# *Supporting Information*

## Aza-oxyallyl cation-mediated synthesis of α-sulfonyl hydroxamic acid derivatives from α-halo hydroxamates and sodium sulfinates

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# Table of Contents

## 1. Experimental Section

### General information

The starting material, α-halohydroxamates and sodium sulfinates were synthesized in the laboratory following literature methods.[1,2] Other reagents and solvents were purchased from various suppliers and used as received. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a BRUKER NMR spectrophotometer operating at 400 MHz and 101 MHz, respectively. $CDCl_3$ was used as a solvent to record NMR spectra. ESI-HRMS Mass spectra were recorded with an Agilent 6530B UHD Q-TOF mass spectrometer.

### 1.1 General procedure for the synthesis of sulfonyl alkyl hydroxamates (3a-3y)

To an oven-dried, clean 25 mL round-bottom flask, the halo hydroxamate **1a** (100 mg, 0.37 mmol, 1.0 equiv.), sodium 4-methylbenzene sulfinate **2a** (79 mg, 0.45 mmol, 1.2 equiv.), $Na_2CO_3$ (78 mg, 0.74 mmol, 2.0 equiv.), HFIP (1 mL) was added, and the reaction mixture was stirred at room temperature under an open-air atmosphere for 1 h. After the completion of the reaction (as confirmed by TLC), the reaction mixture was diluted with dichloromethane and washed three times with water (10 mL each). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (100-200 mesh $SiO_2$) using 25% ethyl acetate in hexane as the eluent, yielding product **3a** in 122 mg, 96% yield.

A similar protocol was used to prepare all the *α*-sulfonyl hydroxamates (**3b-3z**). The time required for completion varied between 1 and 2 hours, and products were isolated using 25-60% ethyl acetate in hexane as the eluent.

### 1.2 Procedure for the gram-scale reaction: synthesis of 3a from 1a.

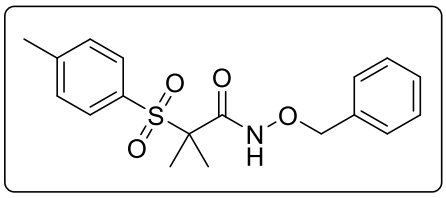
To an oven-dried, clean 25 mL round-bottom flask, the halo hydroxamate **1a** (1 g, 3.7 mmol, 1.0 equiv.), sodium sulfinate **2a** (786 mg, 1.2 equiv.), $Na_2CO_3$ (780 mg, 2.0 equiv.), HFIP (7 mL) was added, and the reaction mixture was stirred at room temperature under an open-air atmosphere for 2.5 h. After the completion of the reaction (as confirmed by TLC), the reaction mixture was diluted with dichloromethane and washed three times with water (25 mL each). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (100-200 mesh SiO2) using 25% ethyl acetate in hexane as the eluent, yielding product **3a** in 1.05 g, 82% yield.

### 1.3 Procedure for the synthesis of 4a from sulfonyl hydroxamates 3a

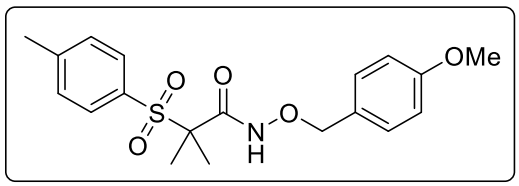
To an oven-dried, clean 50 mL round-bottom flask, the α-sulfonyl alkyl hydroxamate **3a** (0.28 mmol, 1.0 equiv.), *tert*-butyl nitrite (0.48 mmol, 1.5 equiv.), DCM (1 mL) was added, and the reaction mixture was stirred at 0 °C for 1 h. Then, benzyl amine (0.30 mmol, 1.1 equiv.) was added to the reaction mixture and stirred at room temperature for an additional 1 h. After the completion of the reaction (as confirmed by TLC), the reaction mixture was diluted with dichloromethane and washed three times with water (10 mL each). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (100-200 mesh SiO2) using 25% ethyl acetate in hexane as the eluent, yielding product **4a** in 57 mg (60%).

## 2. Characterization data of the isolated compounds:

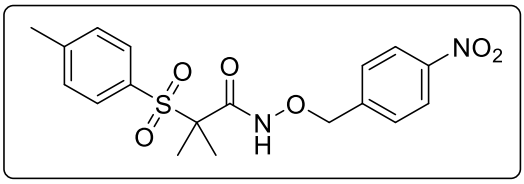
**Compound 3a:** White solid. Eluted with 25% EtOAc/hexane. Yield: 96% (122 mg from 0.37 mmol of corresponding *α*-halo hydroxamate). **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.50 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.37 (m, 5H), 7.33 (d, *J* = 7.6 Hz, 2H), 4.94 (s, 2H), 2.44 (s, 3H), 1.51 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.2, 145.9, 135.0, 131.5, 130.1, 130.0, 129.4, 129.0, 128.7, 78.4, 68.0, 21.8, 20.8. HRMS (ESI) calcd for $C_{18}H_{21}NO_4S$ [M+H] + 348.1264; found 348.1263.



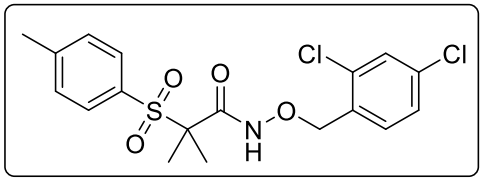
**Compound 3b:** White solid. Eluted with 30% EtOAc/hexane. Yield: 86% (107 mg from 0.3306 mmol of corresponding *α*-halo hydroxamate)**. $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.46 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.8 Hz, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.86 (s, 2H), 3.82 (s, 3H), 2.43 (s, 3H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.1, 160.2, 145.9, 131.5, 131.2, 130.1, 129.9, 127.1, 114.1, 78.1, 68.0, 55.4, 21.8, 20.8. HRMS (ESI) calcd for $C_{19}H_{23}NO_5S$ [M+Na] + 400.1189; found 400.1195.



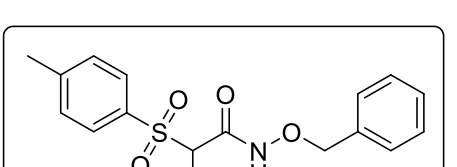
**Compound 3c:** White solid. Eluted with 30% EtOAc/hexane. Yield: 87% (215 mg from 0.6306 mmol of corresponding *α*-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.71 (s, 1H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 2H), 2.44 (s, 3H), 1.51 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.7, 148.2, 146.1, 142.2, 131.2, 130.1, 130.0, 129.7, 77.0, 68.1, 21.8, 20.9. HRMS (ESI) calcd for $C_{18}H_{20}N_2O_6S$ [M+H] + 393.1115; found 393.1108.



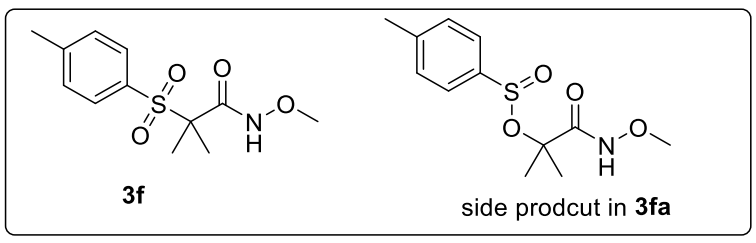

**Compound 3d:** White solid. Eluted with 30% EtOAc/hexane. Yield: 70% (170 mg from 0.5864 mmol of corresponding *α*-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.60 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 -7.42 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 1H), 5.04 (s, 2H), 2.44 (s, 3H), 1.53 (s, 6H**).** **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.7, 146.0, 135.5, 135.2, 132.2, 131.5, 131.4, 130.1, 130.0, 129.6, 127.4, 74.6, 68.1, 21.8, 20.9. HRMS (ESI) calcd for $C_{18}H_{19}Cl_2NO_4S$ [M+H] + 416.0485; found 416.0456.




**Compound 3e** Colorless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 62% (194 mg from 0.9360 mmol of corresponding *α*-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.63 (s, 3H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.21 (m, 5H), 4.78 – 4.77(m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 162.9, 145.6, 134.9, 132.5, 129.8, 129.5, 129.3, 128.7, 128.5, 78.4, 63.6, 21.7, 12.0. HRMS (ESI) calcd for $C_{17}H_{19}NO_4S$ [M+H] + 334.1108; found 334.1120.

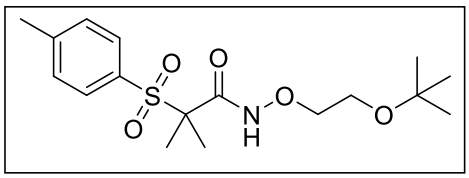



**Compound 3f:** It was isolated as a mixture (**3f:3fa** = ~9:1) with a minor amount of **3fa**. Colorless sticky liquid. Eluted with 15% EtOAc/hexane. Yield: 70% (210 mg from 1.0201 mmol of corresponding *α*-halo hydroxamate)**.** Data for **3f: $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.63 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 2.43 (s, 3H), 1.55 (s, 6H). **$^{13}$C{$^1$H} NMR** (101



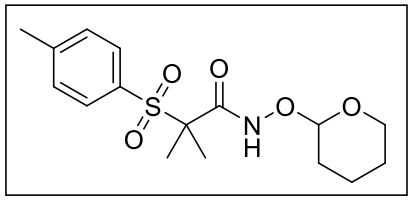
MHz, $CDCl_3$) $\delta$ 166.3, 145.9, 131.5, 130.1, 129.9, 67.9, 64.3, 21.7, 20.7. HRMS (ESI) calcd for $C_{12}H_{17}NO_4S$ [M+H] + 272.0951; found 272.0951.

**Compound 3g:** Colourless sticky liquid. Eluted with 20% EtOAc/hexane. Yield: 74% (192 mg



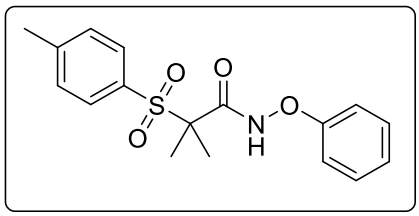
from 0.7963 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.06 (s, 1H), 7.74 (d, $J$ = 7.2 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 4.06 – 4.04 (m, 2H), 3.67 – 3.65 (m, 2H), 2.43 (s, 3H), 1.55 (s, 6H), 1.27 (s, 9H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 165.0, 145.7, 131.7, 130.3, 129.8, 75.8, 74.0, 67.7, 61.5, 27.5, 21.8, 20.6. HRMS (ESI) calcd for $C_{16}H_{25}NO_4S$ [M+Na] + 380.1502; found 380.1508.

**Compound 3h:** Colourless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 75% (192 mg



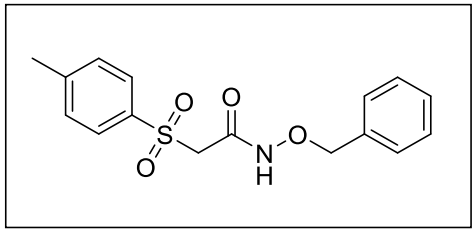
from 0.7543 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.72 (s, 1H), 7.78 (d, $J$ = 8.4 Hz, 4H), 7.34 (d, $J$ = 8.0 Hz, 4H), 4.98 -4.97 (m, 1H), 4.04–3.98 (m, 1H), 3.73 -3.682 (m, 1H), 2.43 (s, 3H), 1.88 – 1.82 (m, 2H), 1.79 – 1.71 (m, 2H), 1.67 – 1.61 (m, 2H), 1.59 (s, 3H), 1.56 (s, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 165.7, 145.8, 131.7, 130.2, 129.9, 102.1, 68.0, 62.4, 27.9, 25.1, 21.7, 20.9, 20.7, 18.4. HRMS (ESI) calcd for $C_{16}H_{23}NO_5S$ [M+H] + 342.1370; found 342.1374.

**Compound 3i:** Colourless semi-solid. Eluted with 15% EtOAc/hexane. Yield: 79% (102 mg



from 0.387 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 10.08 (s, 1H), 7.73 (d, $J$ = 8.3 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.07 (dd, $J$ = 16.6, 8.0 Hz, 3H), 2.45 (s, 3H), 1.62 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 166.96, 159.43, 146.10, 131.28, 130.15, 130.04, 129.62, 123.40, 113.57, 68.43, 21.80, 20.87. HRMS (ESI) calcd for $C_{17}H_{19}NO_4S$ $[M+H]^+$ 334.1108; found 365.1101.

**Compound 3j:** This compound was not formed.

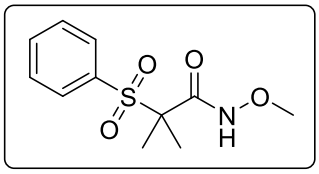


**Compound 3k:** White solid. Eluted with 30% EtOAc/hexane. Yield: 86% (208 mg from 0.6618 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.45 (s, 1H), 7.82 – 7.79 (m, 2H), 7.68 (t, $J$ = 14.8 Hz, 1H), 7.55 (t, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 8.4 Hz, 2H), 6.91 (d, $J$ = 8.4 Hz, 2H), 4.87 (s, 2H), 3.82 (s, 3H), 1.53 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 165.9, 160.3, 134.6, 134.6, 131.2, 130.1, 129.3, 127.0, 114.1, 78.1, 68.0, 55.4, 20.9. HRMS (ESI) calcd for $C_{18}H_{21}NO_5S$ [M+H] + 364.1213; found 364.1210.

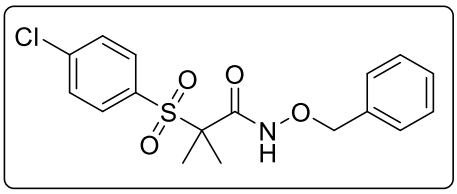
**Compound 3l:** White solid. Eluted with 25% EtOAc/hexane. Yield: 90% (211 mg from 0.5864 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ $^1$H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.82 – 7.80 (m, 2H), 7.69 (t, $J$ = 6.0 Hz, 1H), 7.56 (t, $J$ = 8.0 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.29 – 7.26 (m, 1H), 5.04 (s, 2H), 1.54 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 166.4, 135.5, 135.2, 134.7, 134.4, 132.2, 131.5, 130.1, 129.6, 129.3, 127.4, 74.6, 68.1, 20.8. HRMS (ESI) calcd for $C_{17}H_{17}Cl_2NO_4S$ $[M+H]^+$ 402.0328; found 402.0298.

**Compound 3m:** White solid. Eluted with 35% EtOAc/hexane. Yield: 83% (198 mg from 0.6306 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.70 (s, 1H), 8.23 (d, $J$ = 8.8 Hz, 2H), 7.81 – 7.79 (m, 2H), 7.70 (t, $J$ = 7.6 Hz, 1H), 7.63 – 7.55 (m, 4H), 5.03 (s, 2H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 166.6, 148.2, 142.2, 134.8, 134.3, 130.1, 129.7, 129.3, 123.8, 77.0, 68.1, 20.9. HRMS (ESI) calcd for $C_{17}H_{18}N_2O_6S$ [M+H] + 379.0958; found 379.0931.

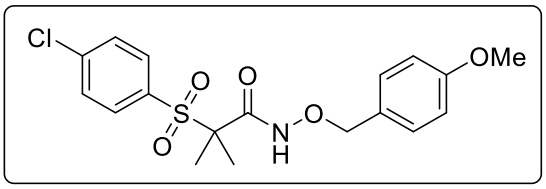
**Compound 3n:** Colorless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 72% (215 mg from 0.9360 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.56 (s, 1H), 7.74 (d, $J$ = 7.6 Hz, 2H), 7.57 (t, $J$ = 7.6 Hz, 1H), 7.45 (t, $J$ = 8.0 Hz, 2H), 7.32 – 7.24 (m, 5H), 4.79 – 4. 78 (m, 2H), 3.79 (q, $J$ = 7.2 Hz, 1H), 1.32 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C {$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 162.8, 135.5, 134.8, 134.5, 129.5, 129.3, 129.2, 128.8, 128.5, 78.4, 63.6, 12.0. HRMS (ESI) calcd for $C_{16}H_{17}NO_4S$ [M+H] + 320.0951; found 320.0954.

**Compound 3o:** Colourless sticky liquid. Eluted with 15% EtOAc/hexane. Yield: 88% (116 mg from 0.5100 mmol of corresponding *α*-halo hydroxamate)**.** 

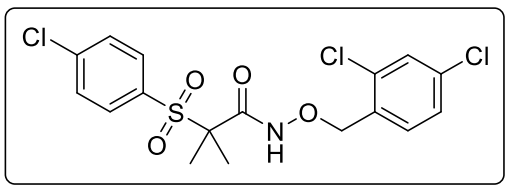
**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.69 (s, 1H), 7.82 – 7.79 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 1.53 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 165.9, 134.6, 134.5, 130.0, 129.1, 67.9, 64.2, 20.5. HRMS (ESI) calcd for $C_{11}H_{15}NO_4S$ [M+H] + 258.0795; found 258.0793.

**Compound 3p:** White solid. Eluted with 25% EtOAc/hexane. Yield: 82% (221 mg from 0.7349 mmol of corresponding *α*-halo hydroxamate)**.** 

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.39 (s, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 6H), 7.43 – 7.38 (m, 5H), 4.93 (s, 2H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 165.7, 141.7, 134.9, 133.0, 131.5, 129.6, 129.4, 129.1, 128.8, 78.4, 68.1, 20.6. HRMS (ESI) calcd for $C_{17}H_{18}ClNO_4S$ [M+H] + 368.0718; found 368.0713.

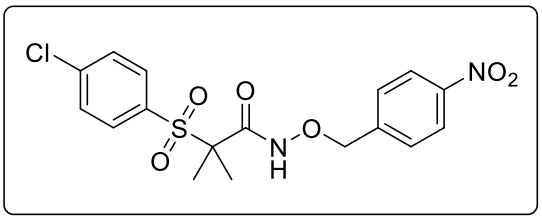
**Compound 3q:** White solid. Eluted with 35% EtOAc/hexane. Yield: 81% (213 mg from 0.6618 mmol of corresponding *α*-halo hydroxamate)**.** 

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.35 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 11.0 Hz, 2H), 4.86 (s, 2H), 3.82 (s, 3H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 165.7, 160.3, 141.6, 133.0, 131.5, 131.2, 129.6, 126.9, 114.1, 78.1, 68.1, 55.4, 20.6. HRMS (ESI) calcd for $C_{18}H_{20}ClNO_5S$ [M+Na] + 420.0643; found 420.0641.

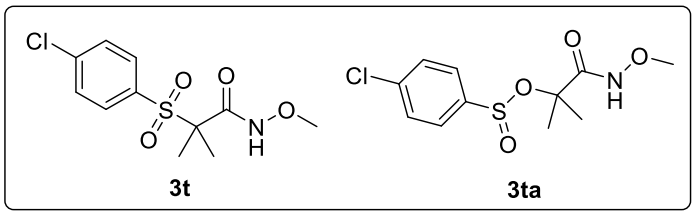
**Compound 3r:** White solid. Eluted with 35% EtOAc/hexane. Yield: 75% (192 mg from 0.5864 mmol of corresponding *α*-halo hydroxamate)**.** 

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.47 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.28 – 7.27 (m, 1H), 5.03 (s, 2H), 1.54 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.3, 141.8, 135.6, 135.3, 132.9, 132.3, 131.5, 131.4, 129.7, 129.6, 127.5, 74.7, 68.3, 20.7. HRMS (ESI) calcd for $C_{17}H_{16}Cl_3NO_4S$ [M+H] + 435.9938; found; 435.9932.

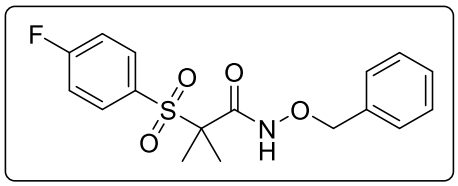
**Compound 3s:** White solid. Eluted with 30% EtOAc/hexane. Yield: 77% (200 mg from 0.6306 mmol of corresponding *α*-halo hydroxamate)**. $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.58 (s, 1H), 8.24 (d, *J* = 6.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 2H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.4, 148.2, 142.1, 141.9, 132.7, 131.5, 129.7, 129.7, 123.9, 77.3, 68.3, 20.7. HRMS (ESI) calcd for $C_{17}H_{17}ClN_2O_6S$ [M+Na] + 435.0388; found 435.0401.



