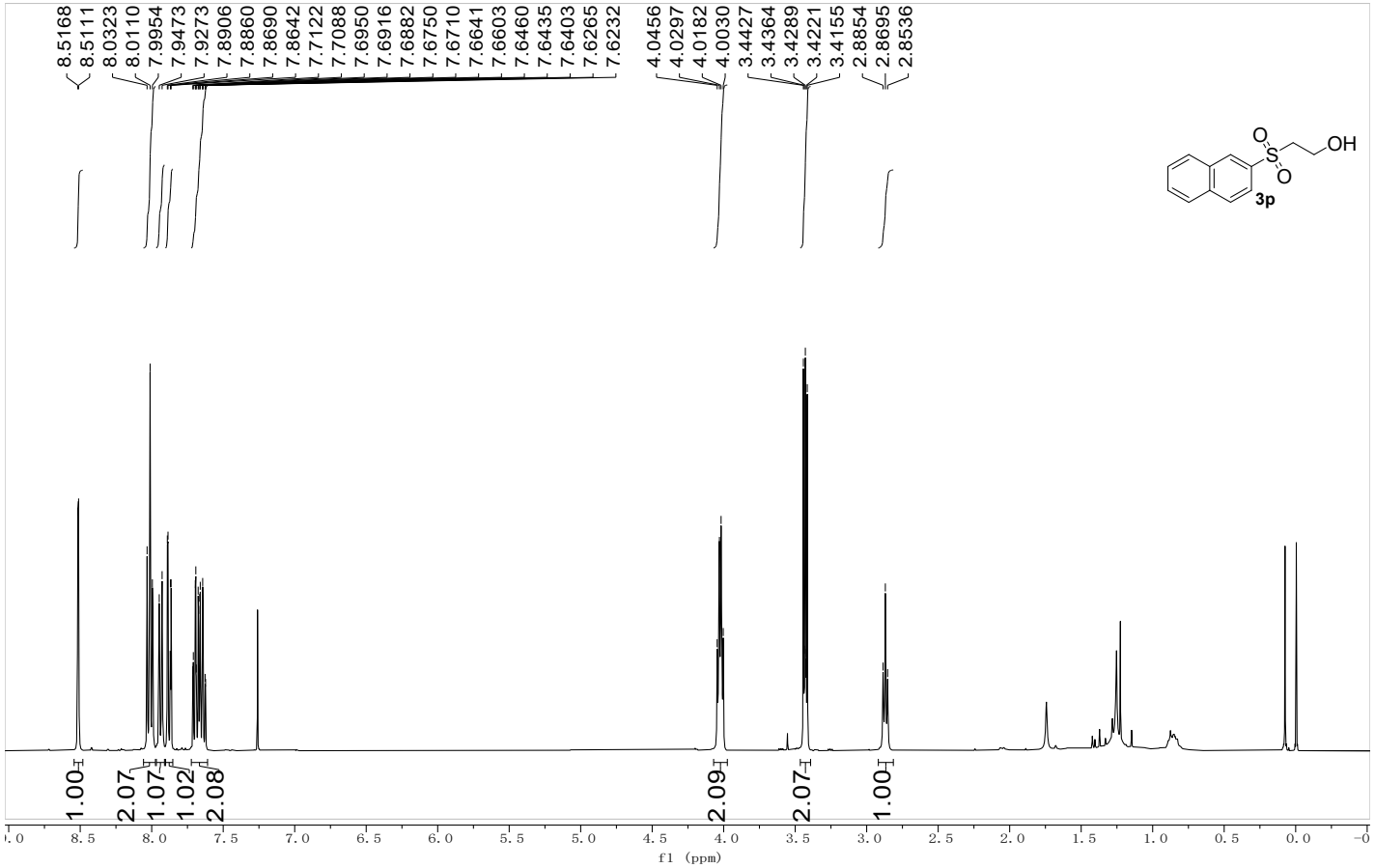
3o ^{1}H NMR (400 MHz, $CDCl_3$)



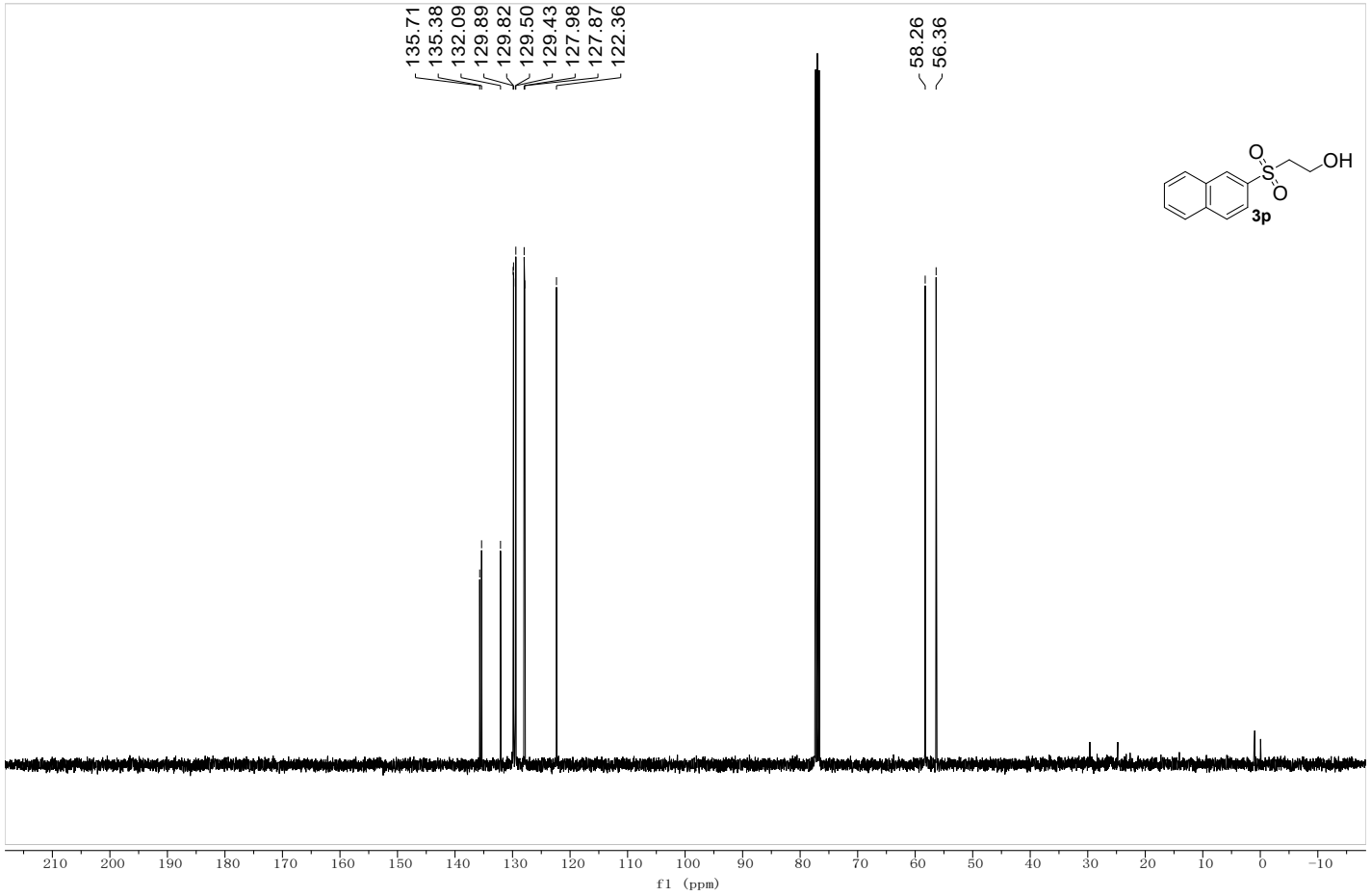
3o $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



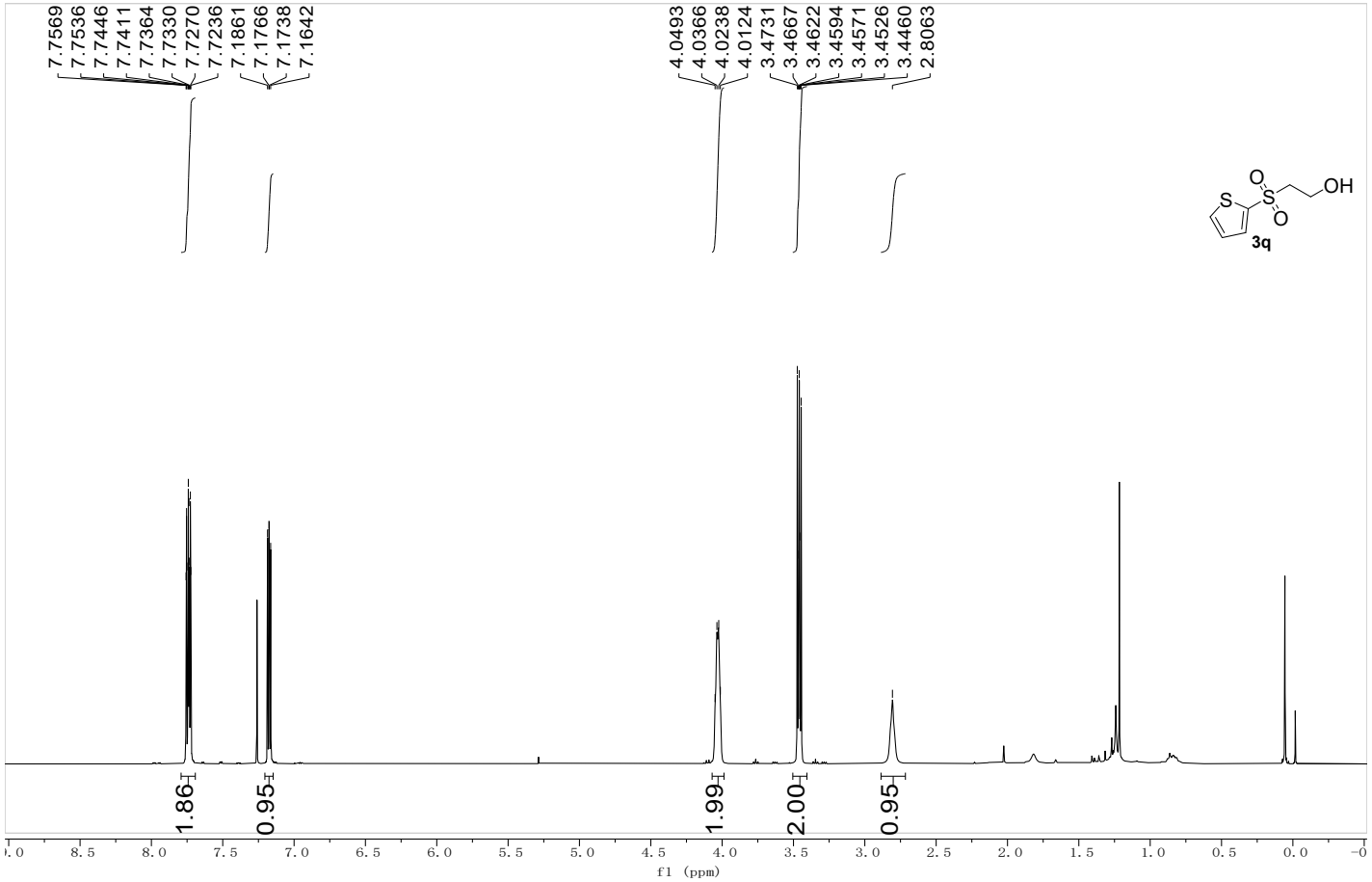
3p ^{1}H NMR (400 MHz, $CDCl_3$)



