Manganese(III) Acetate-Mediated direct C(sp2)-H-Sulfonylation of Enamides with Sodium and Lithium Sulfinates

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Supporting Information

1 General Information

Experimental methods

Reactions. All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H-NMR.

Chromatography. Column chromatography was performed with Silica 60 (0.04-0.063 mm, 230-400 mesh) and the specified solvent mixture. Thin layer chromatography was performed on aluminum sheets coated with SiO_2 (TLC silica gel 60 F_{254}). The spots were visualized by ultraviolet light or iodine.

Solvents Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. All anhydrous solvents were purchased from commercial suppliers and stored over MS4Å under an atmosphere of argon. Solvents for column chromatography were technical standard.

Materials. All starting materials, which were obtained from commercial sources, were used without further purification.

SO_2 (sulfur dioxide, purity 3.8) was used directly without further purification. **SO_2 is a toxic and corrosive gas! It should be handled with care only in a well-ventilated fume-hood with the necessary precaution!** All reactions were performed with a defined amount of liquid SO_2. Therefore, SO_2 was condensed into a dry and Ar-filled Schlenk-flask, cooled to -78 °C. Because of its high heat of evaporation, liquid and cooled SO_2 can be easily handled, measured and transferred with syringes. For small-scale reactions, we recommend this procedure.

Enamides **1a-o** were synthesized from the corresponding *N*-Allylamides via the isomerization-protocol of Halli *et al.*[1] For enamides **1j-*o***, the *E/Z-mixture* obtained after the isomerization was used directly.

All sulfinic acids sodium salts were prepared from the corresponding sulfonyl chlorides using reported procedures.[2,3]

Analytical Data and Instrumentation

NMR spectroscopy. Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon spectra (^{13}C NMR) were recorded at 300, 400 or 500 MHz (^{1}H) and 75, 101 or 126 MHz (^{13}C), respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C). Coupling constants (*J*) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets dqd = doublet of quartets of doublets.

Melting points. Melting points are reported uncorrected.

Mass spectrometry. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) techniques on a Thermo Fisher Q Exactive™ HF Hybrid Quadrupol-Orbitrap mass spectrometer or EI-MS on a Waters GCT Premier.

Infrared spectroscopy. Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm^{-1}).

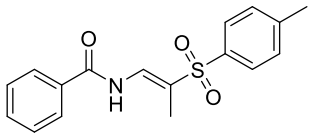
2 Preparation and Analytical Data

2.1 Synthesis of β-Amidovinylsulfones from sodium sulfinates

Typical procedure 1:

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, Enamide derivative **1** (1.0 equiv., 0.2 mmol), sulfinate salt **2** (2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol), and ethanol (2 - 3 mL). The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography afforded the analytically pure product.

2.1.1 (*E*)-N-(2-tosylprop-1-en-1-yl)benzamide **3a**



3a

Prepared from (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (91 mg, 0.181 mmol, 91%).

Prepared from (*Z*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (53 mg, 0.168 mmol, 80 %).

Prepared from (*E*/*Z*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash

column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (53 mg, 0.169 mmol, 85 %).

Prepared from (*E*/*Z*)-Enamide **1a** (806 mg, 5.0 mmol, 1.0 eq, *E*:*Z* = 77:23), sodium 4-methylbenzenesulfinate **2a** (2.0 g, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (2.7 g, 2.0 equiv., 10 mmol) and sodium acetate (820 mg, 2.0 equiv, 10 mmol) according to TP 1 in 15 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as colorless solid (1.12 g, 75%, 3.8 mmol).

m.p. 168 - 172 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.27.

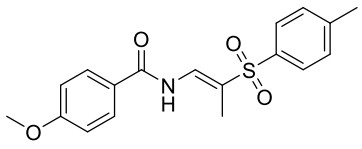
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.38 – 8.27 (m, 1H), 7.90 – 7.79 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 11.9 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.90 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 144.2, 137.0, 133.2, 132.5, 131.4, 130.0, 129.2, 129.2, 128.1, 127.5, 118.5, 21.7, 10.7.

HRMS m/z calcd for $C_{17}H_{17}NO_3S$ 315.0917 $[M]^+$, found 315.0828 $[M]^+$.

IR (ATR, ν in cm^{-1}): 3326 (w), 2939 (w), 2338 (w), 1640 (m), 1600 (m), 1579 (m), 1530 (m), 1488 (m), 1450 (m), 1379 (w), 1287 (s), 1141 (s), 1041 (m), 1017 (m), 1085 (m), 801 (m), 738 (m), 713 (s), 690 (s).

2.1.2 (*E*)-4-methoxy-N-(2-tosylprop-1-en-1-yl)benzamide **3b**



3b

Prepared from (*E*)-Enamide **1b** (38 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (58 mg, 0.166 mmol, 83%).

m.p. 185 – 189 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.12.

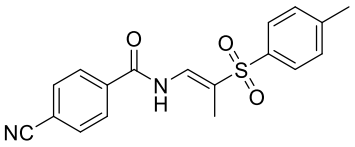
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.28 (dd, *J* = 11.8, 1.5 Hz, 1H), 7.76 (dd, *J* = 21.3, 8.5 Hz, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H), 1.88 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.1, 163.5, 144.1, 137.1, 131.8, 129.9, 129.7, 128.0, 124.5, 117.7, 114.3, 55.7, 21.7, 10.7.

HRMS m/z calcd for $C_{18}H_{19}NO_4S$ 345.1035 $[M]^+$, found 345.1021 $[M]^+$.

IR (ATR, ν in cm^{-1}): 3424 (w), 1684 (m), 1646 (s), 1606 (m), 1576 (m), 1518 (w), 1474 (s), 1439 (m), 1333 (w), 1317 (w), 1285 (m), 1250 (m), 1221 (m), 1183 (m), 1159 (m), 1119 (s), 1077 (m), 1033 (m), 969 (m), 932 (m), 889 (w), 815 (m), 758 (m), 725 (m), 696 (s).

2.1.3 (*E*)-4-cyano-*N*-(2-tosylprop-1-en-1-yl)benzamide **3c**



3c

Prepared from (*E*)-Enamide **1c** (37 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv, 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 2 mL Ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (55 mg, 0.159 mmol 80%).

m.p. 154 – 169 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.29.

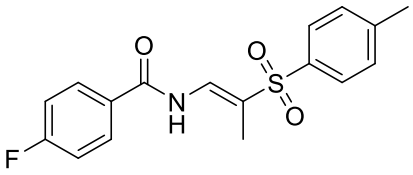
^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.54 (s, 1H), 8.15 – 7.97 (m, 5H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H), 1.92 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, DMSO-d_6*) δ 165.2, 143.9, 136.8, 136.7, 132.4, 131.5, 130.0, 129.3, 127.5, 119.3, 118.2, 114.7, 21.1, 10.8.

HRMS (ESI) m/z calcd for $C_{18}H_{16}N_2O_3S$ 341.0954 $[M+H]^+$, found 341.0956 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3342 (m), 3060 (w), 2925 (w), 2231 (m), 1688 (s), 1646 (s), 1598 (m), 1516 (m), 1483 (m), 1445 (m), 1286 (s), 1260 (s), 1128 (s), 1071 (s), 1019 (w), 921 (m), 876 (m), 852 (m), 769 (w), 706 (m),690 (m).

2.1.4 (*E*)-4-fluoro-*N*-(2-tosylprop-1-en-1-yl)benzamide **3d**



3d

Prepared from (*E*)-Enamide **1d** (36 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv, 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (54 mg, 0.161 mmol, 81%).

m.p. 189 - 193°C.

R_f (*n*-hexane:EtOAc = 7:3) 0.21.

^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.26 (dd, *J* = 11.8, 1.5 Hz, 1H), 7.85 (dd, *J* = 8.9, 5.1 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 2.43 (s, 3H), 1.89 (d, *J* = 1.2 Hz, 3H).

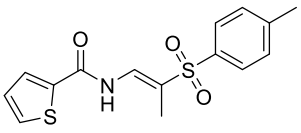
^{13}C NMR (*101 MHz, Chloroform-d*) δ 167.0, 164.4, 163.6, 144.2, 136.9, 131.3, 130.1 (d, *J* = 9.3 Hz), 129.0 (d, *J* = 193.2 Hz), 128.7 (d, *J* = 3.1 Hz), 118.7, 116.4 (d, *J* = 21.9 Hz), 21.7, 10.8.

^{19}F NMR (*376 MHz, Chloroform-d*) δ -103.11 – -106.32 (m).

HRMS (ESI) m/z calcd for $C_{17}H_{16}FNNaO_3S$ 356.0727 $[M+Na]^+$, found 356.0726 $[M+Na]^+$.

IR (ATR, ν in cm^{-1}): 3254 (m), 1671 (m), 1646 (s), 1598 (s), 1522 (w), 1497 (s), 1329 (w), 1301 (m), 1274 (s), 1235 (m), 1202 (m), 1167 (w), 1156 (m), 1132 (s), 1015 (w), 971 (m), 916 (m), 891 (m), 848 (m), 816 (m), 762 (w), 723 (s), 689 (s).

2.1.5 (*E*)-*N*-(2-tosylprop-1-en-1-yl)thiophene-2-carboxamide **3e**



3e

Prepared from (*E*)-Enamide **3e** (33 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (55 mg, 0.170 mmol, 85%).

m.p. 181 - 193 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.12.

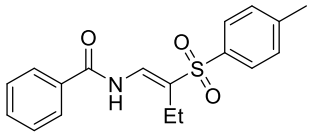
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.24 (dd, *J* = 11.8, 1.4 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.65 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.42 (s, 3H), 1.89 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 158.9, 144.2, 137.0, 136.6, 132.7, 131.0, 130.2, 130.0, 128.3, 128.0, 118.3, 21.7, 10.7.

HRMS (EI) m/z calcd for $C_{15}H_{15}NO_3S$ 321.0493 $[M]^+$, found 321.0486 $[M]^+$.

IR (ATR, ν in cm^{-1}): 3425 (w), 3112 (w), 1672 (s), 1642 (s), 1595 (w), 1523 (m), 1489 (m), 1412 (w),1354 (w), 1287 (m), 1263 (s), 1217 (m), 1166 (m), 1129 (s), 1079 (m), 1033 (m), 969 (m), 906 (w), 870 (w), 846 (m), 816 (m), 755 (w), 721 (s).

2.1.6 (*E*)-*N*-(2-tosylbut-1-en-1-yl)benzamide **3f**



3f

Prepared from (*E*)-Enamide **1f** (35 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3$·2 H_2O (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (50 mg, 0.152 mmol, 76%).

m.p. 171 - 174 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.33.

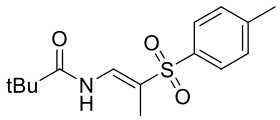
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.29 (d, *J* = 11.9 Hz, 1H), 7.88 – 7.72 (m, 5H), 7.66 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.5, 144.1, 137.7, 133.2, 132.5, 131.4, 129.9, 129.2, 128.1, 127.5, 124.3, 21.7, 19.1, 12.9.

HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_3S$ 330.1158 $[M+H]^+$, found 330.1158 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 2967 (w),2936 (w), 1665 (s), 1639 (s), 1601 (m), 1581 (w), 1518 (s), 1489 (m), 1468 (m), 1445 (w), 1298 (m), 1276 (s), 1205 (m), 1132 (s), 1079 (m), 1020 (m), 937 (m), 842 (w), 701 (m), 669 (m).

2.1.7 (*E*)-*N*-(2-tosylprop-1-en-1-yl)pivalamide **3g**



3g

Prepared from (*E*) – Enamide **1g** (28 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2.0 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (51 mg, 0.172 mmol, 86%). Crystals suitable for X-Ray could be obtained by slow evaporation from ethylacetate.

m.p. 150 - 151 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.43.

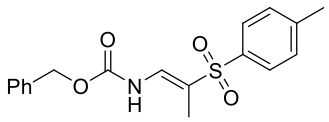
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.09 (dd, *J* = 11.7, 1.3 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.20 (d, *J* = 11.8 Hz, 1H), 2.42 (s, 3H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.7, 144.1, 137.2, 131.4, 129.9, 128.1, 117.6, 39.5, 27.4, 21.7, 10.5.

HRMS (ESI) m/z calcd for $C_{15}H_{22}NO_3S$ 296.1315 $[M+H]^+$, found 296.1315 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3369 (m), 2979 (m), 1703 (s), 1653 (s), 1599 (w), 1494 (m), 1401 (w), 1283 (m), 1233 (m), 1133 (s), 1107 (s), 1076 (s), 1019 (m), 962 (m), 943 (m), 917 (m), 856 (w), 816 (m), 728 (s),660 (s).

2.1.8 Benzyl (*E*)-(2-tosylprop-1-en-1-yl)carbamate **3h**



3h

Prepared from (*E*)-Encarbamate **1h** (38 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (48 mg, 0.140 mmol, 70%).

m.p. 146 – 152 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.48.

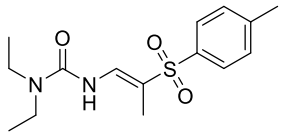
^{1}H NMR (*400 MHz, Chloroform-d*) δ 7.90 (d, *J* = 12.3 Hz, 1H), 7.81 – 7.66 (m, 2H), 7.38 (d, *J* = 2.7 Hz, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.59 (s, 1H), 5.22 (s, 2H), 2.42 (s, 3H), 1.73 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 152.7, 144.0, 137.1, 135.1, 132.8, 129.9, 129.0, 128.9, 128.8, 128.0, 68.6, 21.7, 10.2.

HRMS (ESI) m/z calcd for $C_{18}H_{19}NNaO_4S$ 368.0927 $[M+Na]^+$, found 368.0929 $[M+Na]^+$.

IR (ATR, ν in cm^{-1}): 3308 (m), 1733 (s), 1662 (s), 1594 (w), 1499 (s), 1468 (m), 1457 (m), 1379 (w), 1332 (w), 1286 (m), 1219 (s), 1154 (s), 1123 (s), 1078 (m), 1036 (m), 969 (m), 923 (m), 853 (w), 813 (m), 797 (m), 784 (m), 771 (m), 753 (m).

2.1.9 (*E*)-1,1-diethyl-3-(2-tosylprop-1-en-1-yl)urea **3i**



3i

Prepared from (*E*)-Enamide **1i** (31 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (41 mg, 0.132 mmol, 66%).

m.p. 147 - 150 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.09.

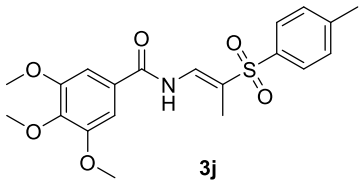
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.14 (dd, *J* = 11.7, 1.3 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 11.6 Hz, 1H), 3.34 (q, *J* = 7.2 Hz, 4H), 2.41 (s, 3H), 1.77 (d, *J* = 1.3 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 152.1, 143.6, 137.8, 134.4, 129.8, 127.9, 112.9, 42.1, 21.7, 13.9, 10.4 .

HRMS (EI) m/z calcd for $C_{15}H_{22}N_2O_3S$ 310.1351 $[M]^+$, found 310.1341 $[M]^+$.

IR (ATR, ν in cm^{-1}): 3441 (w), 1684 (s), 1645 (s), 1594 (w), 1489 (s), 1399 (w), 1362 (w), 1304 (w), 1285 (m), 1245 (s), 1219 (m), 1166 (m), 1145 (m),1126 (s), 1075 (s), 1012 (w), 963 (m), 852 (w), 822 (m), 751 (w), 728 (s).

2.1.10 (*E*)-3,4,5-trimethoxy-*N*-(2-tosylprop-1-en-1-yl)benzamide **3j**



3j

Prepared from (*E*/*Z*)-Enamide **1j** (50 mg, 1.0 equiv., 0.2 mmol; *E*:*Z* = 81:19), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (80 mg, 0.195 mmol, 98%).

m.p. 202 - 213 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.05.

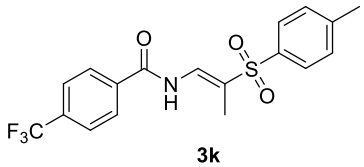
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.48 (dd, *J* = 11.7, 1.5 Hz, 1H), 8.09 (d, *J* = 11.7 Hz, 1H), 8.04 – 7.92 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 4.14 (d, *J* = 1.4 Hz, 9H), 2.68 (s, 3H), 2.13 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.7, 153.5, 144.2, 142.3, 136.9, 131.5, 129.9, 128.0, 127.9, 118.5, 105.2, 61.1, 56.6, 21.7, 10.7.

HRMS (ESI) m/z calcd for $C_{20}H_{24}NO_6S$ 406.1319 $[M+H]^+$, found 406.1319 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 1696 (m), 1651 (s), 1591 (m), 1418 (m), 1339 (m), 1291 (m), 1223 (s), 1155 (m), 1123 (s), 1076 (s), 1036 (m), 963 (m), 934(w), 859 (w), 823 (s), 761 (m), 719 (w).

2.1.11 (*E*)-*N*-(2-tosylprop-1-en-1-yl)-4-(trifluoromethyl)benzamide **3k**



3k

Prepared from **1k** (46 mg, 1.0 equiv., 0.2 mmol; *E*:*Z* = 55:45), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (66 mg, 0.173 mmol, 87%).

m.p. 202 - 223 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.24.

^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.53 (s, 1H), 8.10 (t, *J* = 7.2 Hz, 3H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 2.40 (s, 3H), 1.92 (d, *J* = 1.3 Hz, 3H).

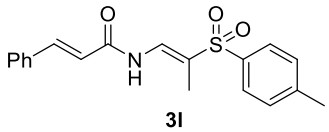
^{13}C NMR (*101 MHz, DMSO-d_6*) δ 165.4, 143.9, 136.7, 136.7, 132.1 (q, *J* = 32.2 Hz), 131.6, 130.0, 129.4, 127.5, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.7 Hz), 119.1, 21.1, 10.8.

^{19}F NMR (*376 MHz*, DMSO-d_6) δ -63.1.

HRMS (ESI) m/z calcd for $C_{18}H_{16}F_3NO_3S$ 384.0876 $[M+H]^+$, found 384.0876 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 1673 (m), 1648 (s), 1526 (m), 1506 (w), 1323 (s), 1276 (m), 1205 (w), 1166 (m), 1127 (s), 1089 (s), 1064 (m), 1017 (m), 965 (w), 918 (w), 891 (m), 853 (m), 815 (w), 732 (m), 704 (w).

2.1.12 *N*-((*E*)-2-tosylprop-1-en-1-yl)cinnamamide **3l**



3l

Prepared from (*E*/*Z*) - Enamide **1l** (38 mg, 1.0 equiv., 0.2 mmol; *E*:*Z* = 48:52), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (60 mg, 0.176 mmol, 88 %). Crystals suitable for X-Ray could be obtained by slow evaporation from ethylacetate.

m.p. 185 - 191 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.15.

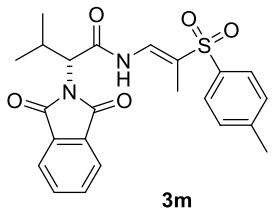
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.24 (d, *J* = 11.8 Hz, 1H), 7.81 (d, *J* = 15.5 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.47 (d, *J* = 12.1 Hz, 1H), 7.38 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 15.5 Hz, 1H), 2.42 (s, 3H), 1.87 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 163.4, 145.4, 144.2, 137.0, 134.2, 131.6, 130.8, 130.0, 129.1, 128.4, 128.0, 118.3, 117.7, 21.7, 10.7.

HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_3S$ 342.1158 $[M+H]^+$, found 342.1155 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3317 (m), 2925 (w), 1701 (s), 1634 (s), 1595 (w), 1497 (s), 1450 (w), 1334 (w), 1286 (s), 1226 (s), 1175 (w), 1135 (s), 1117 (s), 1074 (s), 963 (m), 927 (m), 860 (w), 813 (m), 783 (m), 764 (m), 696 (m).

2.1.13 (*E*)-2-(1,3-dioxoisoindolin-2-yl)-3-methyl-*N*-(2-tosylprop-1-en-1-yl)butanamide **3m**



3m

Prepared from (*E*/*Z*) – Enamide **1m** (57 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 66:34), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol) , $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless, low-melting solid (46 mg, 0.103 mmol, 52%).

R_f (*n*-hexane:EtOAc = 7:3) 0.21.

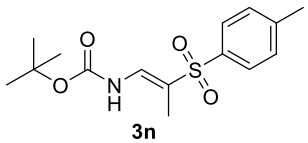
^{1}H NMR (*400 MHz, Chloroform-d*) δ 9.44 (d, *J* = 11.6 Hz, 1H), 8.03 (dd, *J* = 11.6, 1.5 Hz, 1H), 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.56 (d, *J* = 11.7 Hz, 1H), 2.87 – 2.58 (m, 1H), 2.39 (s, 3H), 1.87 (d, *J* = 1.3 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 168.9, 166.8, 144.1, 137.0, 135.1, 131.1, 130.9, 129.8, 128.1, 124.2, 119.4, 63.8, 27.9, 21.7, 19.5, 19.5, 10.8.

HRMS (MALDI) m/z calcd for $C_{23}H_{25}N_2O_5S$ 441.1480 $[M+H]^+$, found 441.1479 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 1768 (w), 1714 (s), 1651 (s), 1598 (w), 1509 (m), 1469 (m), 1383 (s), 1290 (m), 1250 (m), 1212 (m), 1130 (m), 1068 (s), 1018 (m), 966 (m), 913 (m), 888 (m), 848 (w), 813 (m), 712 (s).

2.1.14 *tert*-butyl (*E*)-(2-tosylprop-1-en-1-yl)carbamate **3n**



3n

Prepared from (*E*/*Z*) - Enecarbamate **1n** (31 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 42:58), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (58 mg, 0.186 mmol, 93%).

m.p. 157 - 159 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.31.

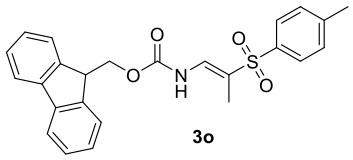
^{1}H NMR (*400 MHz, Chloroform-d*) δ 7.83 (s, 1H), 7.78 – 7.66 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H), 1.74 (d, *J* = 1.1 Hz, 3H), 1.49 (s, 9H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 151.7, 143.8, 137.4, 133.4, 129.8, 127.9, 114.4, 65.5, 28.2, 21.7, 10.2.

HRMS (ESI) m/z calcd for $C_{15}H_{21}NNaO_4S$ 334.1083 $[M+Na]^+$, found 334.1082 $[M+Na]^+$.

IR (ATR, ν in cm^{-1}): 2983 (w), 2929 (w), 1664 (s), 1506 (s), 1394 (w), 1338 (m), 1273 (w), 1232 (s), 1131 (s), 1080 (s), 1019 (m), 912 (m), 804 (m), 710 (s).

2.1.15 (9H-fluoren-9-yl)methyl (*E*)-(2-tosylprop-1-en-1-yl)carbamate **3o**



3o

Prepared from (*E*/*Z*) - Enecarbamate **1o** (56 mg, 1.0 equiv., 0.2 mmol; *E*:*Z* = 54:46), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (61 mg, 0.140 mmol, 70%).

m.p. 191 - 202 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.32.

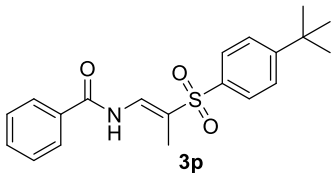
^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.07 (s, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 3H), 7.46 – 7.38 (m, 4H), 7.35 (td, *J* = 7.4, 1.2 Hz, 2H), 4.54 (d, *J* = 6.7 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 1H), 2.39 (s, 3H), 1.80 – 1.68 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 156.6, 143.7, 143.4, 140.8, 137.0, 133.7, 130.0, 127.8, 127.3, 127.2, 125.2, 120.3, 79.2, 67.1, 46.4, 21.0, 10.2.