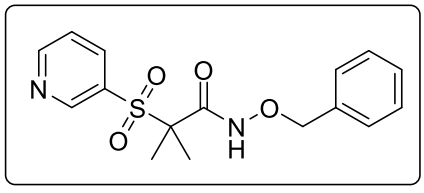

**Compound 3t:** It was isolated as a mixture (**3t:3ta** = ~8.5:1.5) with a minor amount of **3ta.** Colorless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 64% (190 mg from 1.0201 mmol of corresponding *α*-halo hydroxamate)**.** Data for **3t: $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.51 (s, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 1.56 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.0, 141.7, 131.5, 129.6, 126.4, 68.2, 64.4, 20.6. HRMS (ESI) calcd for $C_{11}H_{14}ClNO_4S$ [M+H] + 292.0405; found 292.0415.



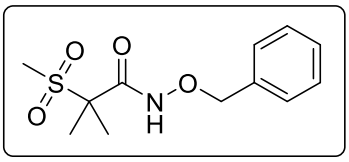

**Compound 3u:** Off white sticky liquid. Eluted with 30% EtOAc/hexane. Yield: 81% (208 mg from 0.7349 mmol of corresponding *α*-halo hydroxamate)**. $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.41 (s, 1H), 7.81 – 7.78 (m, 2H), 7.41 – 7.37 (m, 5H), 7.23 – 7.19 (m, 2H), 4.93 (s, 2H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 167.0 (d, *J* = 261 Hz), 165.9, 134.9, 133.0, 132.9, 130.6 (d, *J* = 3.1 Hz), 129.4, 129.1, 128.8, 116.8, 116.6, 78.4, 68.1, 20.7. HRMS (ESI) calcd for $C_{17}H_{18}FNO_4S$ [M+H] + 352.1013; found; 352.1008.



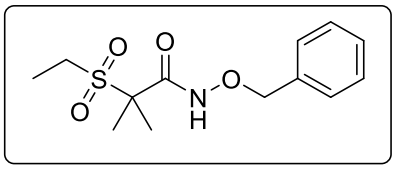

**Compound 3v:** Pale yellow sticky liquid. Eluted with 40% EtOAc/hexane. Yield: 57% (142 mg from 0.6306 mmol of corresponding *α*-halo hydroxamate)**. $^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.17 (s, 1H), 8.92 (d, *J* = 1.6 Hz, 1H), 8.79 – 8.78 (m, 1H), 7.96 – 7.93 (m, 1H), 7.41 – 7.39 (m, 1H), 7.32 – 7. 28 (m, 5H), 4.84 (s, 2H), 1.46 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 165.5, 155.0, 150.7, 137.9,



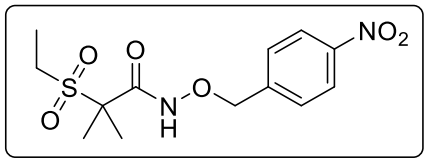
134.8, 131.5, 129.5, 129.2, 128.8, 123.9, 78.6, 68.4, 20.5. HRMS (ESI) calcd for $C_{16}H_{18}N_2O_4S$ [M+H] + 335.1060; found 335.1064.

**Compound 3w:** Colourless sticky liquid. Eluted with 20% EtOAc/hexane. Yield: 91% (182 mg from 0.7349 mmol of corresponding *α*-halo hydroxamate)**.** 

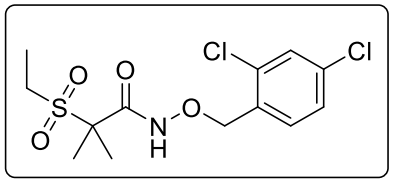
**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.21 (s, 1H), 7.40 – 7.36 (m, 5H), 4.91 (s, 2H), 2.85 (s, 3H), 1.59 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.3, 134.7, 129.4, 129.1, 128.7, 78.4, 66.7, 36.4, 19.5. HRMS (ESI) calcd for $C_{12}H_{17}NO_4S$ [M+H] + 272.0951; found 272.0957.

**Compound 3x:** Colourless sticky liquid. Eluted with 20% EtOAc/hexane. Yield: 92% (192 mg from 0.7349 mmol of corresponding *α*-halo hydroxamate)**.** 

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.23 (s, 2H), 7.39 – 7.36 (m, 5H), 4.92 (s, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.59 (s, 6H), 1.34 (t, *J* = 7.6 Hz, 8H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.4, 134.7, 129.3, 129.0, 128.6, 78.2, 66.4, 42.9, 19.7, 5.2. HRMS (ESI) calcd for $C_{13}H_{19}NO_4S$ [M+H] + 286.1108; found 286.1109.

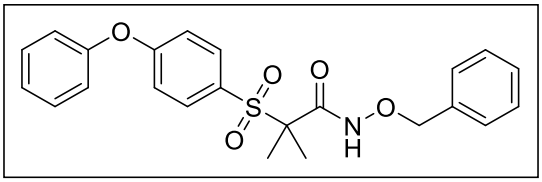
**Compound 3y:** Colourless sticky liquid. Eluted with 20% EtOAc/hexane. Yield: 96% (200 mg from 0.6306 mmol of corresponding *α*-halo hydroxamate)**.** 

**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.20 (s, 1H), 7.40 – 7.37 (m, 4H), 4.92 (s, 2H), 2.98 (q, *J* = 7.6 Hz, 2H), 1.60 (s, 6H), 1.35 (t, *J* = 7.6 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.5, 134.8, 129.4, 129.1, 128.8, 78.4, 66.5, 43.0, 19.8, 5.3. HRMS (ESI) calcd for $C_{13}H_{18}N_2O_6S$ [M+Na] + 353.0778; found 353.0786.

**Compound 3z:** Colourless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 94% (195 mg from 0.5864 mmol of corresponding *α*-halo hydroxamate)**.** 

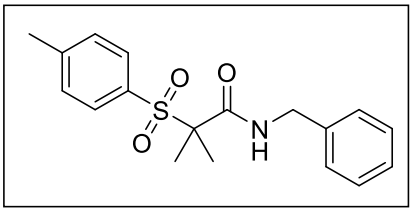
**$^1$H NMR** (400 MHz, $CDCl_3$) *δ* 9.37 (s, 1H), 7.38 – 7.34 (m, 2H), 7.21 – 7.18 (m, 1H), 4.94 (s, 2H), 2.99 (q, *J* = 7.6 Hz, 2H), 1.55 (s, 6H), 1.31 (t, *J* = 7.6 Hz, 3H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) *δ* 166.9, 135.4, 135.1, 132.1, 131.2, 129.4, 127.3, 74.4, 66.5, 42.9, 19.6, 5.2. HRMS (ESI) calcd for $C_{13}H_{17}Cl_2NO_4S$ [M+H] + 354.0328; found 354.0329.

**Compound 3aa:** Colourless sticky liquid. Eluted with 25% EtOAc/hexane. Yield: 50% (78 mg



from 0.3688 mmol of corresponding $\alpha$-halo hydroxamate)**.** **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.48 (s, 1H), 7.70 (d, $J$ = 8.8 Hz, 2H), 7.42– 7.36 (m, 7H), 7.24 – 7.23 (m, 1H), 7.08 (d, $J$ = 7.6 Hz, 2H), 7.02 (d, $J$ = 8.8 Hz, 2H), 4.93 (s, 2H), 1.52 (s, 6H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 166.2, 163.5, 154.6, 135.0, 132.4, 130.4, 129.4, 129.0, 128.7, 127.6, 125.5, 120.8, 117.3, 78.4, 68.1, 20.8. HRMS (ESI) calcd for $C_{23}H_{23}NO_5S$ [M+H] + 426.1370; found 426.1371.

**Compound 4a:** Yellow sticky liquid. Eluted with 20% EtOAc/hexane. Yield: 60% (57 mg from



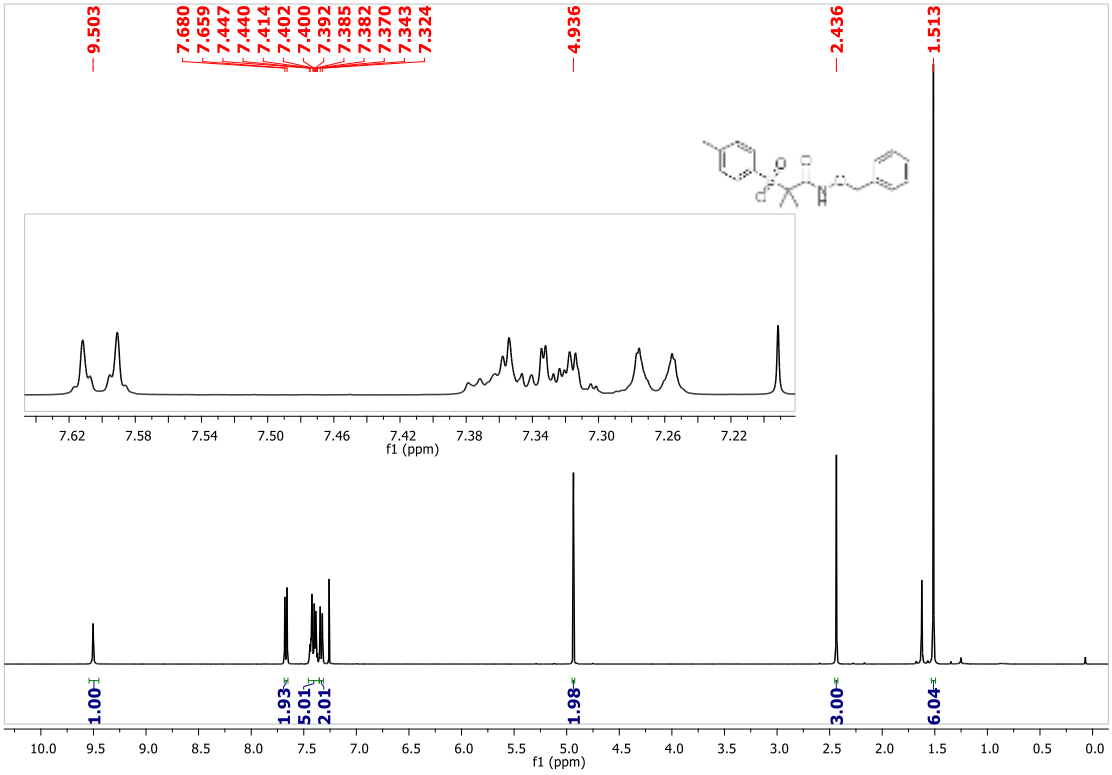
0.2878 mmol of corresponding $\alpha$-sulfonyl hydroxamic acid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.55 (d, $J$ = 8.4 Hz, 2H), 7.42 (s, 1H), 7.37-7.32 (m, 5H), 7.23 (d, $J$ = 8.0 Hz, 2H), 4.47 (d, $J$ = 5.6 Hz, 2H), 2.42 (s, 3H), 1.58 (s, 6H). **$^{13}$C {$^1$H} NMR** (101 MHz, $CDCl_3$) $\delta$ 166.8, 144.5, 136.7, 131.0, 129.1, 128.8, 127.9, 127.2, 126.8, 67.1, 43.4, 20.7, 19.9. HRMS (ESI) calcd for $C_{18}H_{21}NO_3S$ [M+H] + 332.1315; found 332.1319.

**References:**

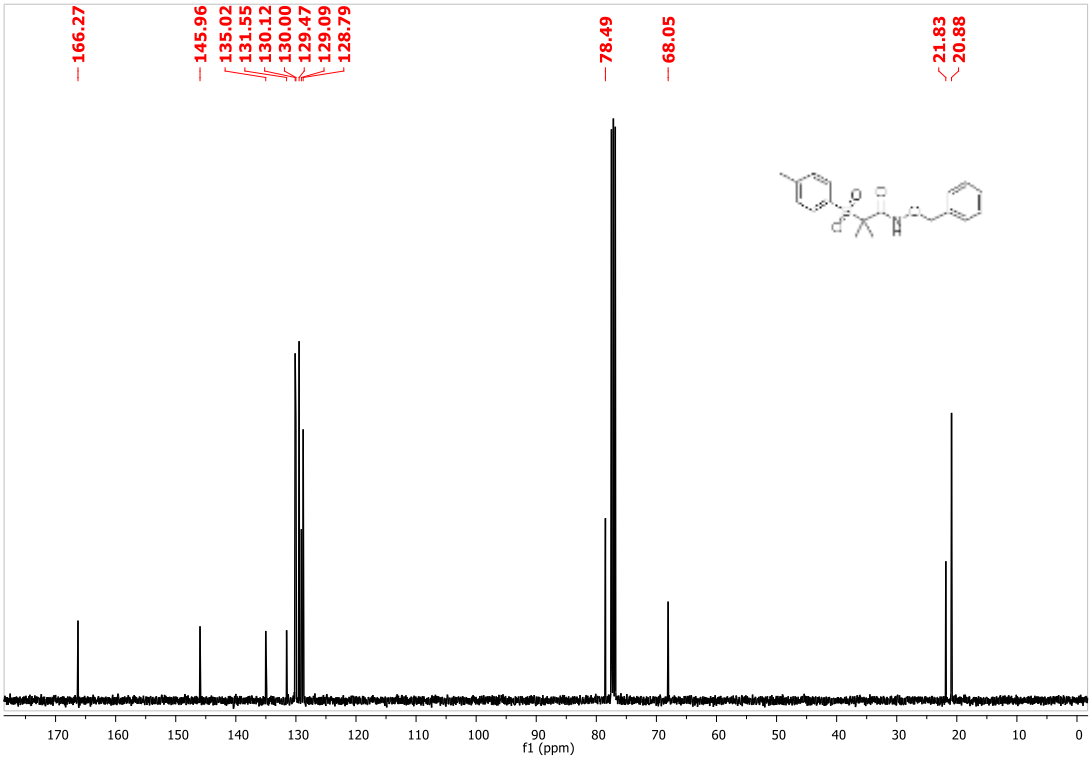

1. C. S. Jeffrey.; K. L. Barnes, K. L.; Eickhoff, J. A and Carson, C. R. *J. Am. Chem. Soc.,* 2011, **133,** 7688.
2. X. Zhou, J. Luo, J. Liu, S. Peng and G. J. Deng, *Org. Lett*. 2011, **13**, 1432

## H and $^{13}$C spectra of isolated compounds

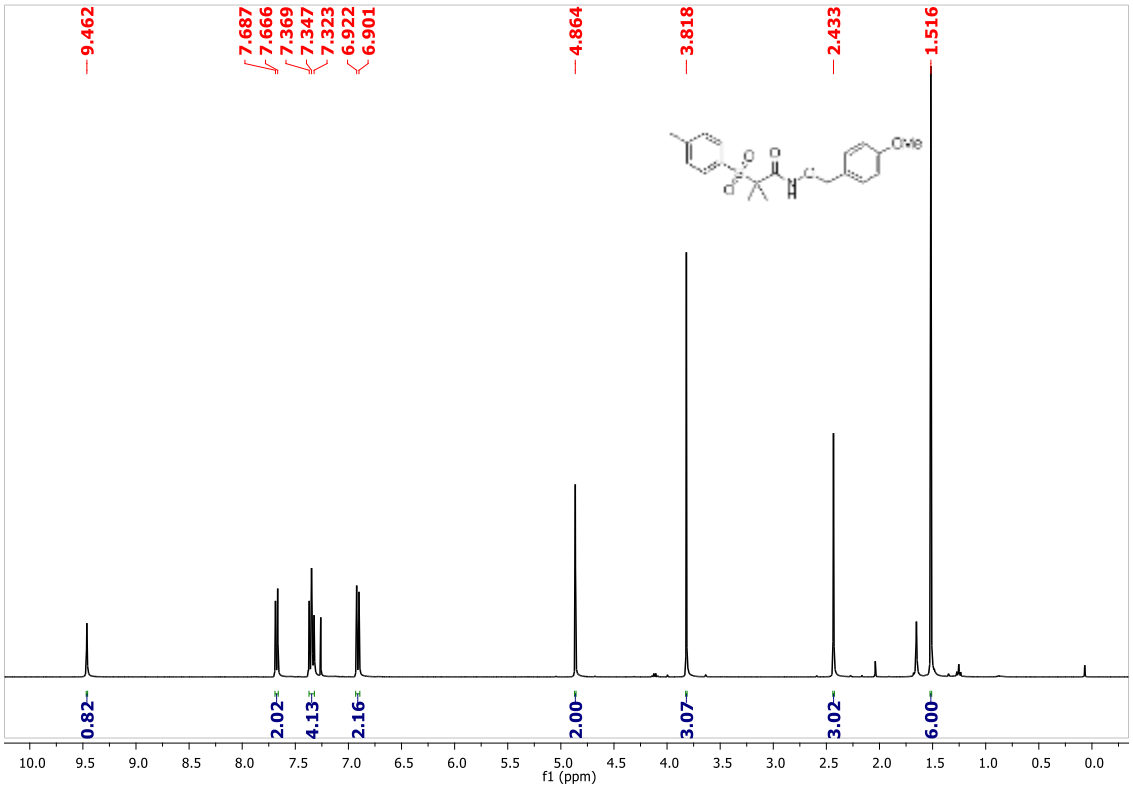
### $^{1}$H NMR (400 MHz, $CDCl_3$) of 3a



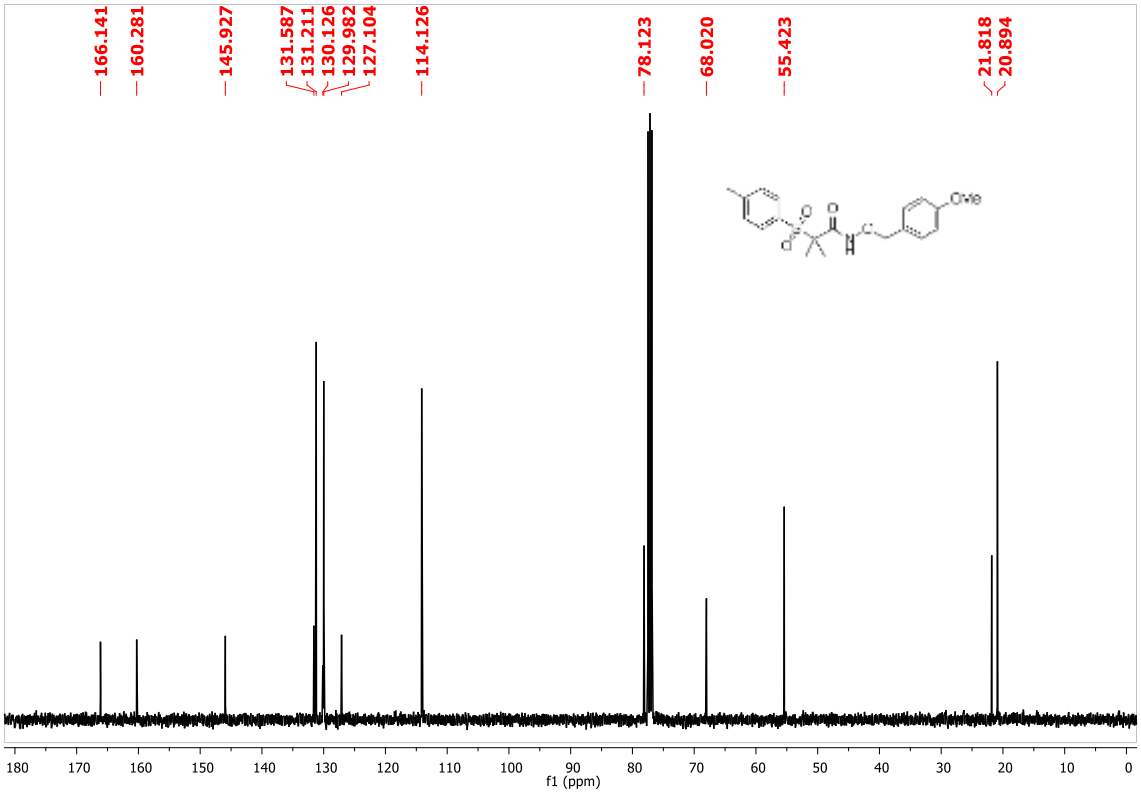

### $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3a



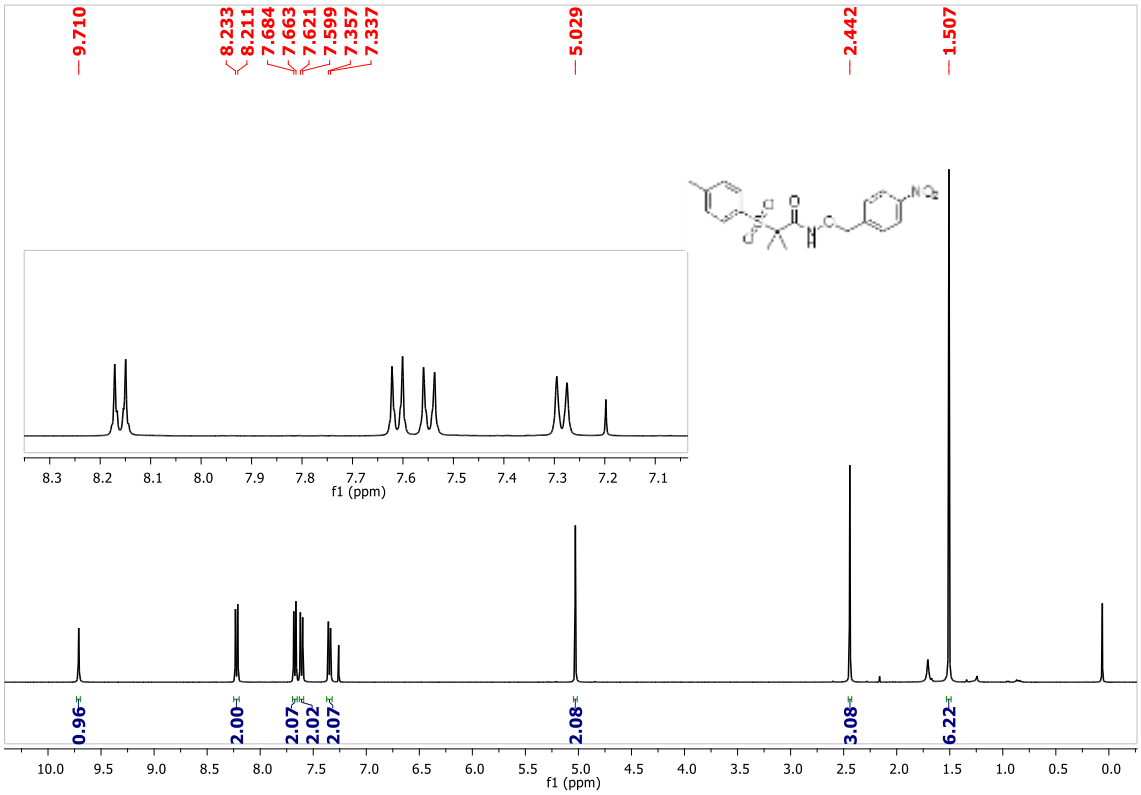
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3b