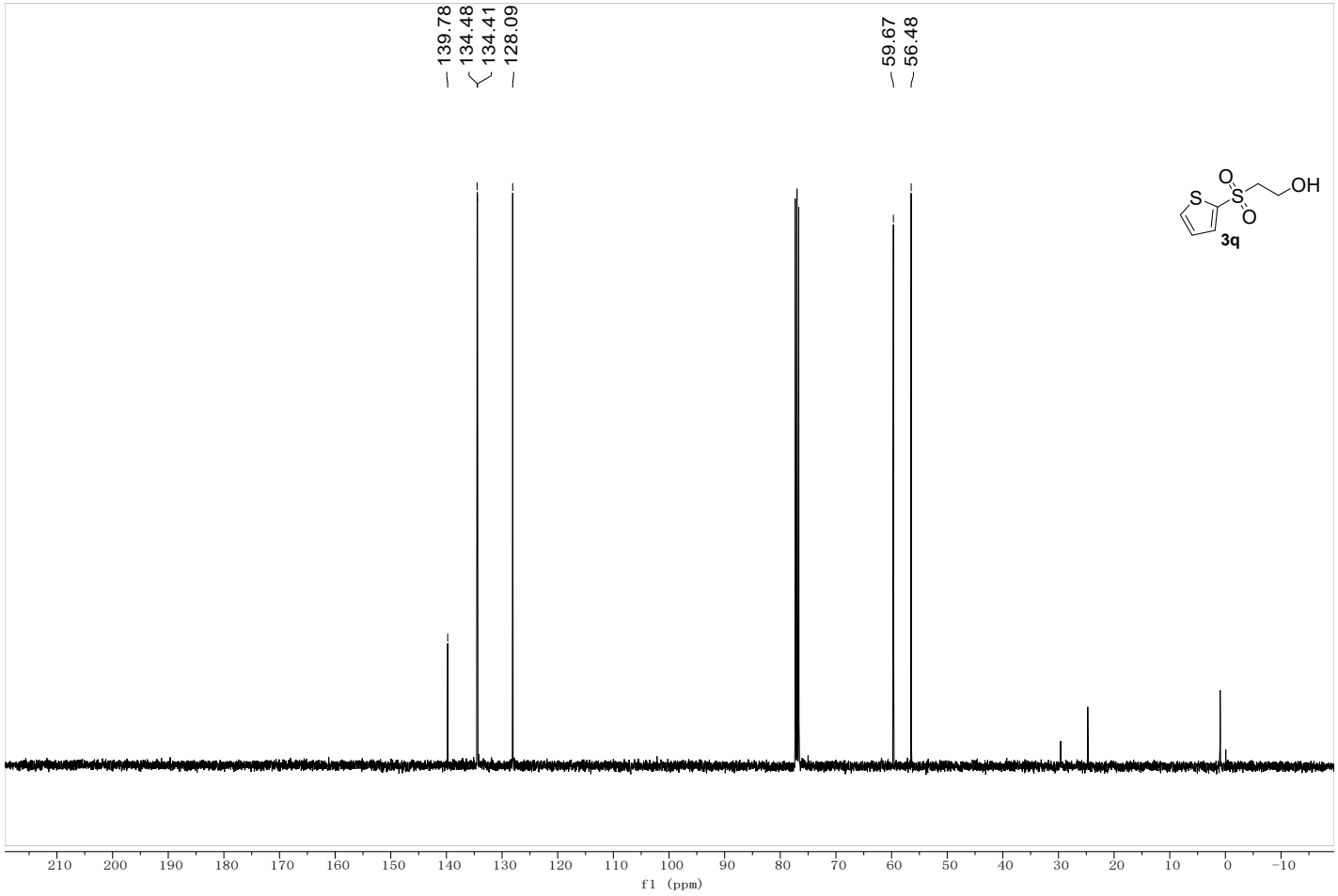
3p $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



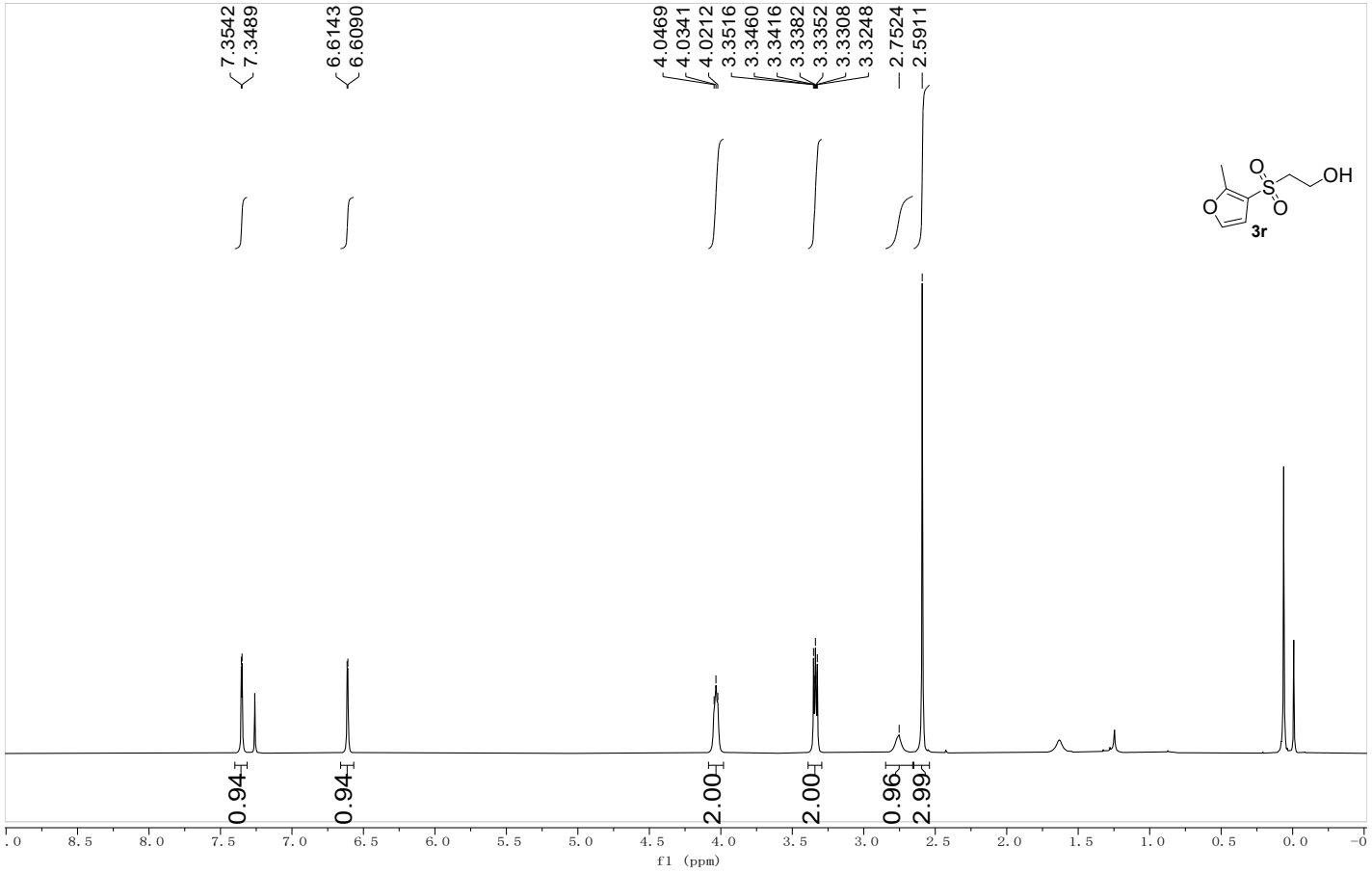
3q ^{1}H NMR (400 MHz, $CDCl_3$)



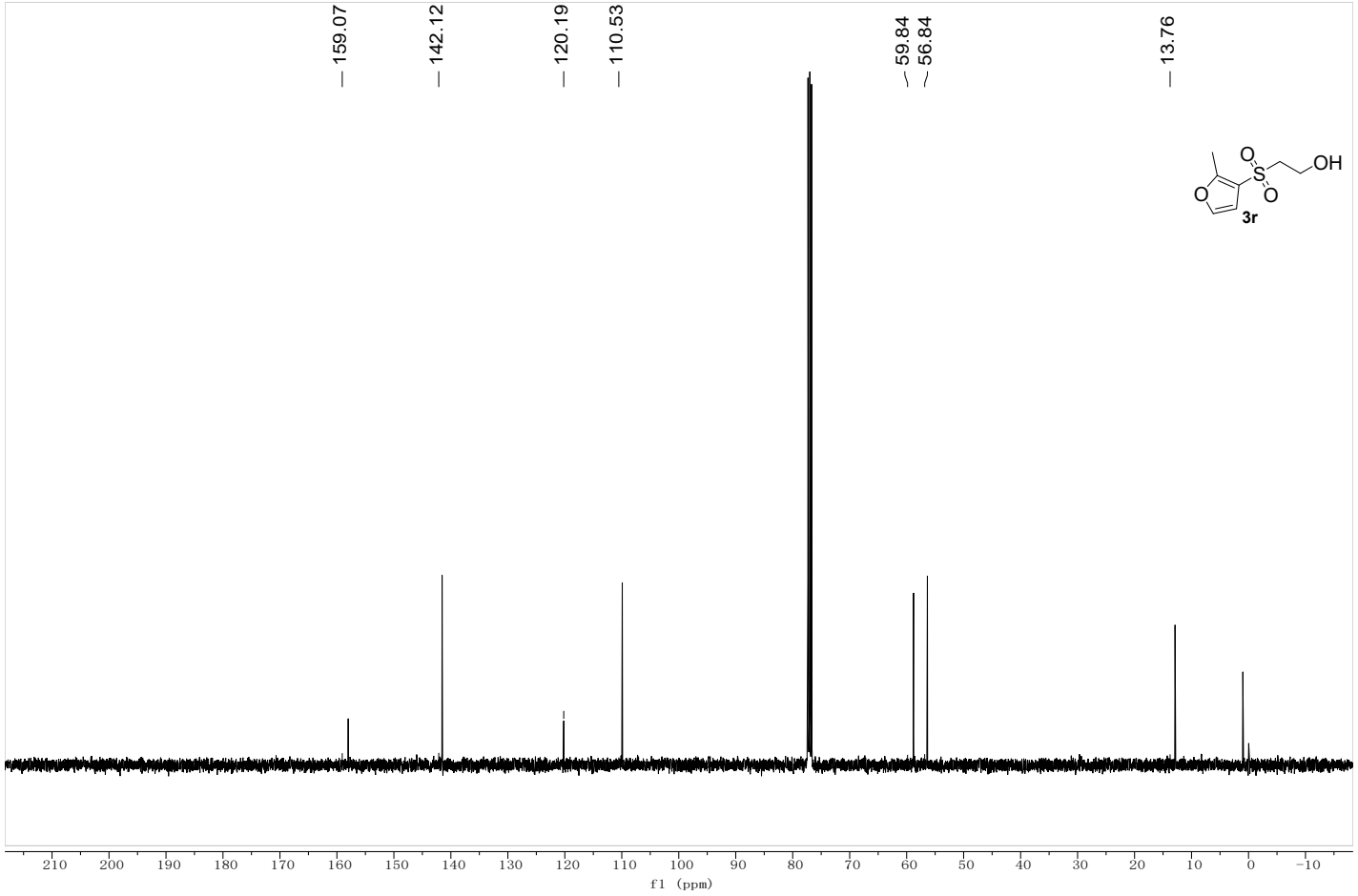
3q $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