HRMS (ESI) m/z calcd for $C_{25}H_{23}NO_4S$ 434.1423 $[M+H]^+$, found 434.1421 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3338 (w), 1678 (s), 1600 (w), 1509 (m), 1299 (w), 1202 (s), 1073 (s), 969 (m), 889 (m), 712 (s).

2.1.16 (*E*)-*N*-(2-((4-(tert-butyl)phenyl)sulfonyl)prop-1-en-1-yl)benzamide **3p**



3p

Prepared from (*E*) - Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-tert-butylbenzenesulfinate **2b** (91 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (60 mg, 0.167 mmol, 84%).

m.p. 148-155 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.2.

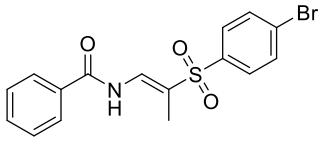
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 11.7, 1.5 Hz, 1H), 7.90 (d, *J* = 11.6 Hz, 1H), 7.85 – 7.71 (m, 4H), 7.59 – 7.54 (m, 1H), 7.53 – 7.44 (m, 4H), 1.90 (d, *J* = 1.2 Hz, 3H), 1.33 (s, 9H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.8, 157.1, 136.9, 133.1, 132.5, 131.5, 129.1, 127.8, 127.6, 126.3, 118.5, 35.3, 31.2, 10.8.

HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_3S$ 358.1471 $[M+H]^+$, found 358.1472 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 2961 (m), 1677 (m), 1649 (s), 1506 (m), 1476 (s), 1402 (w), 1292 (s), 1158 (s),1076 (s), 966 (m), 887 (w), 838 (s),762 (w).

2.1.17 (*E*)-*N*-(2-((4-bromophenyl)sulfonyl)prop-1-en-1-yl)benzamide **3q**



3q

Prepared from (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-bromobenzenesulfinate **2c** (97 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (56 mg, 0.148 mmol, 74%).

m.p. 160 - 161 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.43.

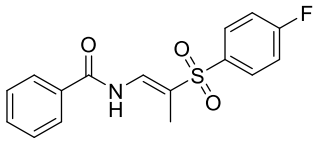
^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.41 (s, 1H), 8.14 (s, 1H), 8.02 – 7.91 (m, 2H), 7.89 – 7.74 (m, 4H), 7.69 – 7.61 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 1.94 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (*101 MHz, DMSO-d_6*) δ 166.3, 139.1, 132.8, 132.6, 132.6, 132.6, 129.4, 128.5, 128.4, 127.4, 117.2, 10.7.

HRMS (ESI) m/z calcd for $C_{16}H_{15}BrNO_3S$ 379.9951 $[M+H]^+$, found 379.9950 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3364 (w), 3082 (w), 1695 (m), 1648 (m), 1601 (m), 1570 (m), 1506 (m), 1466 (s), 1386 (m), 1302 (s), 1276 (m), 1244 (m), 1122 (s), 1064 (s), 1027 (w), 1004 (s), 962 (w), 925 (w), 826 (w), 798 (w), 745 (m).

2.1.18 (*E*)-*N*-(2-((4-fluorophenyl)sulfonyl)prop-1-en-1-yl)benzamide **3r**



3r

Prepared from (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2d** (75 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (37 mg, 0.117 mmol, 59 %).

m.p. 153 - 158 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.24.

^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.32 (dd, *J* = 11.8, 1.5 Hz, 1H), 8.03 – 7.87 (m, 2H), 7.85 – 7.76 (m, 2H), 7.74 (d, *J* = 11.9 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.50 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H), 1.91 (d, *J* = 1.3 Hz, 3H).

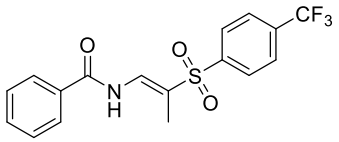
^{13}C NMR (*101 MHz, Chloroform-d*) δ 166.8, 164.4 (d, *J* = 24.6 Hz), 136.1 (d, *J* = 3.2 Hz), 133.3, 132.4, 132.0, 130.8 (d, *J* = 9.5 Hz), 129.2, 127.5, 117.9, 116.6 (d, *J* = 22.6 Hz), 10.7.

^{19}F NMR (*376 MHz, Chloroform-d*) δ -104.48 (ddd, *J* = 13.4, 8.6, 5.1 Hz).

HRMS m/z calcd for $C_{16}H_{16}FNO_3S$ 319.0678 $[M]^+$, found 319.0665 $[M]^+$.

IR (ATR, ν in cm^{-1}): 3351 (m), 3077 (w), 1737 (w), 1693 (m), 1652 (s), 1584 (m), 1507 (m), 1474 (m), 1336 (w), 1306 (w), 1294 (w), 1283 (m), 1255 (m), 1211 (m), 1165 (s), 1126 (s), 1074 (s), 1026 (w), 1010 (w), 963 (m), 925 (w), 832 (m), 815 (m), 740 (m), 703 (s), 671 (m).

2.1.19 (*E*)-*N*-(2-((4-(trifluoromethyl)phenyl)sulfonyl)prop-1-en-1-yl)benzamide **3s**



3s

Prepared from (*E*/*Z*) – Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-trifluoromethylbenzenesulfinate **2e** (95 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (46 mg, 0.124 mmol, 62%).

m.p. 166 - 180 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.2.

^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.46 (d, *J* = 11.0 Hz, 1H), 8.18 (dd, *J* = 11.0, 1.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.96 – 7.90 (m, 2H), 7.67 – 7.63 (m, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 1.95 (d, *J* = 1.1 Hz, 3H).

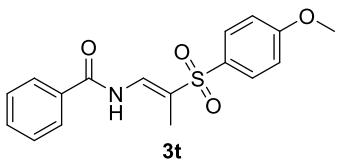
^{13}C NMR (*101 MHz, DMSO-d_6*) δ 166.3, 143.8, 133.6, 132.7, 132.6, 128.5, 128.5, 128.4, 126.8 (q, *J* = 3.5 Hz), 124.8, 122.1, 116.6, 10.7.

^{19}F NMR (*376 MHz, DMSO-d_6*) δ -61.7.

HRMS (ESI) m/z calcd for $C_{17}H_{14}F_3NO_3S$ 370.0719 $[M+H]^+$, found 370.0719 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3273 (w), 2925 (w), 1737 (m), 1678 (m), 1646 (s), 1602 (w), 1517 (m), 1477 (m), 1405 (m), 1322 (s), 1270 (m), 1129 (s), 1090 (m), 1062 (s), 1017 (m), 966 (m), 924 (m), 891 (m), 851 (m), 820 (w), 796 (m), 704 (s),656 (w).

2.1.20 (*E*)-*N*-(2-((4-methoxyphenyl)sulfonyl)prop-1-en-1-yl)benzamide **3t**



3t

Prepared from (*E*/*Z*) – Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol, *E*:*Z* = 77:23), sodium 4-methoxybenzenesulfinate **2f** (81 mg, 2.0 equiv, 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv, 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by

flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (37 mg, 0.11 mmol, 55%).

m.p. 126 - 144 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.18.

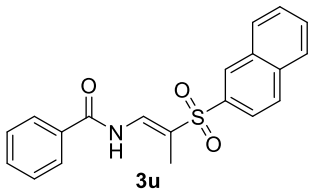
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 11.7 Hz, 1H), 7.90 (d, *J* = 11.5 Hz, 1H), 7.79 (dd, *J* = 12.7, 8.1 Hz, 4H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 163.4, 133.1, 132.5, 131.4, 131.0, 130.2, 129.1, 127.6, 118.8, 114.5, 55.8, 10.7.

HRMS (MALDI) m/z calcd for $C_{27}H_{18}NO_4S$ 332.0951 $[M+H]^+$, found 332.0951 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 1671 (m), 1647 (s), 1598 (m), 1498 (m), 1266 (s), 1206 (m), 1163 (m), 1134 (s), 1076 (m), 1023 (m), 967 (w), 911 (w), 887 (w), 803 (m), 737 (m), 701 (s).

2.1.21 (*E*)-*N*-(2-(naphthalen-2-ylsulfonyl)prop-1-en-1-yl)benzamide **3u**



3u

Prepared from **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2g** (86 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (53 mg, 0.151 mmol, 76%).

m.p. 168 - 169 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.19.

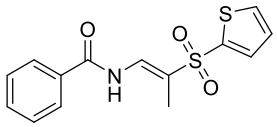
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.45 (d, *J* = 1.8 Hz, 1H), 8.38 (dd, *J* = 11.8, 1.5 Hz, 1H), 8.01 – 7.88 (m, 4H), 7.80 (ddd, *J* = 12.1, 8.4, 1.5 Hz, 3H), 7.63 (dqd, *J* = 8.4, 7.0, 1.4 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H), 1.92 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.8, 136.7, 135.1, 133.1, 132.4, 132.3, 132.0, 129.7, 129.5, 129.4, 129.2, 129.1, 128.0, 127.7, 127.6, 122.9, 118.1, 10.8.

HRMS (ESI) m/z calcd for $C_{20}H_{17}NNaO_3S$ 374.0821 $[M+Na]^+$, found 374.0822 $[M+Na]^+$.

IR (ATR, ν in cm^{-1}): 3275 (w), 1669 (m), 1644 (s), 1602 (w), 1514 (m), 1488 (m), 1386 (w), 1303 (s), 1270 (s), 1162 (m), 1141 (m), 1117 (s), 1087 (m), 1067 (m), 1026 (w), 965 (m), 910 (m), 887 (m), 856 (m), 816 (m), 797 (w), 748 (m), 735 (m), 694 (s).

2.1.22 (E)-N-(2-(thiophen-2-ylsulfonyl)prop-1-en-1-yl)benzamide **3v**



3v

Prepared from **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium thiophene-2-sulfinate **2h** (70 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (39 mg, 0.128 mmol, 64%).

m.p. 143 - 149 °C.

R_f (*n*-hexane:EtOAc = 7:3) 0.13.

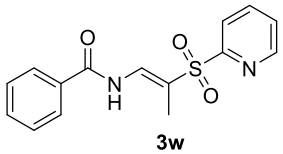
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.32 (dd, *J* = 11.8, 1.5 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.77 (d, *J* = 11.9 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.63 – 7.56 (m, 1H), 7.50 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.11 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.01 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.6, 141.6, 133.6, 133.6, 133.3, 132.4, 131.8, 129.2, 127.9, 127.6, 118.7, 10.8.

HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_3S_2$ 308.0410 $[M+H]^+$, found 308.0408 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3435 (w), 3104 (w), 2924 (w), 1737 (w), 1679 (s), 1647 (s), 1602 (m), 1583 (w), 1506 (m), 1467 (m), 1343 (w), 1303 (s), 1231 (m), 1168 (m), 1120 (s), 1088 (m), 1016 (m), 964 (m), 858 (m), 798 (w), 736 (m), 699 (s), 685 (s), 662 (s).

2.1.23 (*E*)-*N*-(2-(pyridin-2-ylsulfonyl)prop-1-en-1-yl)benzamide **3w**



3w

Prepared from (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium pyridine-2-sulfinate **2i** (66 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 3 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (28 mg, 0.092 mmol, 46%).

m.p. 108 - 115 °C.

R_f (*n*-hexane:EtOAc = 1:1) 0.21.

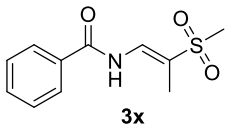
^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.47 (d, *J* = 11.2 Hz, 1H), 8.94 – 8.53 (m, 1H), 8.20 – 8.06 (m, 3H), 8.00 – 7.89 (m, 2H), 7.72 (ddd, *J* = 7.4, 4.7, 1.4 Hz, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 2.09 – 1.80 (m, 3H).

^{13}C NMR (*101 MHz, DMSO-d_6*) δ 166.3, 157.2, 150.5, 139.0, 134.2, 132.7, 132.6, 128.5, 128.4, 127.6, 122.2, 115.7, 11.1.

HRMS (ESI) m/z calcd for $C_{15}H_{14}N_2O_3S$ 303.0798 $[M+H]^+$, found 303.0798 $[M+H]^+$.

IR (*ATR, ν in cm^{-1}*): 3271 (m), 2924 (w), 1749 (w), 1671 (m), 1645 (s), 1602 (w), 1579 (w), 1517 (m), 1487 (m), 1449 (w), 1428 (w), 1307 (s), 1274 (s), 1206 (m), 1147 (m), 1102 (s), 1075 (s), 1027 (w), 991 (w), 968 (m), 931 (w), 907 (m), 797 (w), 779 (m), 691 (s).

2.1.24 (*E*)-*N*-(2-(methylsulfonyl)prop-1-en-1-yl)benzamide **3x**



3x

Prepared from (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium methylsulfinate **2j** (41 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3 \cdot 2\,H_2O$ (111 mg, 2.0 equiv., 0.4 mmol) and sodium acetate (33 mg, 2.0 equiv., 0.4 mmol) according to TP 1 in 2 mL ethanol. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid solid (35 mg, 0.147mmol, 74%).

m.p. 157 - 160 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.07.

^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.28 – 8.12 (m, 1H), 7.92 – 7.79 (m, 2H), 7.76 (d, *J* = 11.9 Hz, 1H), 7.70 – 7.58 (m, 1H), 7.56 – 7.49 (m, 2H), 2.94 (s, 3H), 2.11 (d, *J* = 1.3 Hz, 3H).

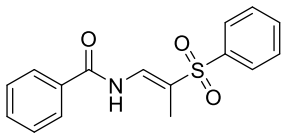
^{13}C NMR (*101 MHz, Chloroform-d*) δ 133.3, 132.4, 132.4, 129.2, 127.6, 117.4, 41.6, 10.9.

HRMS (MALDI) m/z calcd for $C_{11}H_{14}NO_3S$ 240.0689 $[M+H]^+$, found 240.0688 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3338 (w), 2924 (w), 1678 (m), 1648 (s), 1600 (w), 1581 (w), 1509 (m), 1479 (s), 1336 (w), 1299 (m), 1263 (s), 1202 (s), 1160 (s), 1113 (s), 1073 (m), 1028 (w), 969 (m), 951 (m), 925 (m), 890 (m), 799 (w), 768 (m), 711 (s), 685 (s).

2.2 Synthesis of β-Amidovinylsulfones from lithium sulfinates

2.2.1 (*E*)-*N*-(2-(phenylsulfonyl)prop-1-en-1-yl)benzamide **3y**



3y

Lithium benzenesulfinate (**12a**):

A dry, N_2-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with phenyllithium (14.6 mL, 23 mmol, 1.55 M solution in Et_2O, 1.0 equiv) and cooled to −40 °C. At this temperature, liquid SO_2 (0.5 mL, 25 mmol, 1.1 equiv) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with CH_2Cl_2 (150 mL) to afford the solid benzenesulfinic lithium salt **12a** (4.3 g). This procedure affords sulfinate **12a** sufficiently pure for the following transformation.

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, The obtained lithium benzenesulfinate **12a** (59 mg, 2.0 equiv., 0.4 mmol), (*E*)-enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), $Mn(OAc)_3{\cdot}2\ H_2O$ (111 mg, 2.0 equiv., 0.4 mmol), and ethanol (2 mL). The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product a colorless solid solid (28 mg, 0.093 mmol, 47%).

m.p. 175 - 177 °C.

R_f (*n*-hexane:EtOAc = 6:4) 0.29.

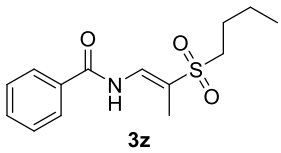
^{1}H NMR (*400 MHz, Chloroform-d*) δ 8.31 (d, *J* = 11.8, 1.5 Hz, 1H), 7.91 – 7.77 (m, 5H), 7.62 – 7.43 (m, 7H), 1.90 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 164.7, 139.9, 133.2, 133.2, 132.4, 131.9, 129.3, 129.1, 128.0, 127.6, 118.1, 10.8.

HRMS m/z calcd for $C_{16}H_{15}NO_3S$ 301.0773 $[M]^+$, found 301.0782 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 3394 (w), 3076 (w), 1701 (m), 1644 (s), 1604 (w), 1505 (w), 1471 (m), 1443 (m), 1325 (w), 1287 (m), 1242 (m), 1159 (m), 1123 (m), 1072 (s), 999 (m), 963 (m), 931 (m), 887 (m), 795 (w), 762 (m), 739 (m), 703 (s).

2.2.2 (*E*)-*N*-(2-(butylsulfonyl)prop-1-en-1-yl)benzamide **3z**



3z

Lithium butane-1-sulfinate (**12b**):

A dry, N_2-flushed Schlenk-flask equipped with a magnetic stirrer and a rubber septum was charged with nBuLi (1.63 mL, 3.8 mmol, 2.34 M) and THF (5 mL), then cooled to −40 °C. At this temperature, liquid SO_2 (0.5 mL, 25 mmol) was added and the reaction mixture was allowed to warm to 25 °C within 90 min. It was then concentrated under reduced pressure and coevaporated two times with CH_2Cl_2 (150 mL) to afford the solid lithium salt **12b** (500 mg).

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, the obtained lithium butane-1-sulfinate **12b** (51 mg, 2.0 equiv, 0.4 mmol), (*E*)-enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (111 mg, 2.0 equiv., 0.4 mmol), and ethanol (2 mL). The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless, low-melting solid (16 mg, 0.056 mmol, 36%).

R_f (*n*-hexane:EtOAc = 7:3) 0.06.

^{1}H NMR (*400 MHz, DMSO-d_6*) δ 10.33 (d, *J* = 11.0 Hz, 1H), 8.02 – 7.90 (m, 2H), 7.84 (dd, *J* = 11.0, 1.5 Hz, 1H), 7.80 – 7.60 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 3.18 – 2.97 (m, 2H), 2.09 (d, *J* = 1.2 Hz, 3H), 1.54 (tt, *J* = 7.9, 6.2 Hz, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (*101 MHz, DMSO-d_6*) δ 166.2, 132.7, 132.6, 132.4, 128.4, 127.5, 116.7, 51.1, 24.3, 20.8, 13.6, 11.0.

HRMS (MALDI) m/z calcd for $C_{14}H_{19}NNaO_3S$ 304.0978 $[M+H]^+$, found 304.0980 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 2961 (w), 2876 (w), 1683 (s), 1649 (m), 1603 (w), 1582 (w), 1507 (m), 1480 (m), 1258 (s), 1209 (m), 1161 (m), 1106 (s), 1066 (m), 1026 (m), 965 (m), 915 (m), 888 (m), 795 (m),768 (m).

2.2.3 (*E*)-N-(2-tosylprop-1-en-1-yl)benzamide **3a**

A solution of 1-Iodo-4-methylbenzene **13** (1.6 g, 7.5 mmol, 1.0 equiv) in Et_2O (15 mL) was treated with nBuLi (2.9 mL, 2.58 M in hexane, 7.5 mmol, 1.0 equiv) dropwise at 0 °C (ice bath cooling). The mixture was allowed to stir at 0 °C for 30 min. After cooling to -40 °C, liquid SO_2 (0.5 mL, 25 mmol, 3.3 equiv) was added and the reaction mixture was allowed to warm to 25 °C for 90 min. The resulting suspension was filtered. The obtained solid was washed with EtOAc (3x 30 mL) and DCM (3x 30 mL) to give sulfinate **12c** as a colorless solid solid (870 mg, 72%). The crude sulfinate is sufficiently pure to be used directly in the next step.

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, the obtained Lithiumsulfinate **12c** (65 mg, 2.0 equiv, 0.4 mmol), (*E*)-enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), $Mn(OAc)_3$·2 H_2O (111 mg, 2.0 equiv., 0.4 mmol), and ethanol (2 mL). The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as white solid (51 mg, 0.162 mmol, 81%).

*Analytical data match those of **3a** prepared from the corresponding sodium sulfinate.*

2.3 Control experiments

2.3.1 Trapping experiments with DPE

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium benzenesulfinate **2a** (67 mg, 0.4 mmol, 2.0 equiv), $Mn(OAc)_3$·2 H_2O (111 mg, 2.0 equiv., 0.2 mmol), 1,1-diphenylethylene (72 mg, 4.0 equiv., 0.4 mmol) and 2 mL ethanol. The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography afforded **6** as a colorless oil in 19 mg (0.057 mmol, 14 %).

Analytical data of **6** are consistent with literature.[4]

^{1}H NMR (*400 MHz, Chloroform-d*) δ 7.81 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.74 – 7.69 (m, 1H), 7.62 – 7.42 (m, 11H), 7.34 – 7.28 (m, 2H).
MS (ESI) m/z calcd $C_{20}H_{17}O_2S$ 321.09 $[M+H]^+$, found 321.08 $[M+H]^+$.

2.3.2 Trapping experiments with BHT

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, (*E*)-Enamide **1a** (32 mg, 1.0 equiv., 0.2 mmol), sodium 4-methylbenzenesulfinate **2a** (74 mg, 2.0 equiv), $Mn(OAc)_3 \cdot 2\ H_2O$ (111 mg, 2.0 equiv., 0.2 mmol), 2,6-di-*tert*-butyl-4-methylphenol (98 mg, 2.2 equiv., 0.44 mmol) and 3 mL ethanol. The tube was closed with a rubber septum, and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography afforded (*E*)-N-(2-tosylprop-1-en-1-yl)benzamide **3y** as a colorless solid in 23 mg (0.073 mmol, 36%). Compound **17** could be detected by ESI-HRMS of the reaction mixture after filtration

HRMS (ESI) m/z calcd $C_{32}H_{42}NO_4S$ 536.2829 $[M+H]^+$, found 536.2826.
m/z calcd $C_{32}H_{42}NO_4S$ 558.2649 $[M+Na]^+$, found 558.2649.