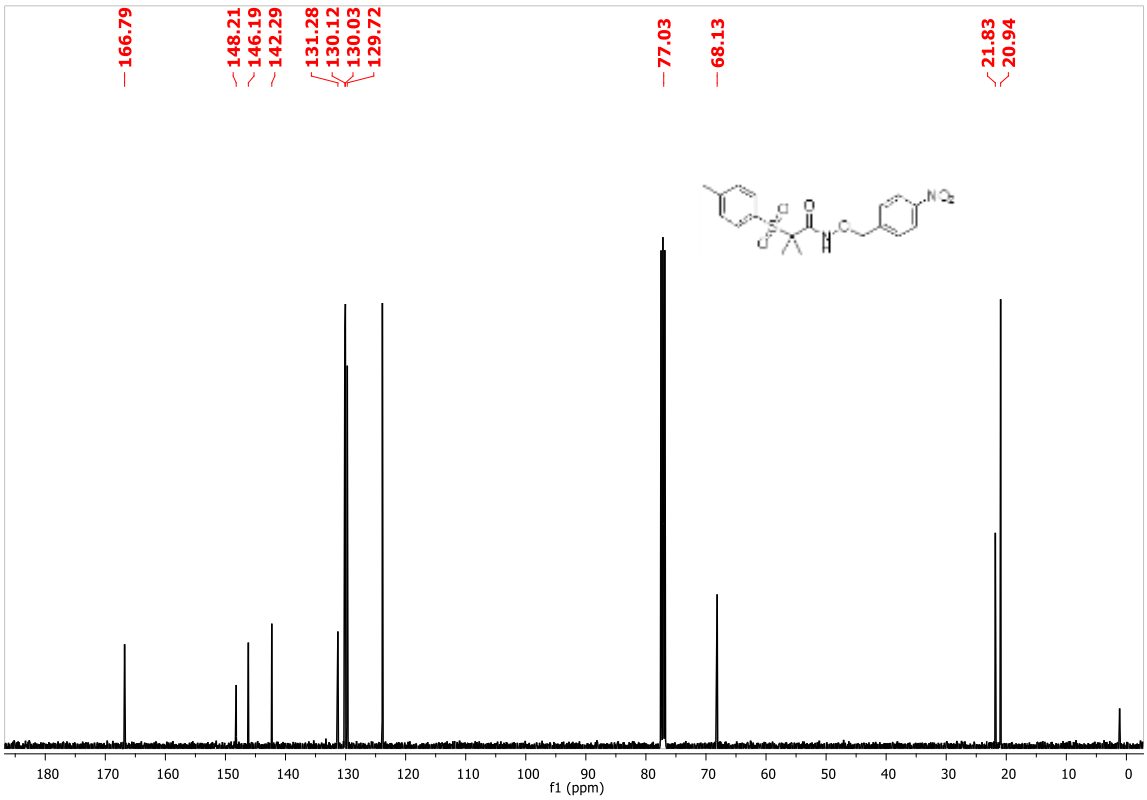

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3b



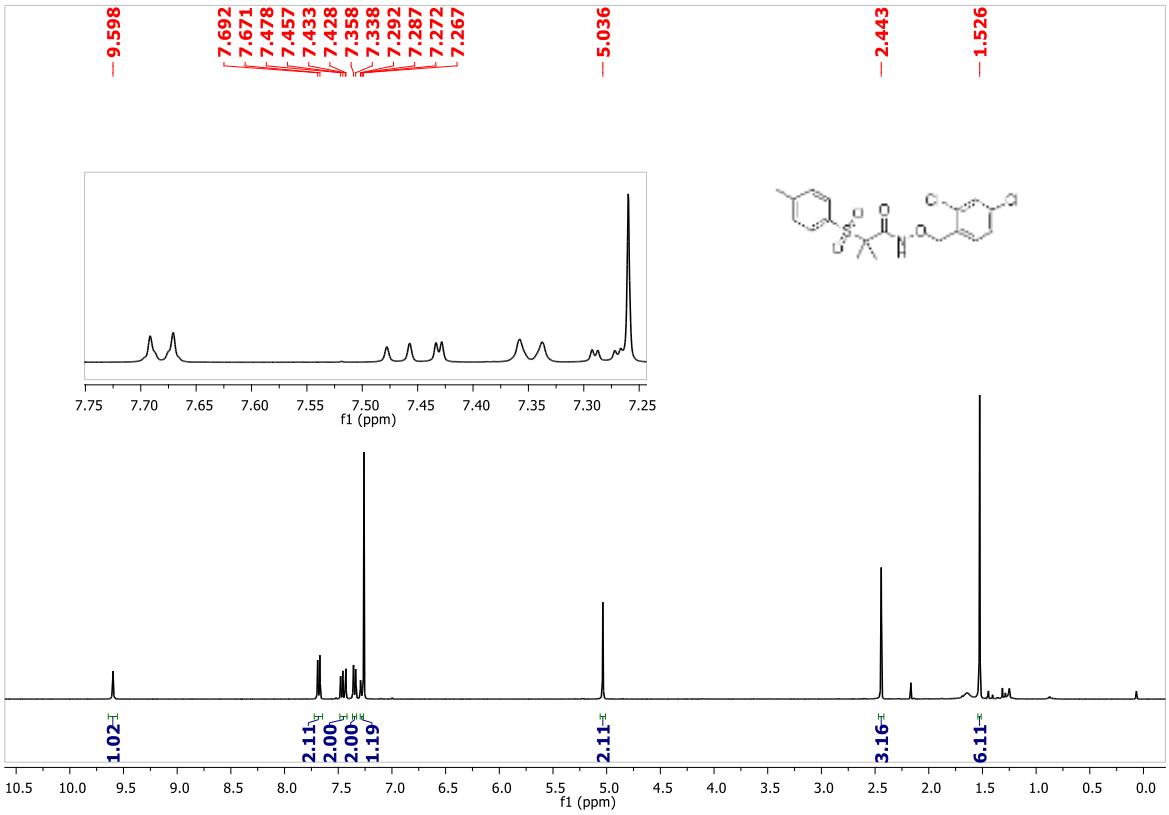
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3c**



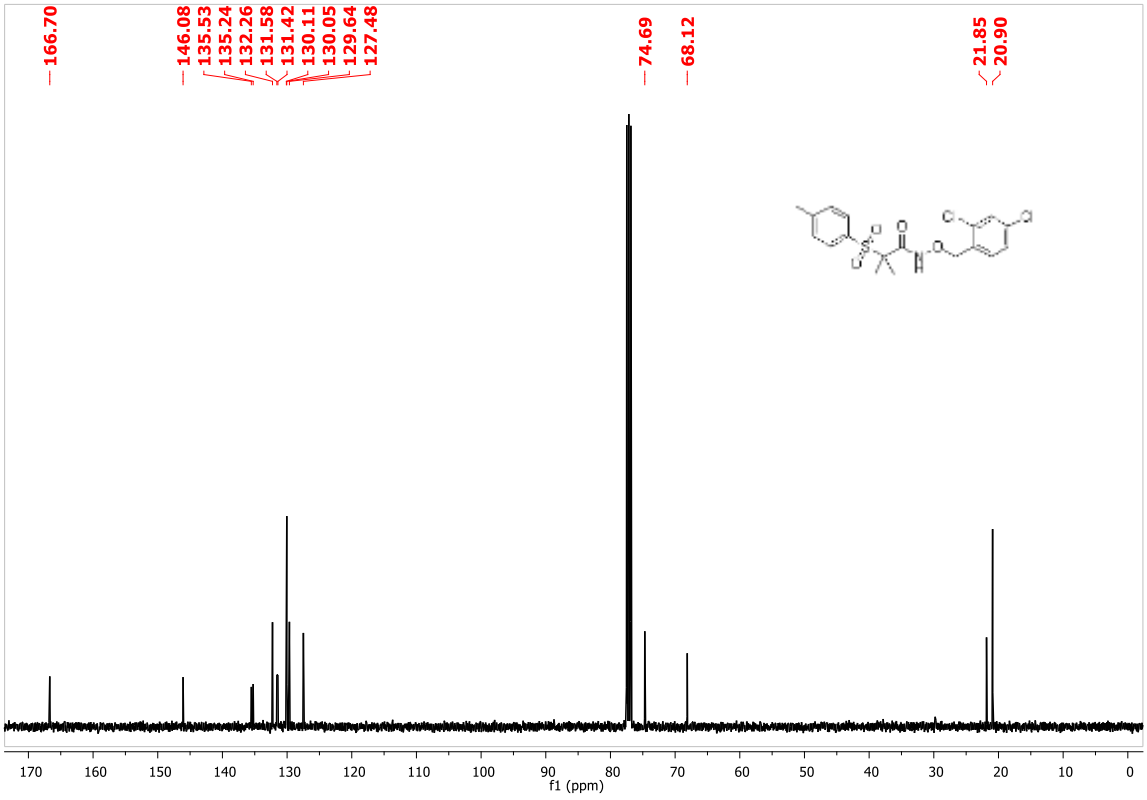

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3c**



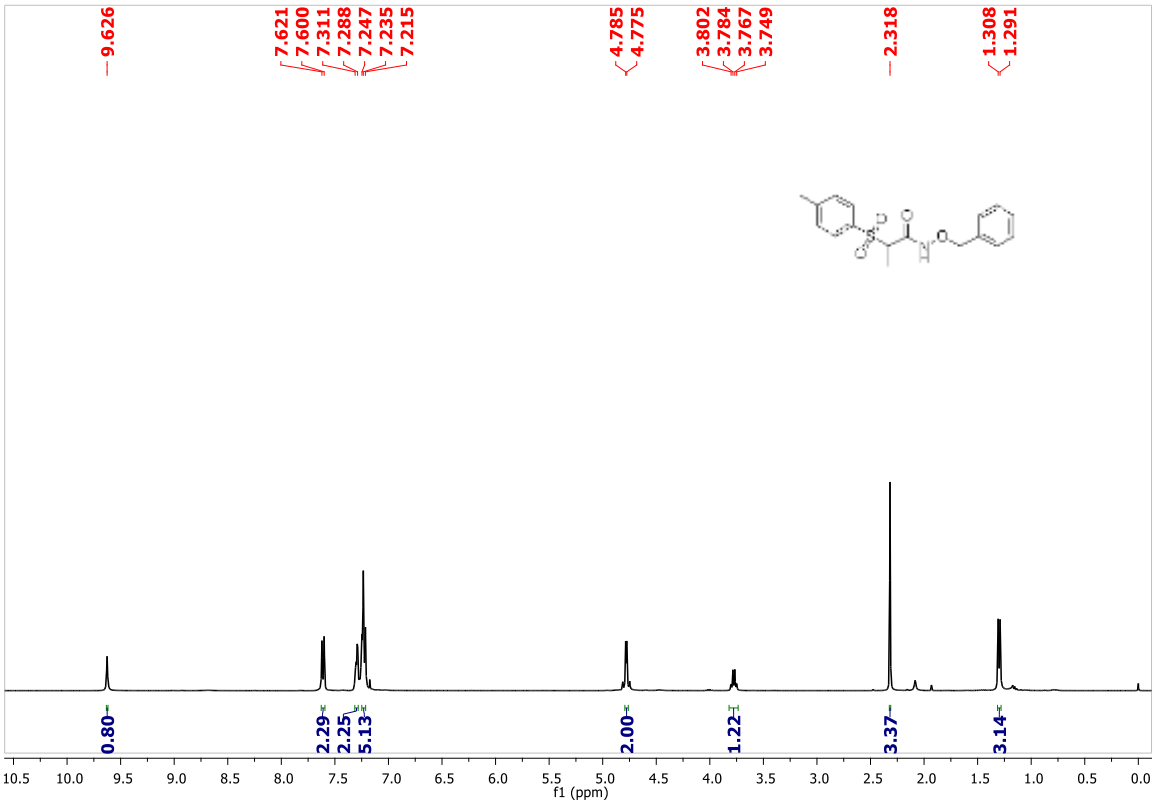
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3d



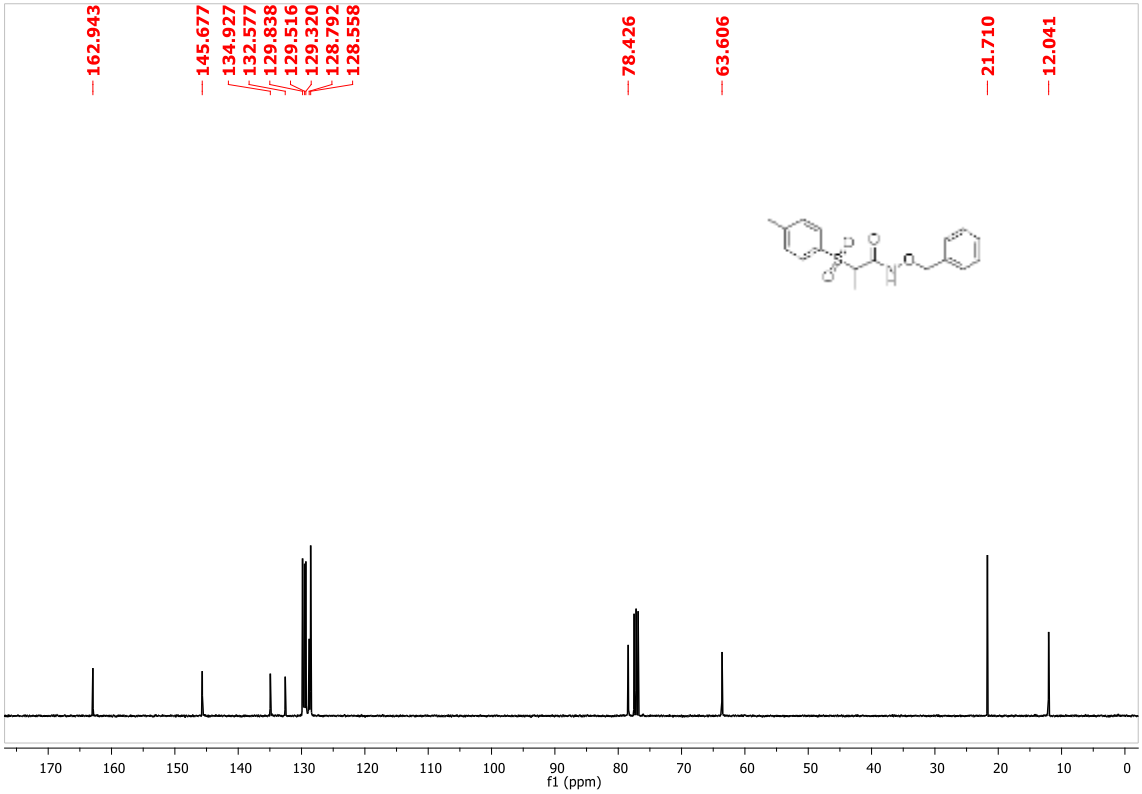

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3d



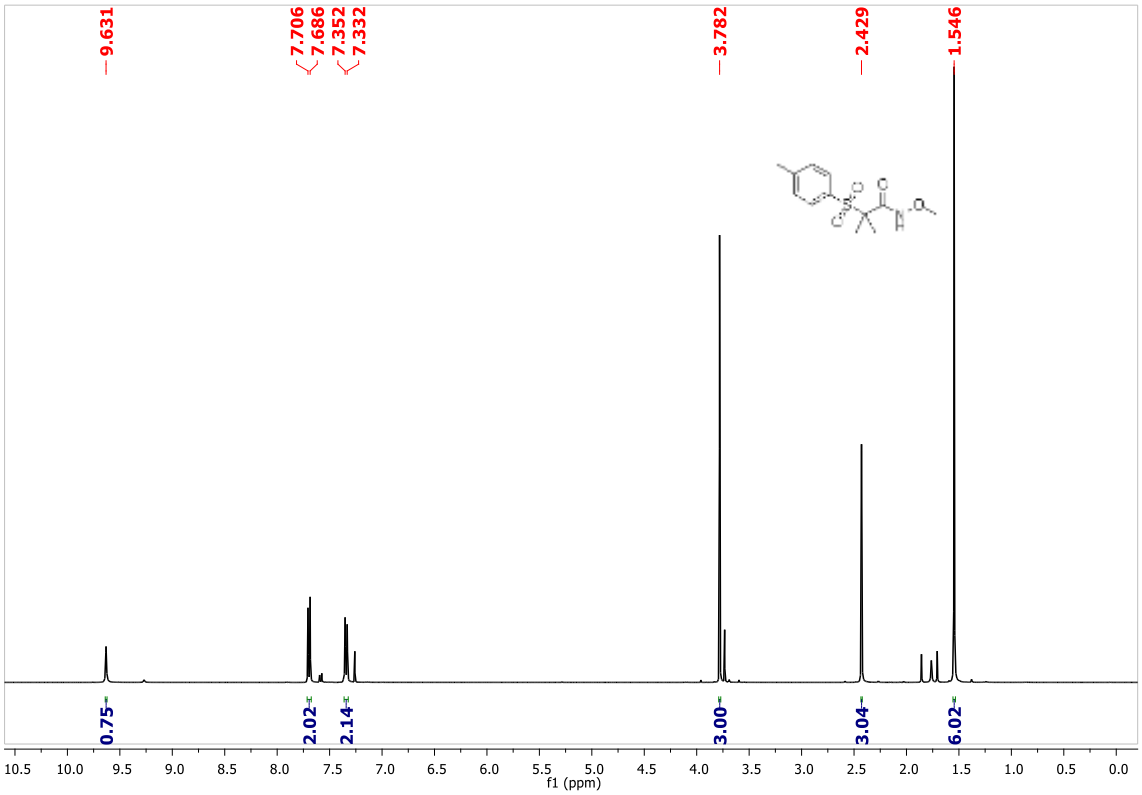
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3e