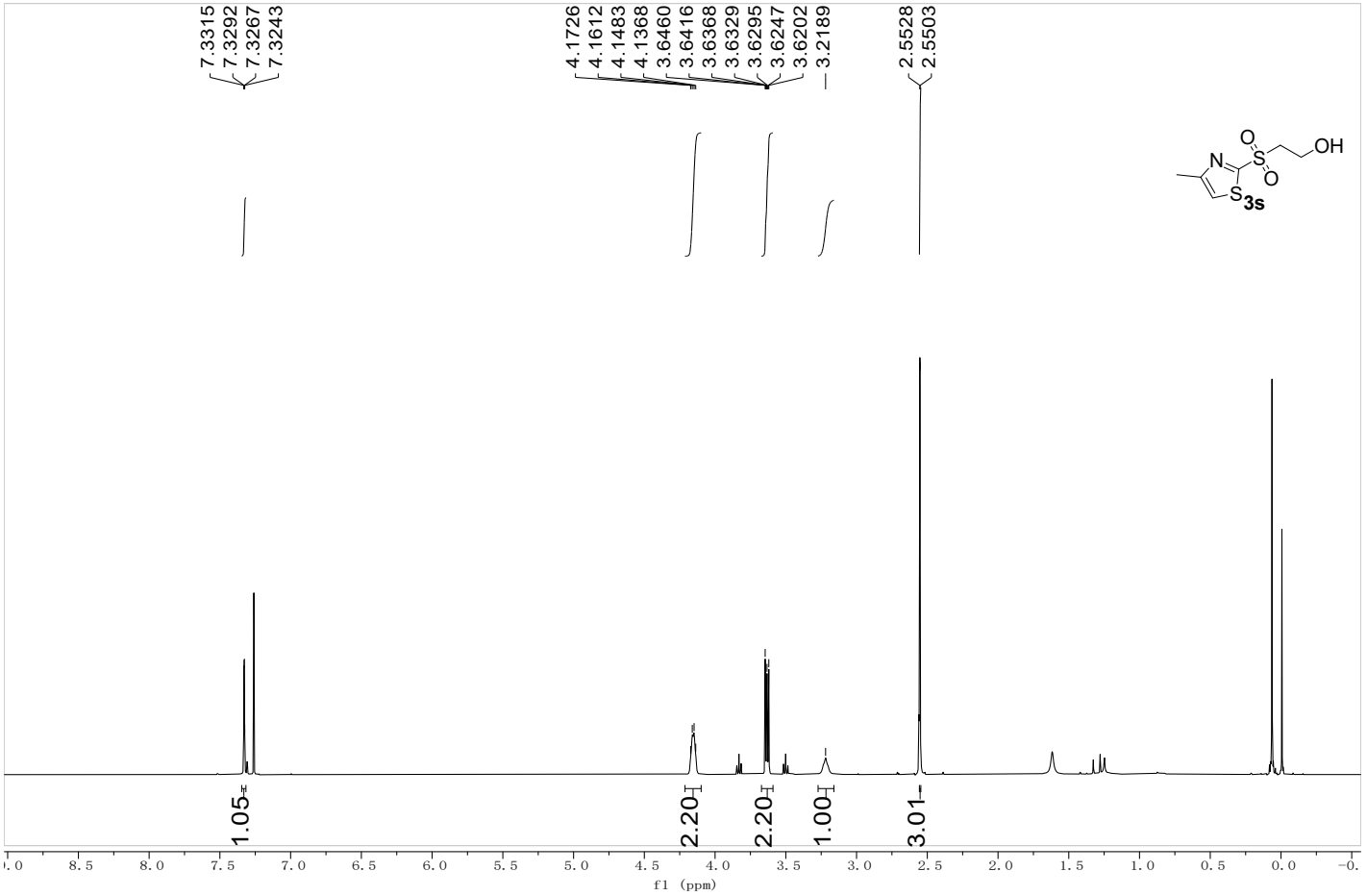
3r ^{1}H NMR (400 MHz, $CDCl_3$)



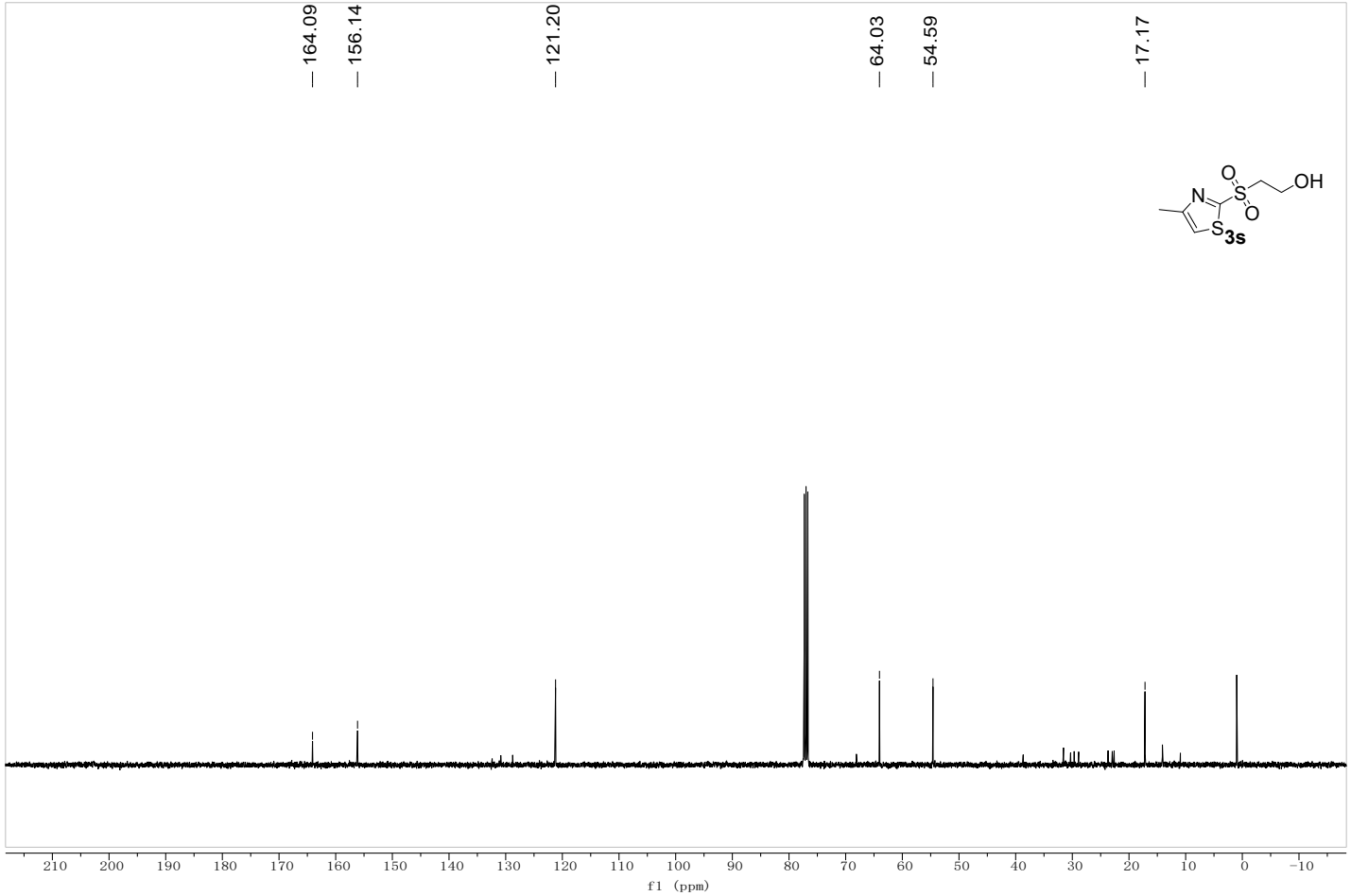
3r $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



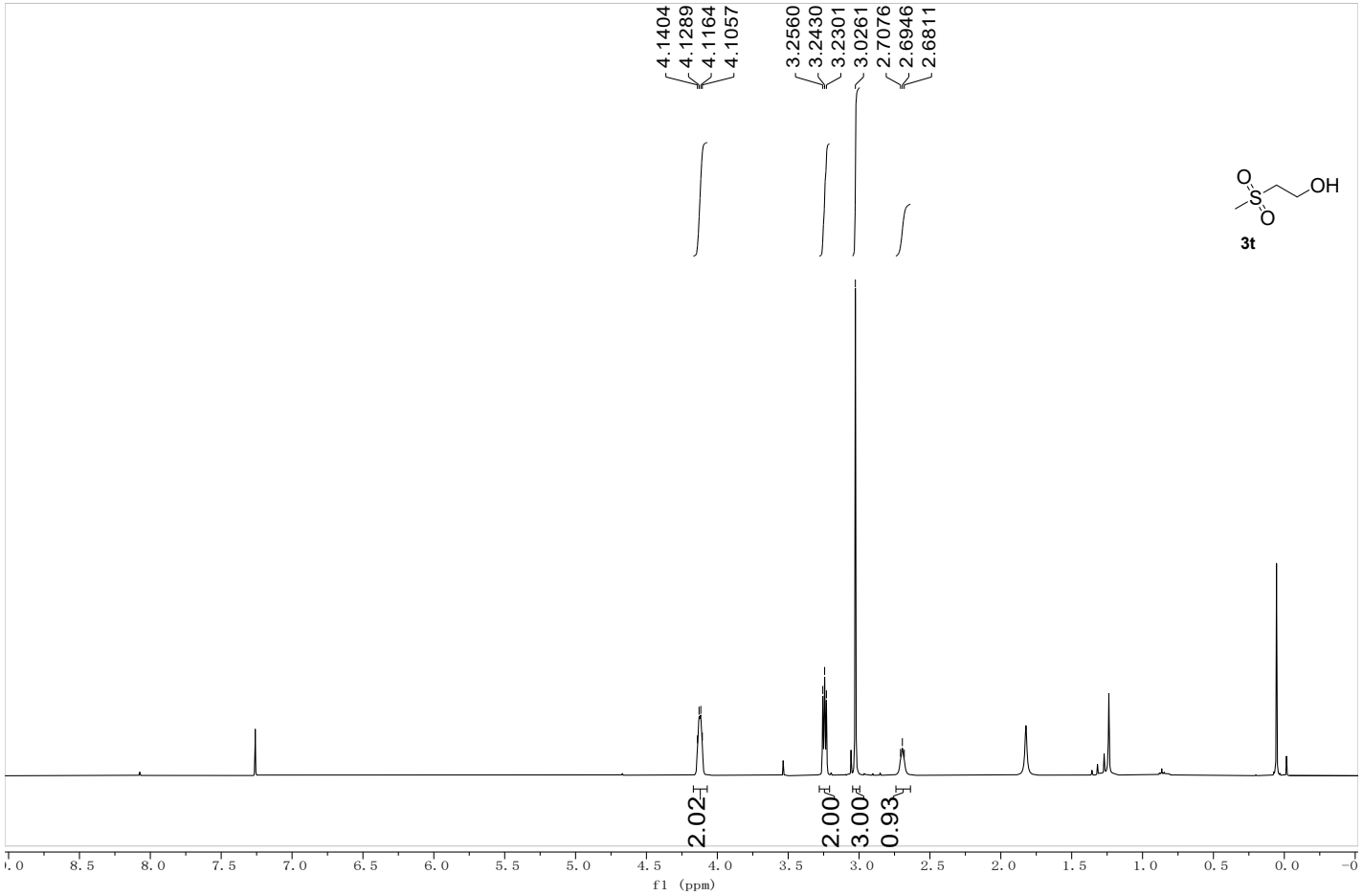
3s ^{1}H NMR (400 MHz, $CDCl_3$)