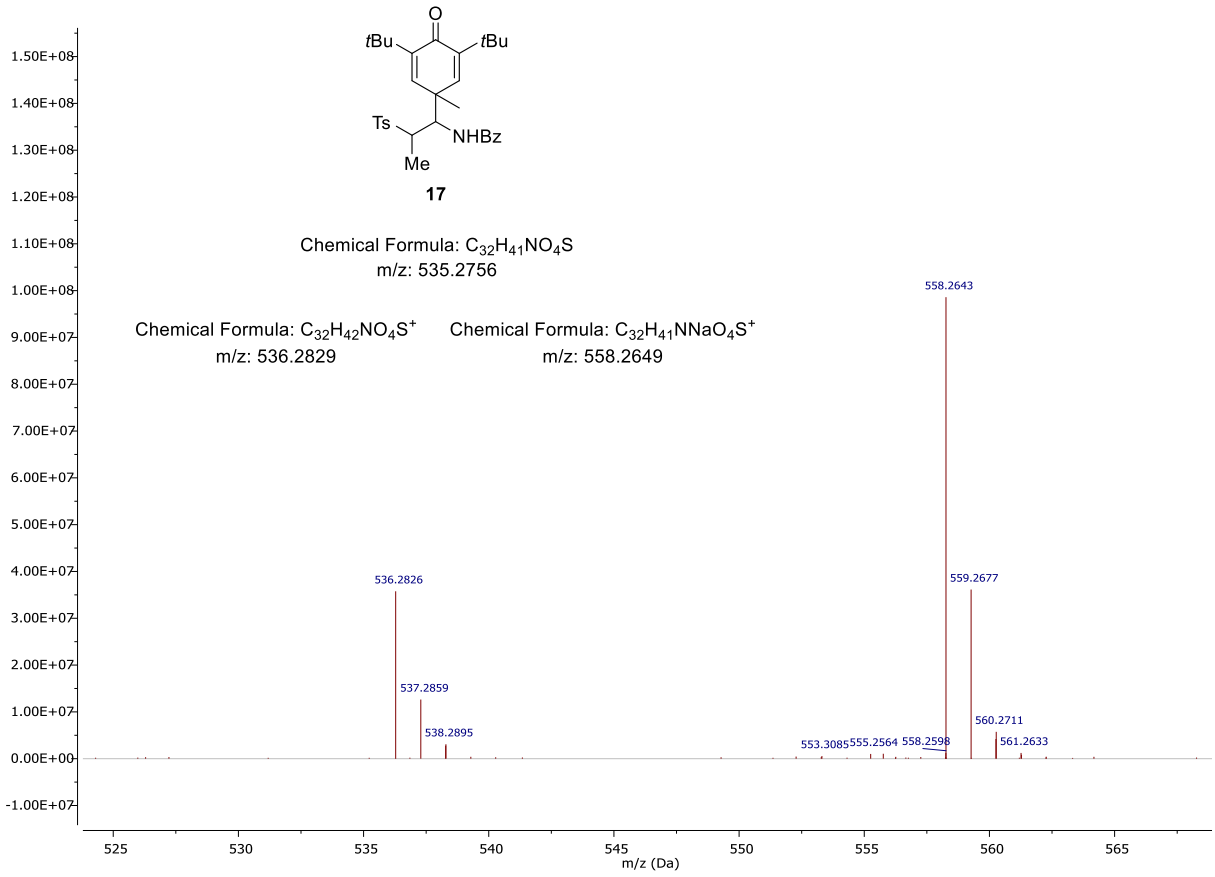
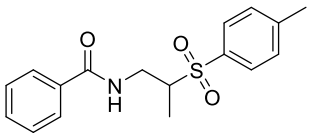


*Figure 1: ESI-MS Spectrum of Compound **17**.*

2.4 Hydrogenation of **3a** to **15**



15

A stainless-steel autoclave was tube was charged with a magnetic stirring bar, (*E*)-N-(2-tosylprop-1-en-1-yl)benzamide **3a** (1.0 equiv., 0.1 mmol, 32 mg), Wilkinson catalyst (10 mol%, 9 mg, 100 µmol) and 5 mL MeOH. The autoclave was flushed three times with hydrogen until a pressure of 20 bar was achieved. The reaction was then heated to 60 °C and the reaction was stirred for 24 h. Upon completion of the reaction the mixture was evaporated to dryness. Purification of the crude residue by flash column chromatography afforded compound **15** the analytically pure product as a yellow oil (26 mg, 81µmol, 85%).

R_f (*n*-hexane:EtOAc = 7:3) 0.25.

^{1}H NMR (*400 MHz, Chloroform-d*) δ 7.84 – 7.73 (m, 4H), 7.55 – 7.49 (m, 1H), 7.44 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 5.9 Hz, 1H), 3.93 (ddd, *J* = 14.9, 6.6, 3.3 Hz, 1H), 3.74 (ddd, *J* = 14.8, 7.9, 5.3 Hz, 1H), 3.37 (pd, *J* = 7.2, 3.4 Hz, 1H), 2.44 (s, 3H), 1.29 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (*101 MHz, Chloroform-d*) δ 167.5, 145.5, 133.9, 133.9, 131.9, 130.2, 128.9, 128.8, 127.1, 59.7, 39.4, 21.8, 12.7.

HRMS (MALDI) m/z calcd for $C_{17}H_{19}NO_3S$ 318.1158 $[M+H]^+$, found 318.1158 $[M+H]^+$.

IR (ATR, ν in cm^{-1}): 2938 (w), 1645 (s), 1598 (w), 1580 (w), 1533 (s), 1489 (m), 1449 (m), 1382 (w), 1287 (s), 1141 (s), 1085 (m), 1018 (w), 914 (w), 802 (m), 712 (s), 692 (m).

2.5 Telescoped processed for **3a**

An oven-dried, 10 mL tube was charged with a magnetic stirring bar, $Ni(PPh_3)_2$[NaphthylBr] (5 mol%, 0.05 mmol) and 2 mL Ethanol and capped with a rubber septum. The resulting suspension was degassed by slowly bubbling nitrogen through the mixture for 10 min with simultaneous sonication in an ultrasound bath. The *N*-allylamide **14** (161 mg, 1.0 equiv., 1 mmol) was added at room temperature under vigorous stirring. The reaction mixture was stirred for 24 h time. After completion of the reaction (controlled by TLC) sulfinate salt **2a** (369 mg, 2.0 equiv., 0.4 mmol), $Mn(OAc)_3$·2 H_2O (574 mg, 2.0 equiv., 2 mmol) and NaOAc (164 mg, 2.0 eq., 2mmol) were added to reaction mixture. The resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a short plug of Celite and silica gel. The filter pad was rinsed with additional ethyl acetate and the solution was concentrated under reduced pressure. Purification by flash column chromatography (n-Hexane/EtOAc) afforded the analytically pure product as a colorless solid (276 mg, 0.87 mmol, 87%).

*Analytical data match those of **3a**.*

3 NMR Data

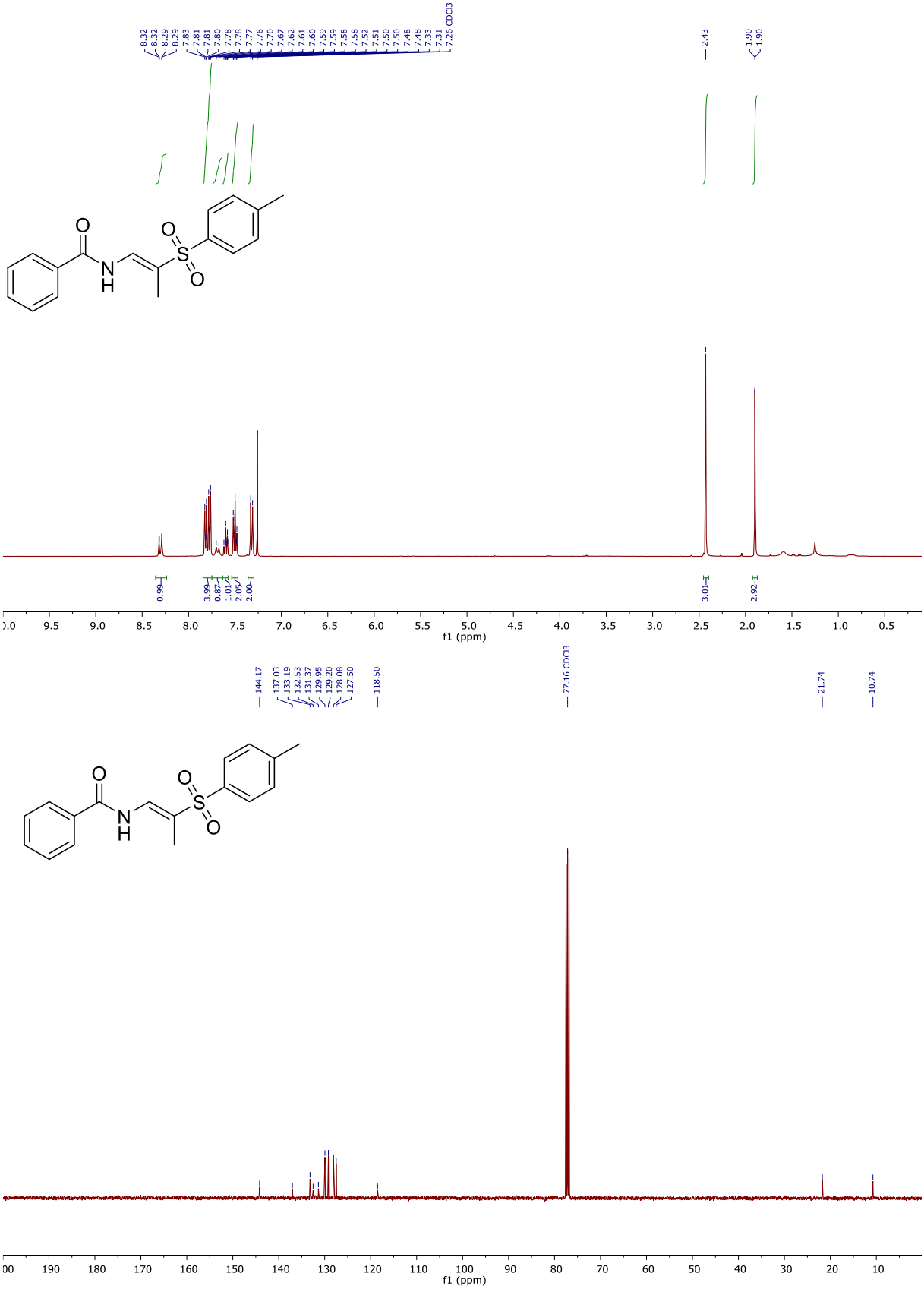


*Figure 2: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3a** in $CDCl_3$.*

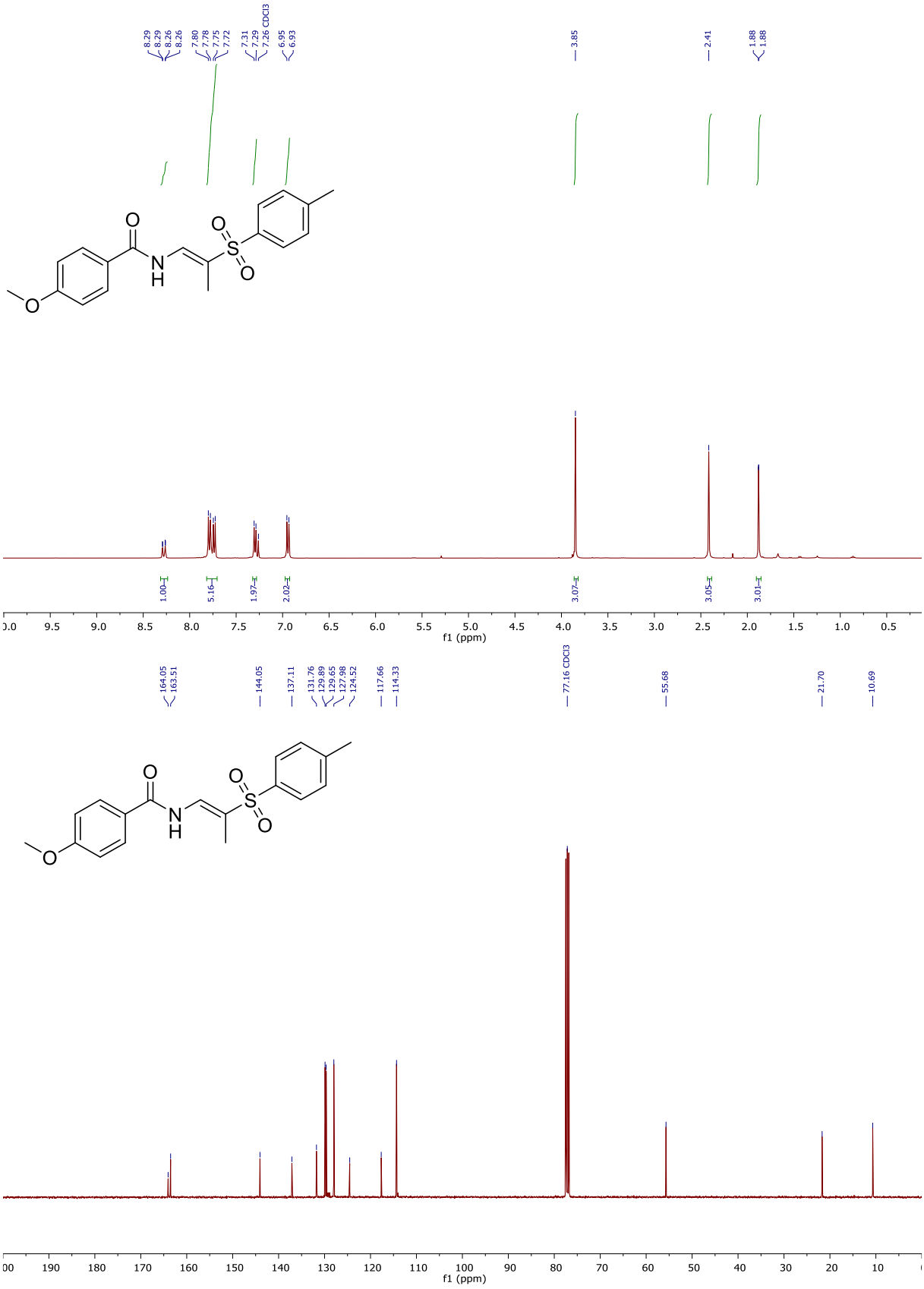


*Figure 3: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3b** in $CDCl_3$.*

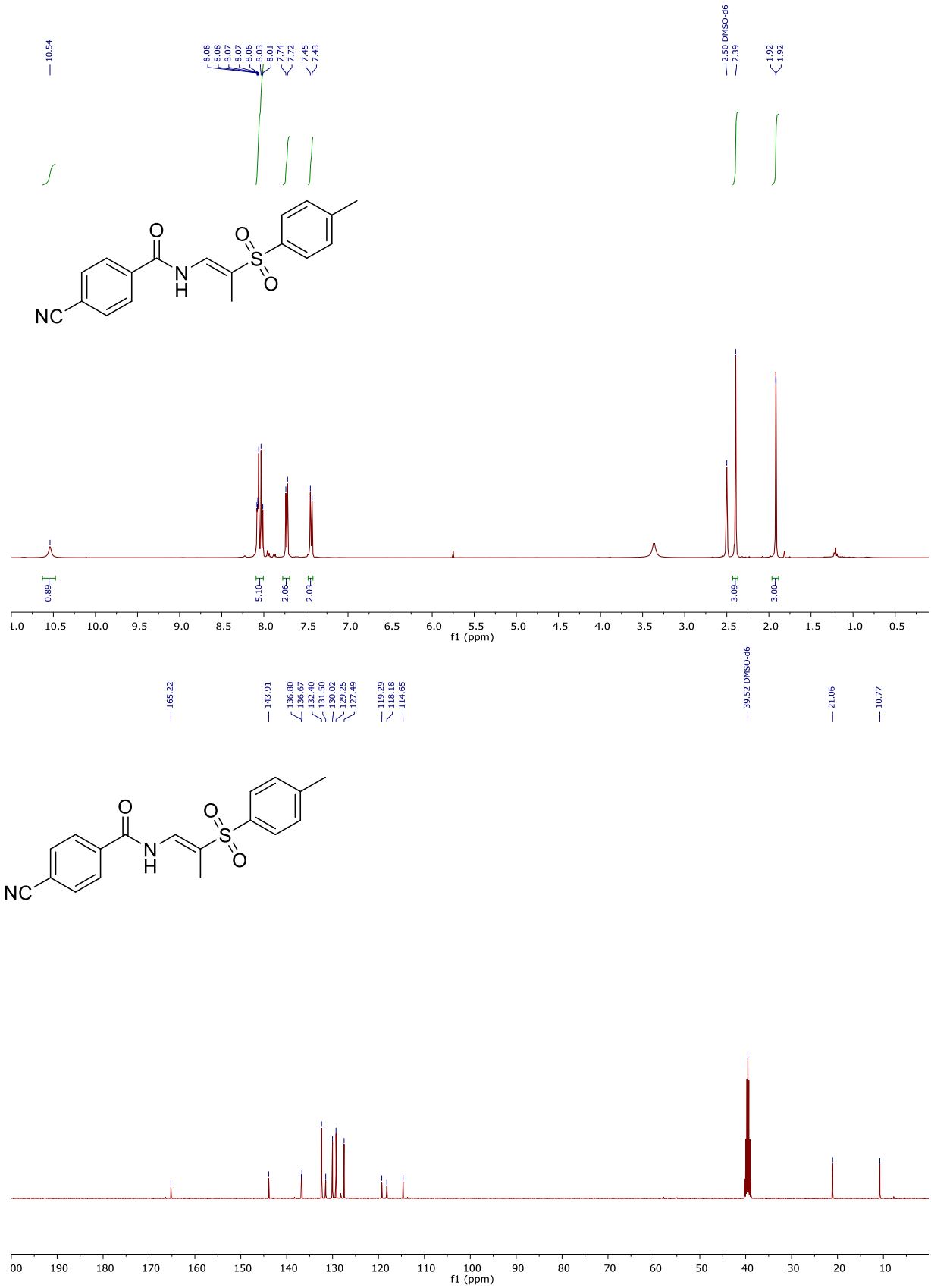
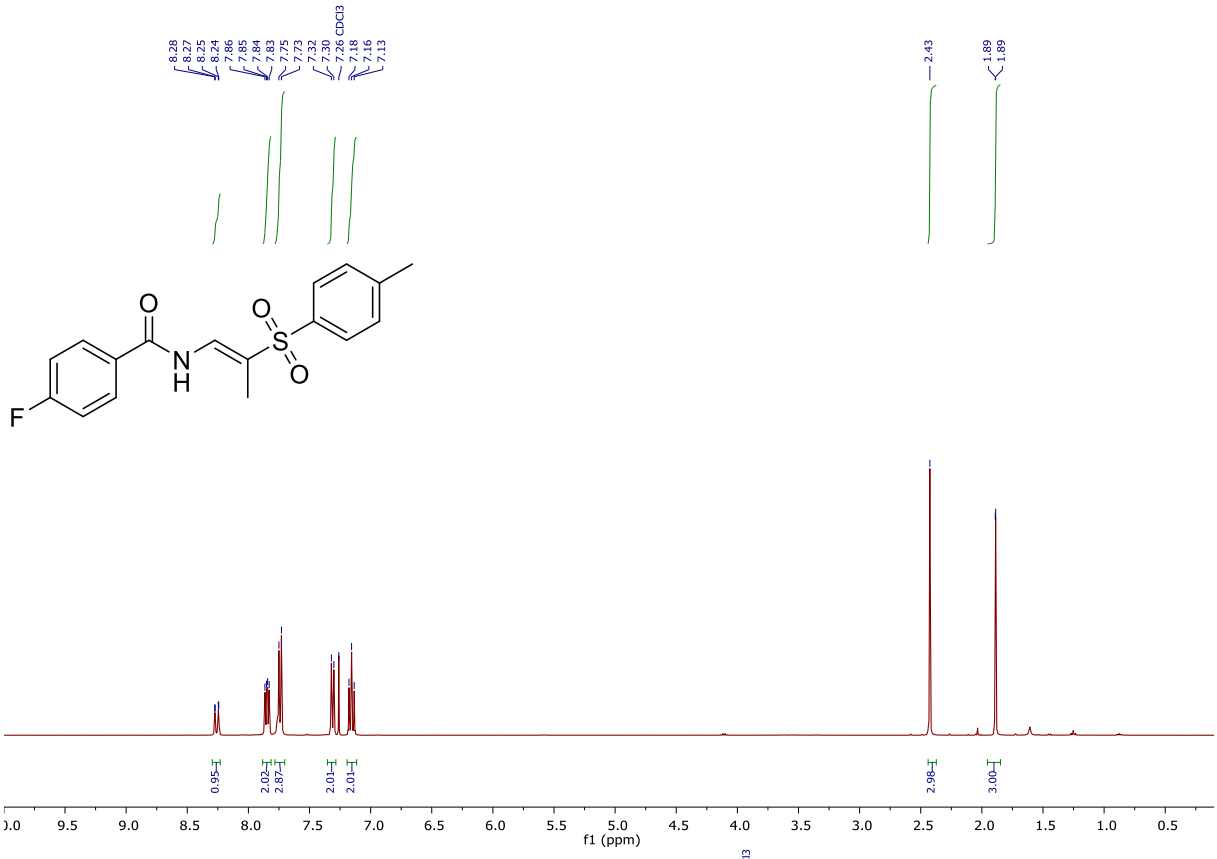
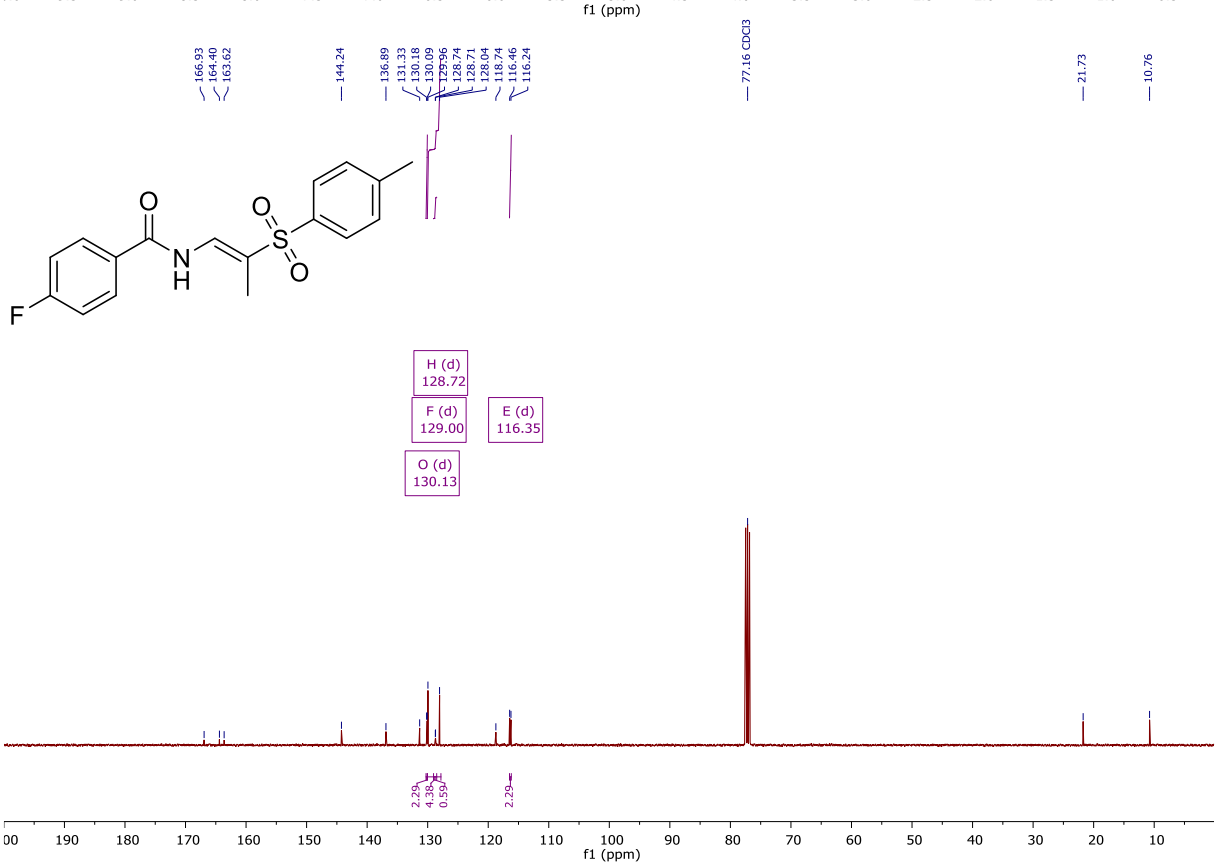


*Figure 4: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3c** in DMSO-d_6.*


8.28
8.27
8.25
8.24
7.86
7.85
7.84
7.83
7.75
7.73
7.32
7.30
7.26 CDCl3
7.18
7.16
7.13
2.43
1.89
1.89
O
N
H
S
O
O
F
0.95
2.02
2.87
2.01
2.01
2.98
3.00
f1 (ppm)