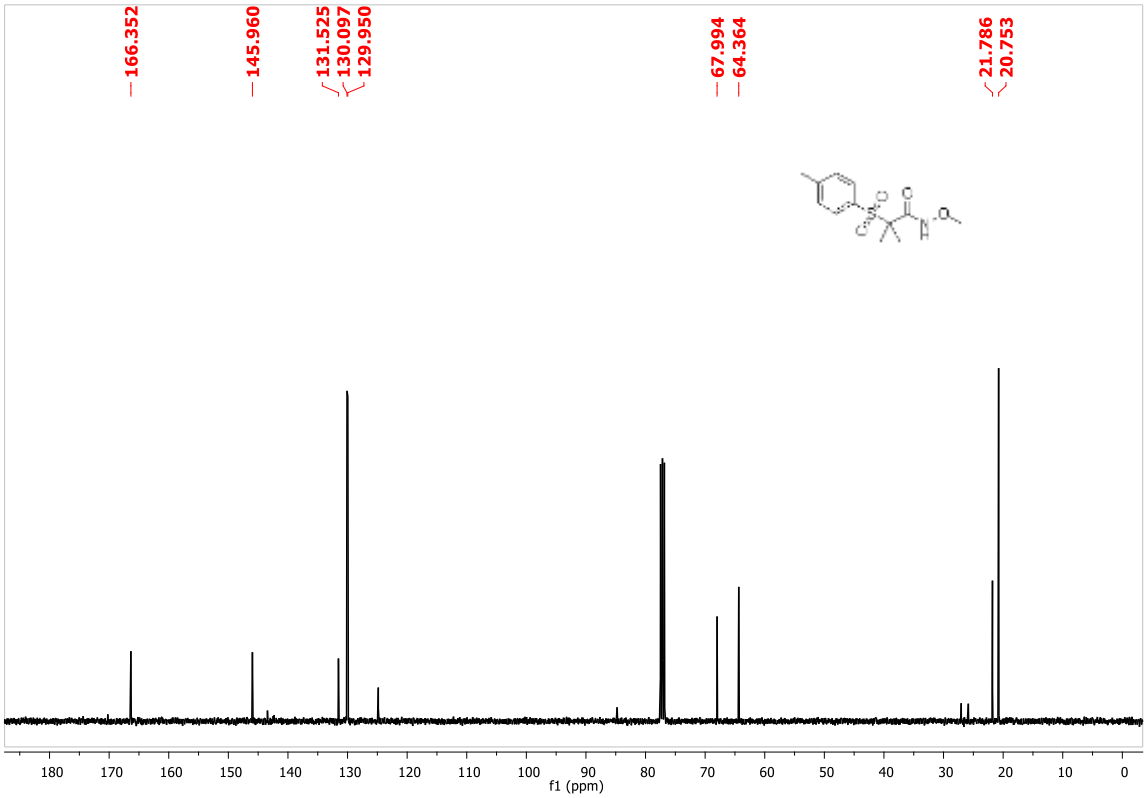

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3e



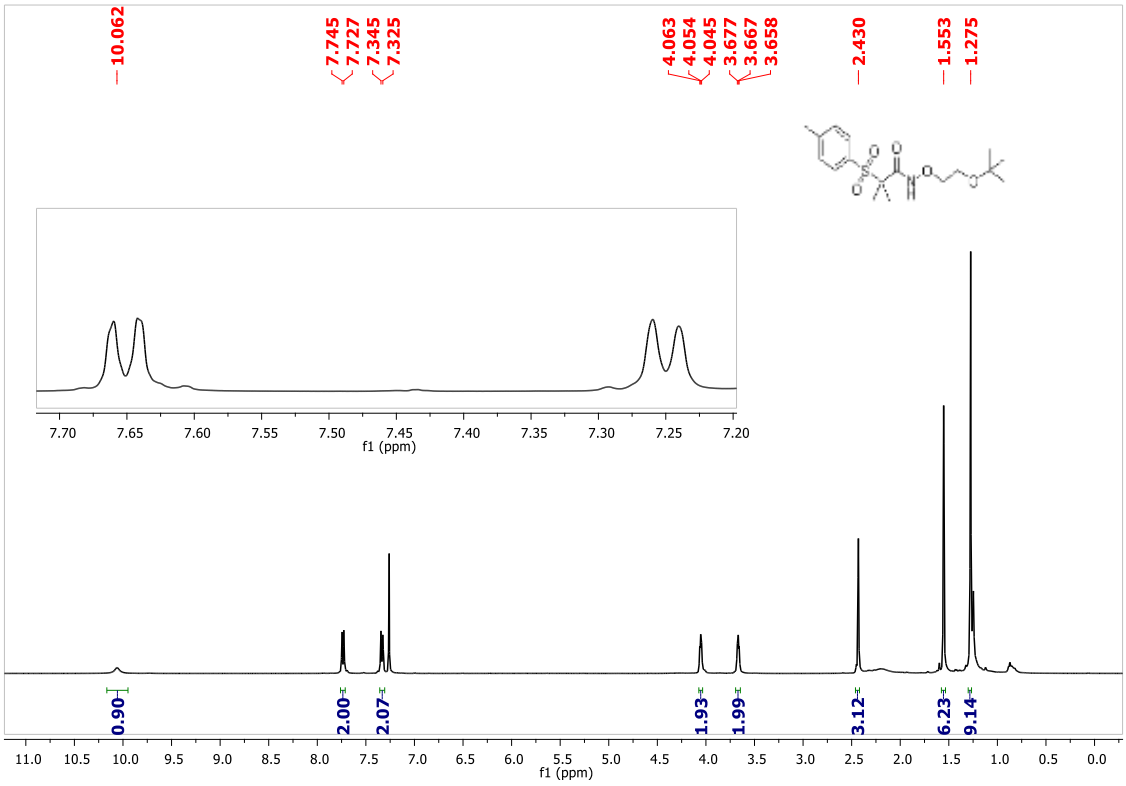
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3f



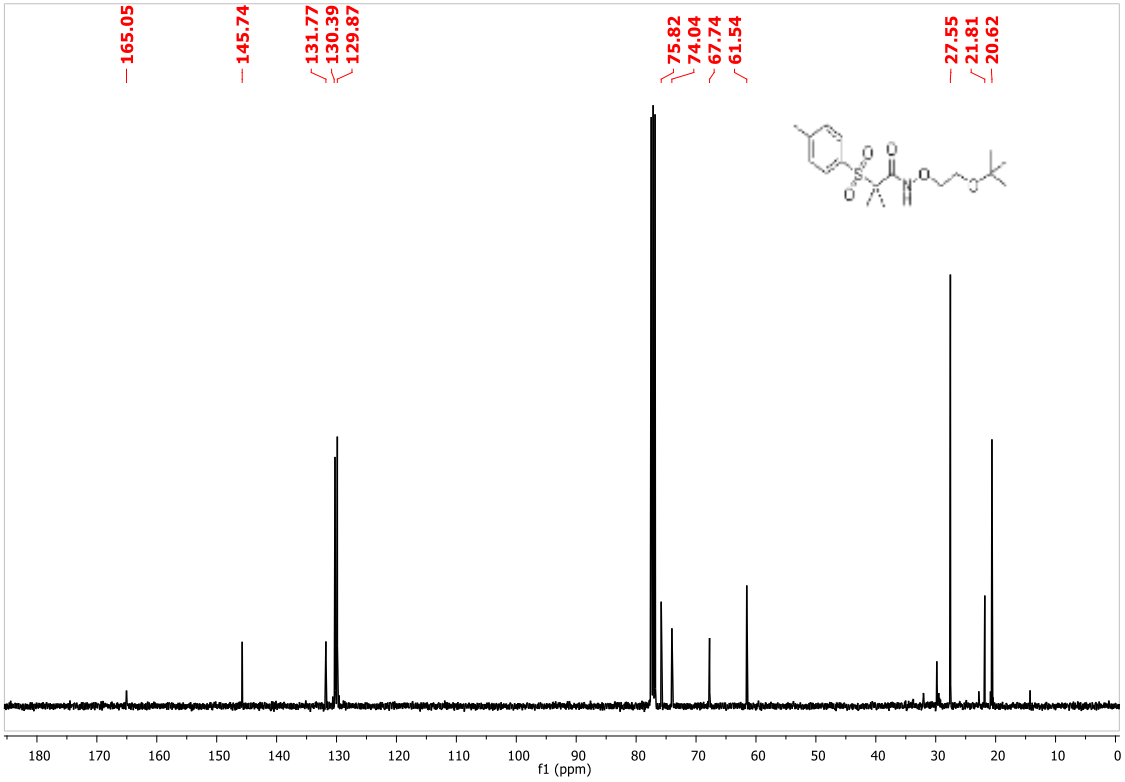

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3f



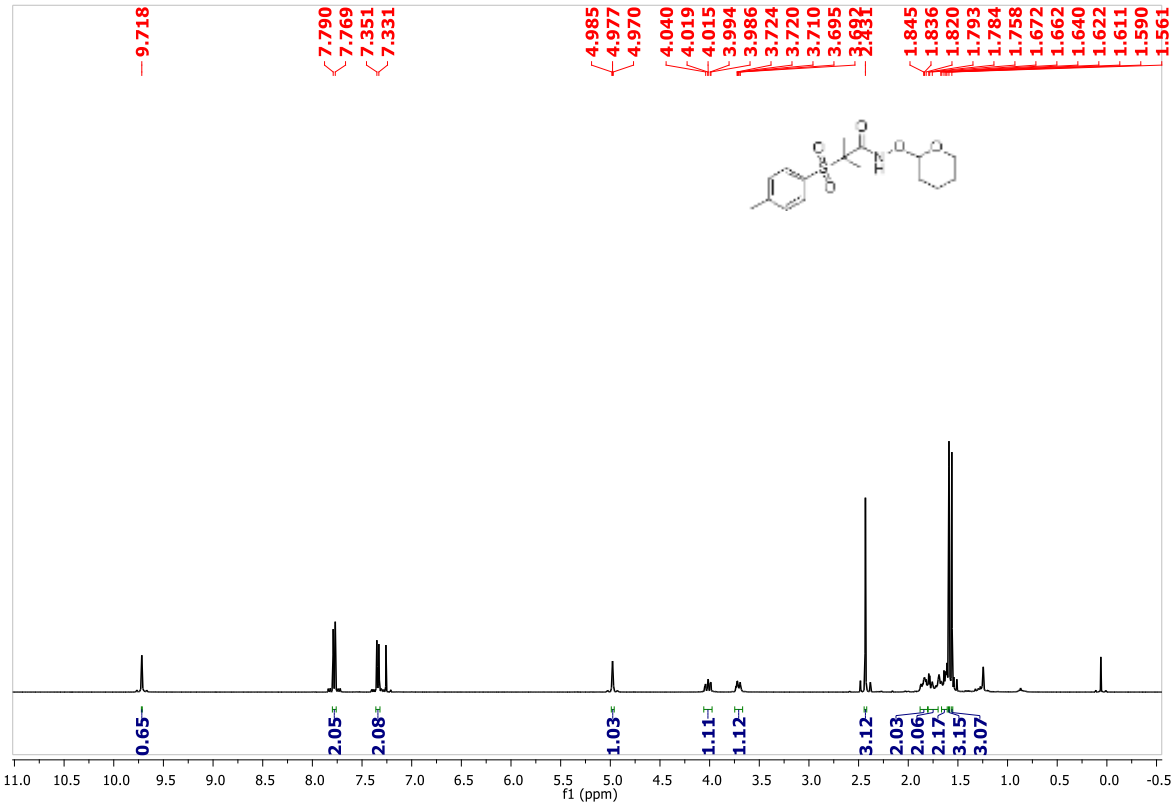
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3g



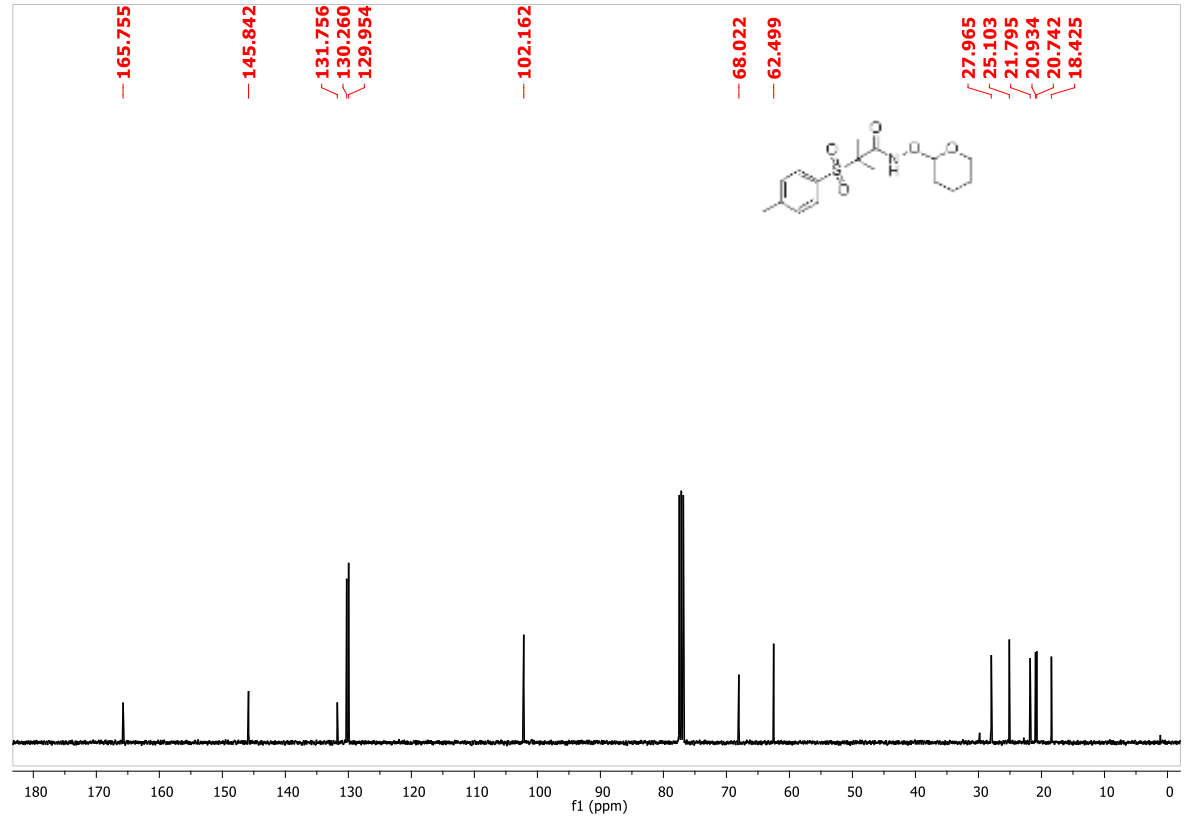

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3g



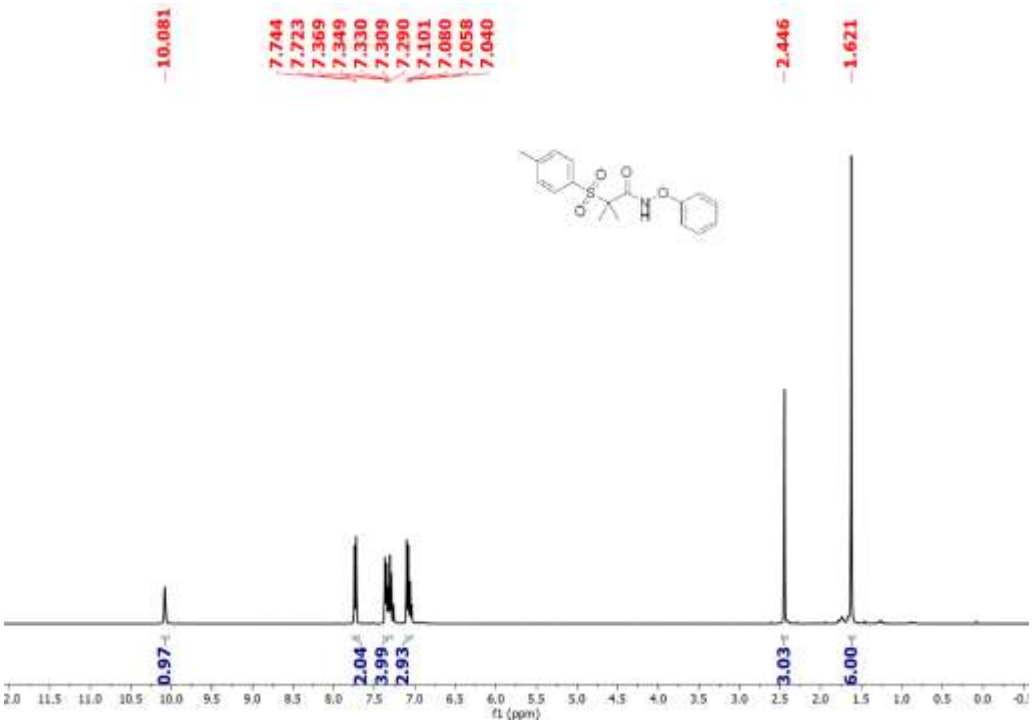
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3h**



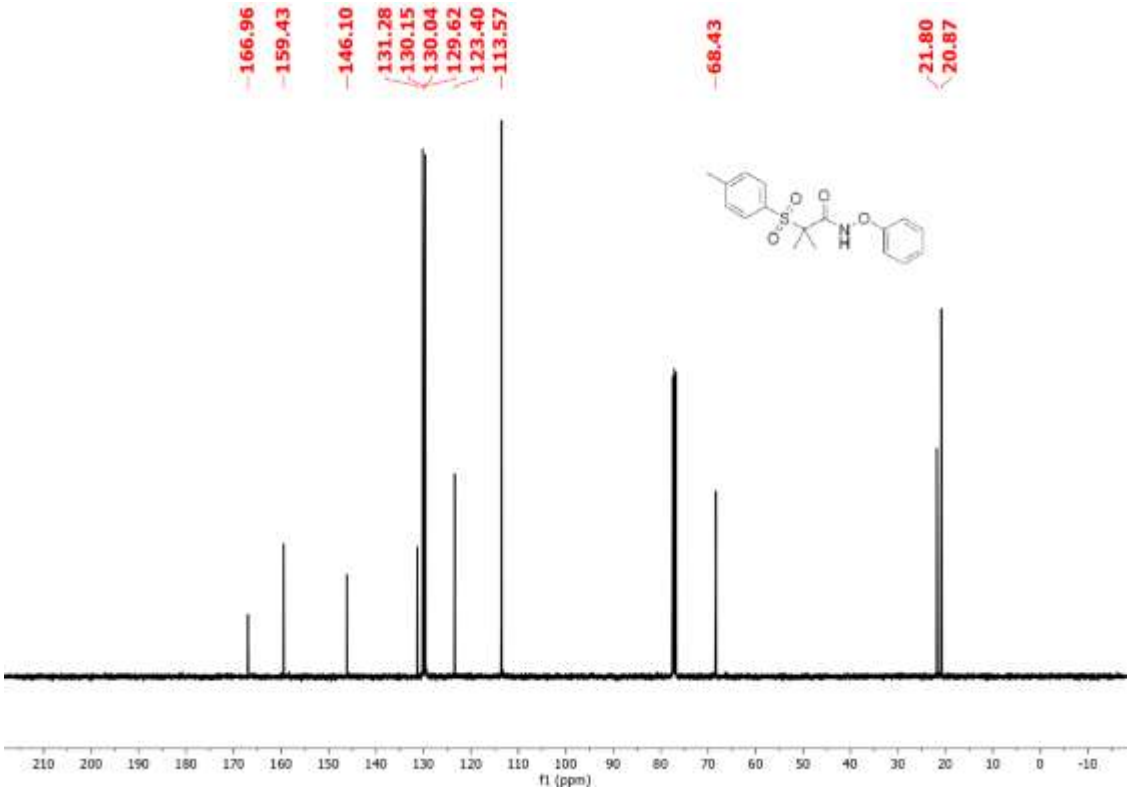

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3h**



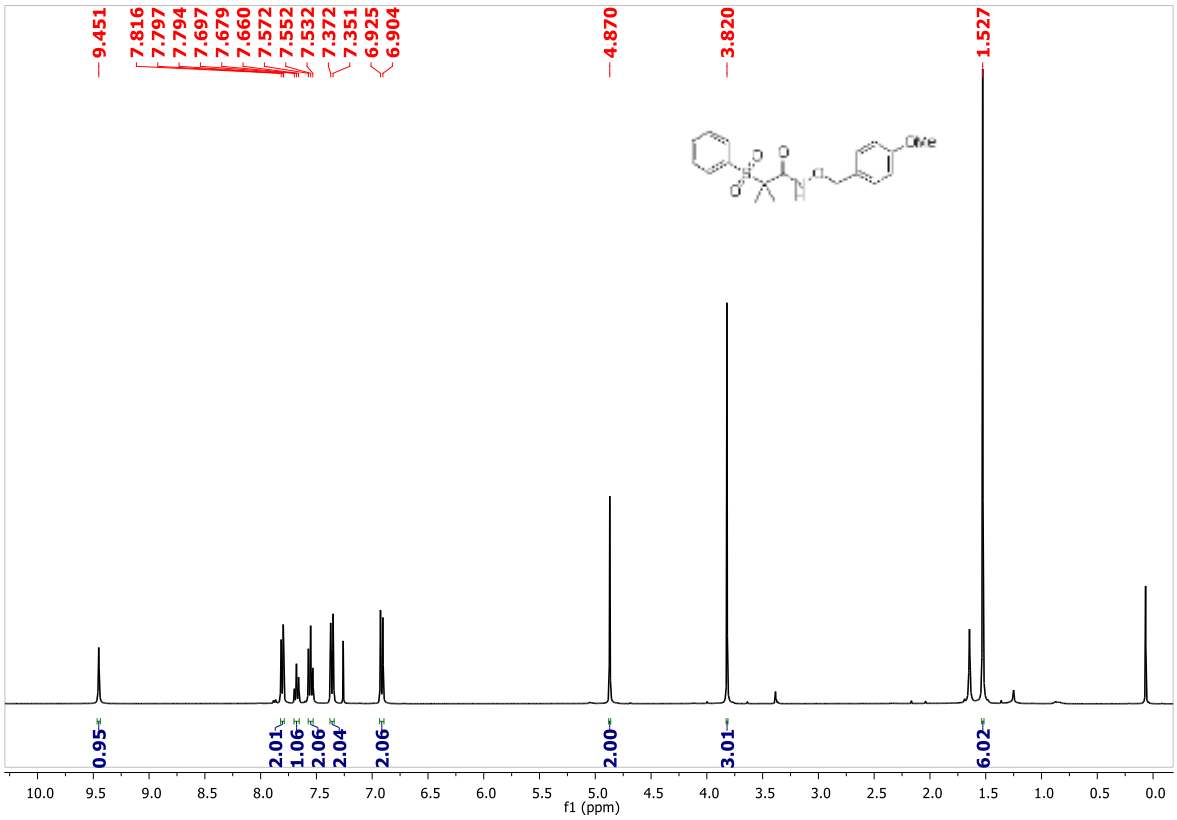
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3i**