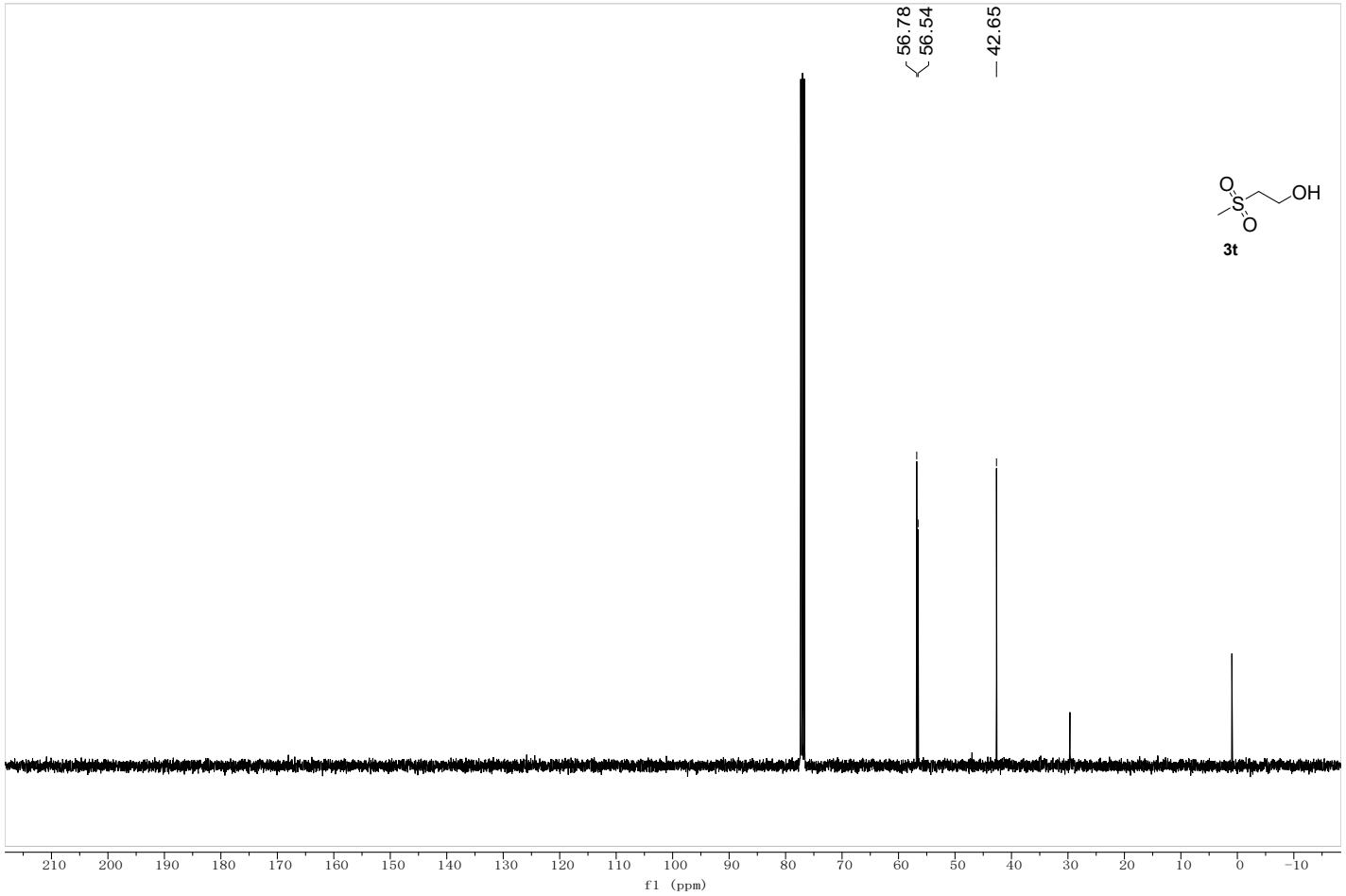
3s $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



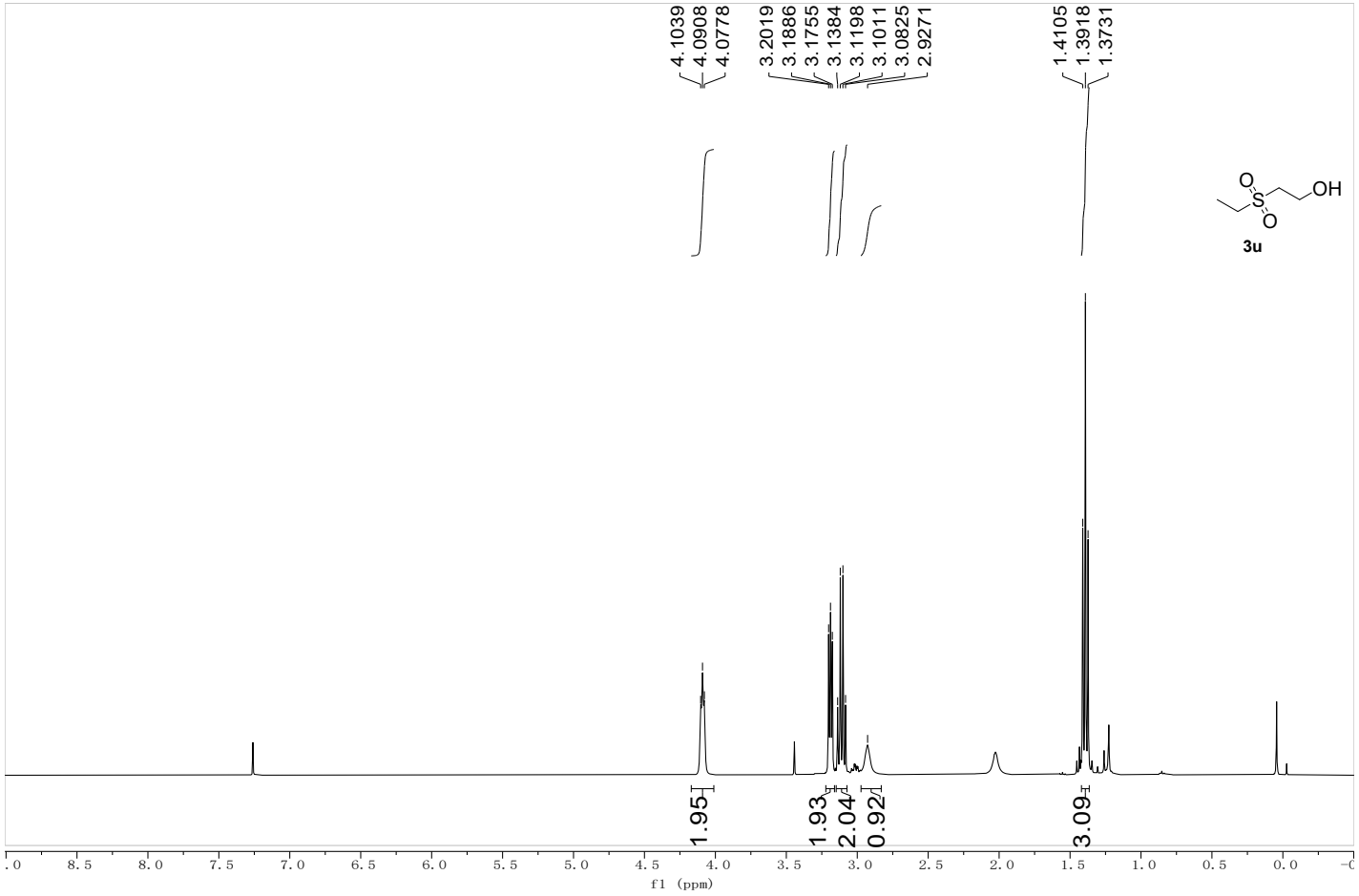
3t ^{1}H NMR (400 MHz, $CDCl_3$)



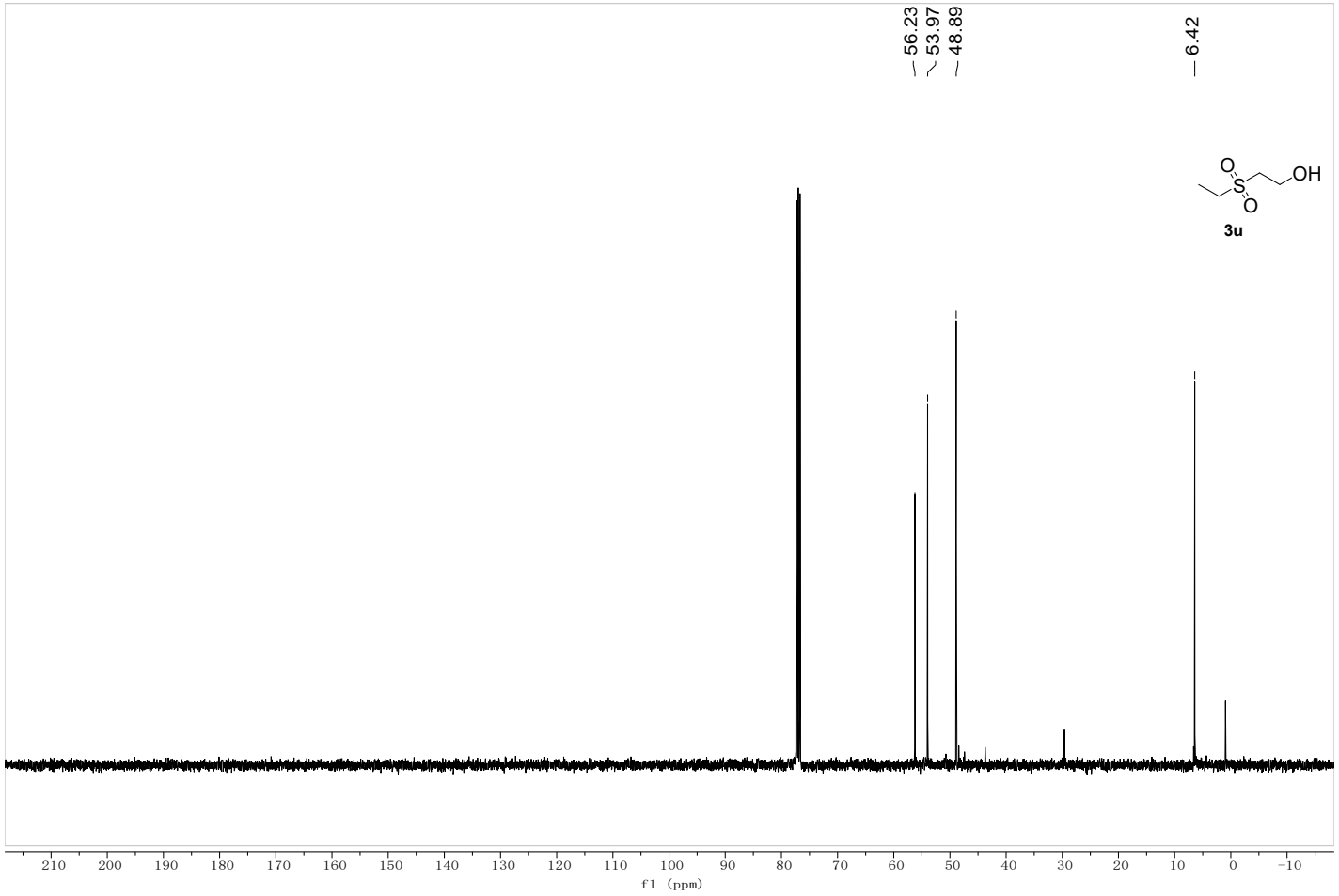
3t $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