166.93
164.40
163.62
144.24
136.89
131.33
130.18
130.09
129.96
128.74
128.71
128.04
118.74
116.46
116.24
77.16 CDCl3
21.73
10.76
O
N
H
S
O
O
F
H (d)
128.72
F (d)
129.00
E (d)
116.35
O (d)
130.13
2.29
4.38
0.59
2.29
f1 (ppm)

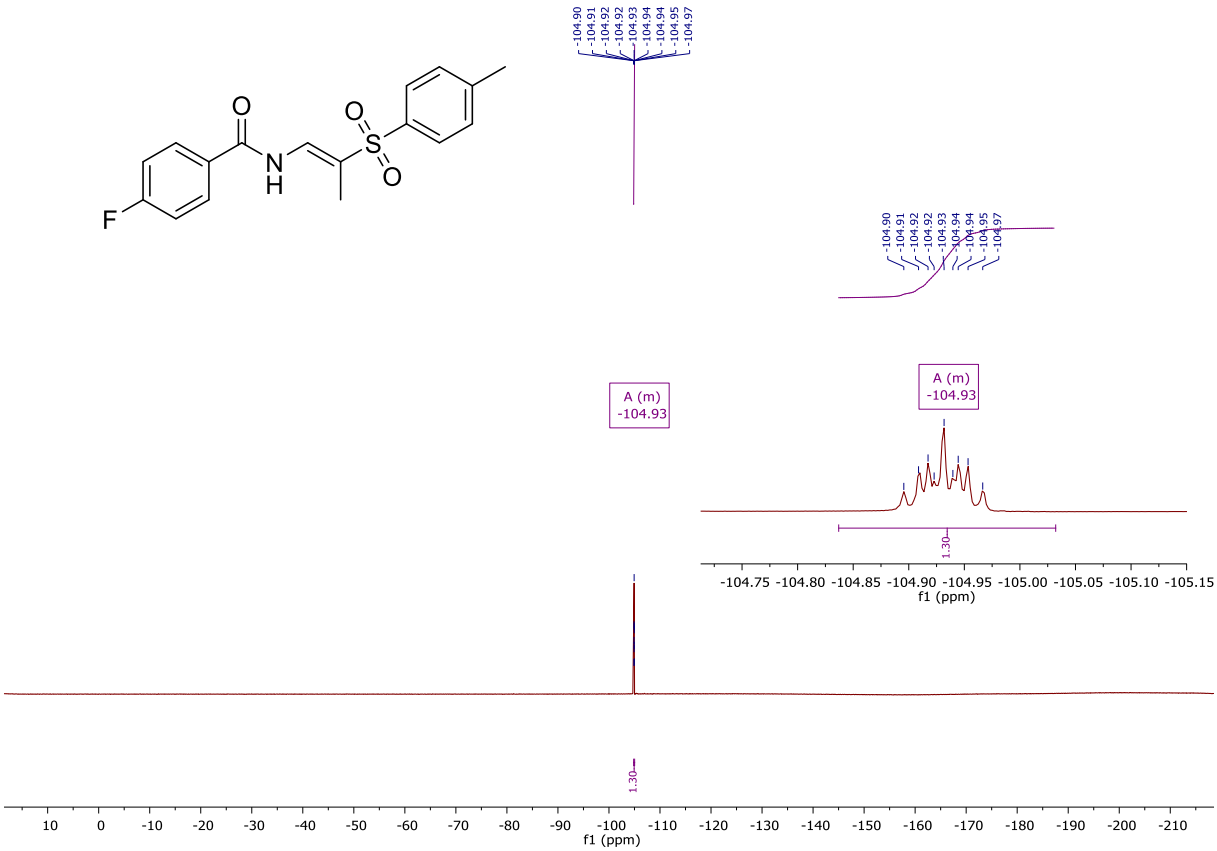


*Figure 5: ^{1}H (400 MHz), ^{13}C (101 MHz) ^{19}F (476 MHz) NMR spectra of **3d** in DMSO-d_6.*

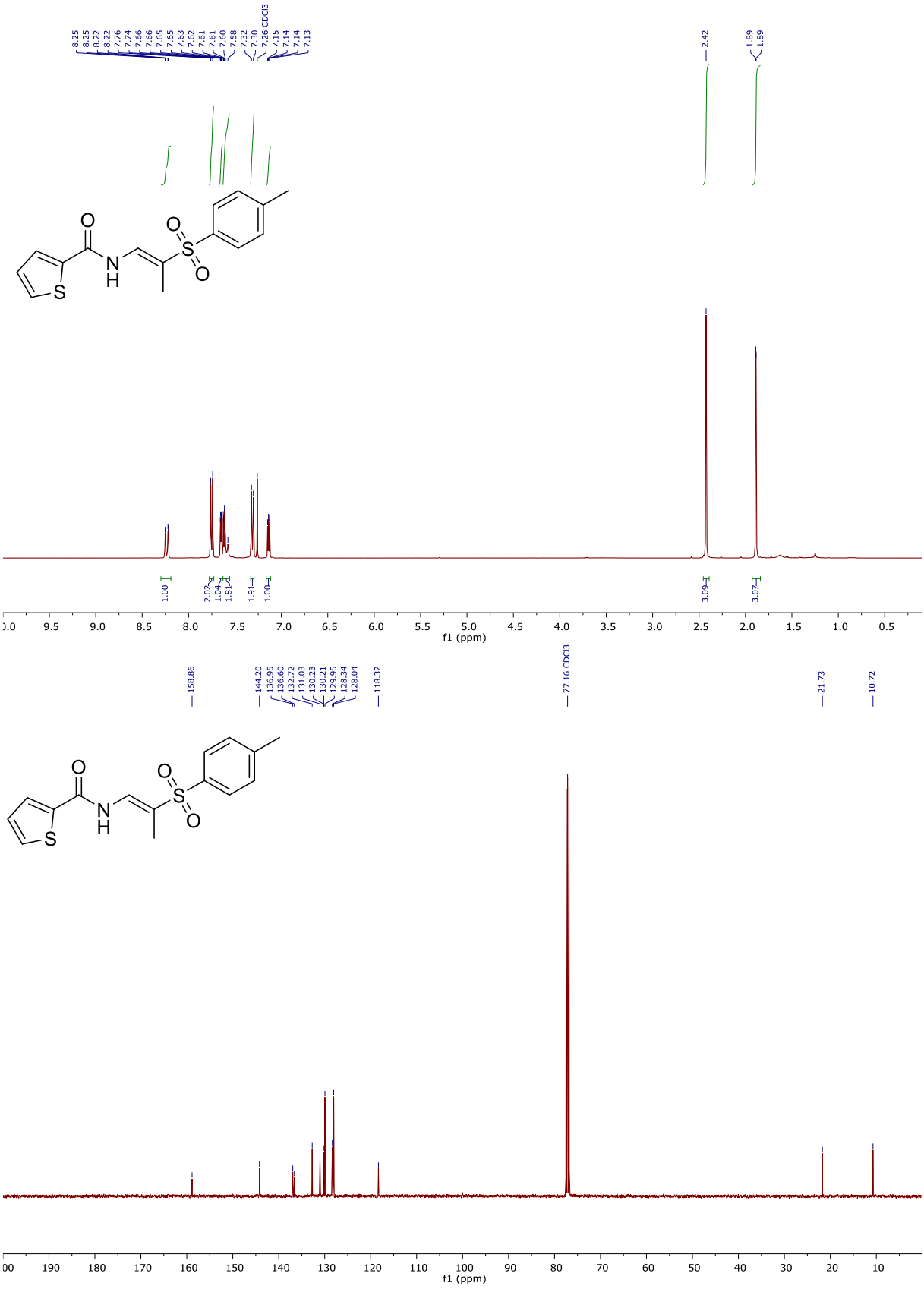


*Figure 6: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3e** in $CDCl_3$.*

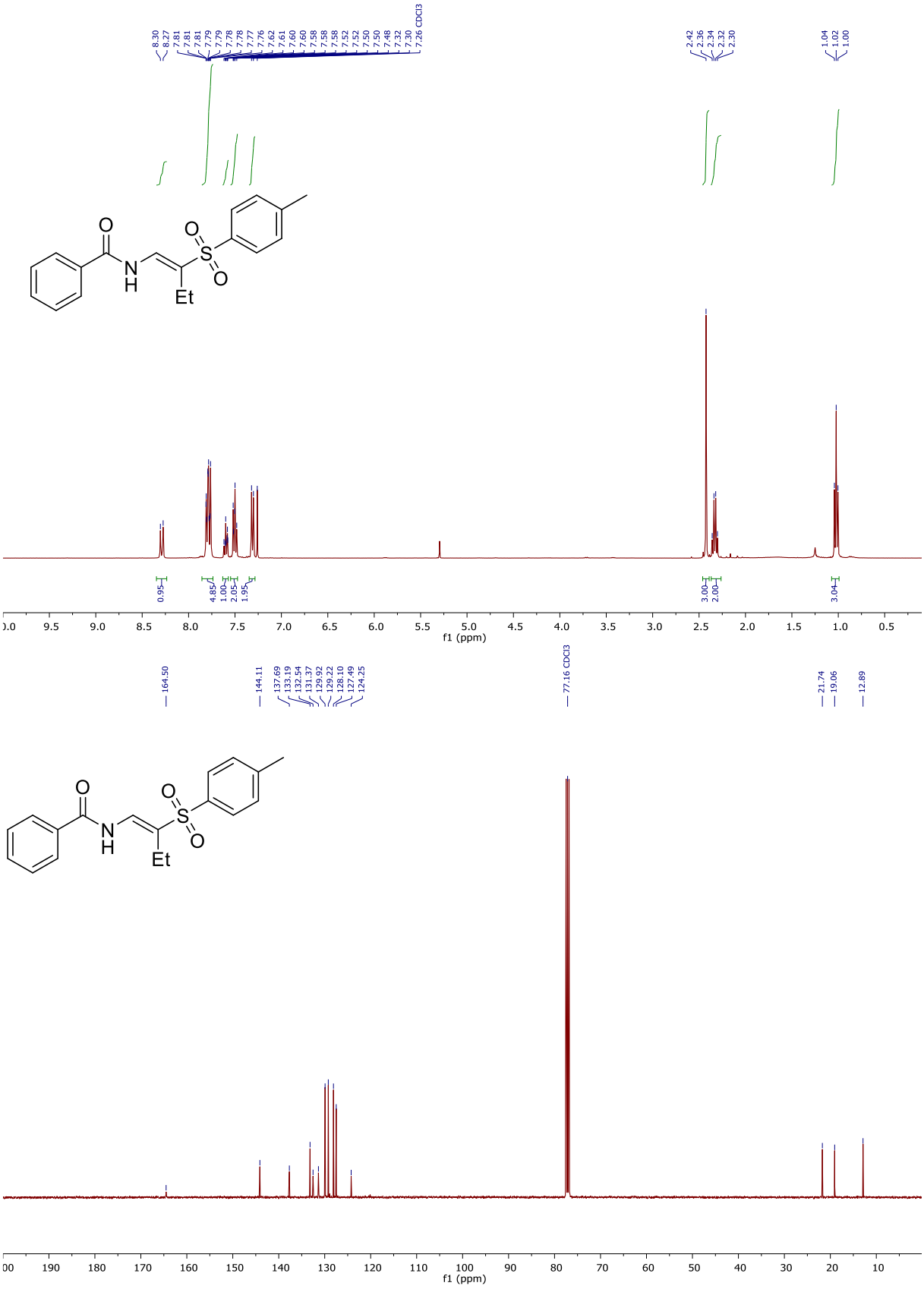


*Figure 7: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3f** in $CDCl_3$.*

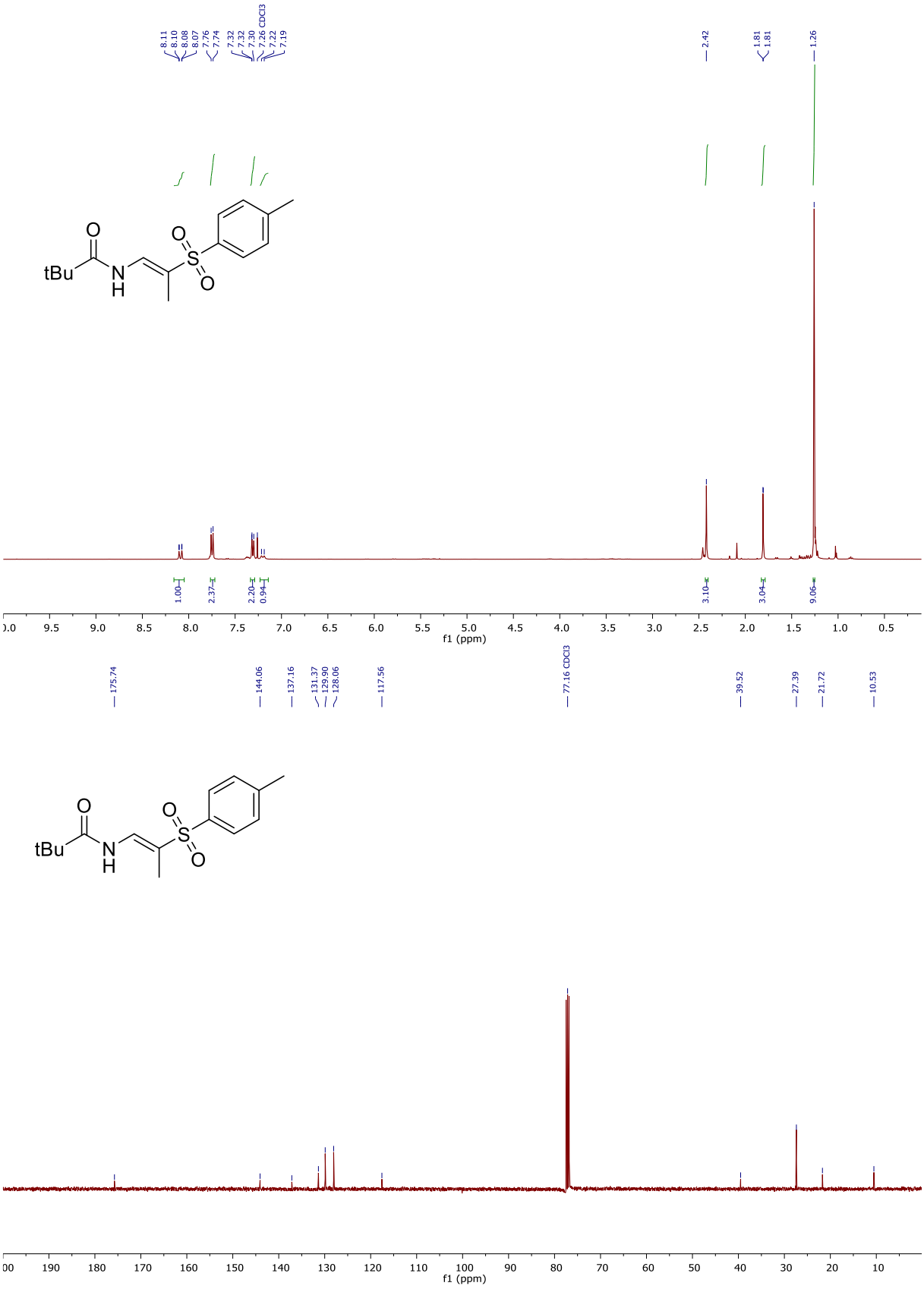


*Figure 8: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3g** in $CDCl_3$.*

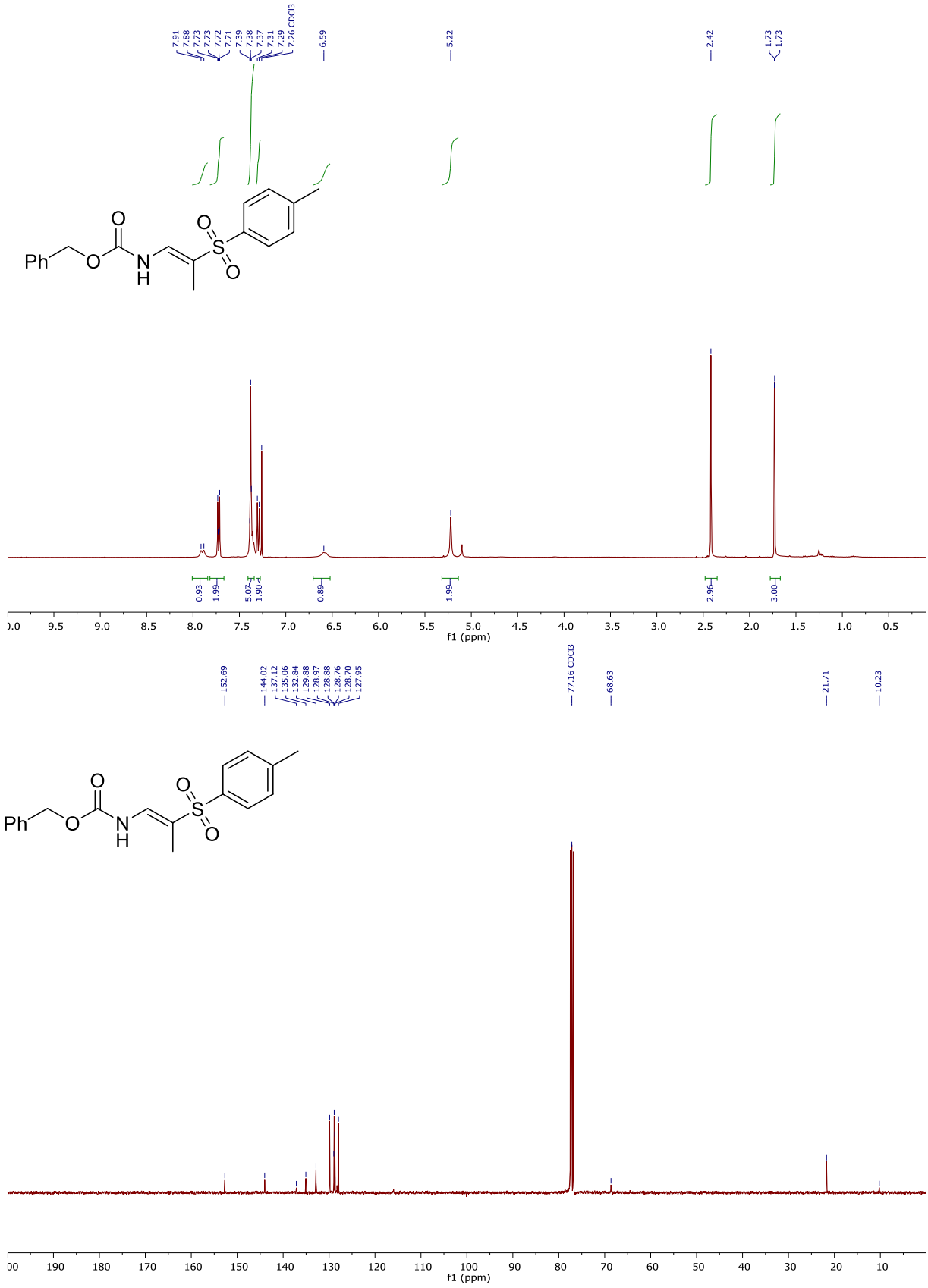


*Figure 9: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3h** in $CDCl_3$.*

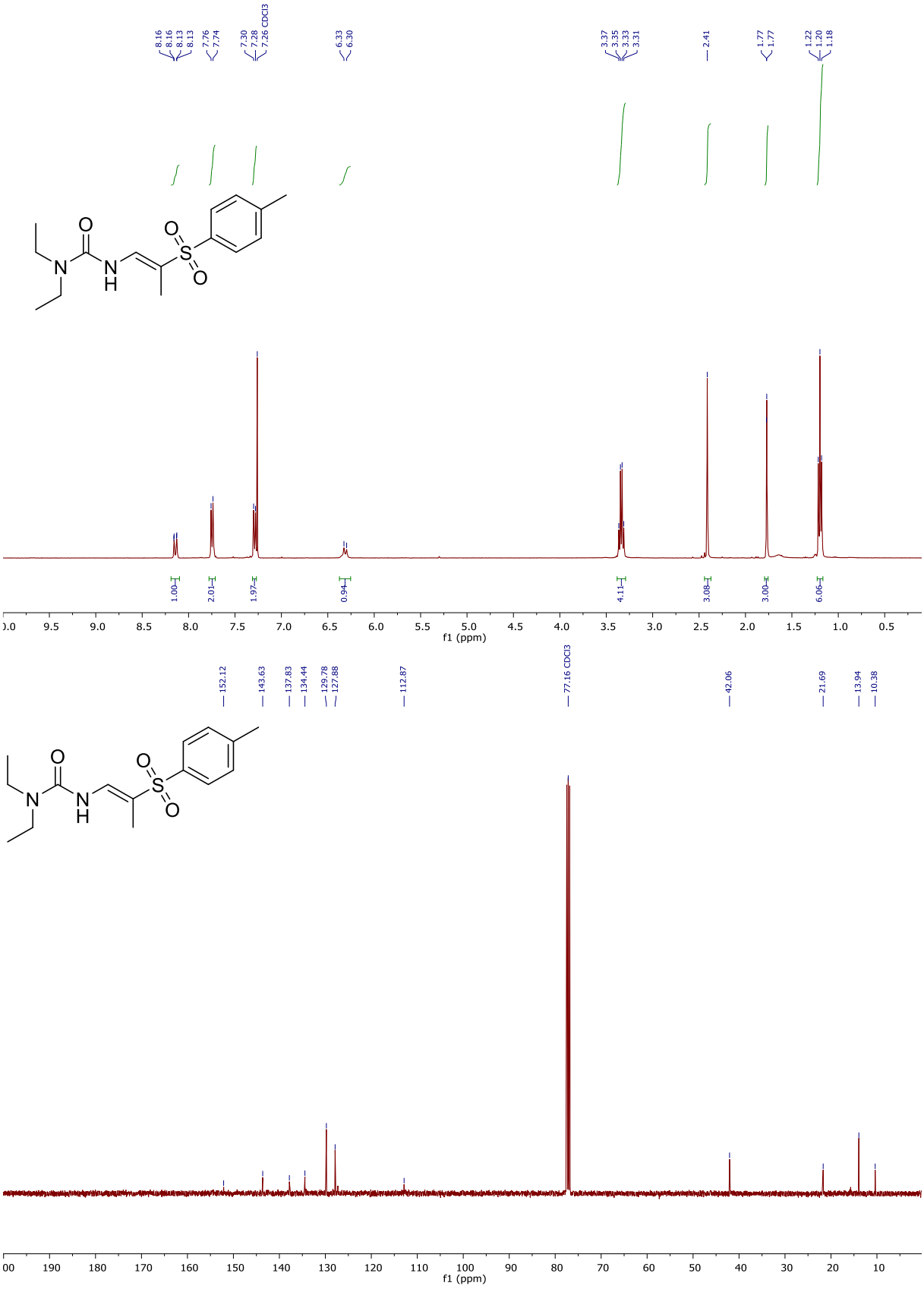


*Figure 10: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3i** in $CDCl_3$.*