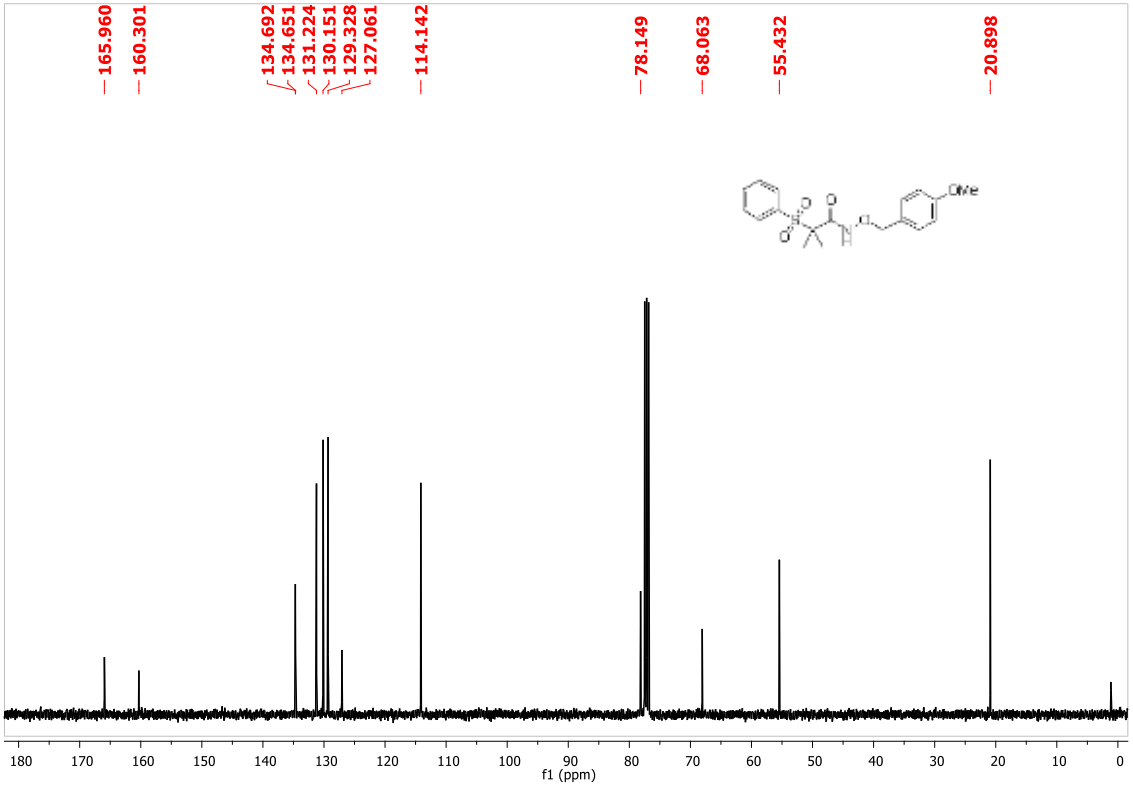

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3i**



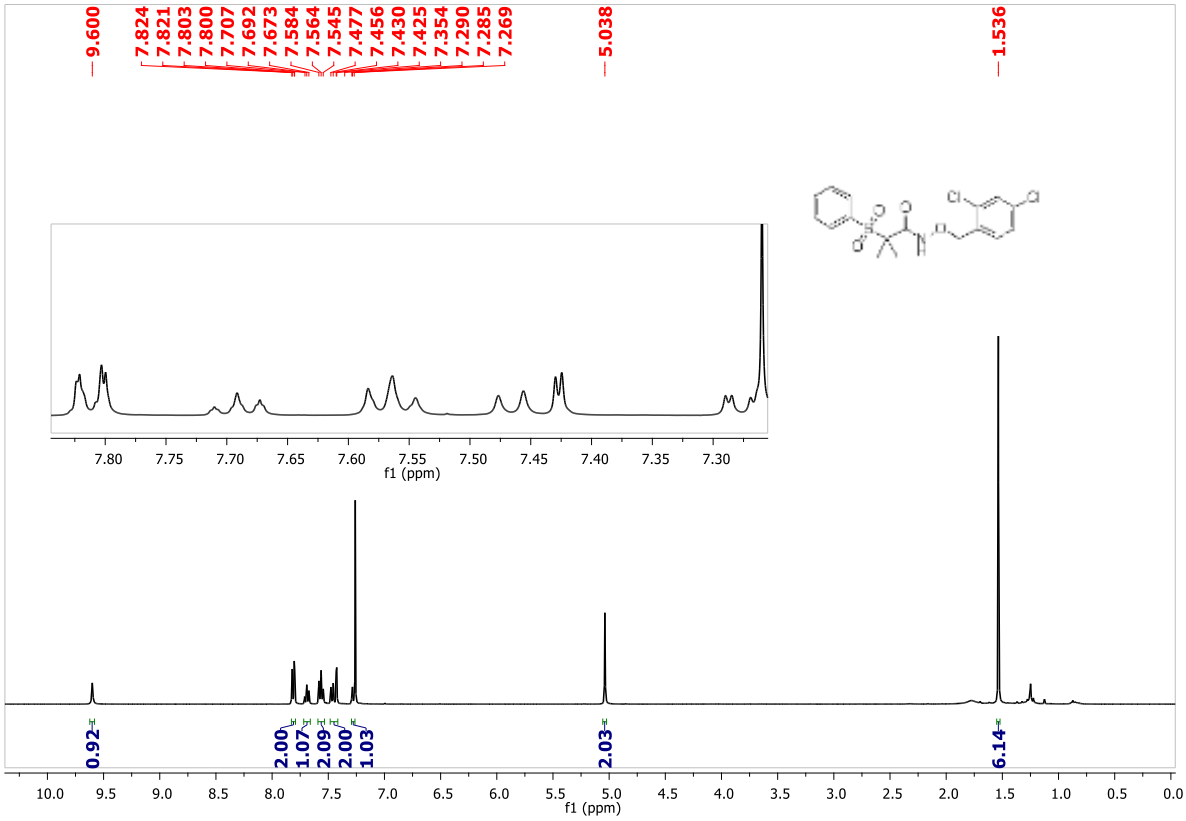
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3k



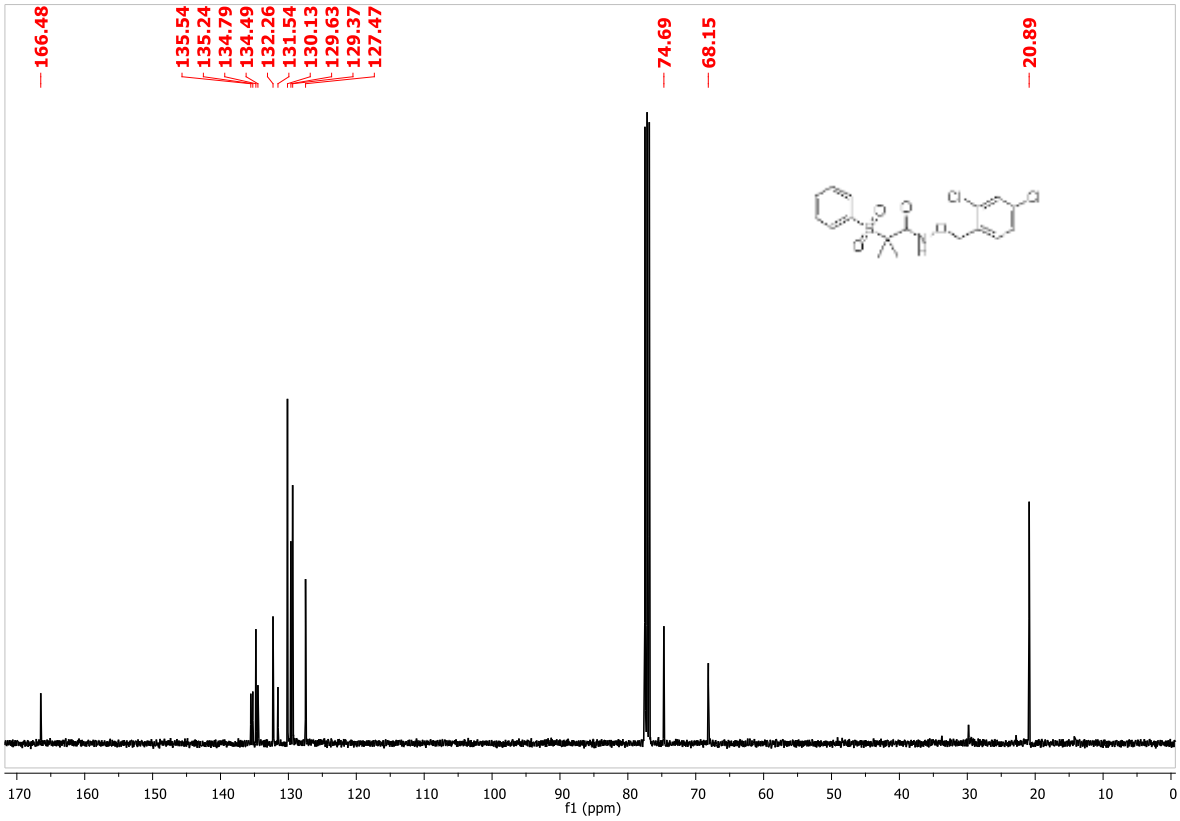

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3k



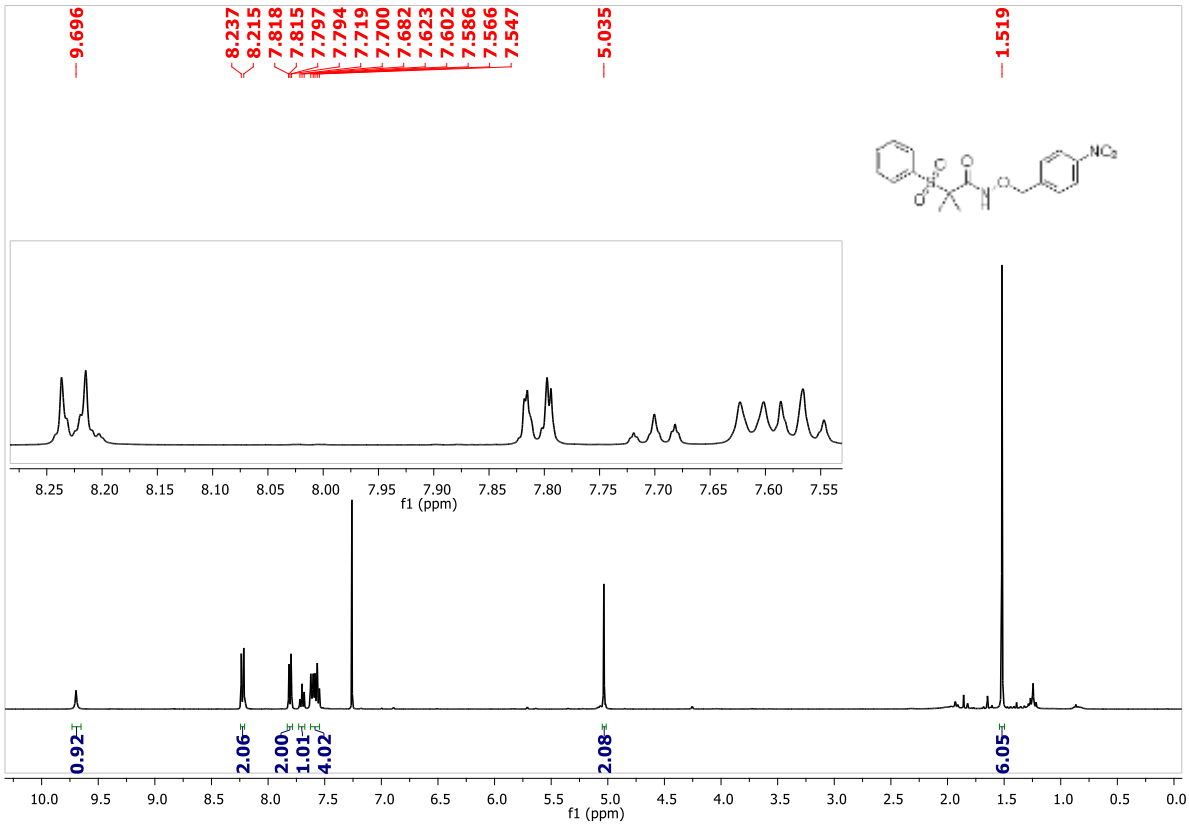
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3l



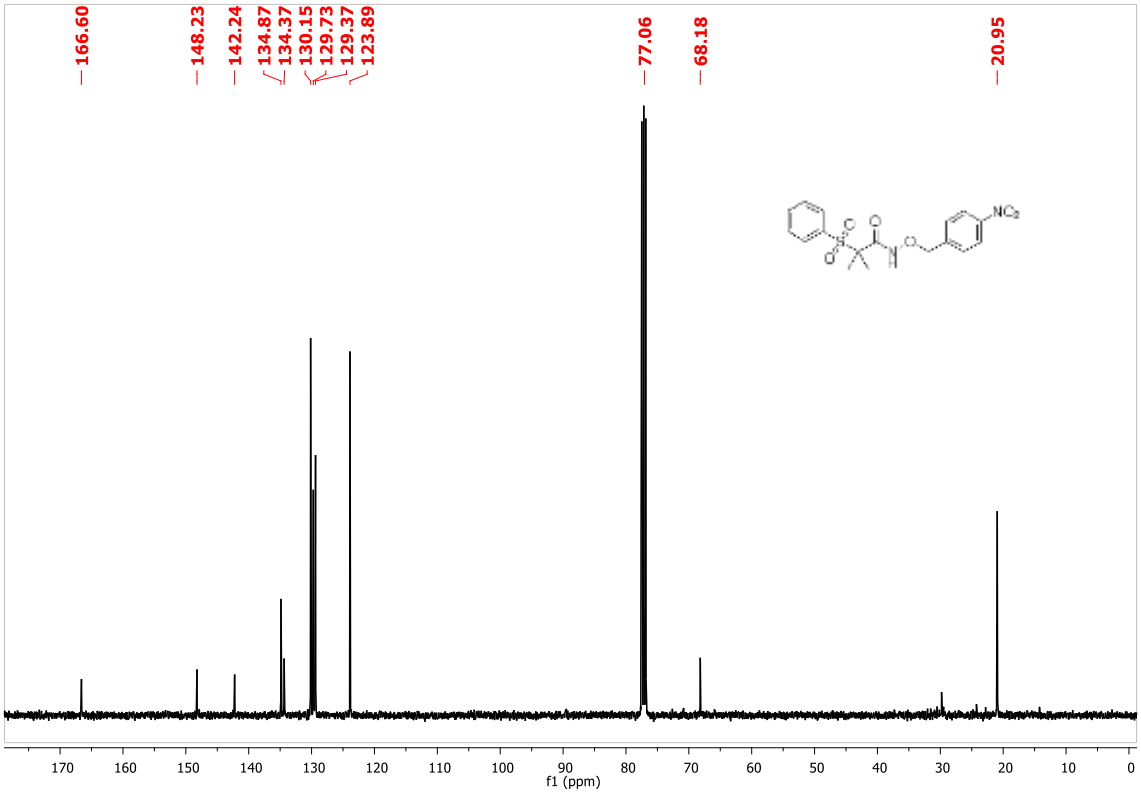

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3l



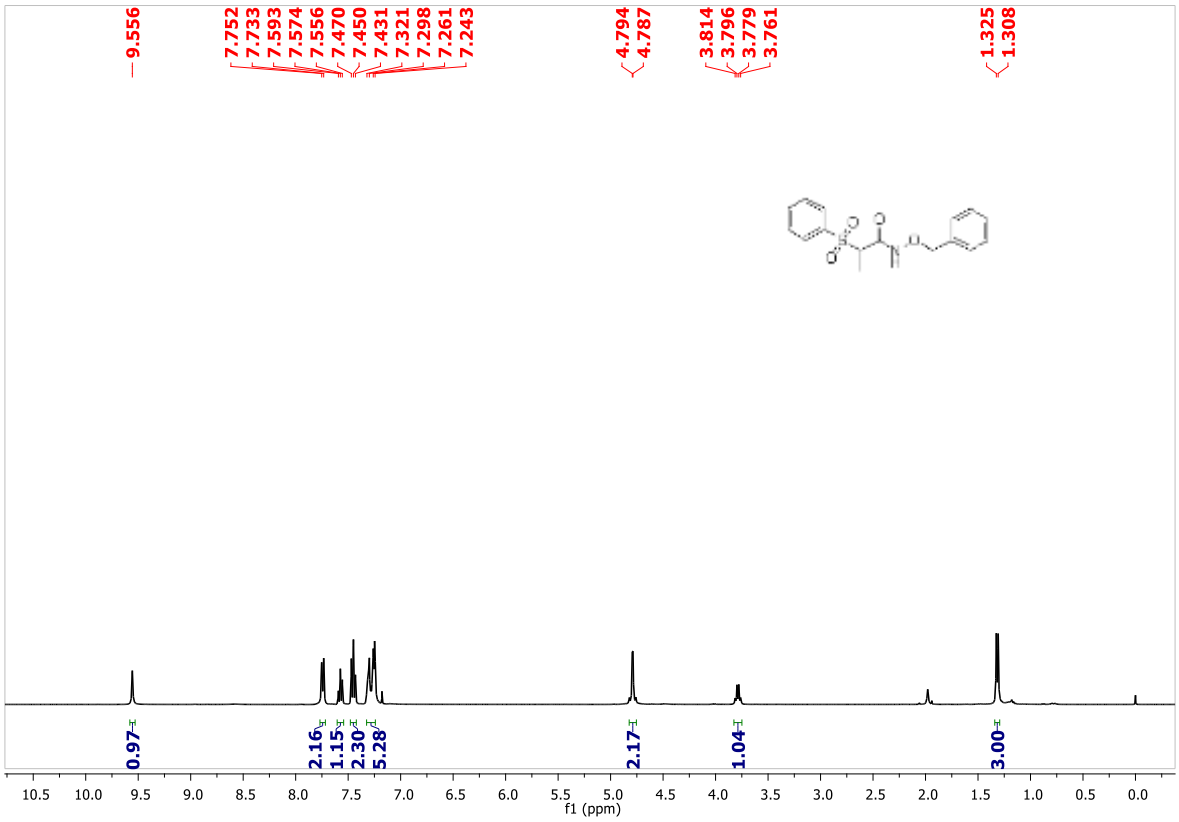
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3m