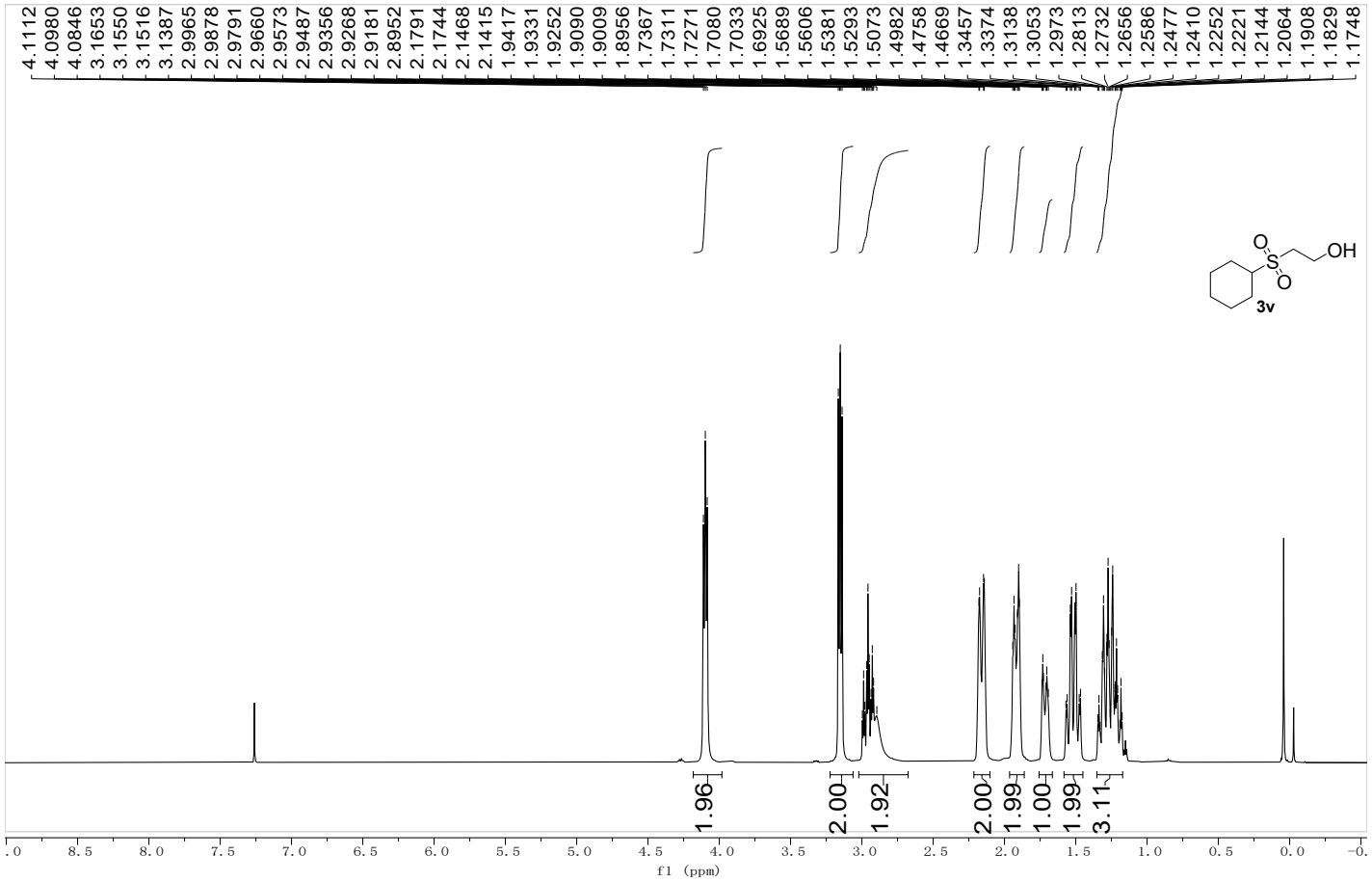
3u ^{1}H NMR (400 MHz, $CDCl_3$)



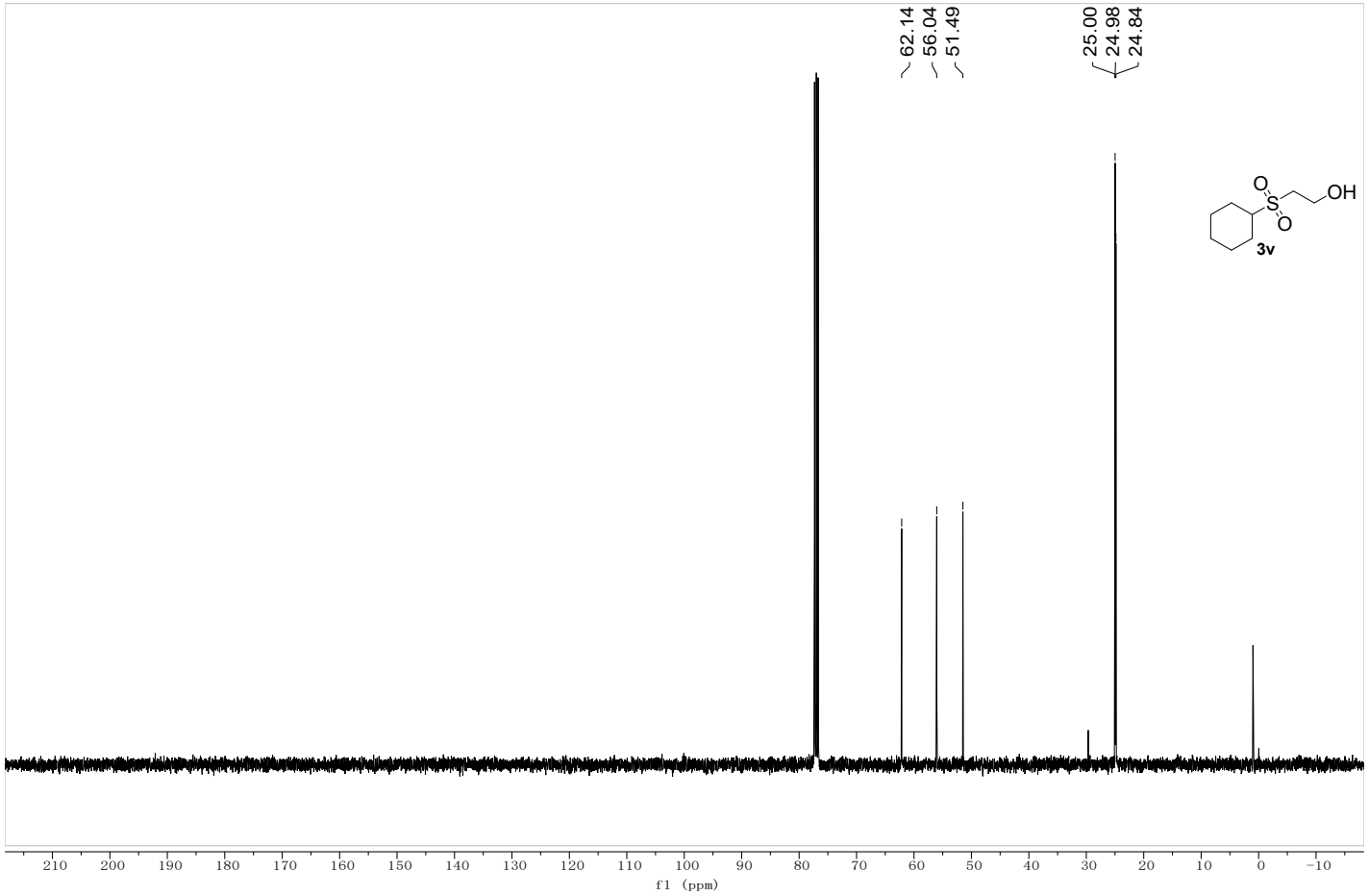
3u $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