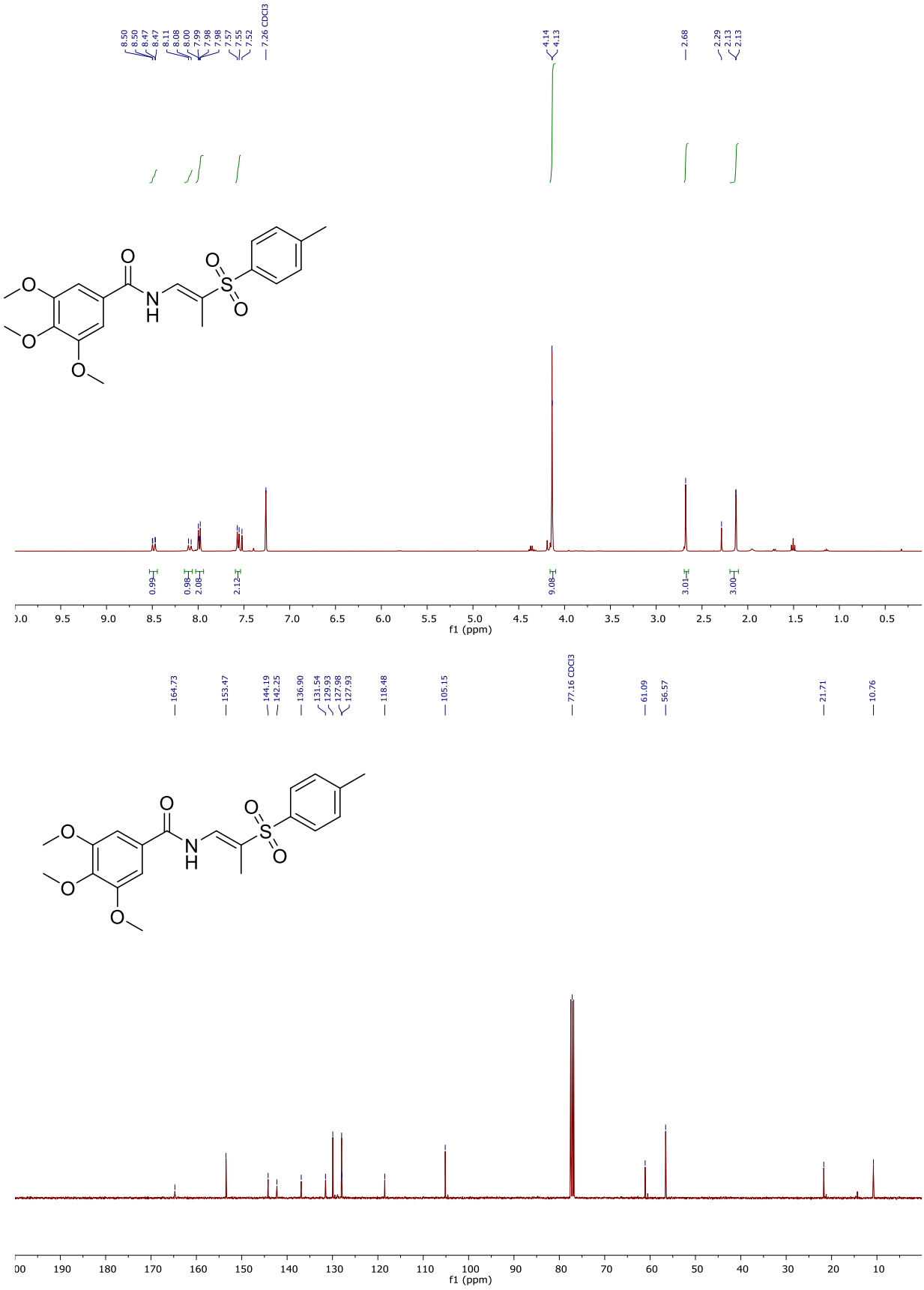
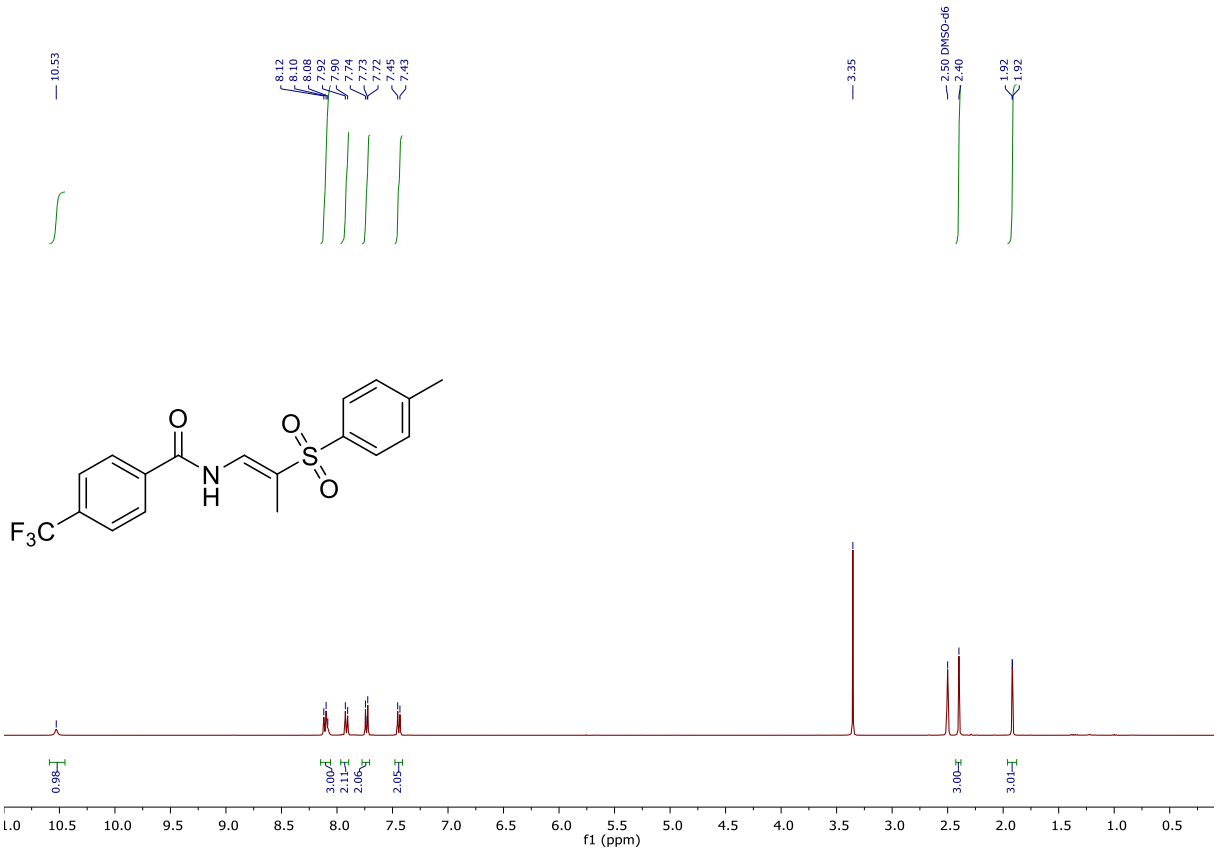
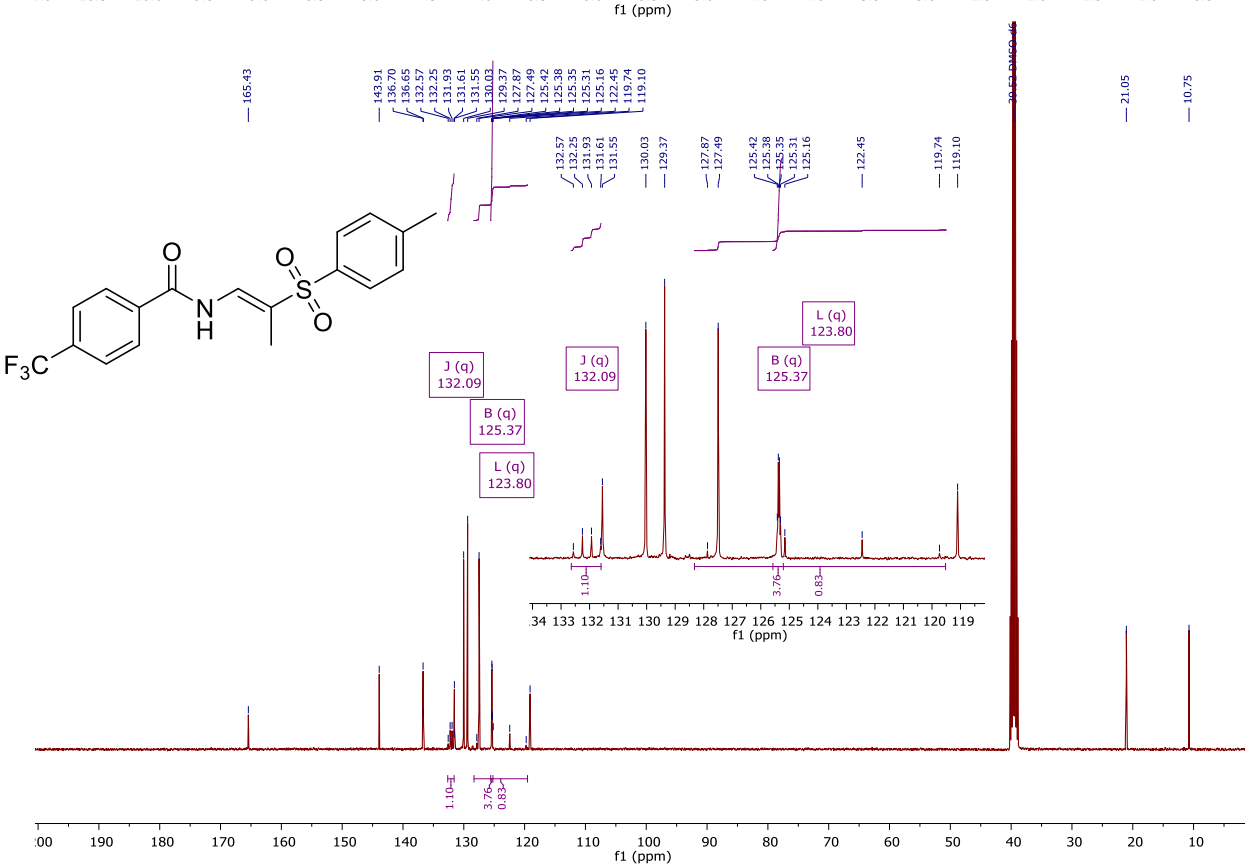


*Figure 11: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3j** in $CDCl_3$.*


10.53
8.12
8.10
8.08
7.92
7.90
7.74
7.73
7.72
7.45
7.43
3.35
2.50 DMSO-d6
2.40
1.92
1.92
O
N
H
O
S
O
F3C
0.98
3.00
2.11
2.06
2.05
3.00
3.01
f1 (ppm)


165.43
143.91
136.70
136.65
132.57
132.25
131.93
131.61
131.55
130.03
129.37
127.87
127.49
125.42
125.38
125.35
125.31
125.16
122.45
119.74
119.10
39.52 DMSO-d6
21.05
10.75
O
N
H
O
S
O
F3C
J (q)
132.09
B (q)
125.37
L (q)
123.80
J (q)
132.09
B (q)
125.37
L (q)
123.80
1.10
3.76
0.83
f1 (ppm)

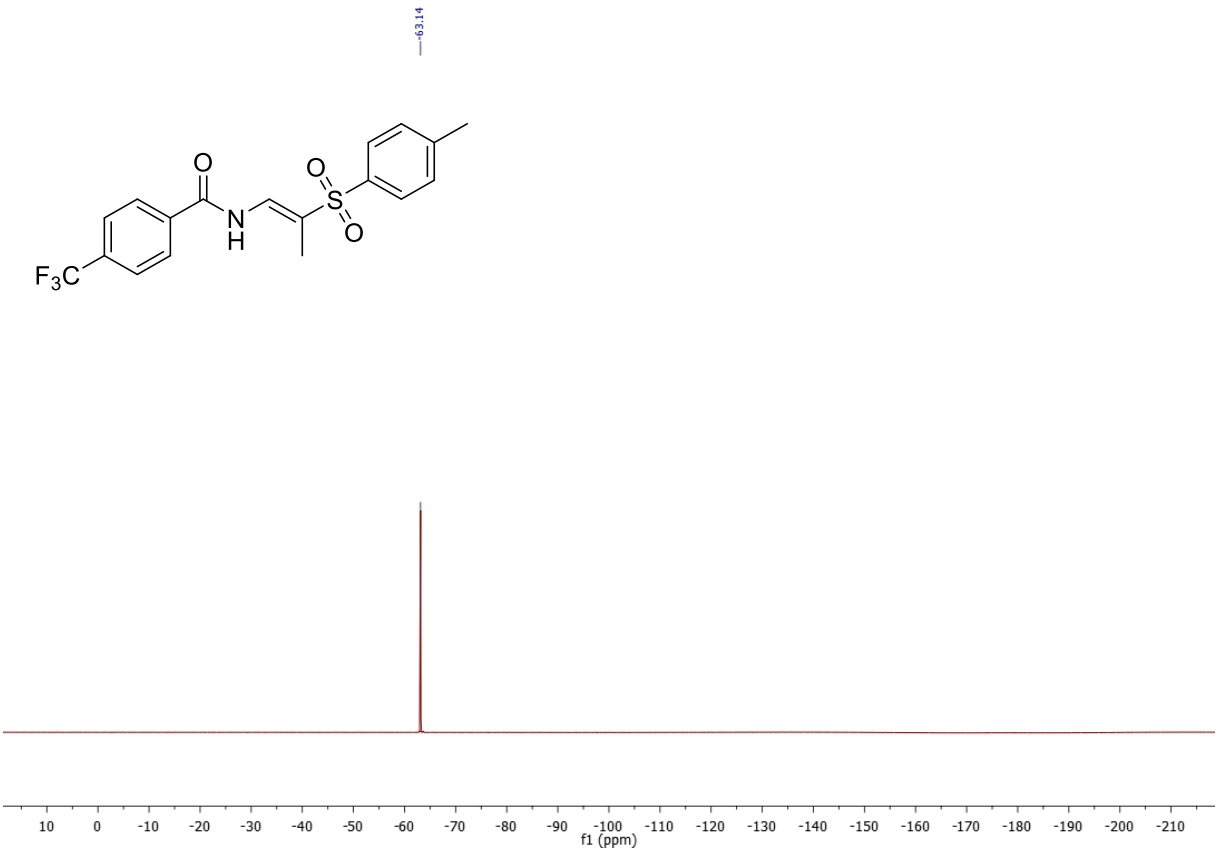


*Figure 12: ^{1}H (400 MHz), ^{13}C (101 MHz) ^{19}F (476 MHz)NMR spectra of **3k** in DMSO-d_6.*

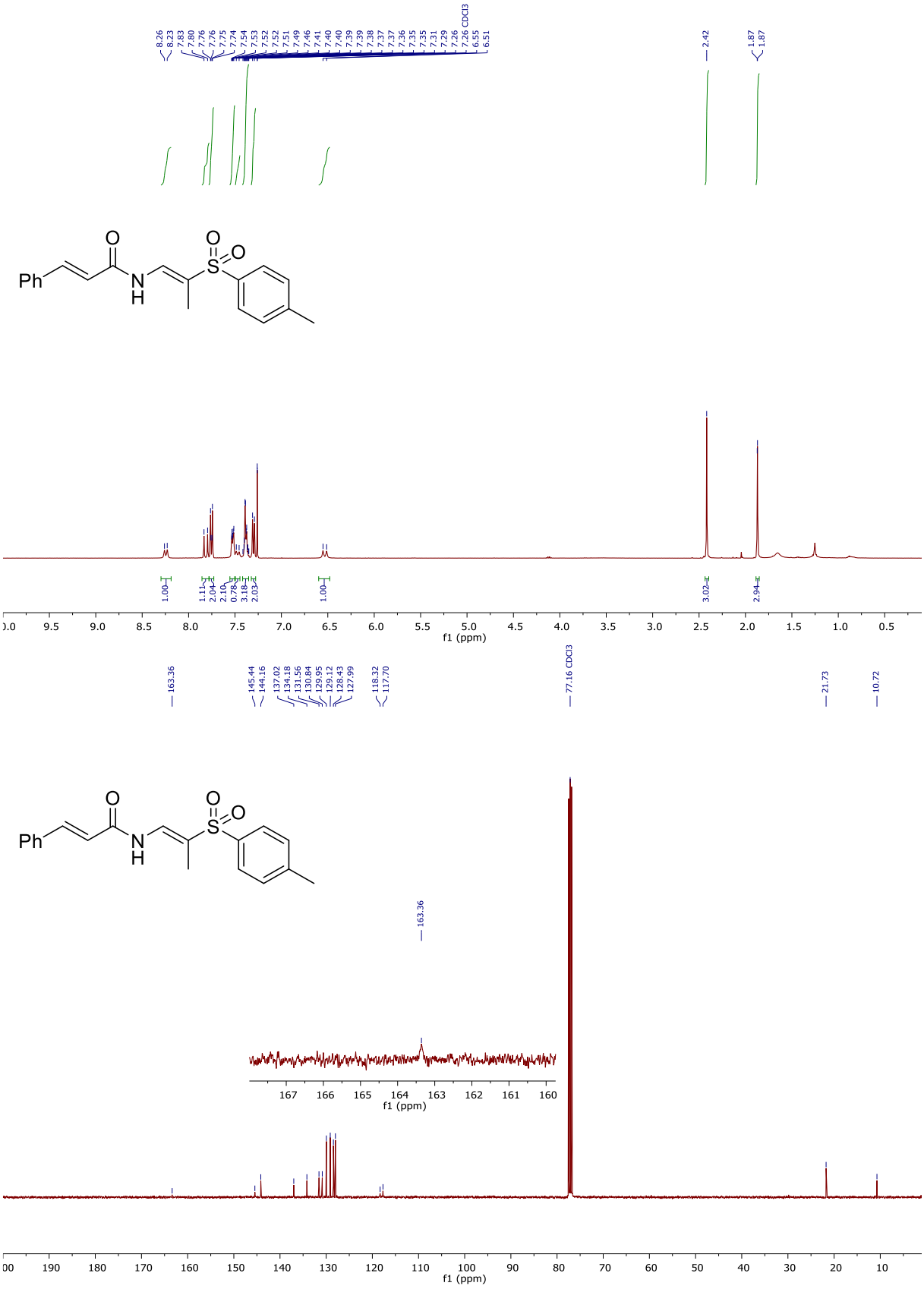


*Figure 13: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3l** in $CDCl_3$.*

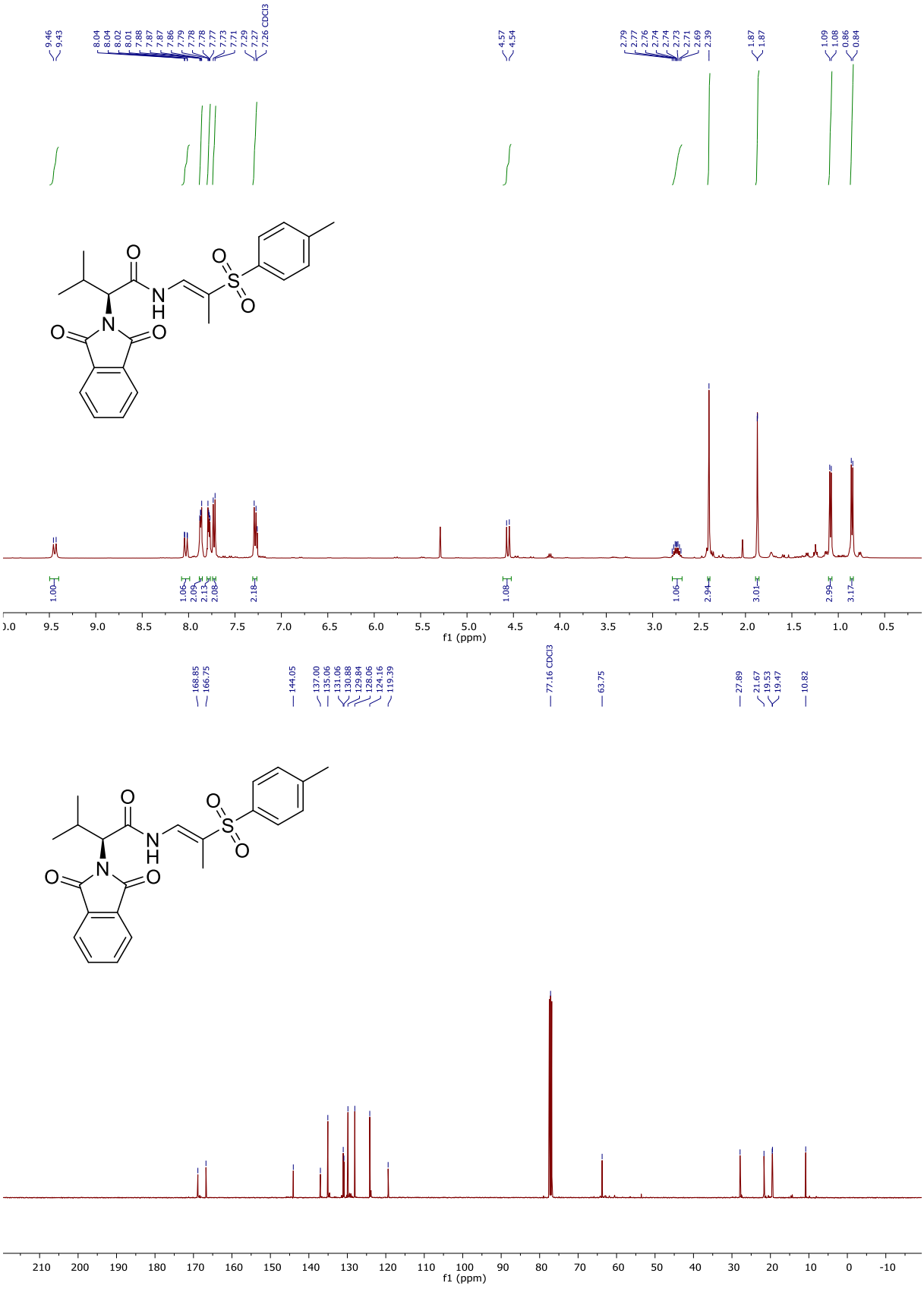


*Figure 14: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3m** in $CDCl_3$.*