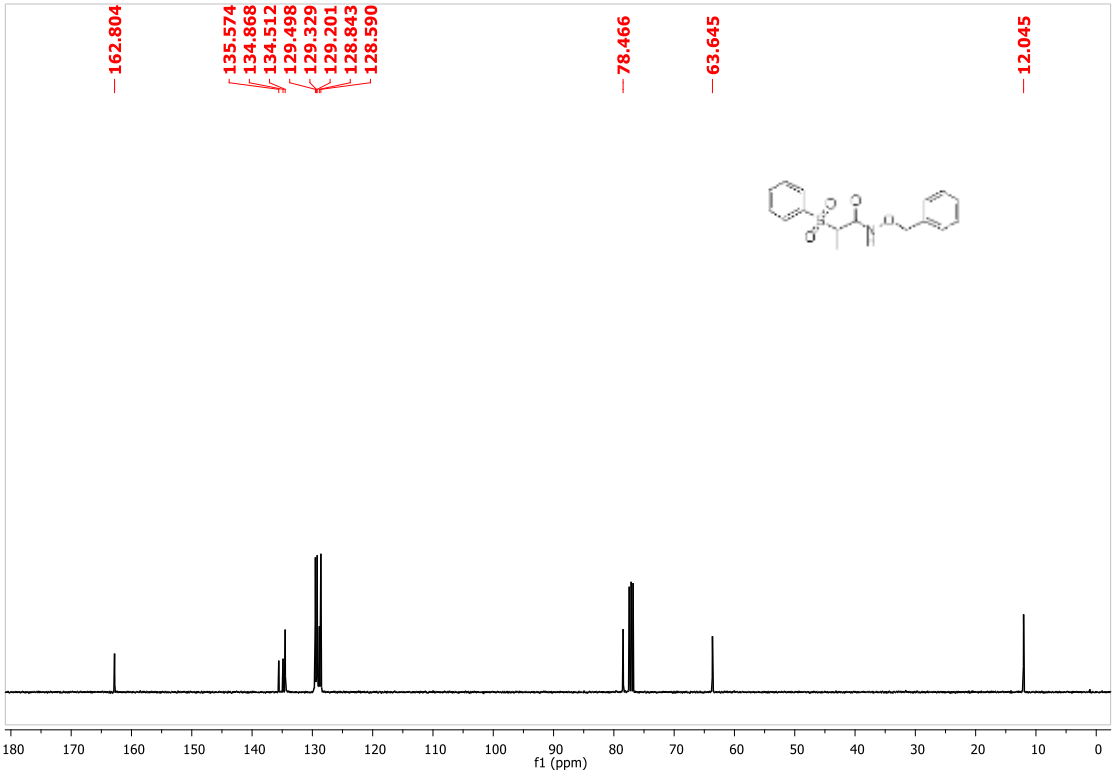

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3m



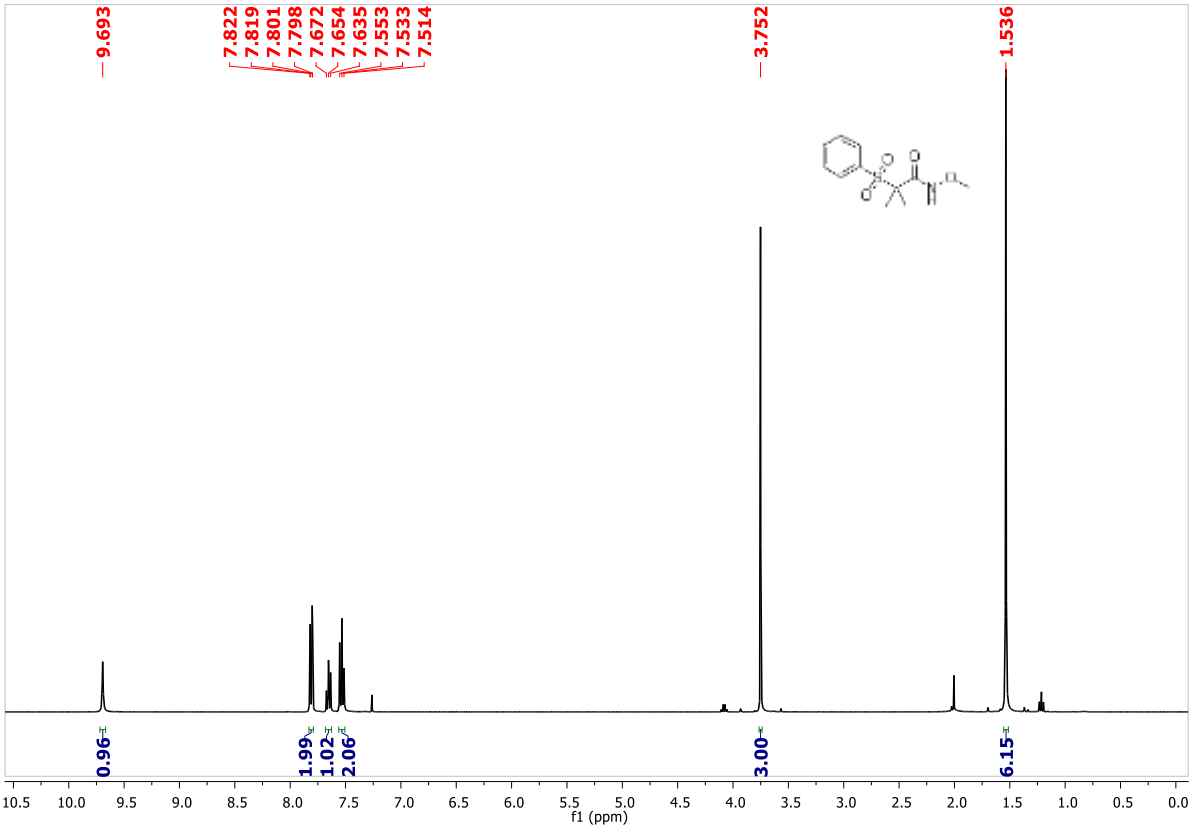
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3n**



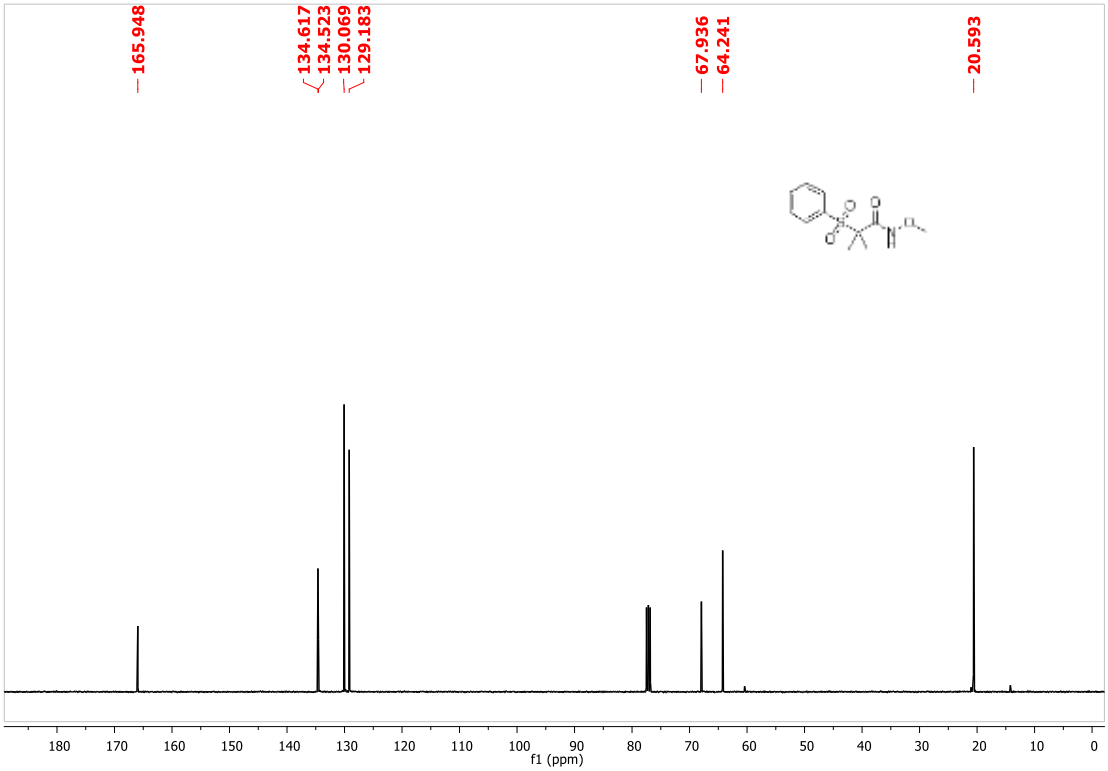

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3n**



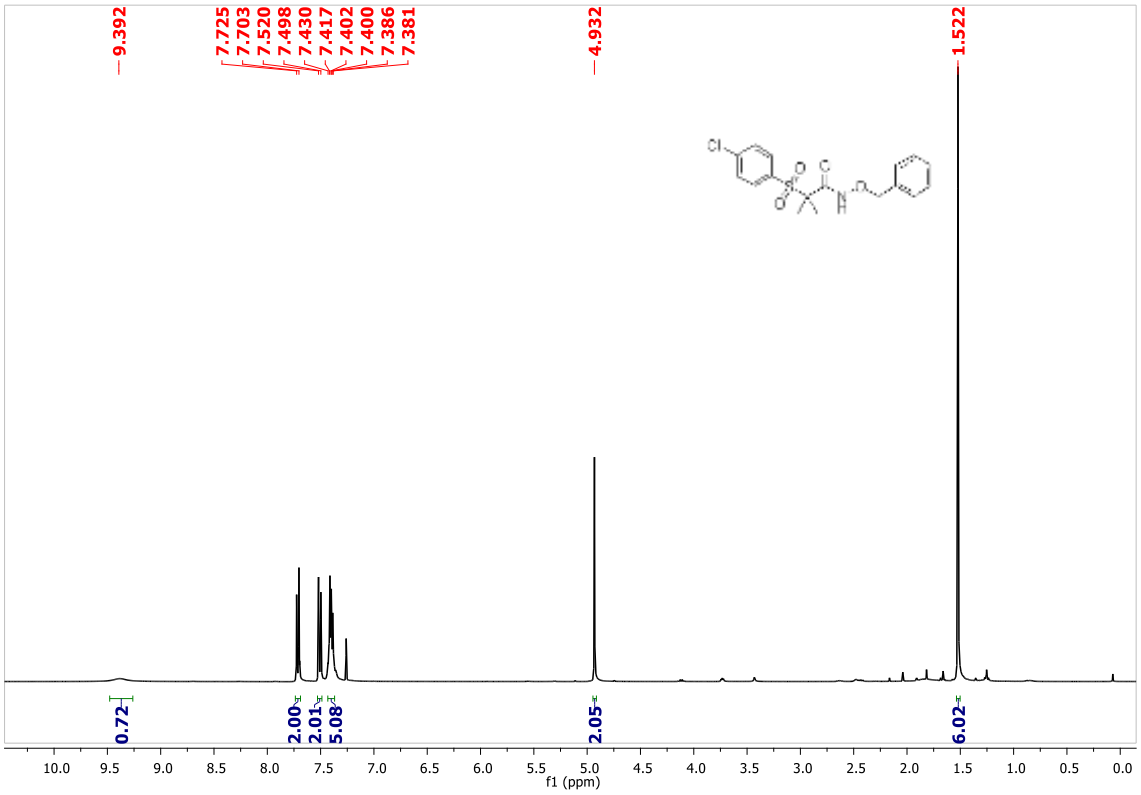
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3o



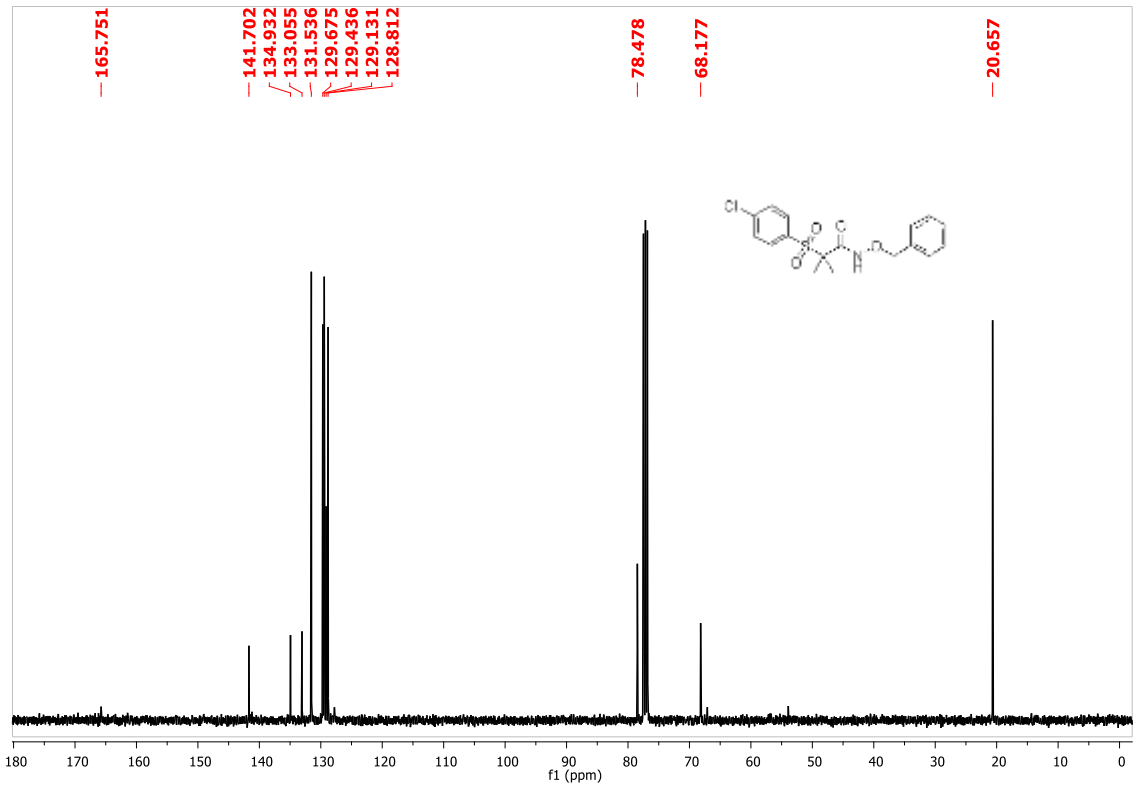

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3o



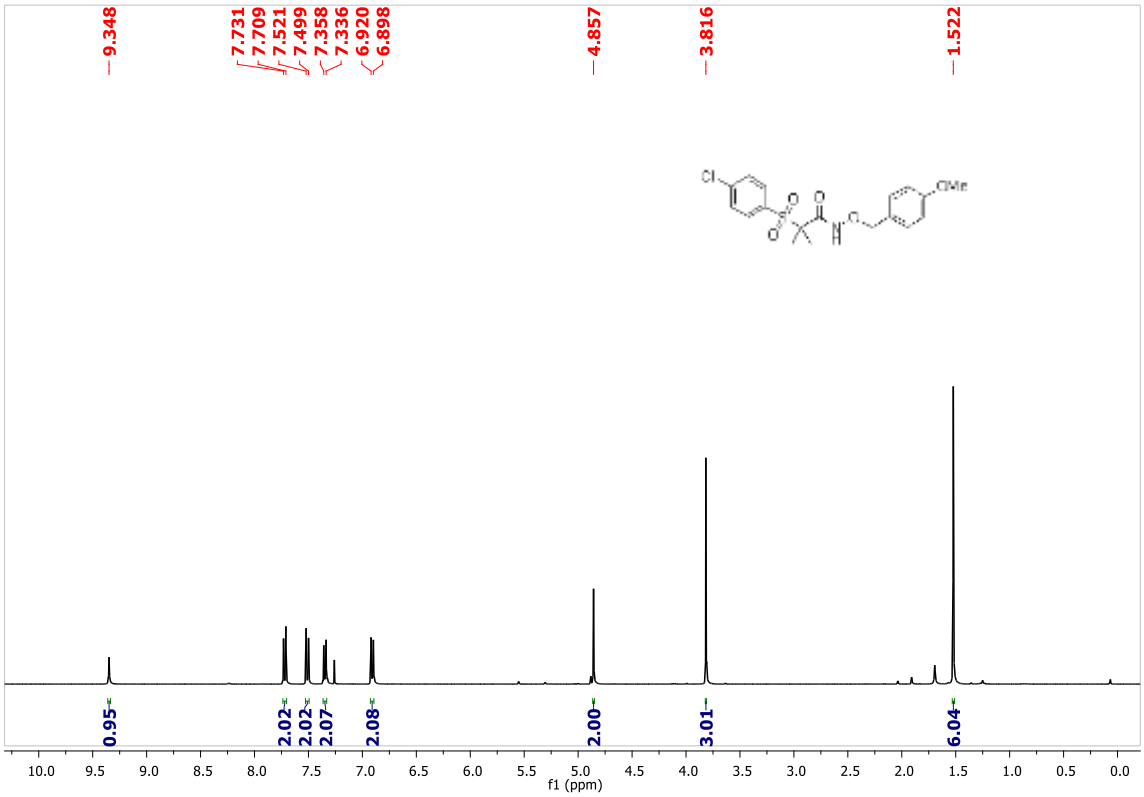
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3p**