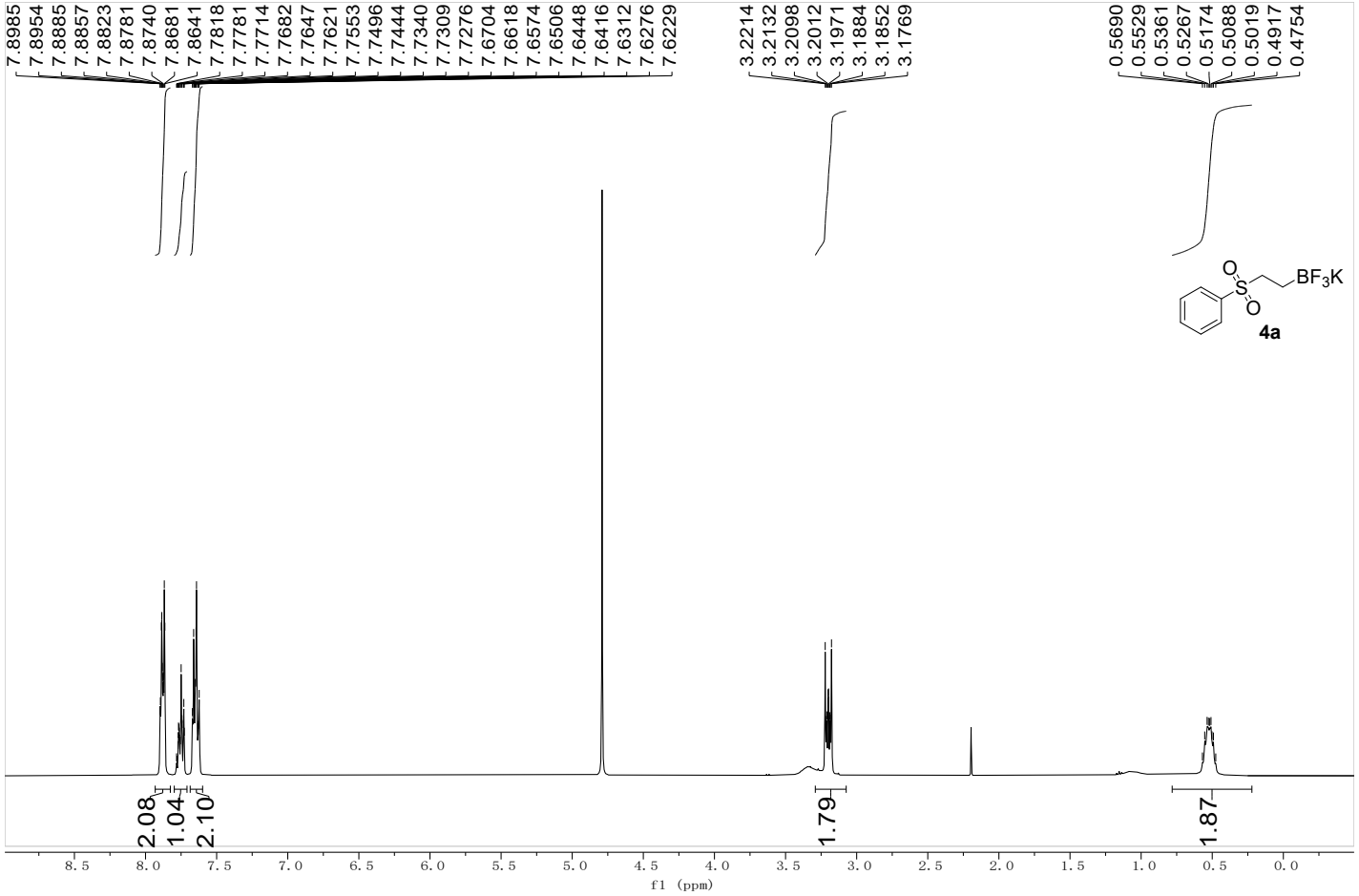
3v ^{1}H NMR (400 MHz, $CDCl_3$)



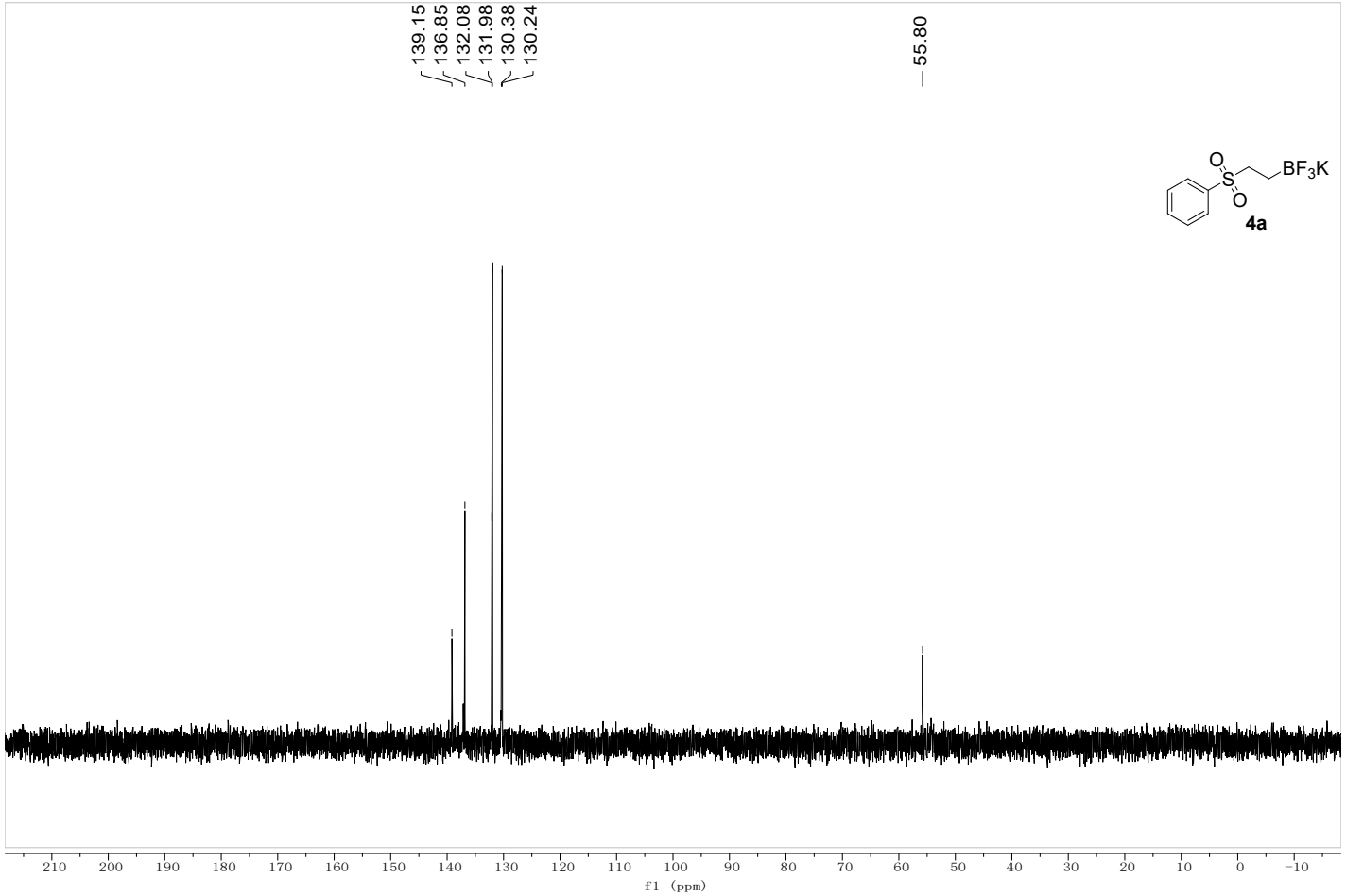
3v $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



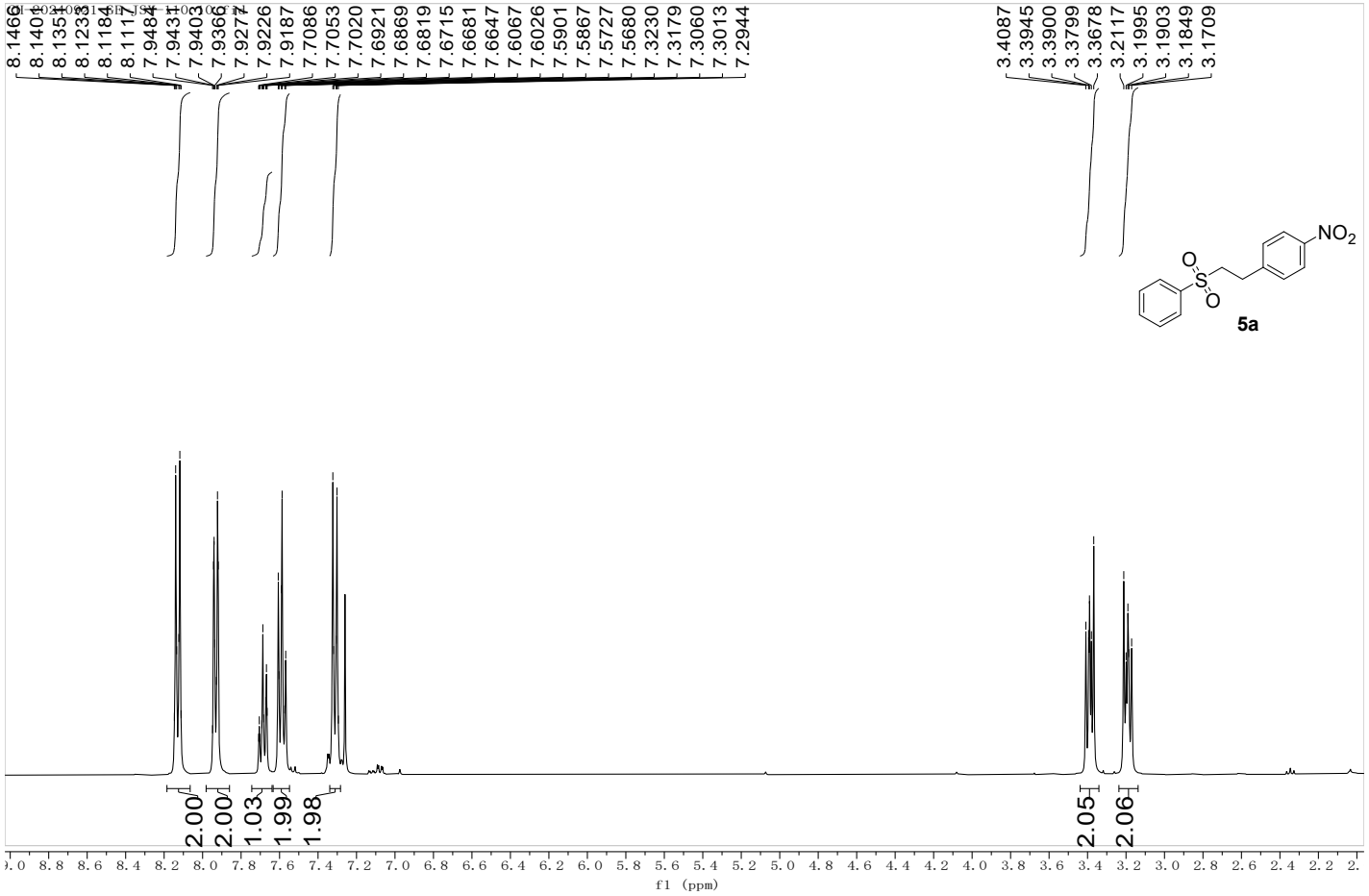
4a ^{1}H NMR (400 MHz, D_2O)