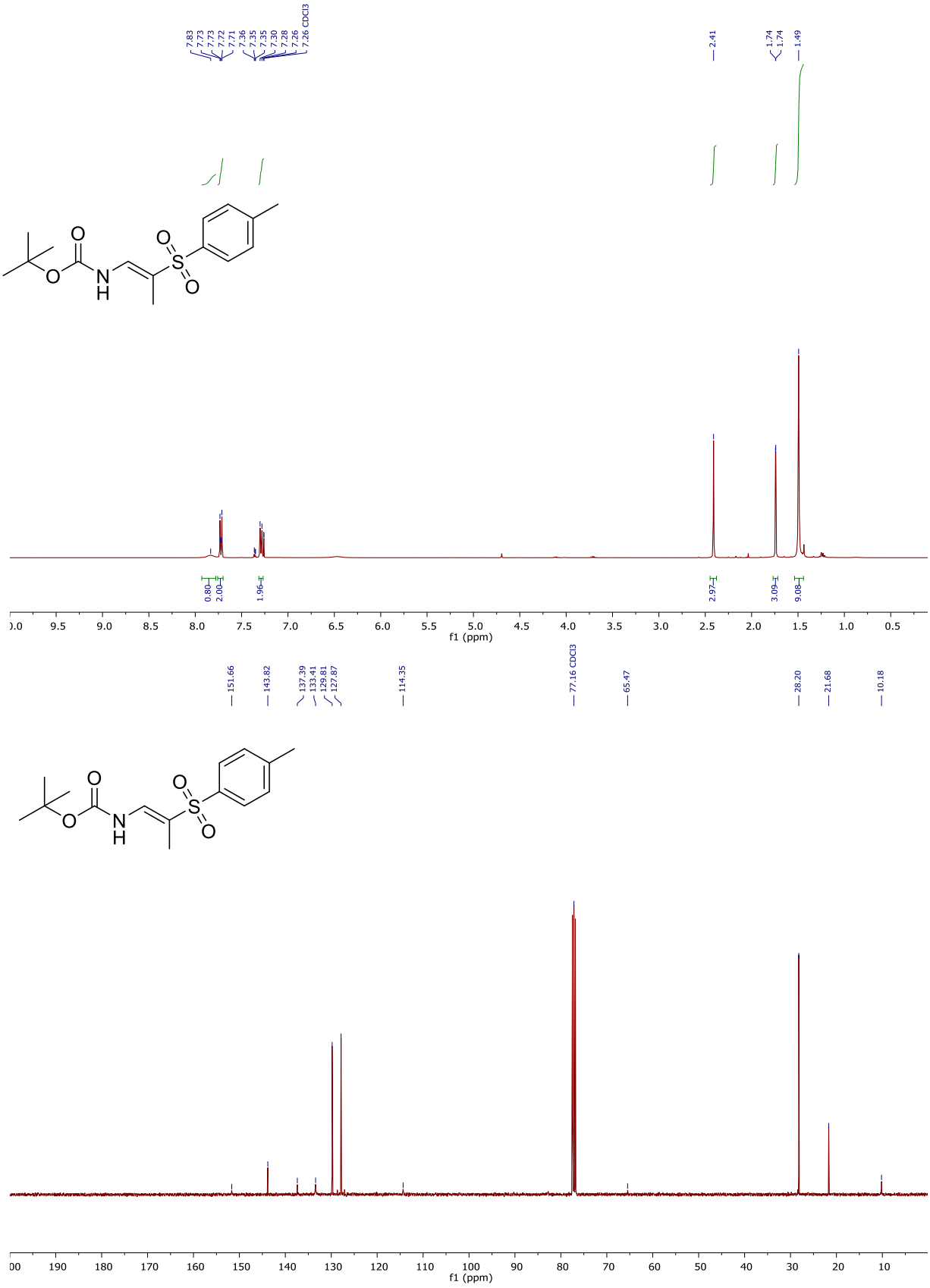


*Figure 15: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3n** in $CDCl_3$.*

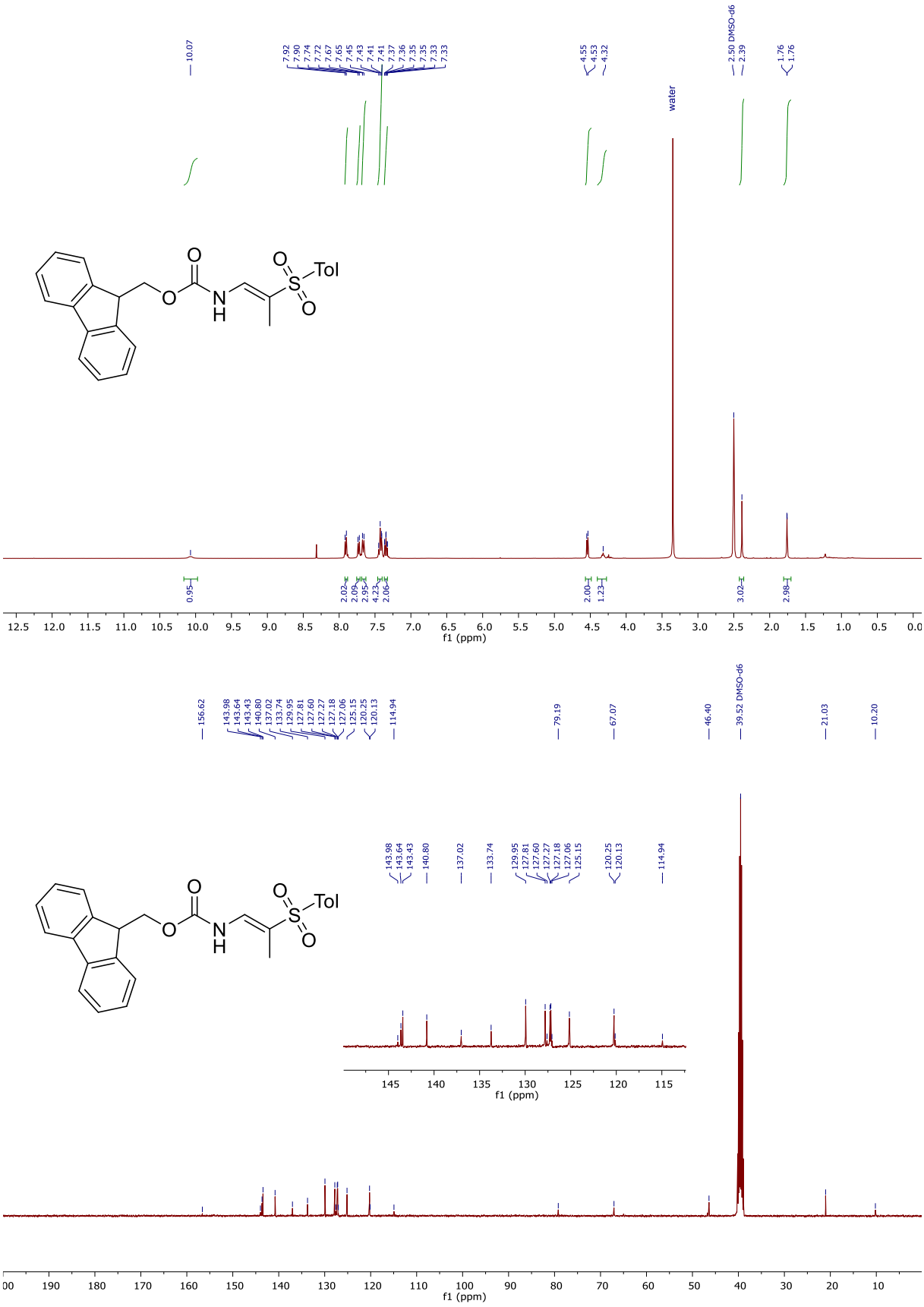


*Figure 16: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3o** in DMSO-d_6.*

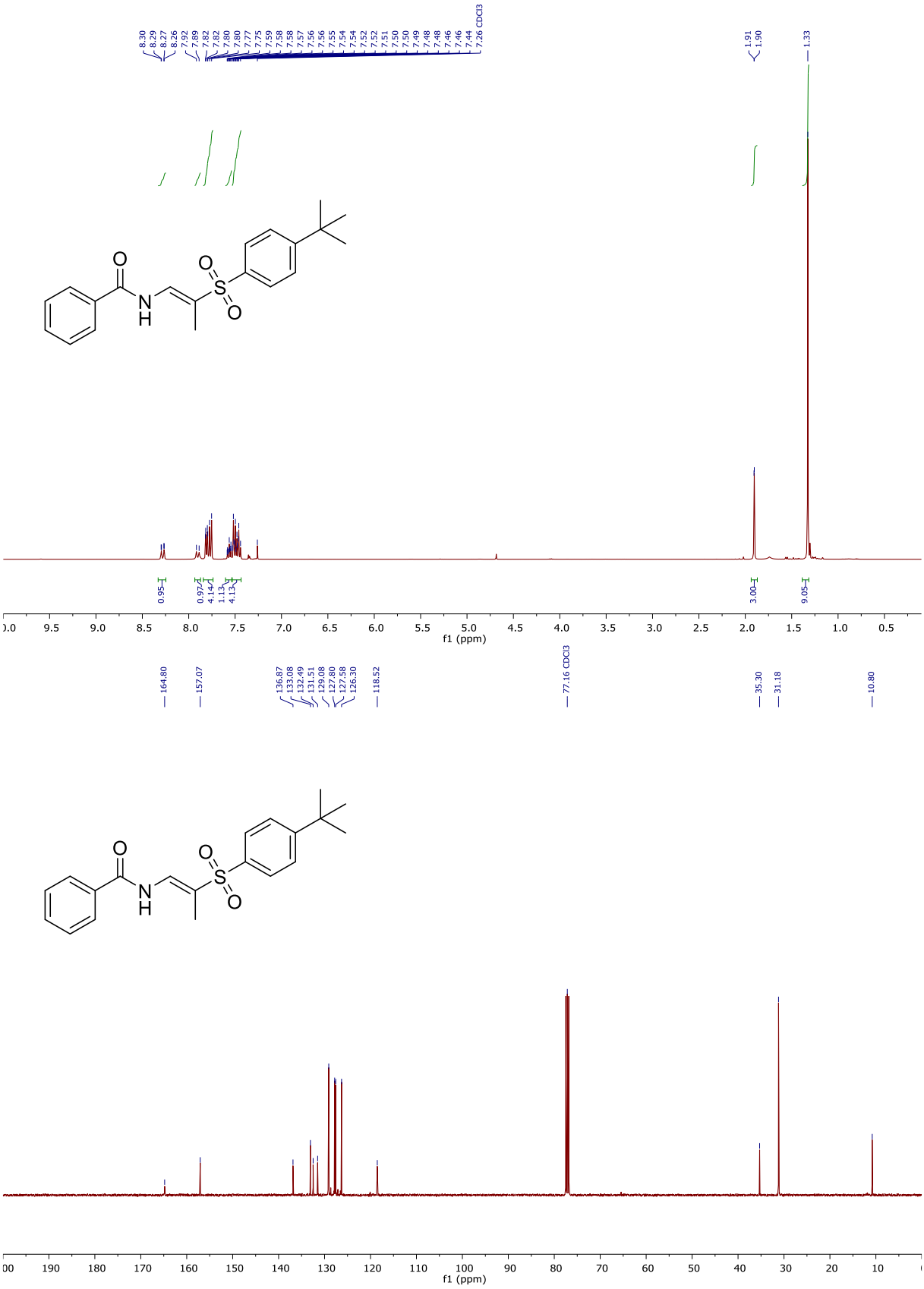


*Figure 17. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3p** in $CDCl_3$.*

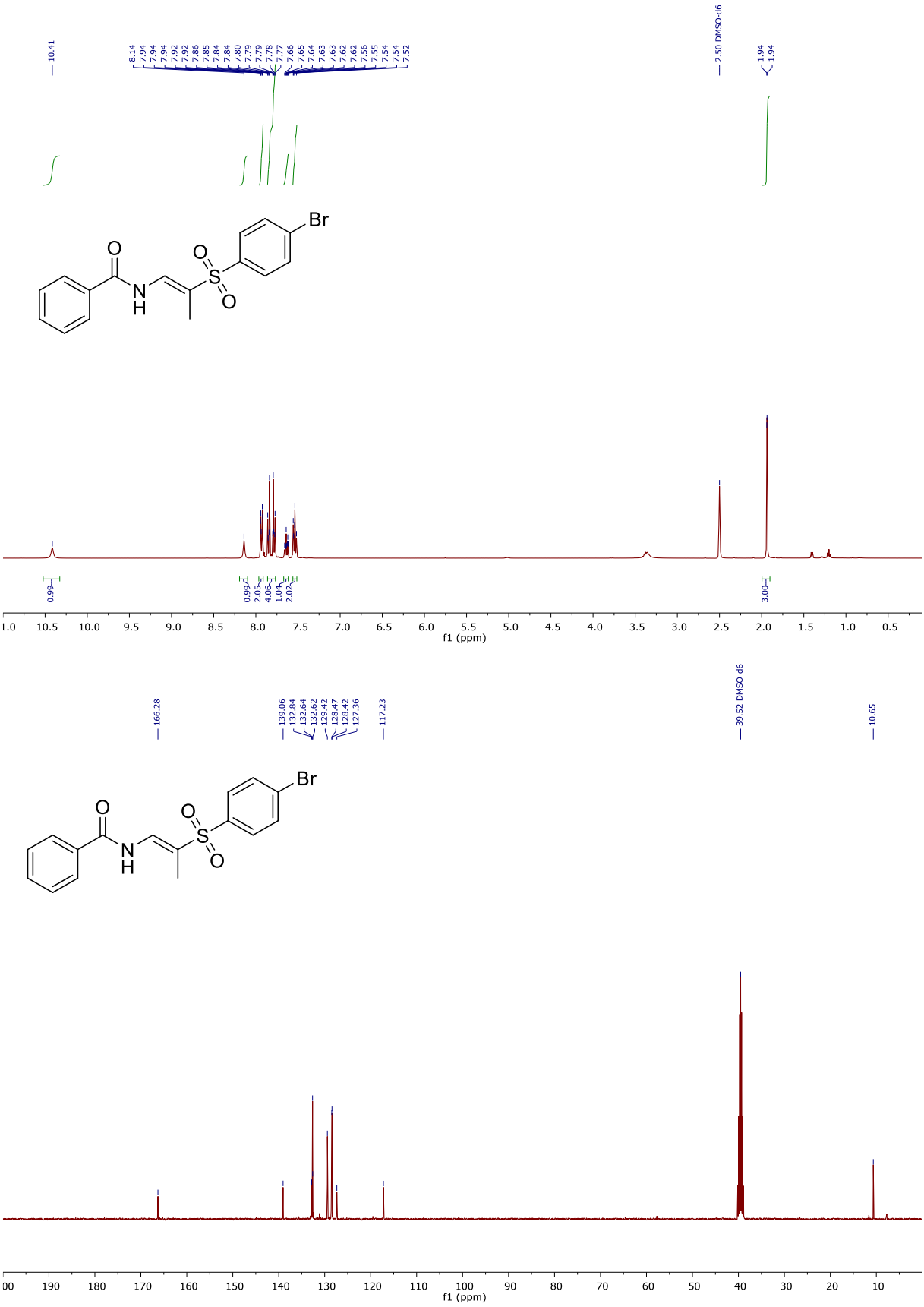
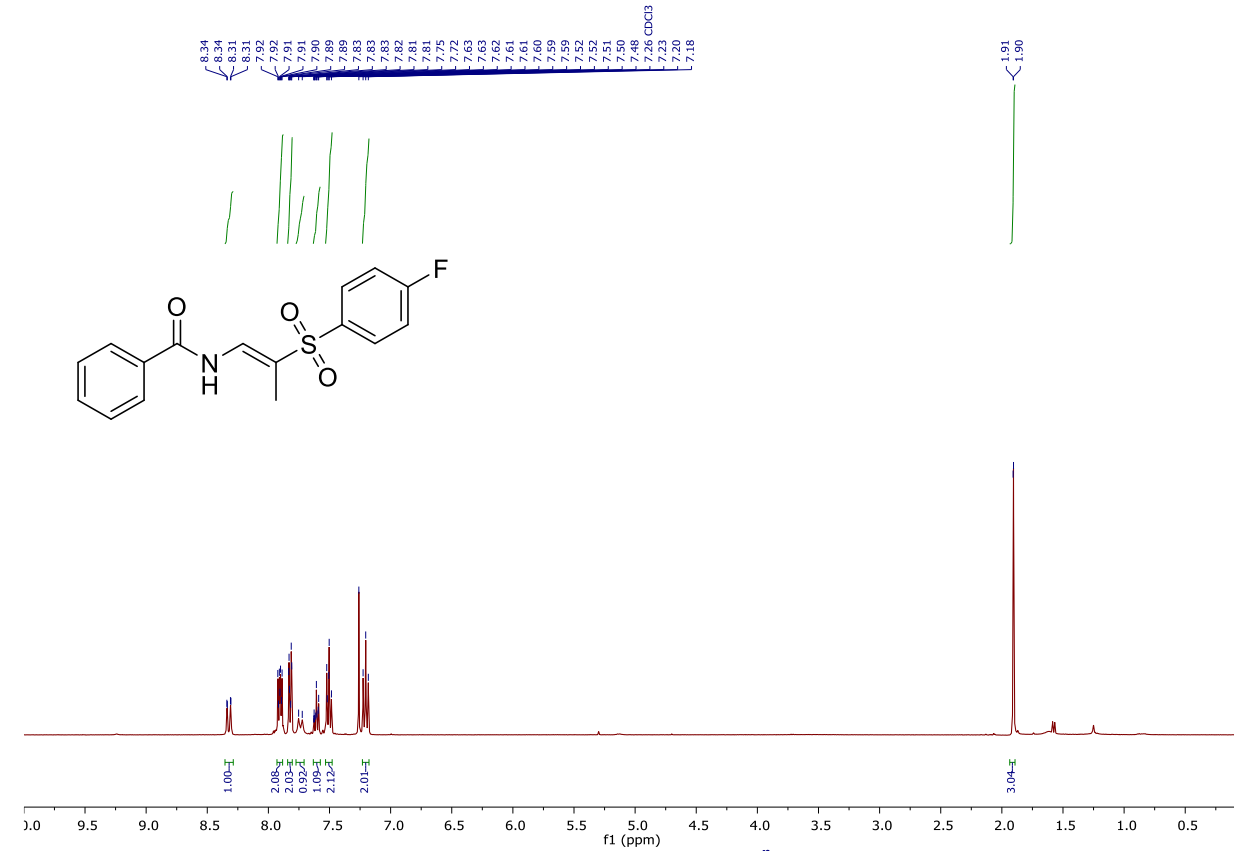
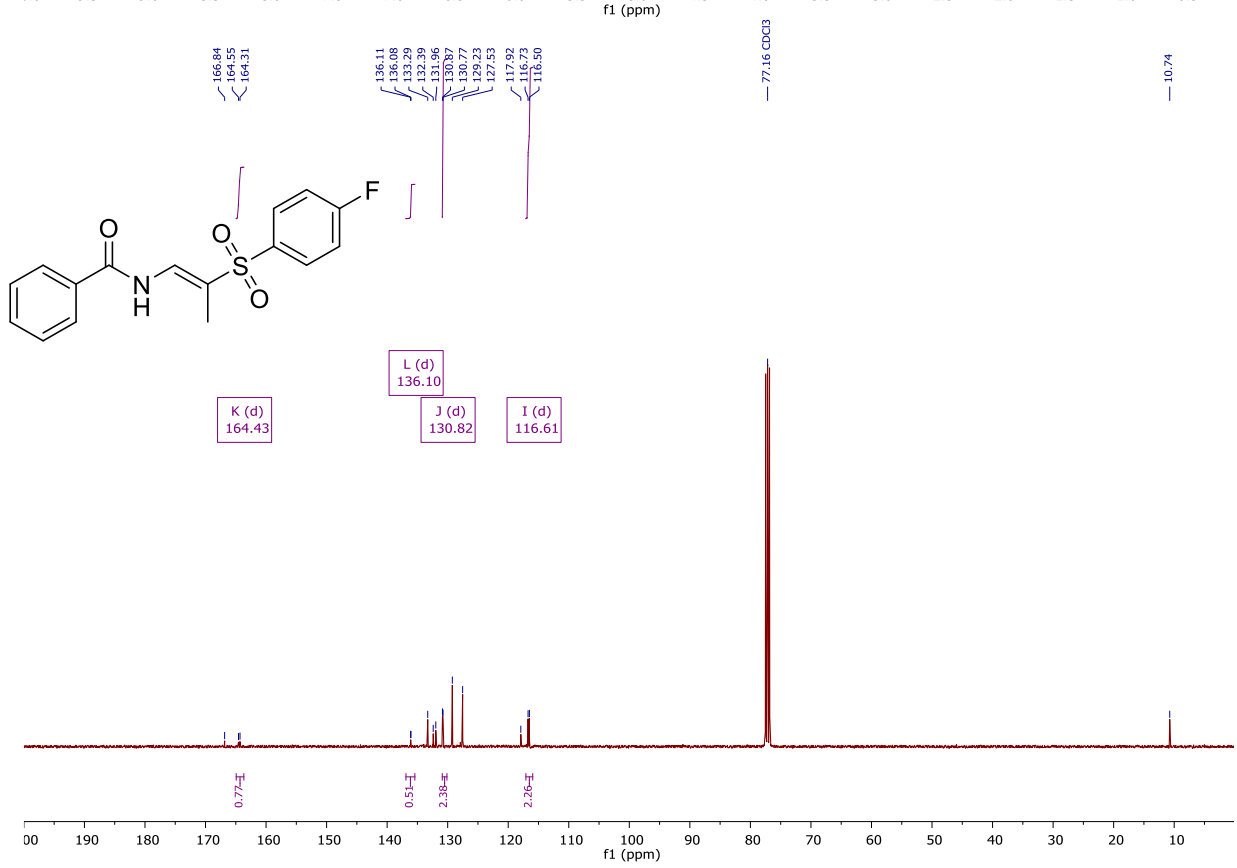


*Figure 18: ^{1}H (400 MHz), ^{13}C (101 MHz) ^{19}F (476 MHz)NMR spectra of **3q** in DMSO-d_6.*


8.34
8.34
8.31
8.31
7.92
7.92
7.91
7.91
7.90
7.89
7.89
7.83
7.83
7.83
7.82
7.81
7.81
7.75
7.72
7.63
7.63
7.62
7.61
7.61
7.60
7.59
7.59
7.52
7.52
7.51
7.50
7.48
7.26 CDCl3
7.23
7.20
7.18
1.91
1.90
F
O
N
H
O
S
O
1.00
2.08
2.03
0.92
1.09
2.12
2.01
3.04
f1 (ppm)


166.84
164.55
164.31
136.11
136.08
133.29
132.39
131.96
130.37
130.77
129.23
127.53
117.92
116.73
116.50
77.16 CDCl3
10.74
F
O
N
H
O
S
O
L (d)
136.10
K (d)
164.43
J (d)
130.82
I (d)
116.61
0.77
0.51
2.38
2.26
f1 (ppm)