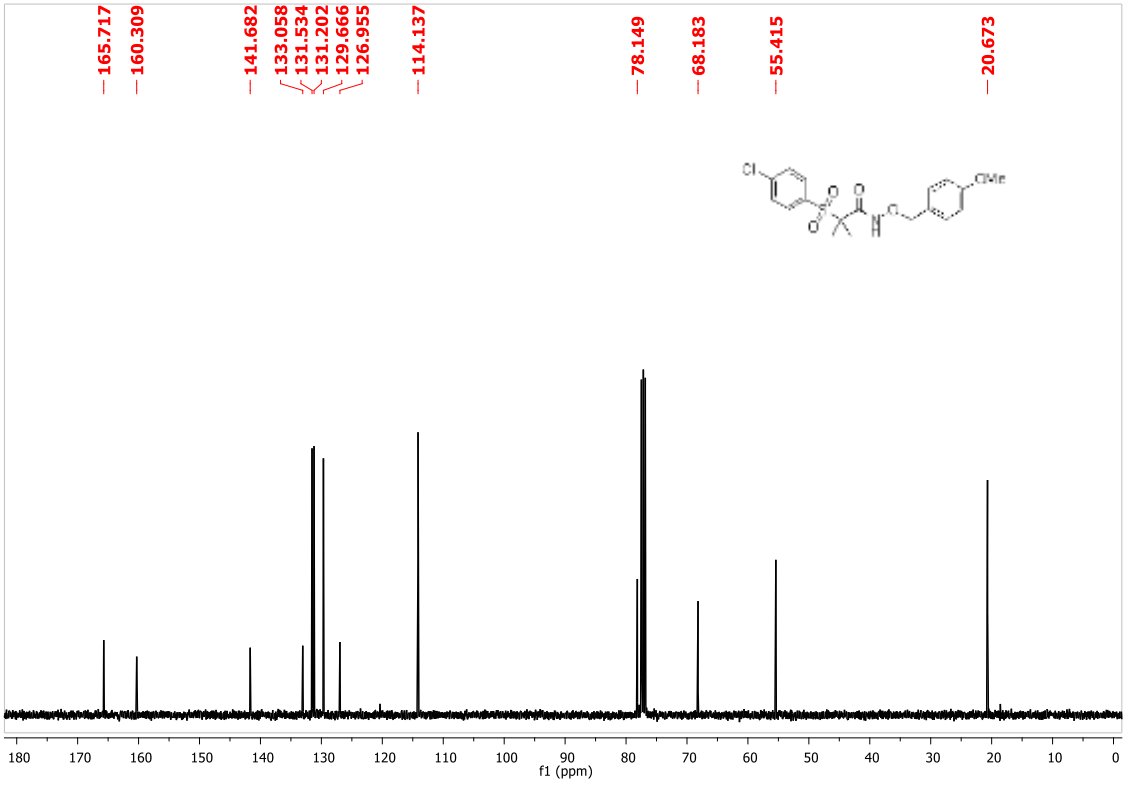

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3p**



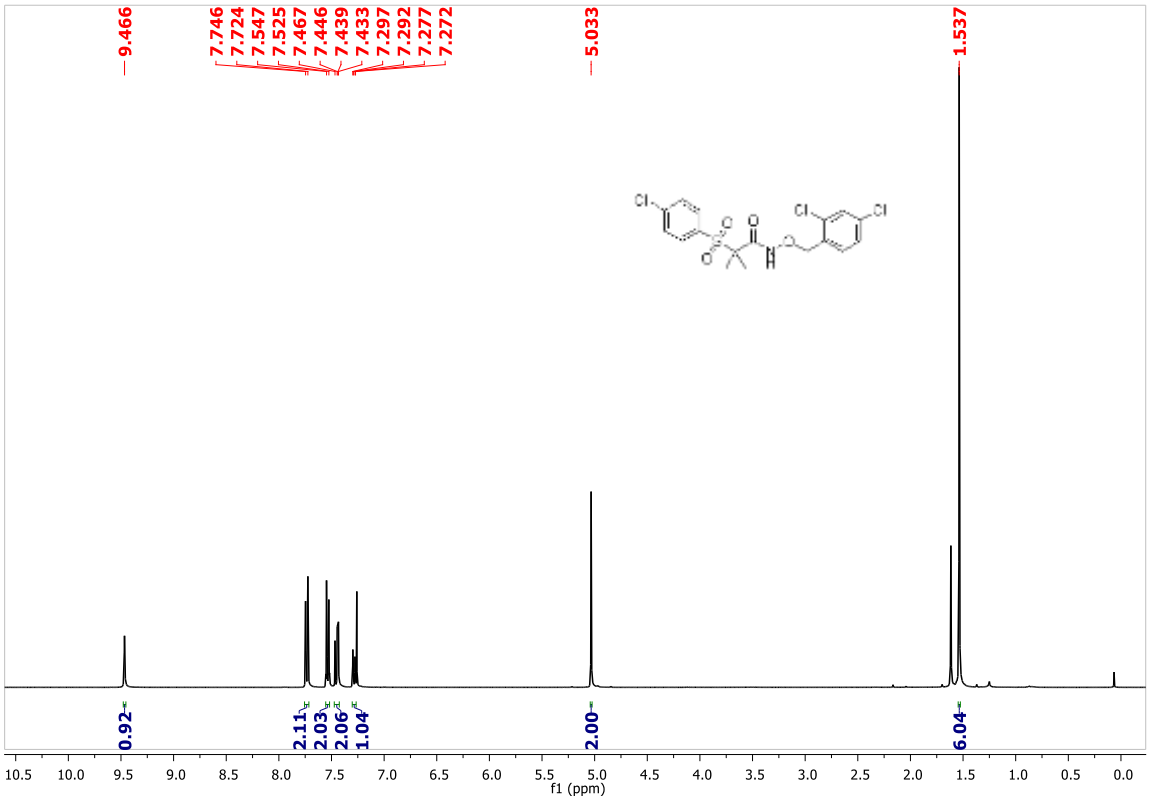
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3q



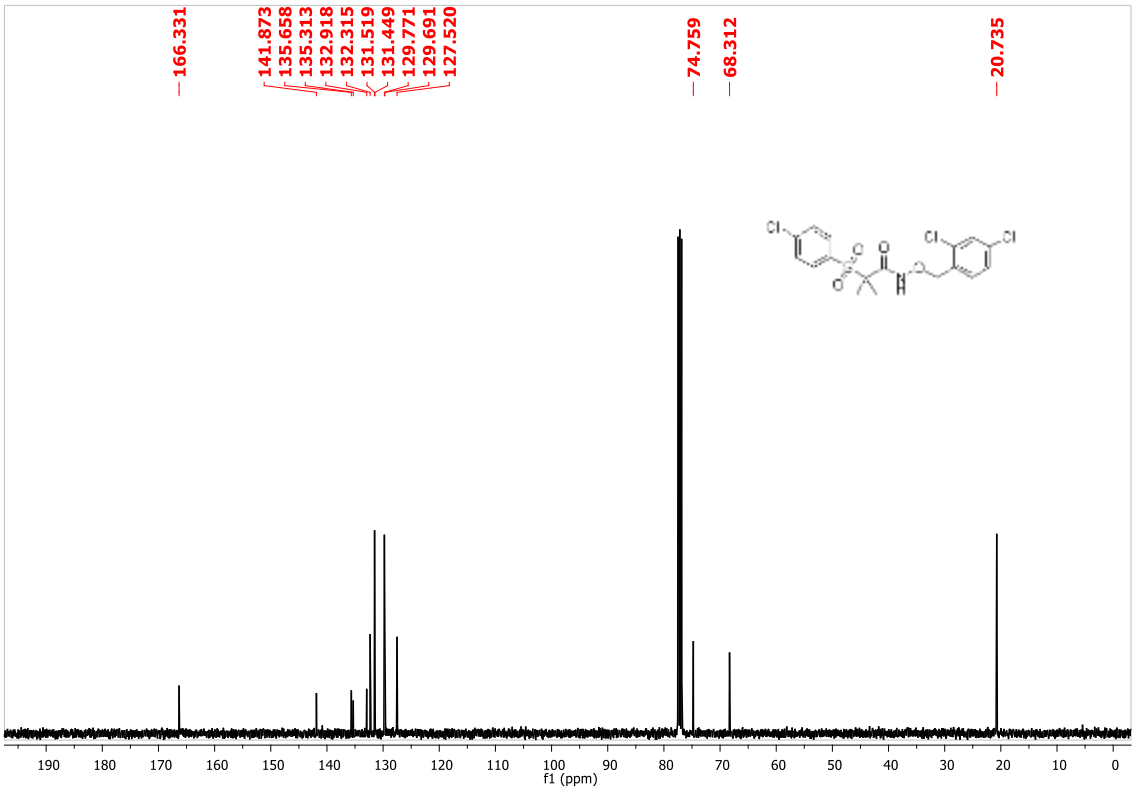

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3q



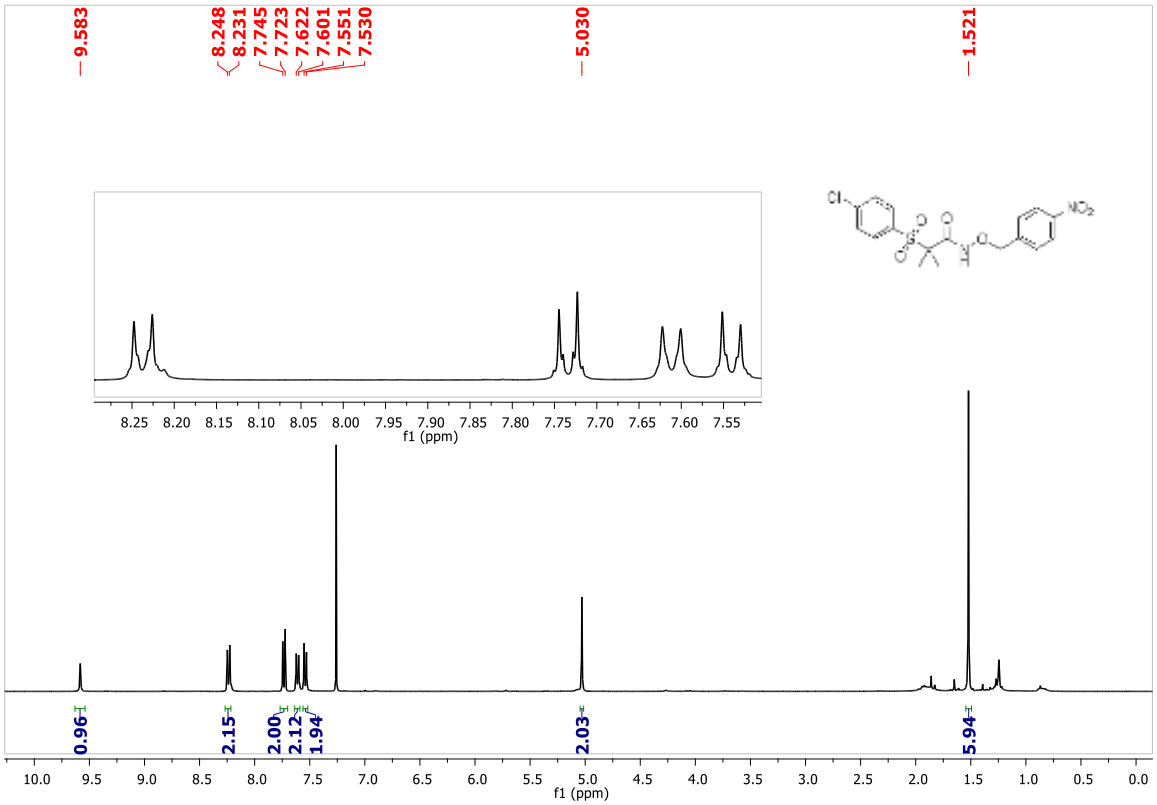
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3r**



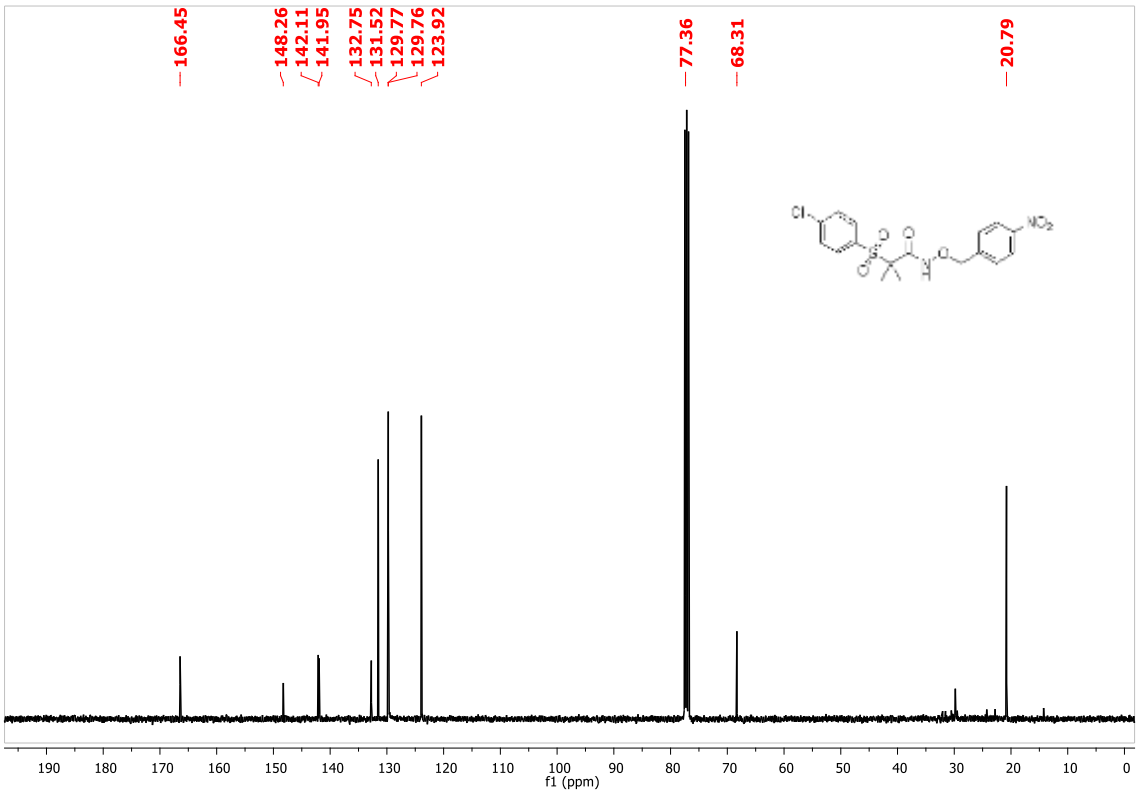

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3r**



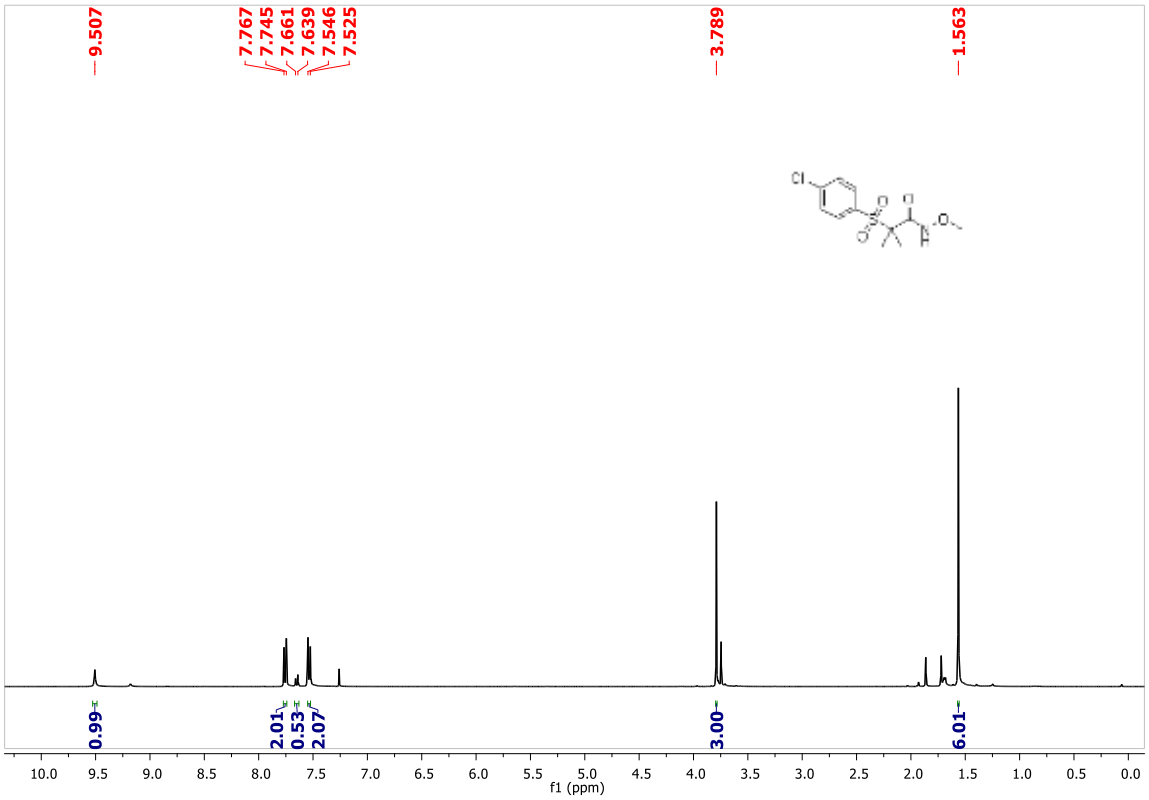
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3s



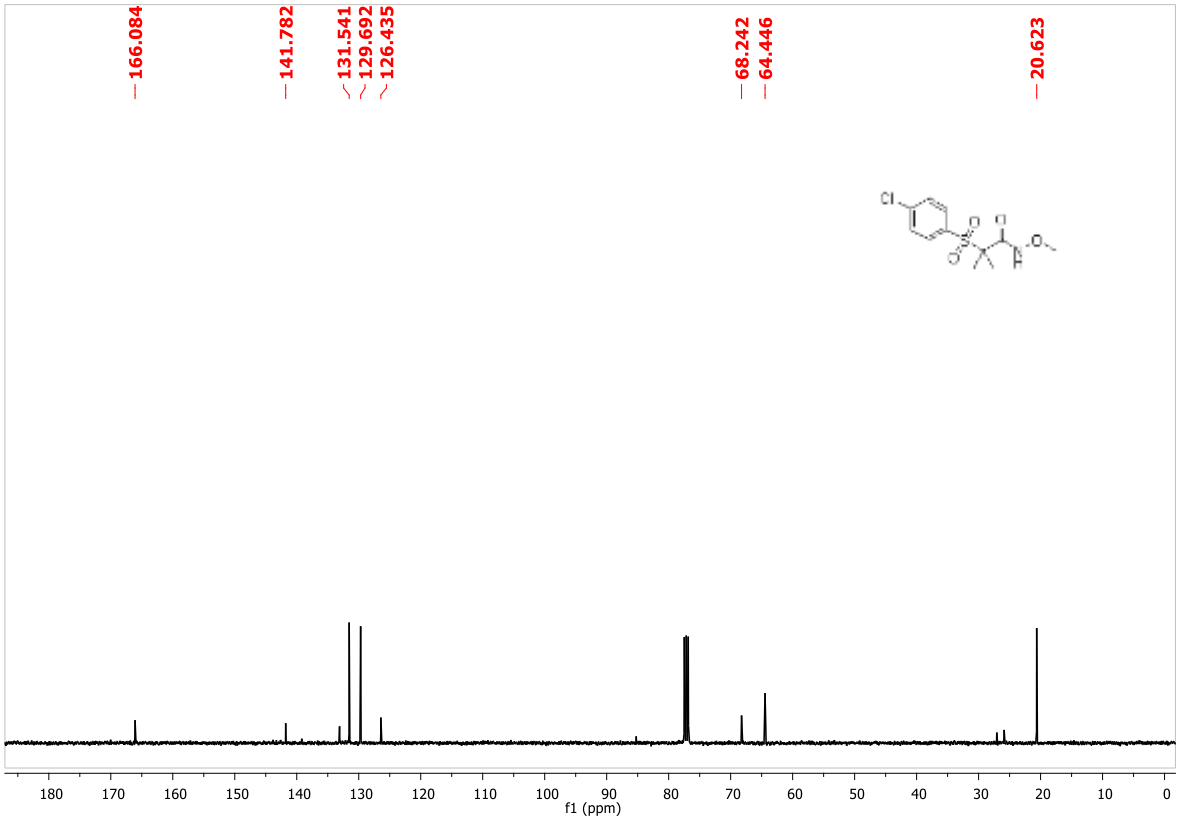

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3s



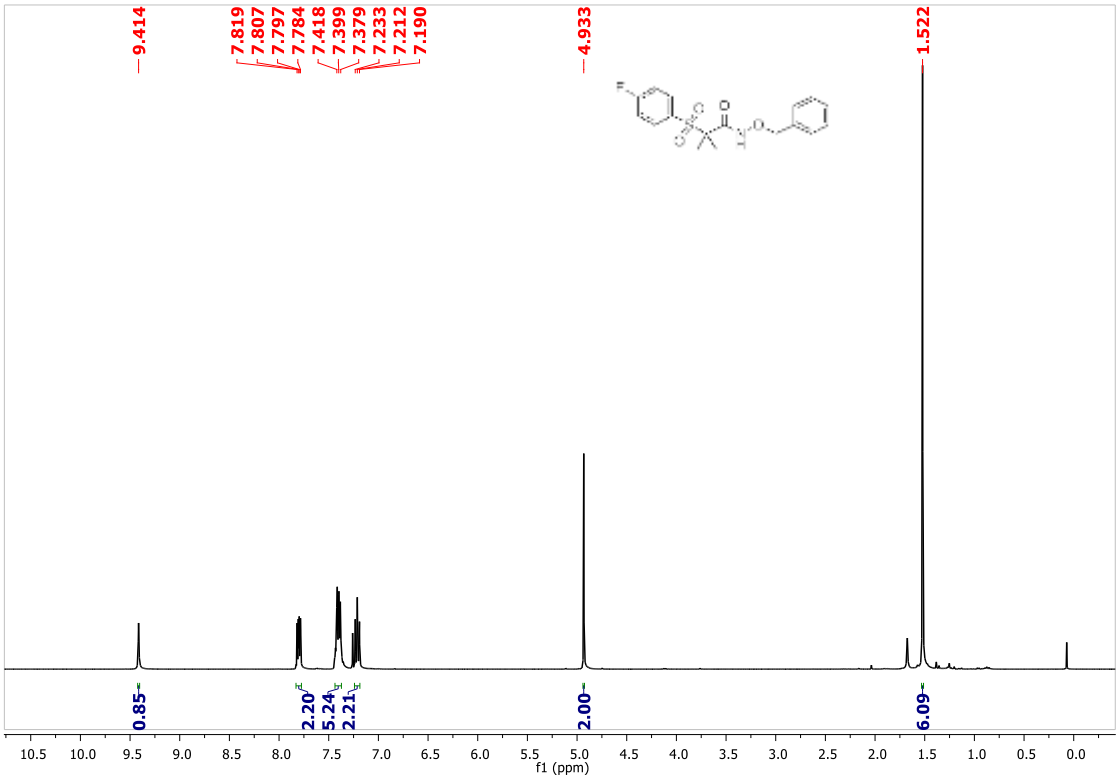
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3t**