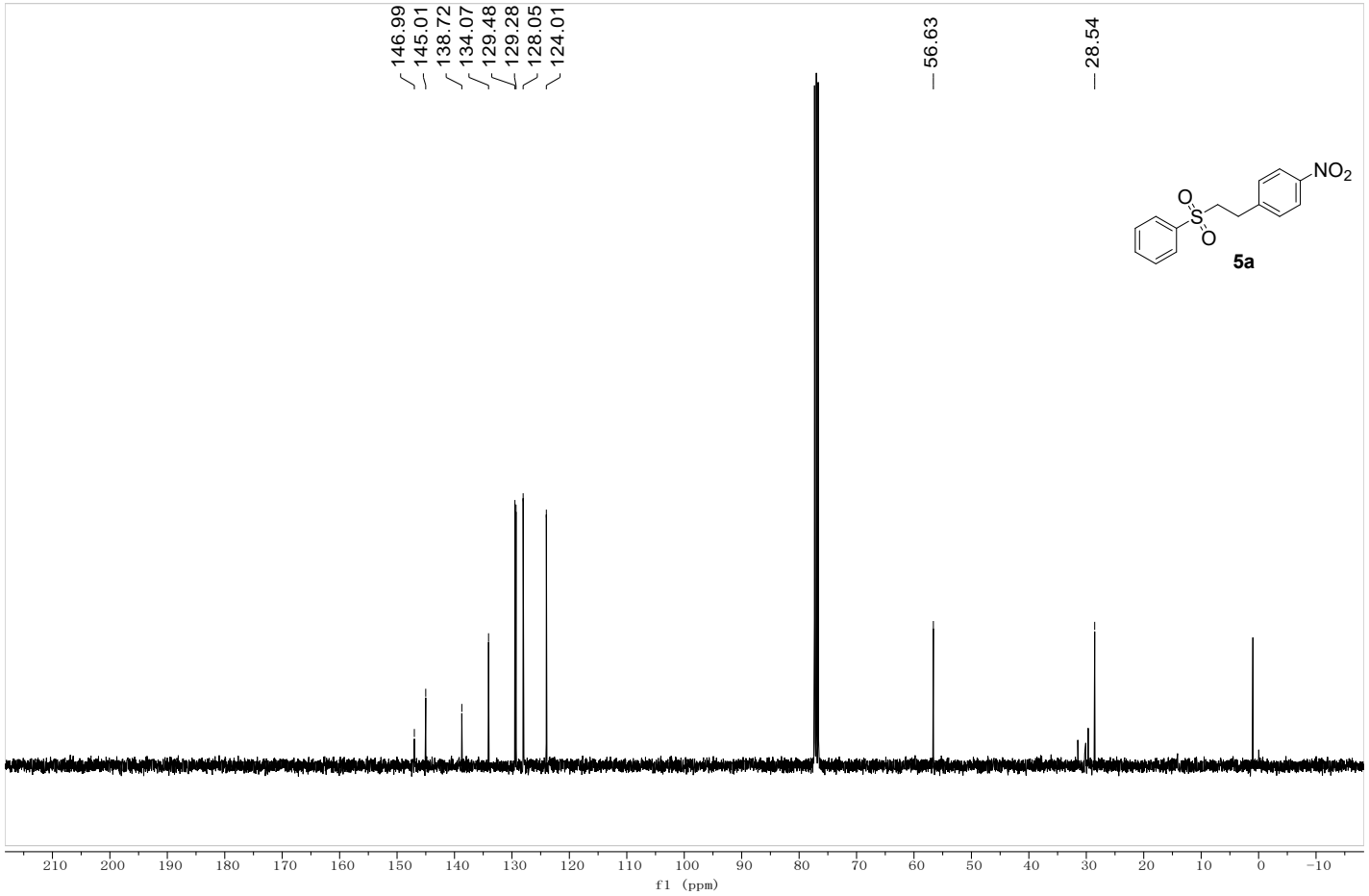
4a $^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O)



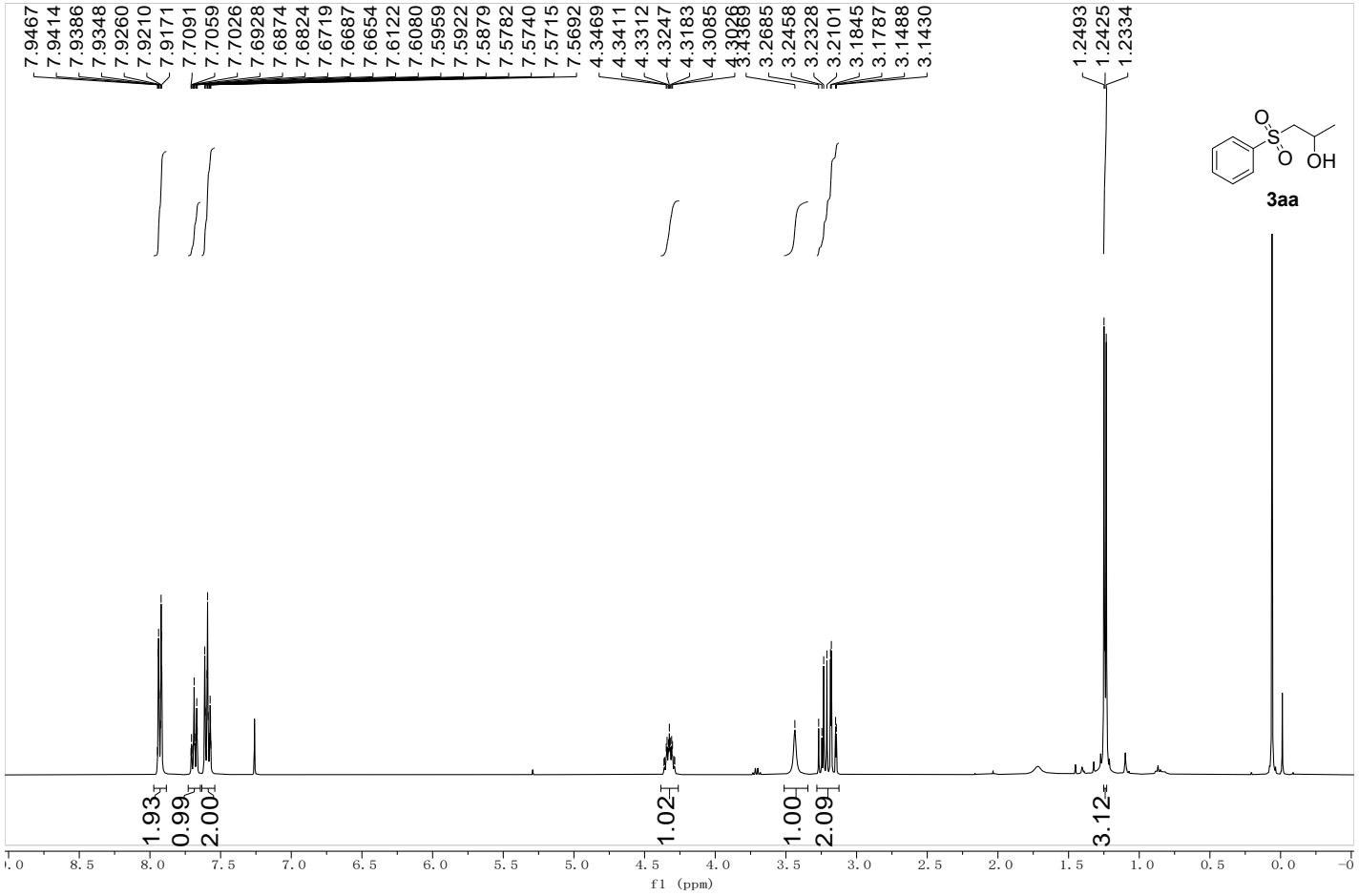
5a ^{1}H NMR (400 MHz, $CDCl_3$)



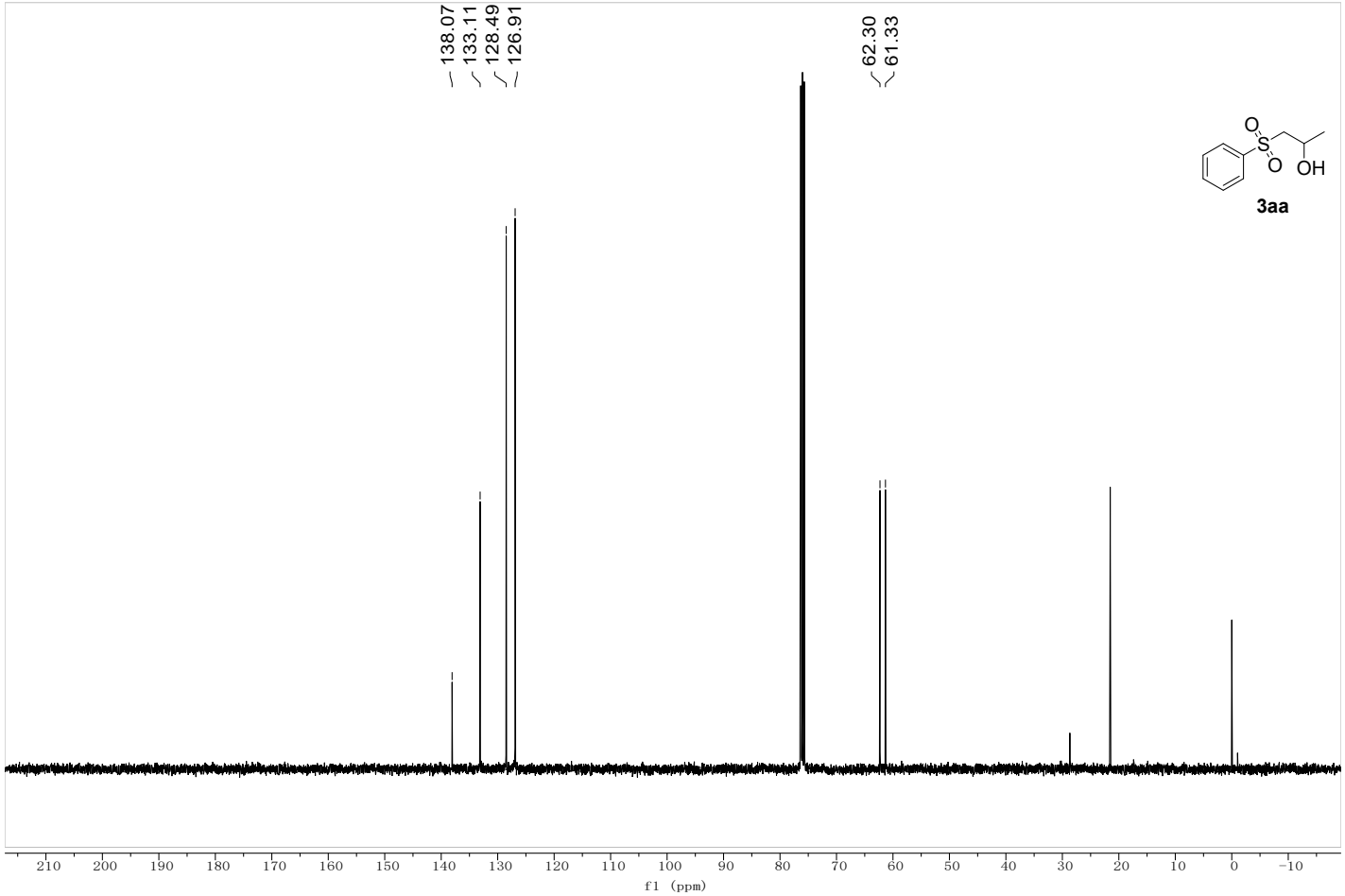
5a $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