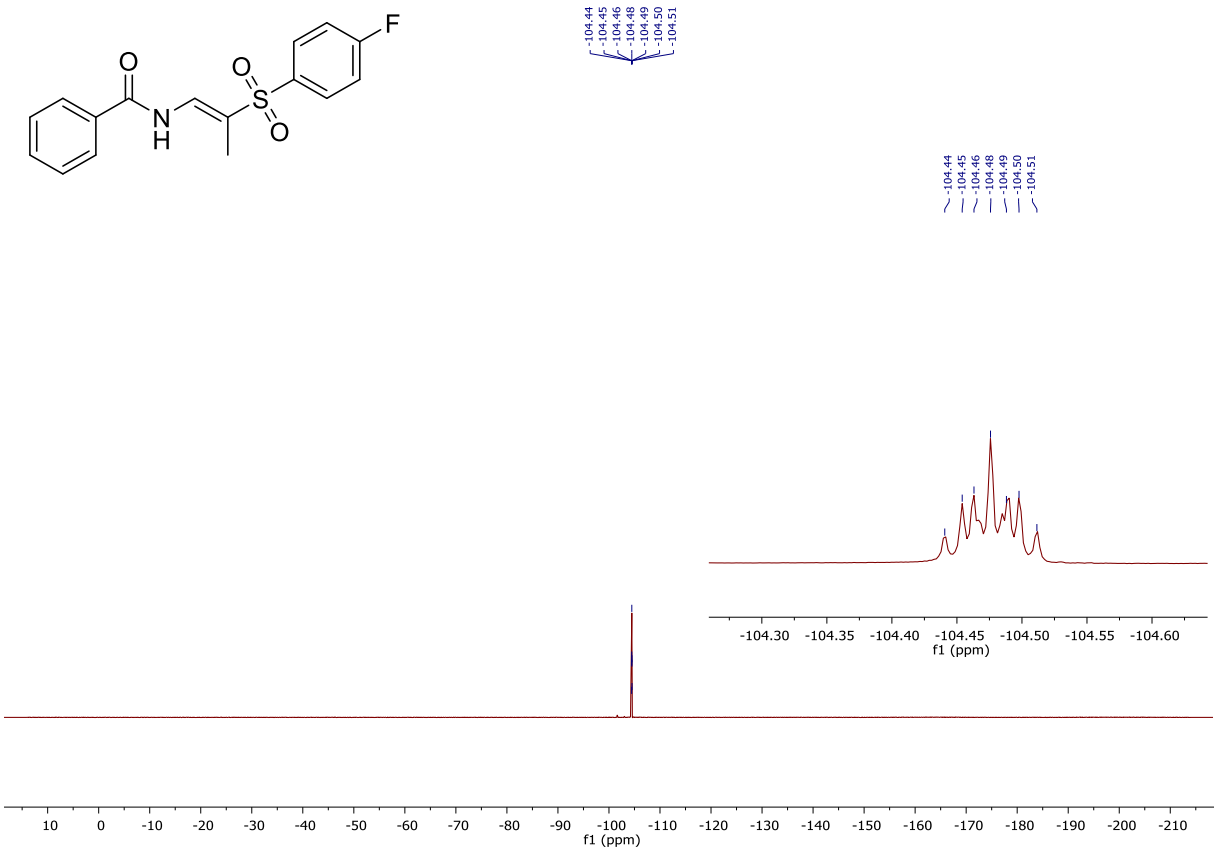
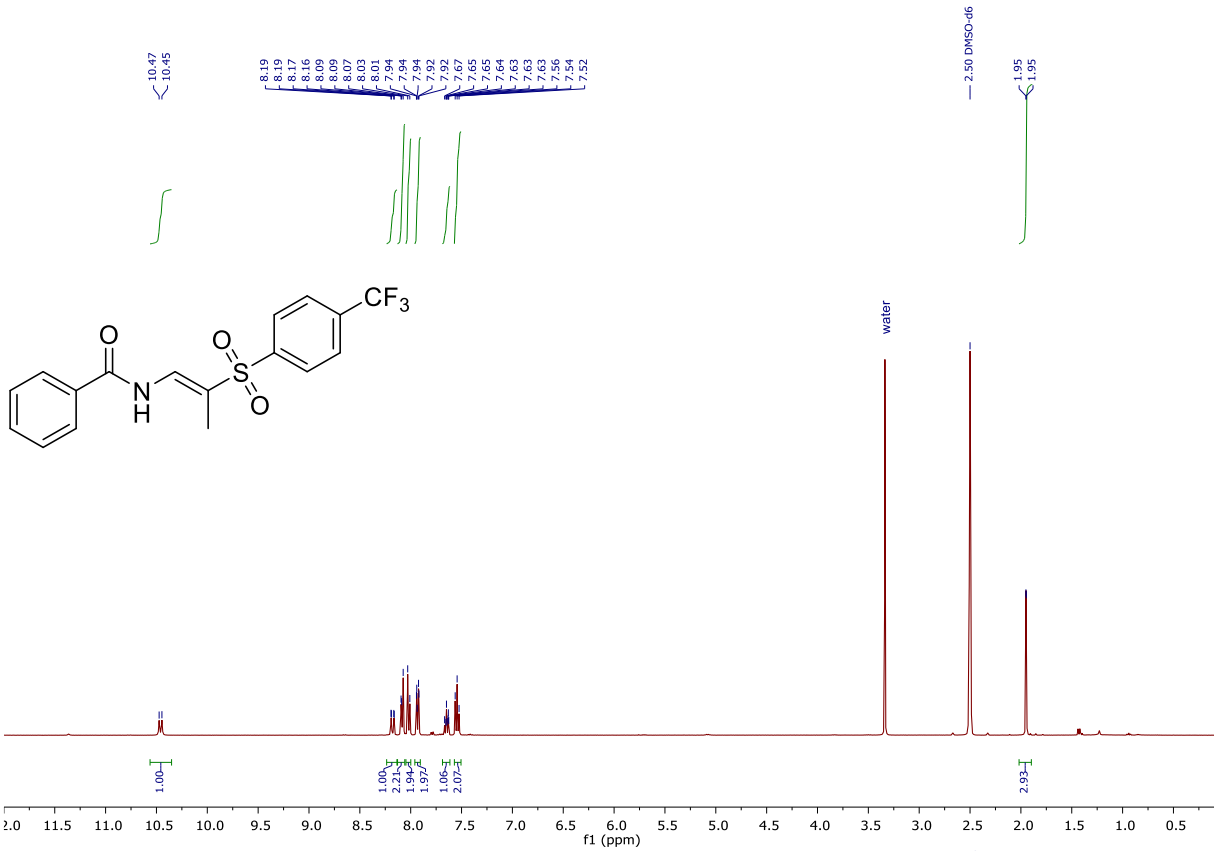
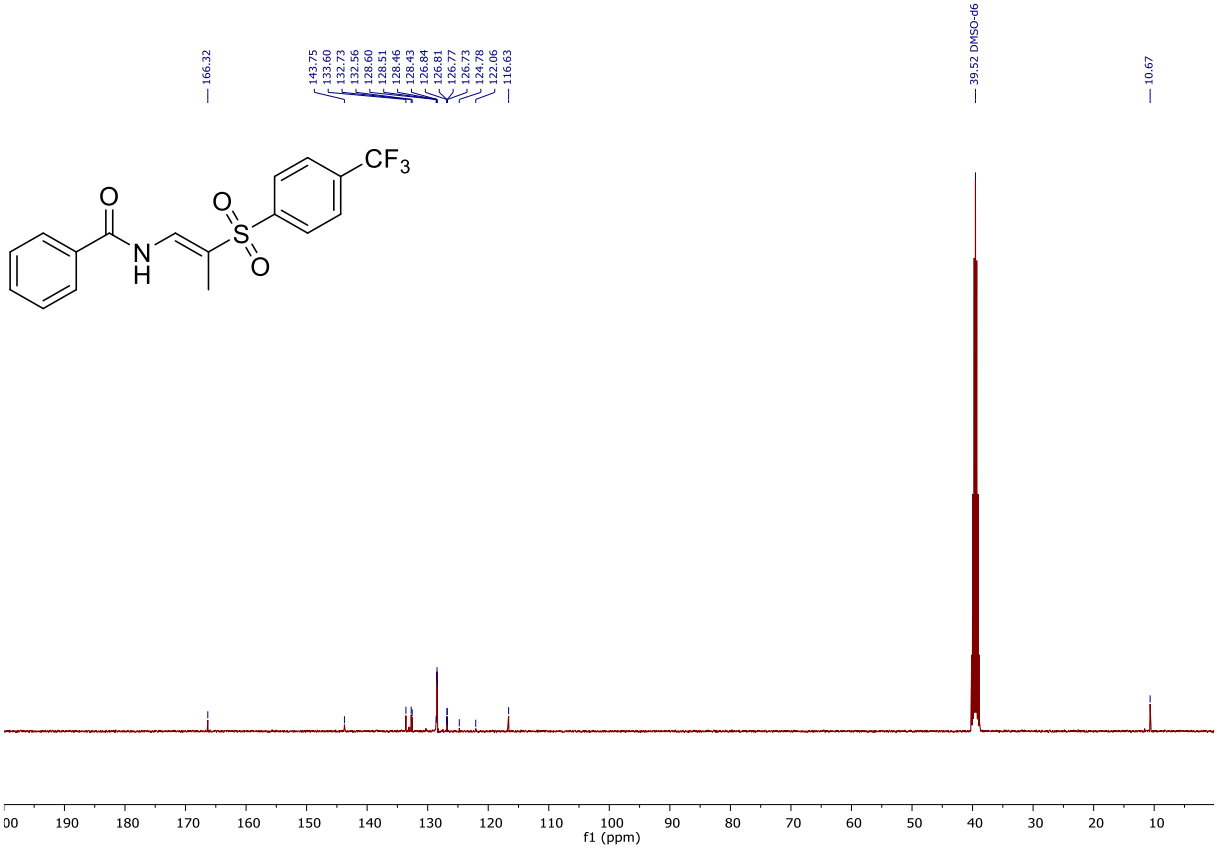


*Figure 19: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3r** in $CDCl_3$.*


10.47
10.45
8.19
8.19
8.17
8.16
8.09
8.09
8.07
8.03
8.01
7.94
7.94
7.94
7.92
7.67
7.65
7.65
7.64
7.63
7.63
7.56
7.54
7.52
2.50 DMSO-d6
1.95
1.95
water
CF3
O
N
H
S
1.00
1.00
2.21
1.94
1.97
1.06
2.07
2.93
f1 (ppm)


166.32
143.75
133.60
132.73
132.56
128.60
128.51
128.46
128.43
126.84
126.81
126.77
126.73
124.78
122.06
116.63
39.52 DMSO-d6
10.67
CF3
O
N
H
S
f1 (ppm)

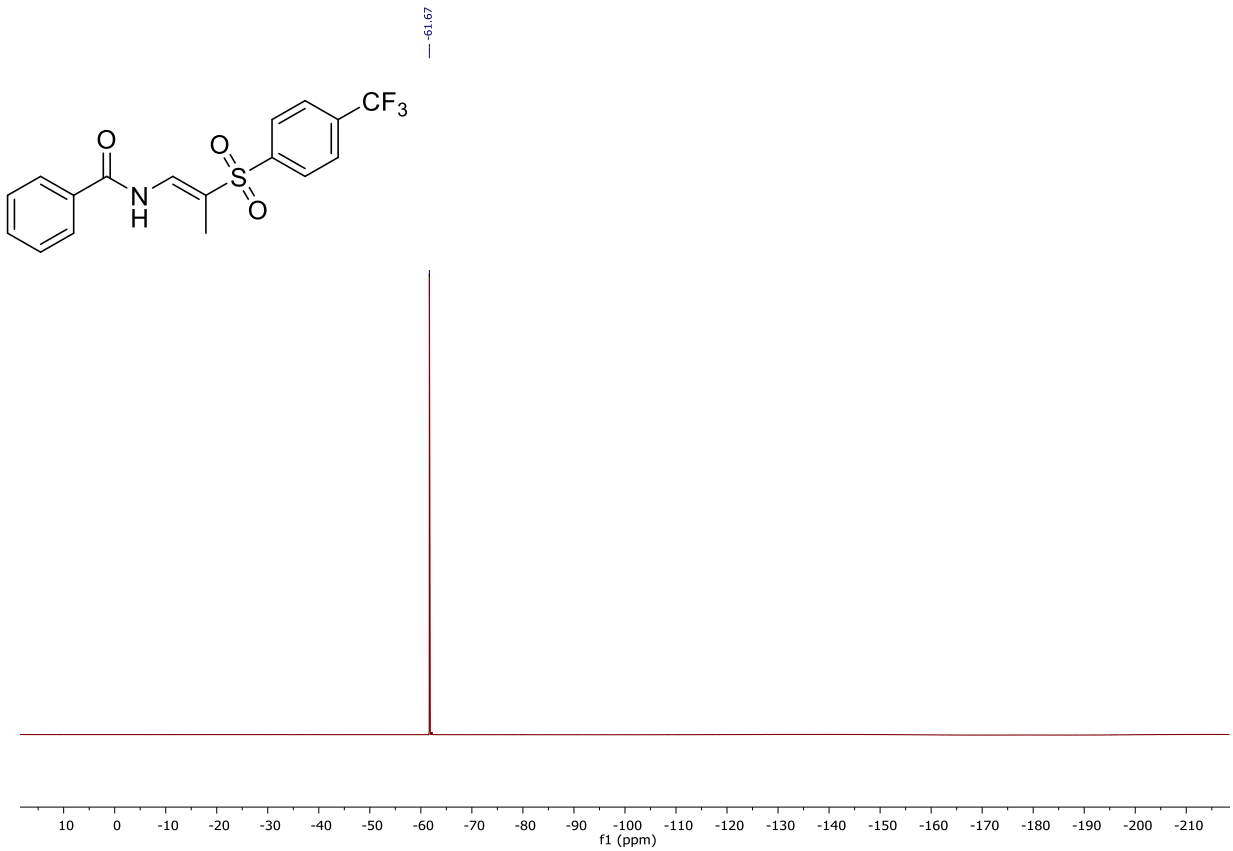


*Figure 20: ^{1}H (400 MHz), ^{13}C (101 MHz) ^{19}F (476 MHz)NMR spectra of **3s** in DMSO-d_6.*

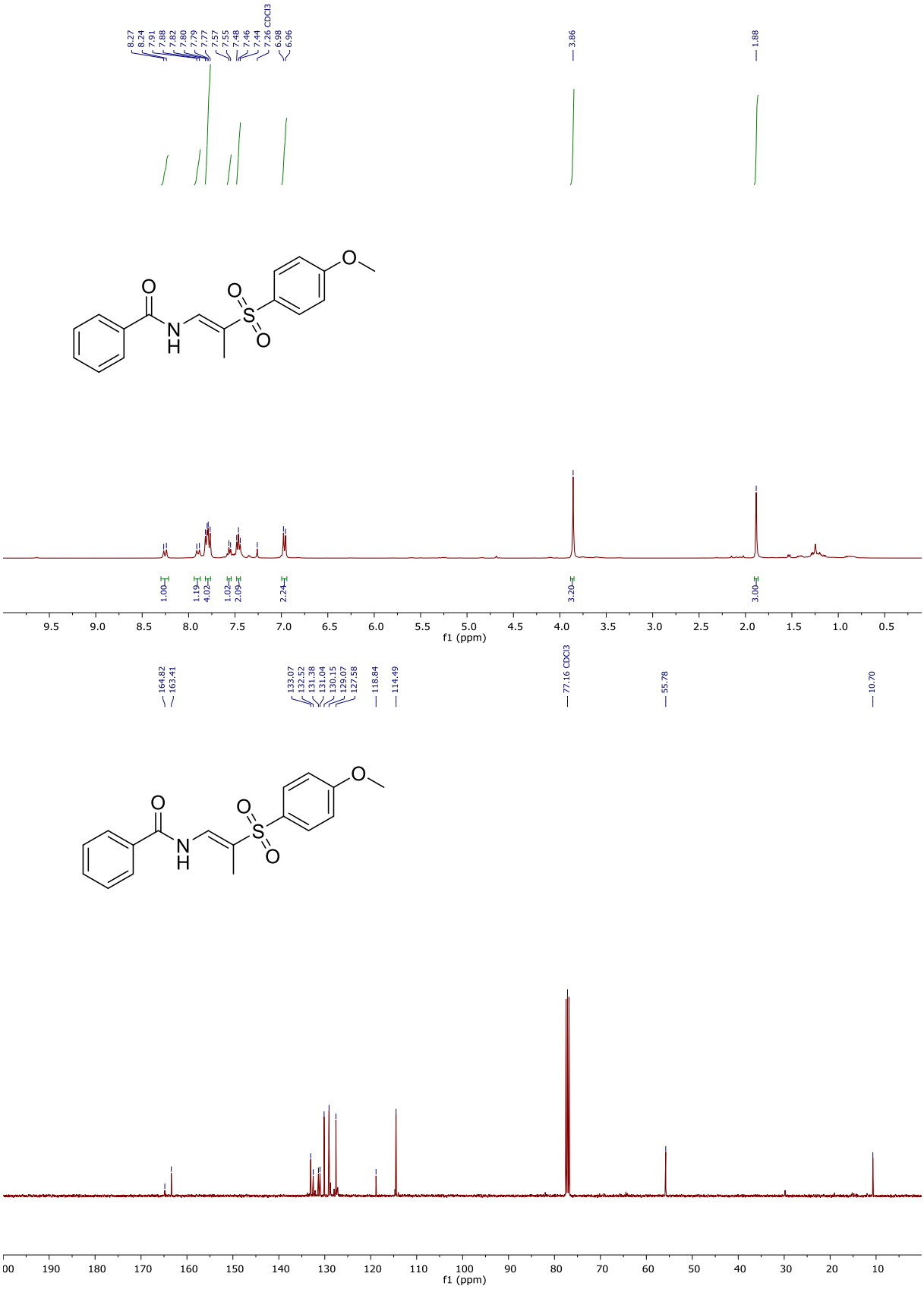


*Figure 21: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3t** in $CDCl_3$.*

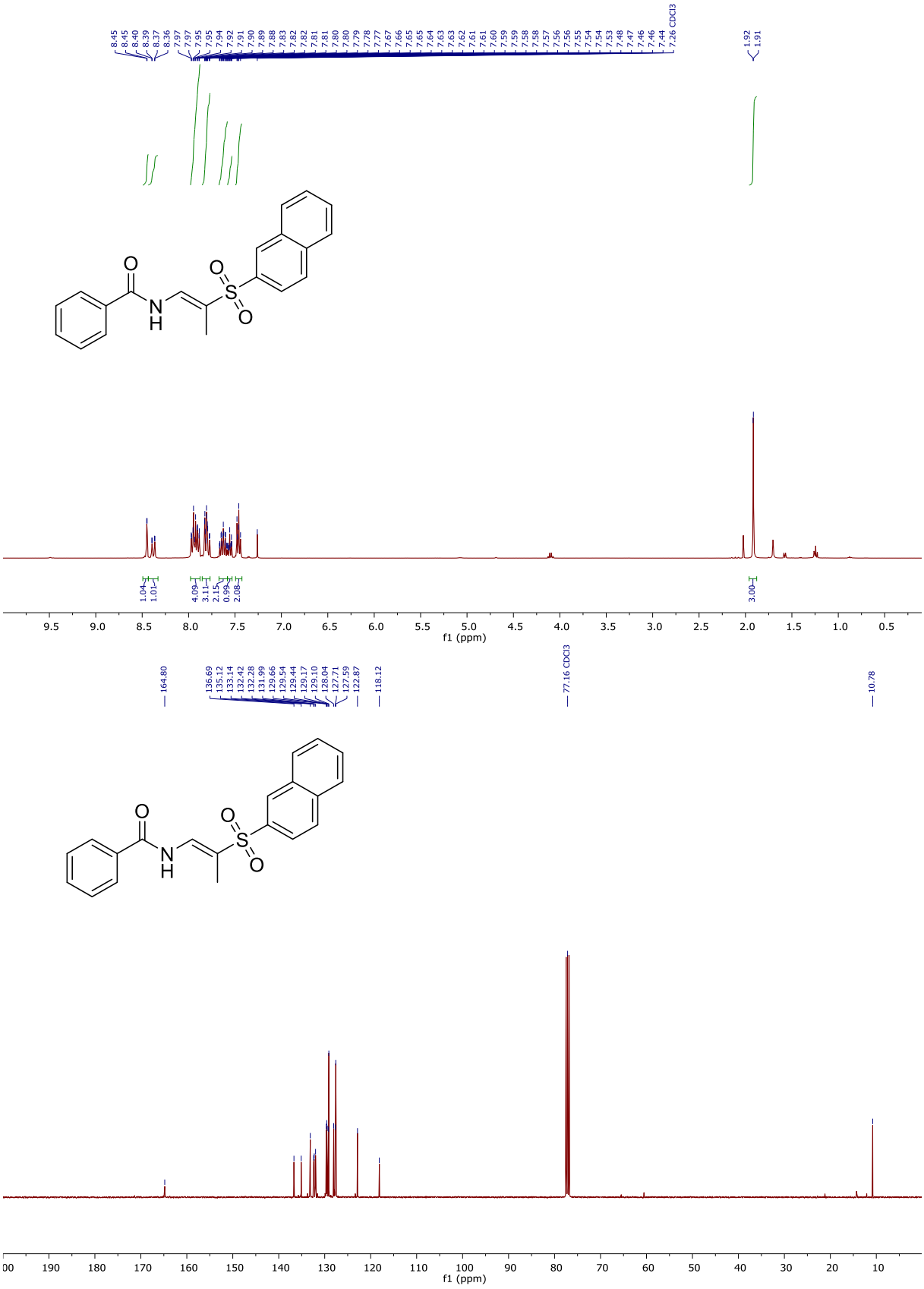


*Figure 22: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3u** in $CDCl_3$.*

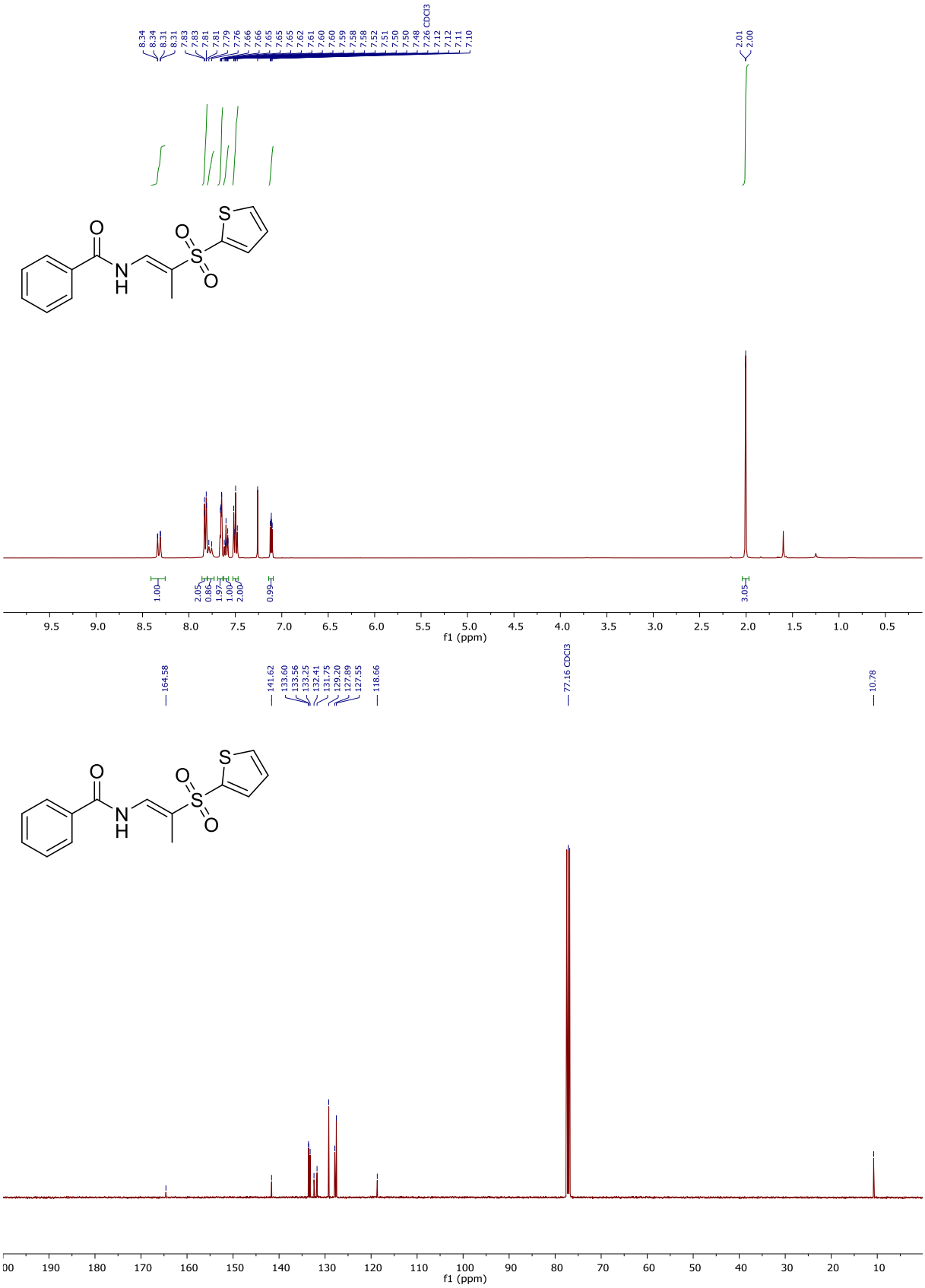


*Figure 23: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3v** in $CDCl_3$.*