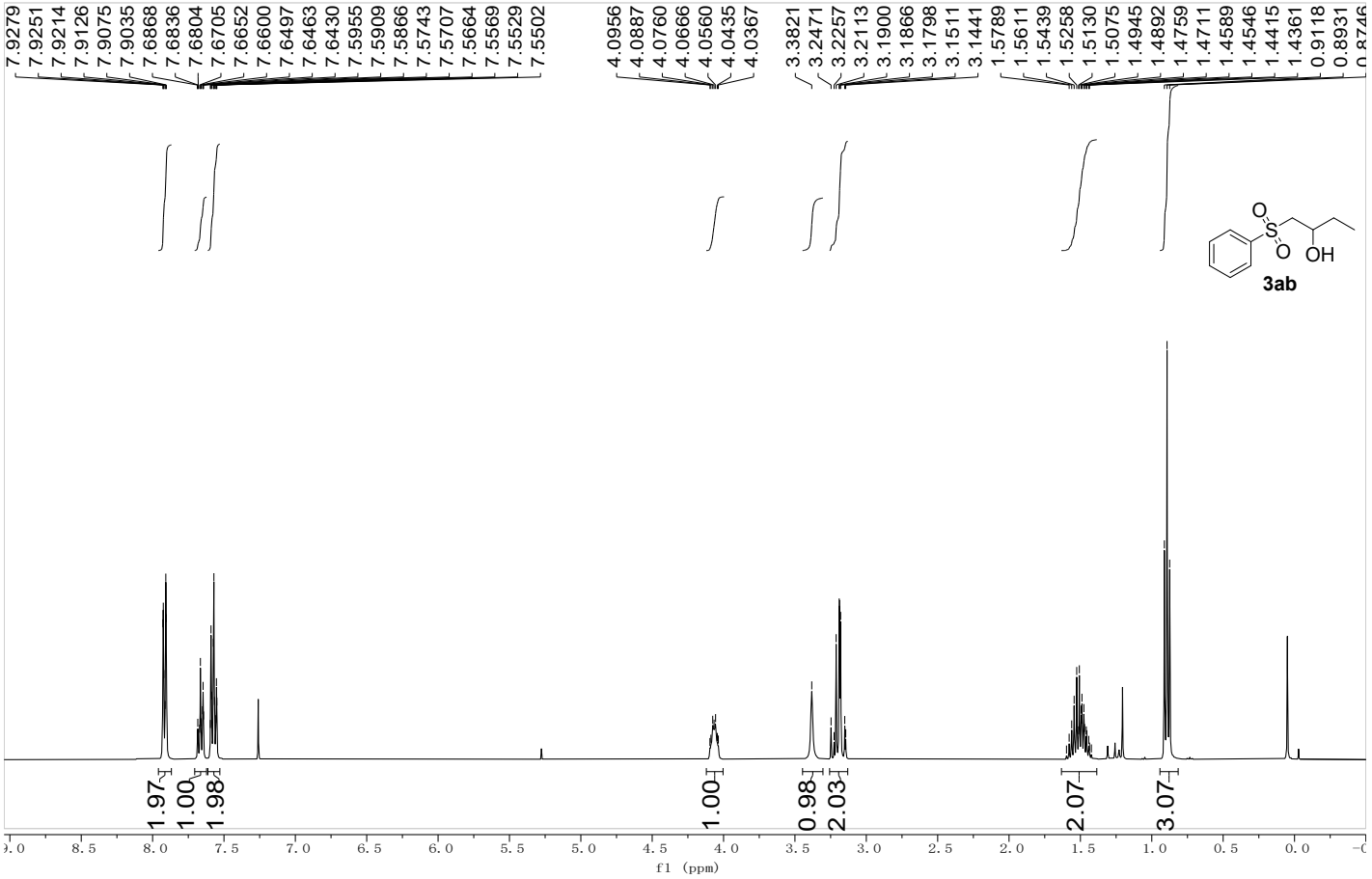
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



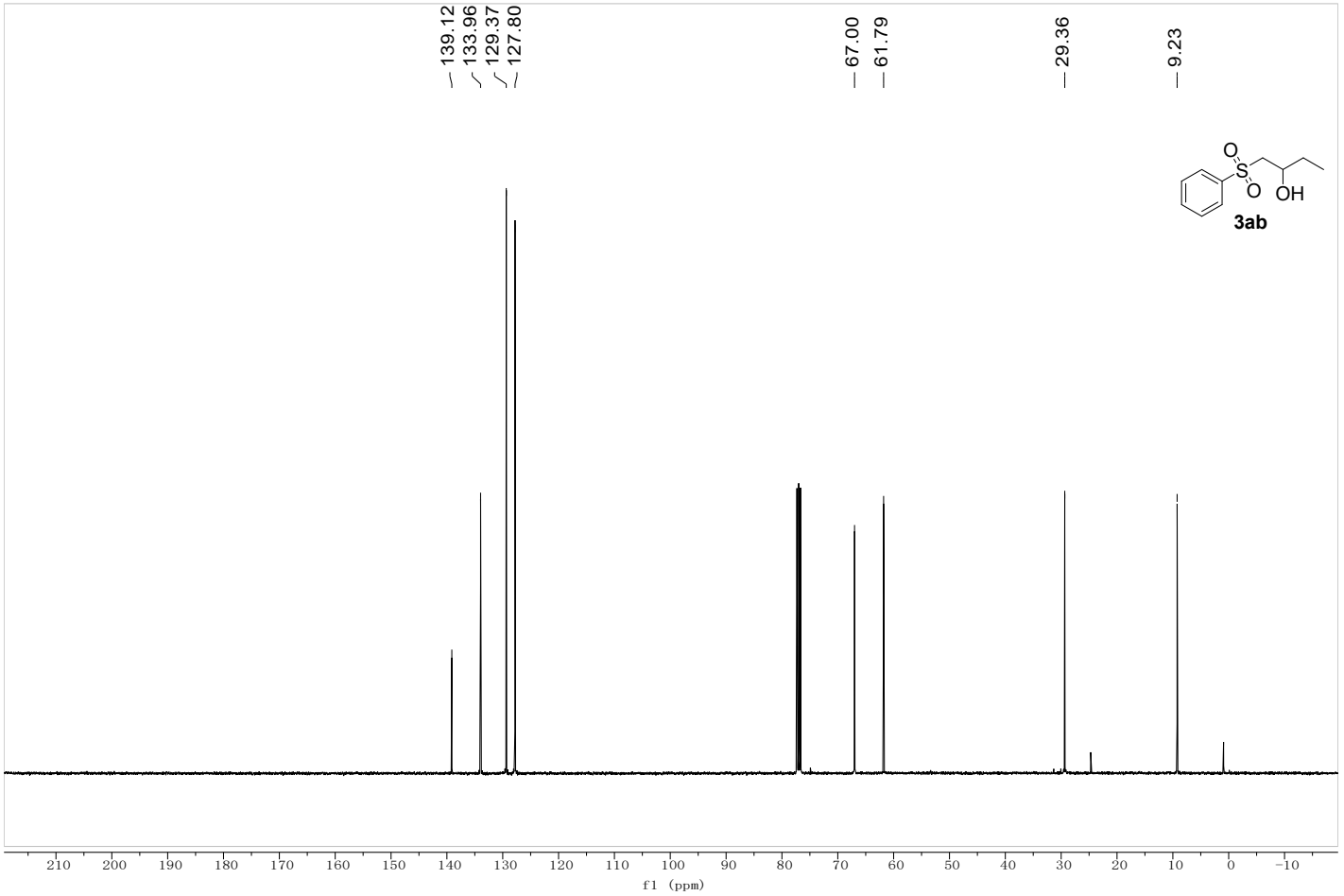
3aa $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



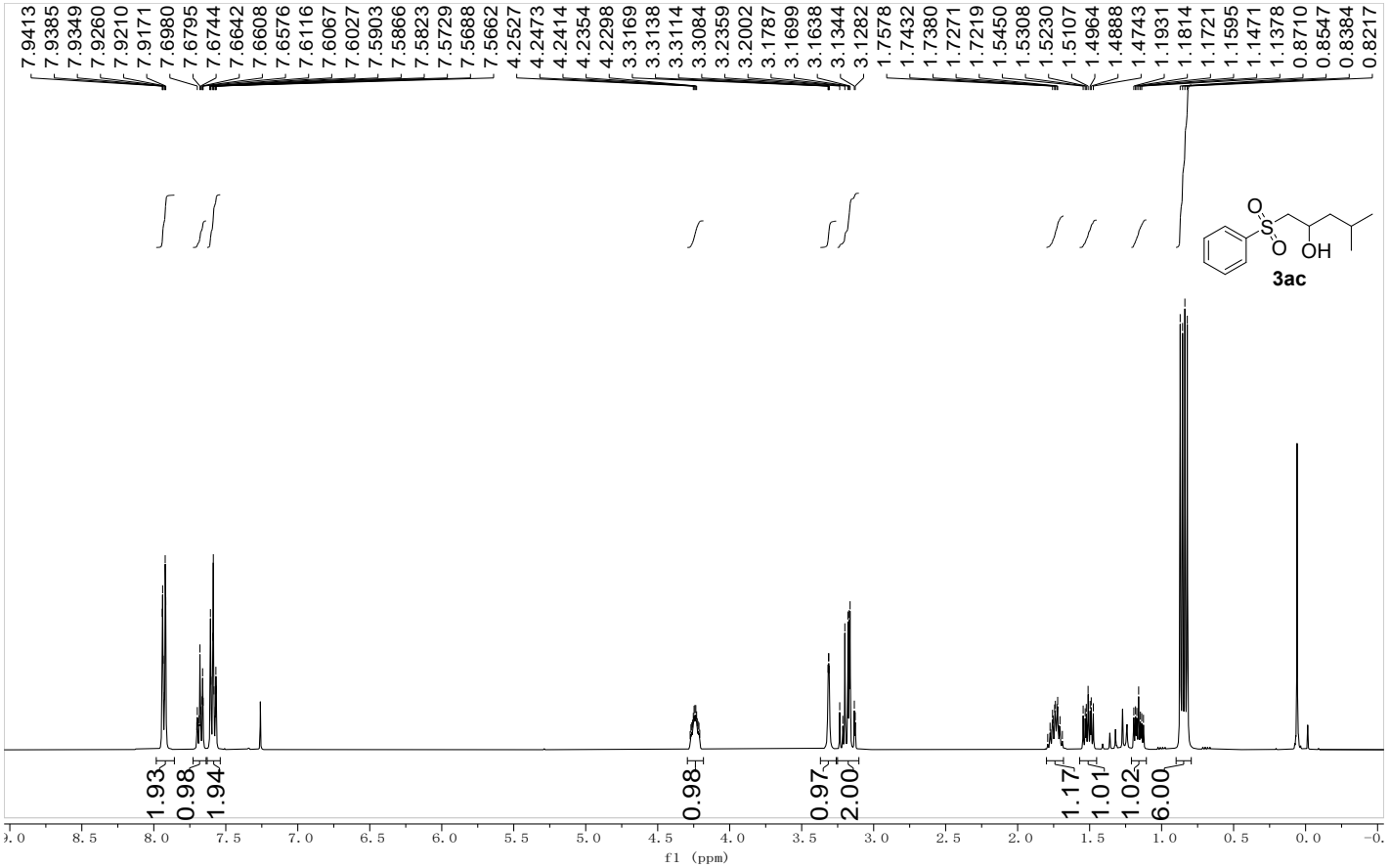
3ab ^{1}H NMR (400 MHz, $CDCl_3$)



3ab $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



3ac ^{1}H NMR (400 MHz, $CDCl_3$)



3ac $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)