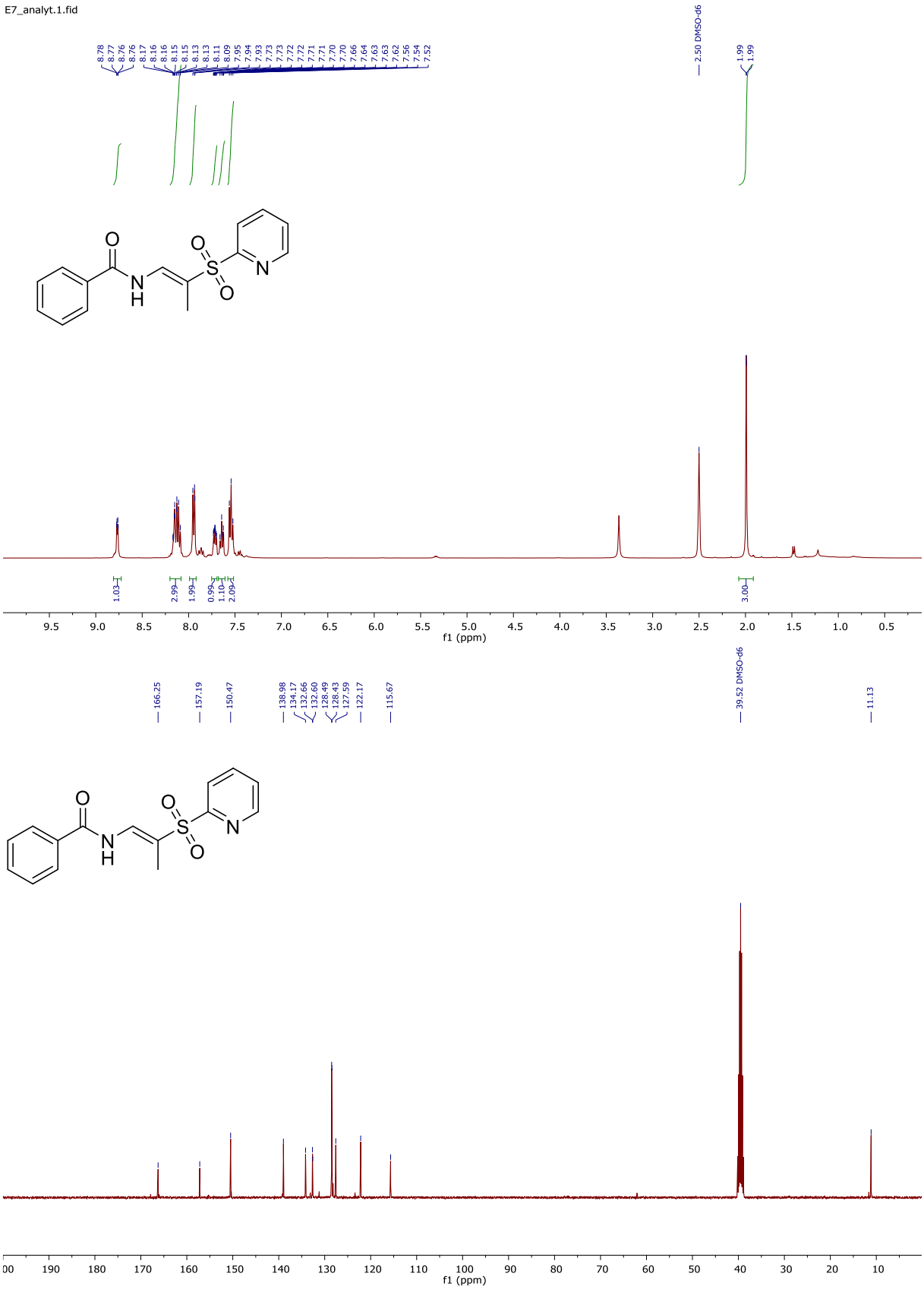


*Figure 24: ^{1}H (400 MHz), ^{13}C (101 MHz) ^{19}F (476 MHz)NMR spectra of **3w** in DMSO-d_6.*

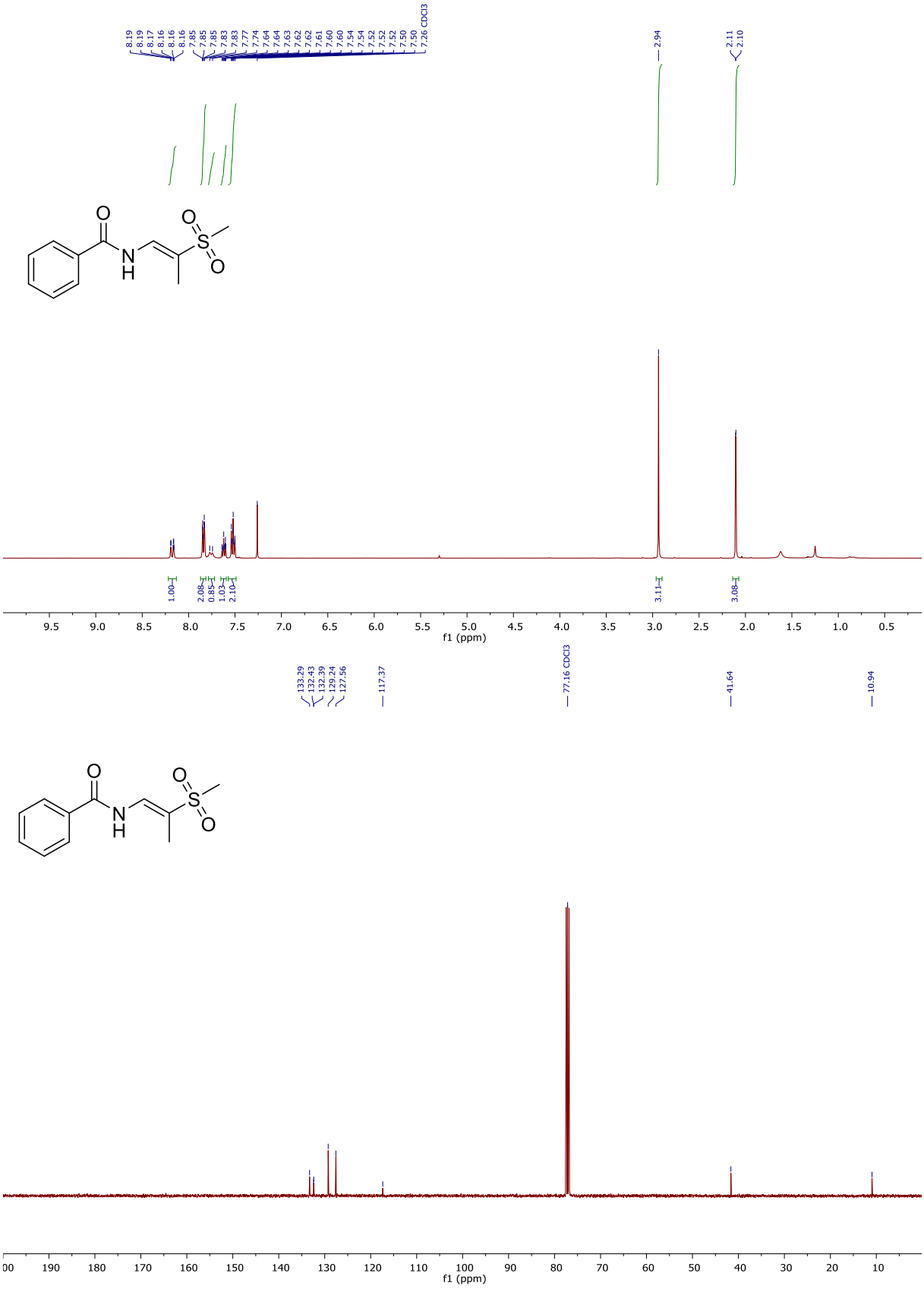


*Figure 25: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3x** in $CDCl_3$.*

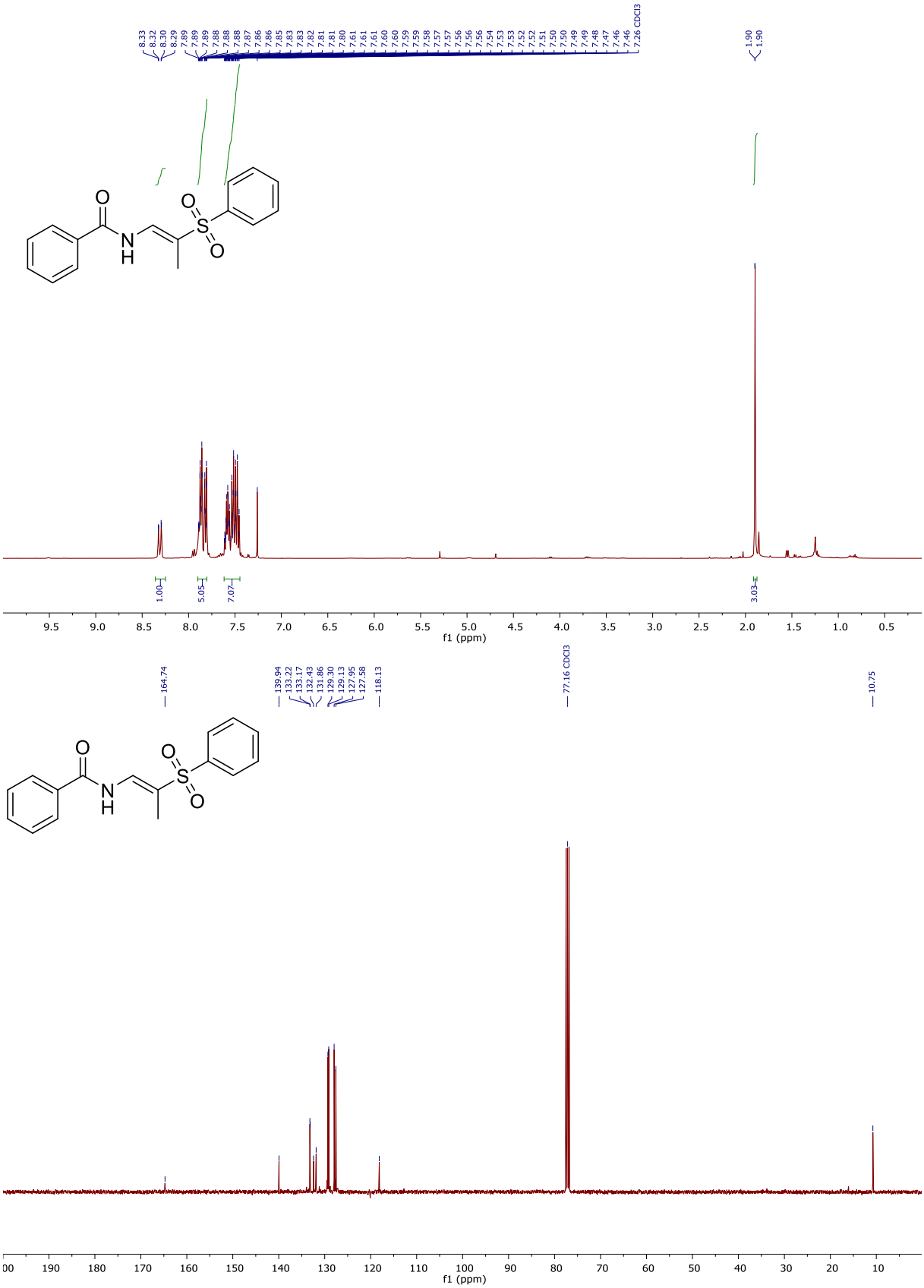


*Figure 26: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **3y** in $CDCl_3$.*

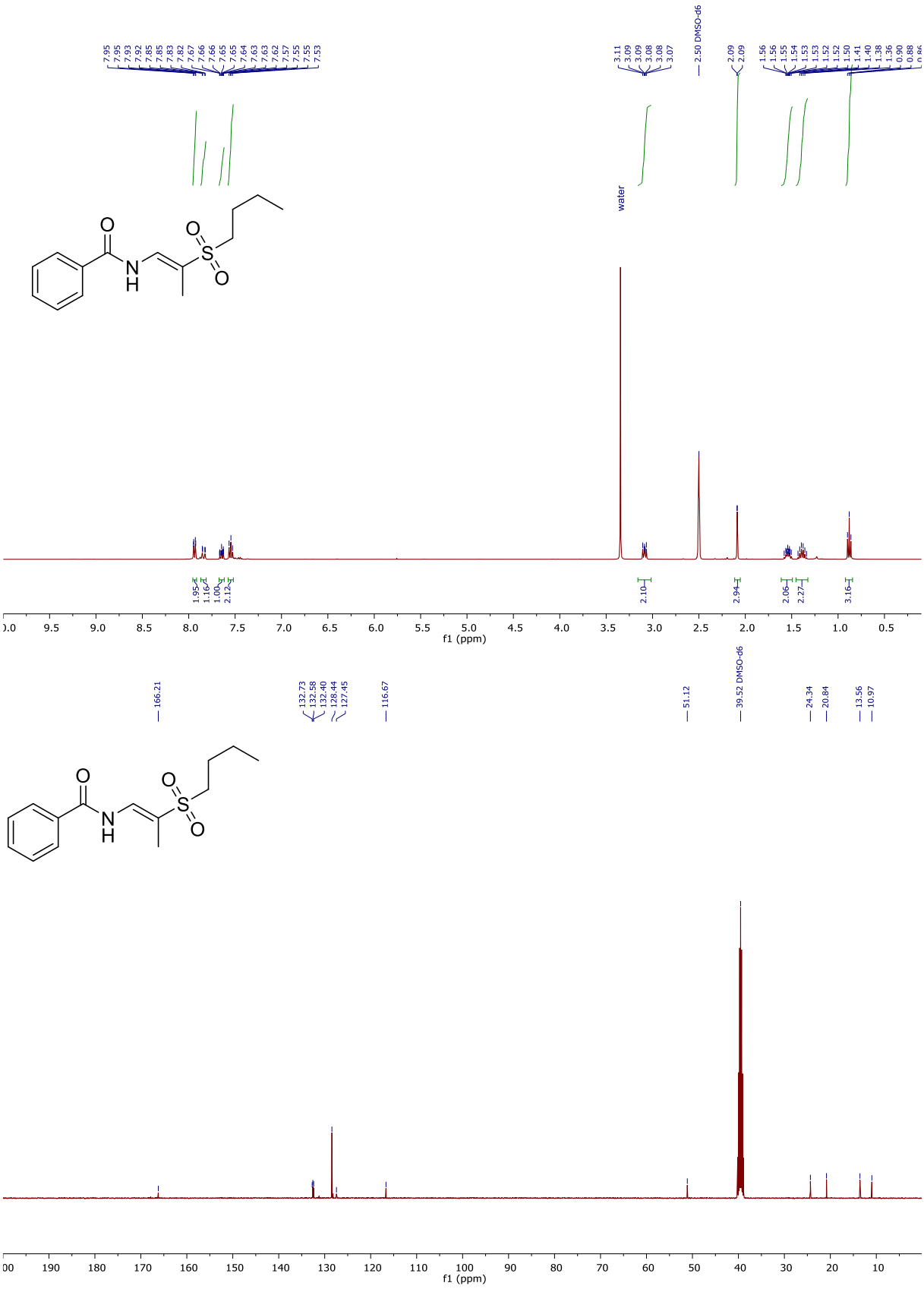


*Figure 27: ^{1}H (400 MHz), ^{13}C (101 MHz) spectra of **3z** in DMSO-d_6.*

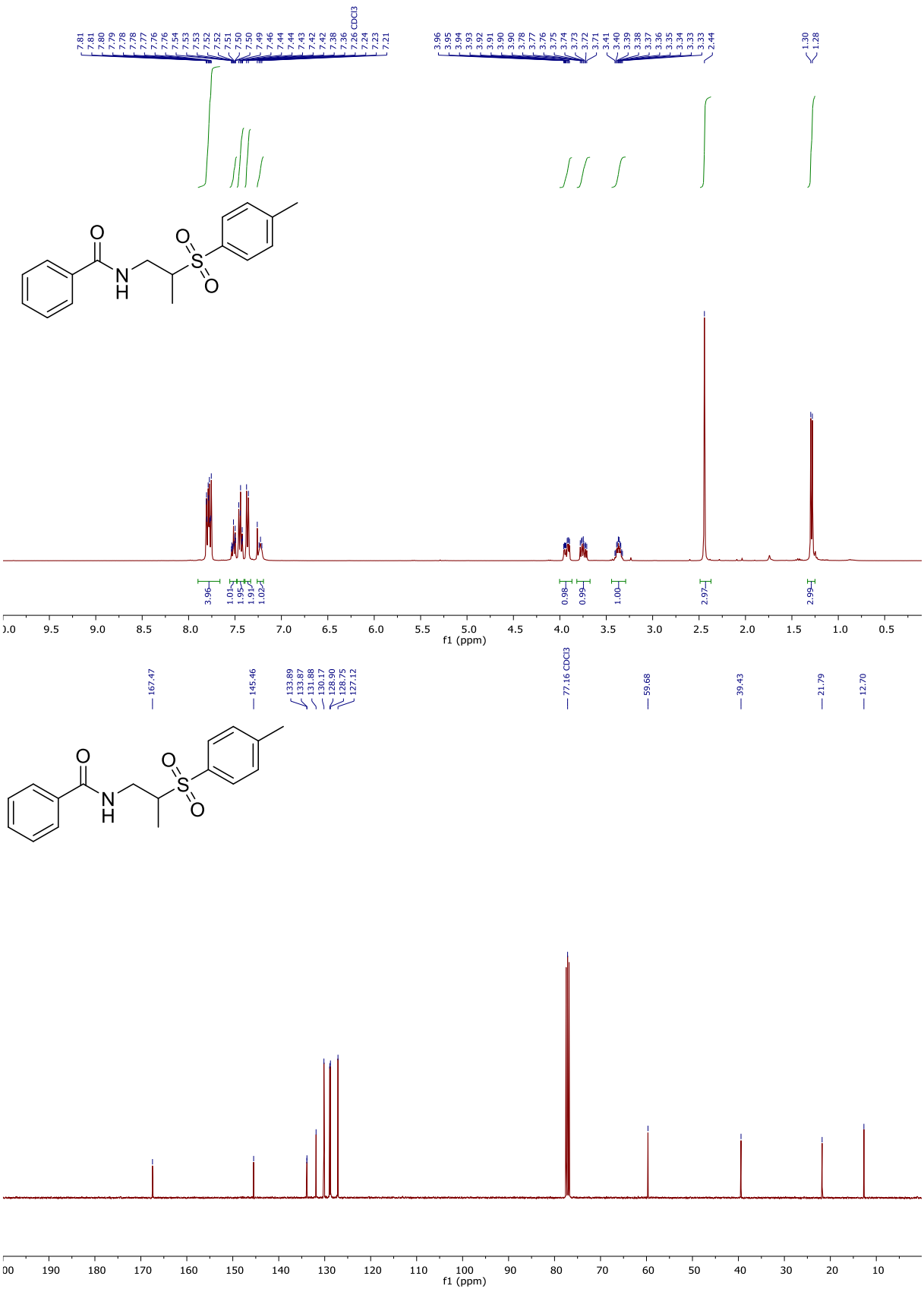


*Figure 28: ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra of **15** in $CDCl_3$.*

4 X-ray Data

Crystal structure determination.[5] Data for **3g**, and **3l** (CCDC 1908089-1908090) were collected at 150.0(1) K on a Rigaku/Oxford diffraction Xcalibur/Gemini dual wavelength diffractometer with a Cu-Kα (λ = 1.54184 Å) radiation X-ray source. Program CrysAlisPro5 was used for the data collection and reduction. The structures were solved by direct methods using the program SHELXS (SHELXS-2014/78) and refined by full-matrix least squares on F^2 using SHELXL-2014/78 program.

All the hydrogen atoms were refined using riding models.

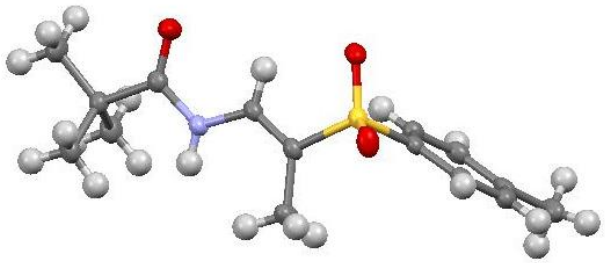


Table 1. Crystal data and structure refinement for **3g**. Displacement ellipsoids are shown at the 50% probability level.

Empirical formula	C_{15} H_{21} N O_3 S	
Formula weight	295.39	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.1301(2) Å	α= 90°.
	b = 6.63950(10) Å	β= 91.894(2)°.
	c = 23.1337(5) Å	γ = 90°.
Volume	1555.10(5) $Å^3$	
Z	4	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	1.908 mm^{-1}	
F(000)	632	
Crystal size	0.330 x 0.200 x 0.100 mm^3	
Theta range for data collection	3.824 to 62.681°.	
Index ranges	-10<=h<=11, -6<=k<=7, -24<=l<=26	
Reflections collected	5938	
Independent reflections	2495 [R(int) = 0.0215]	
Completeness to theta = 62.681°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.826 and 0.526	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2495 / 0 / 186	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0946	
R indices (all data)	R1 = 0.0376, wR2 = 0.0972	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.224 and -0.397 $e.Å^{-3}$	

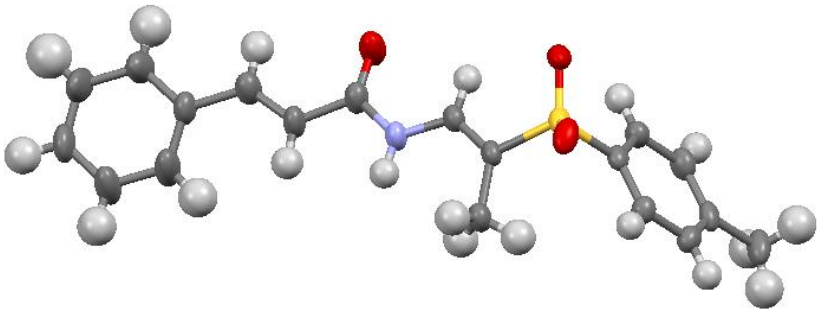


Table 2. Crystal data and structure refinement for **3l**. Displacement ellipsoids are shown at the 50% probability level.

Empirical formula	C_{19} H_{19} N O_3 S	
Formula weight	341.41	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.5801(5) Å	α= 90.562(6)°.
	b = 10.7434(8) Å	β= 95.920(5)°.
	c = 19.1136(12) Å	γ = 97.534(6)°.
Volume	1736.9(2) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	1.791 mm^{-1}	
F(000)	720	
Crystal size	0.220 x 0.030 x 0.020 mm^3	
Theta range for data collection	4.152 to 62.660°.	
Index ranges	-9<=h<=9, -7<=k<=12, -21<=l<=21	
Reflections collected	10720	
Independent reflections	5511 [R(int) = 0.0402]	
Completeness to theta = 62.660°	99.0 %	
Absorption correction	Analytical	
Max. and min. transmission	0.948 and 0.762	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5511 / 0 / 437	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1093	
R indices (all data)	R1 = 0.0646, wR2 = 0.1210	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.271 and -0.375 e.$Å^{-3}$	

5 References

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