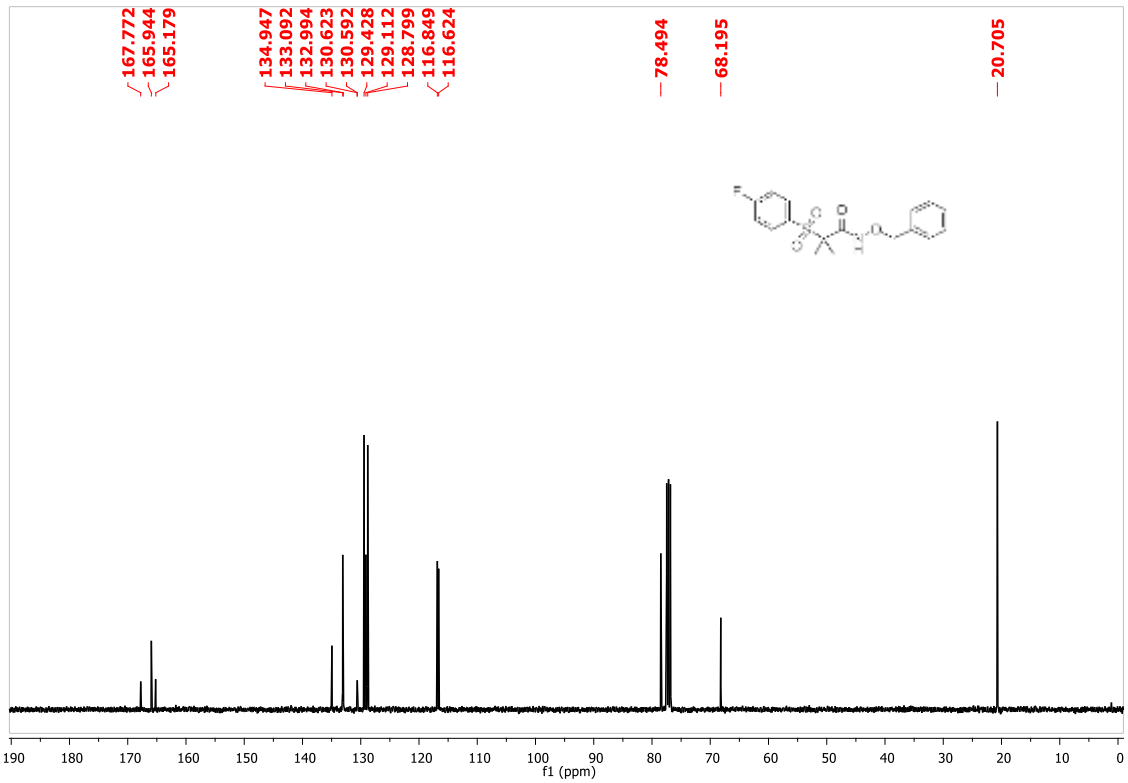

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3t**



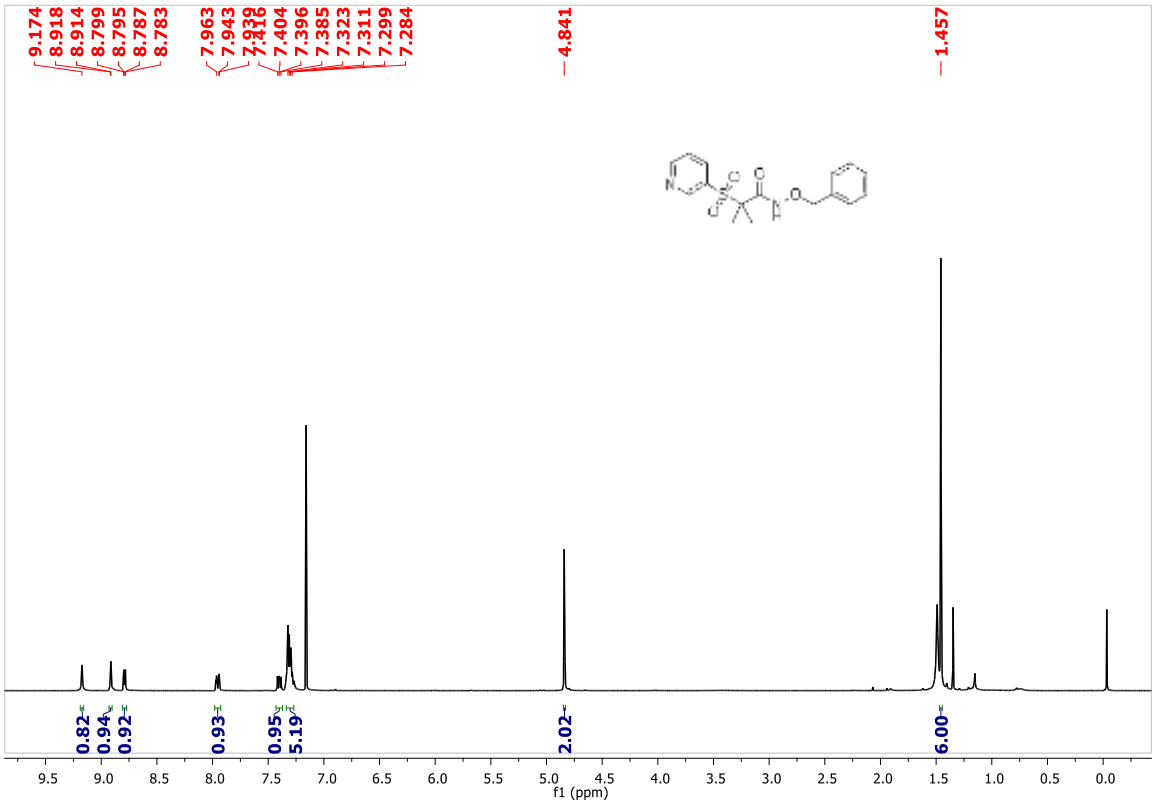
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3u**



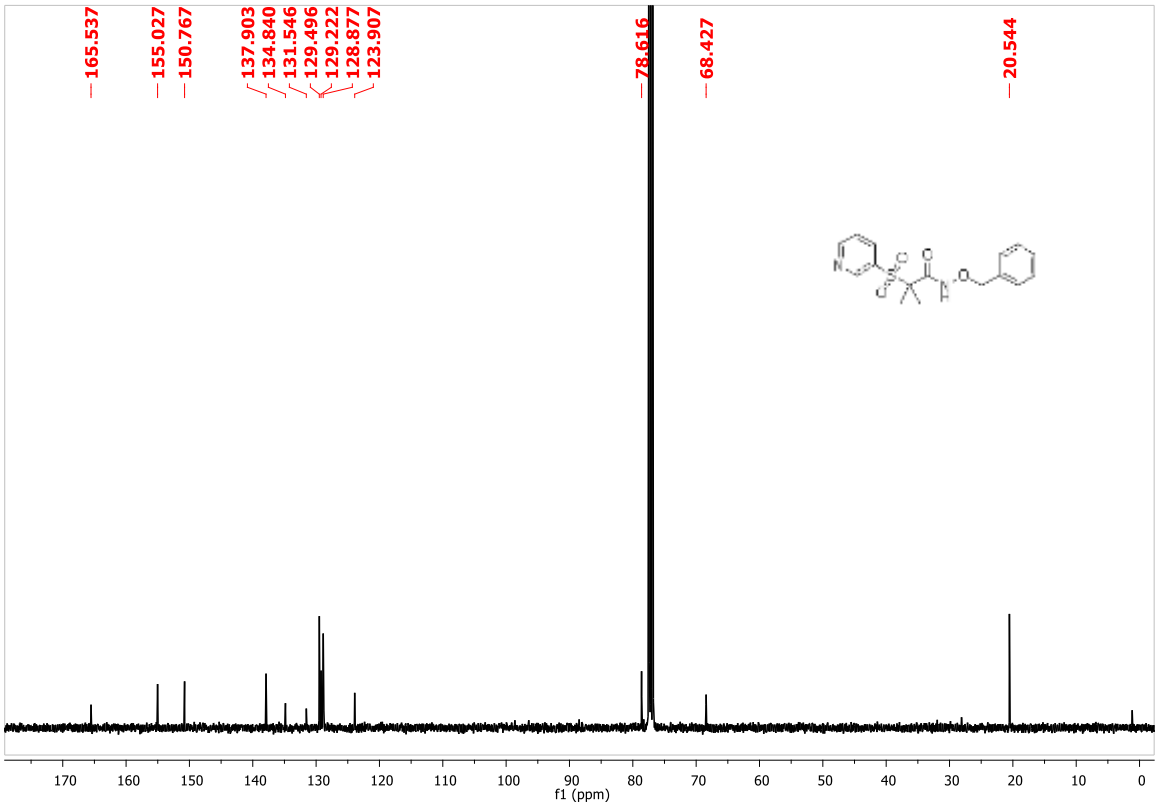

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3u**



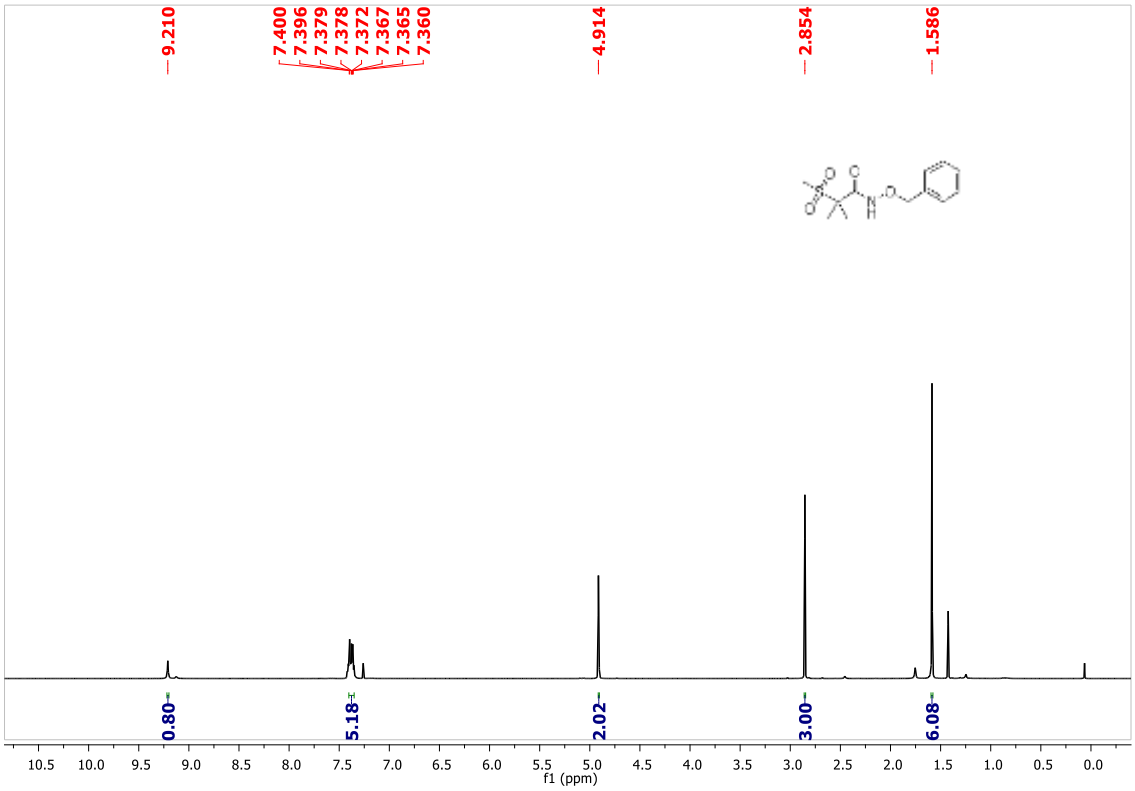
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3v**



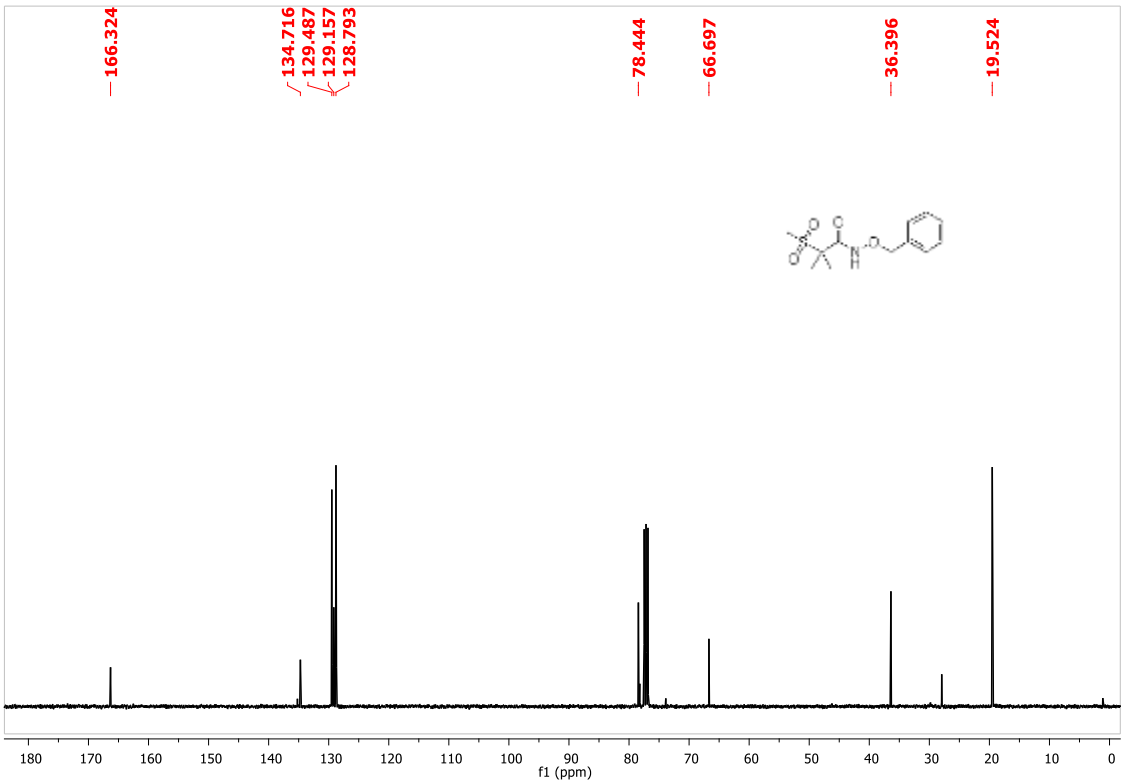

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3v**



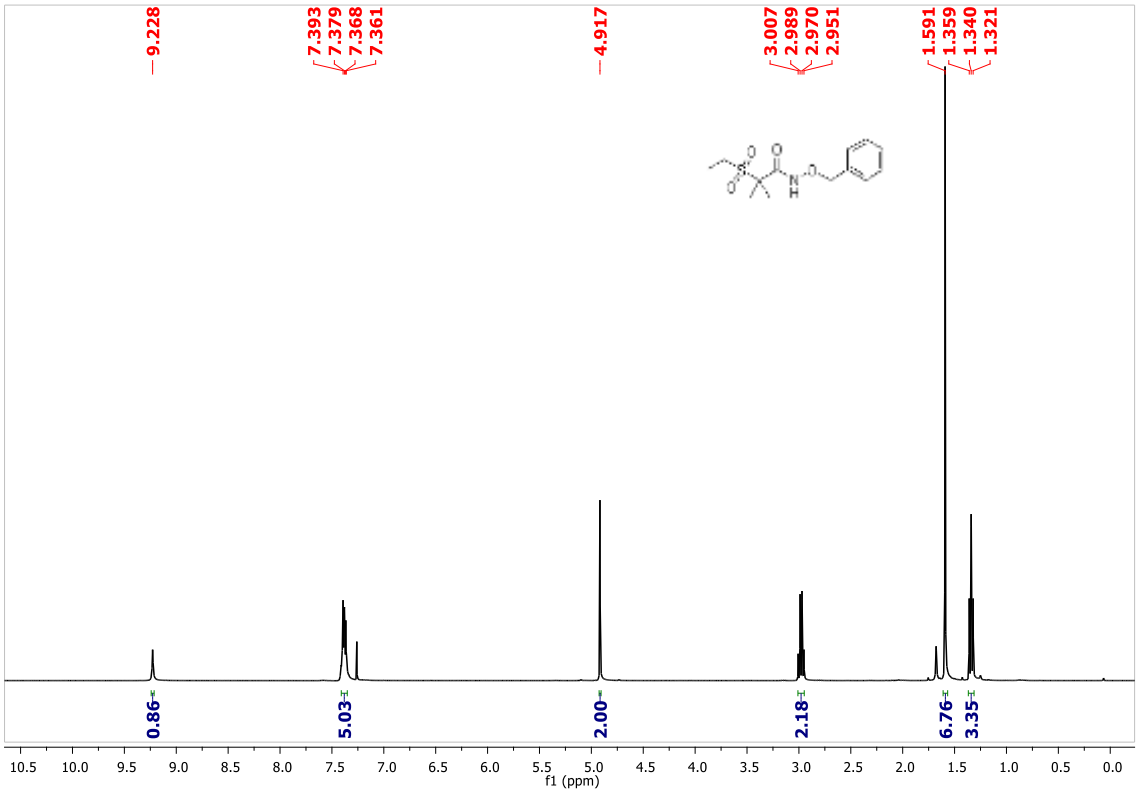
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3w**



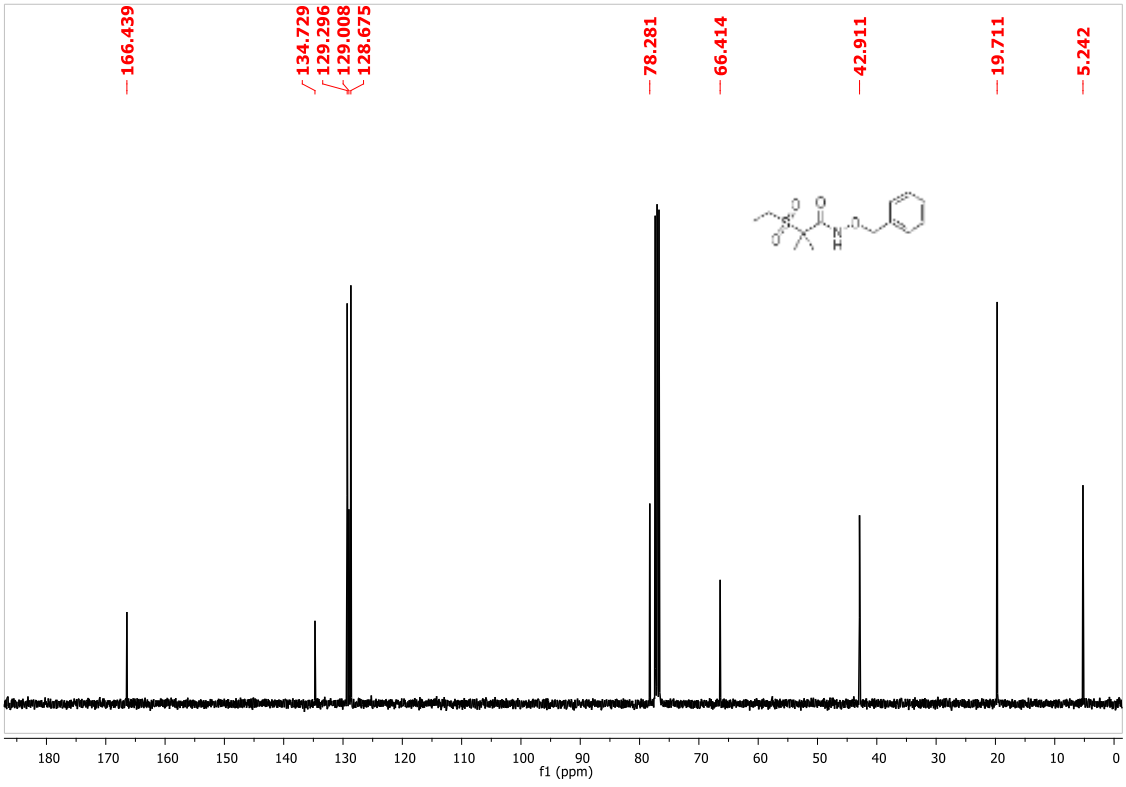

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3w**



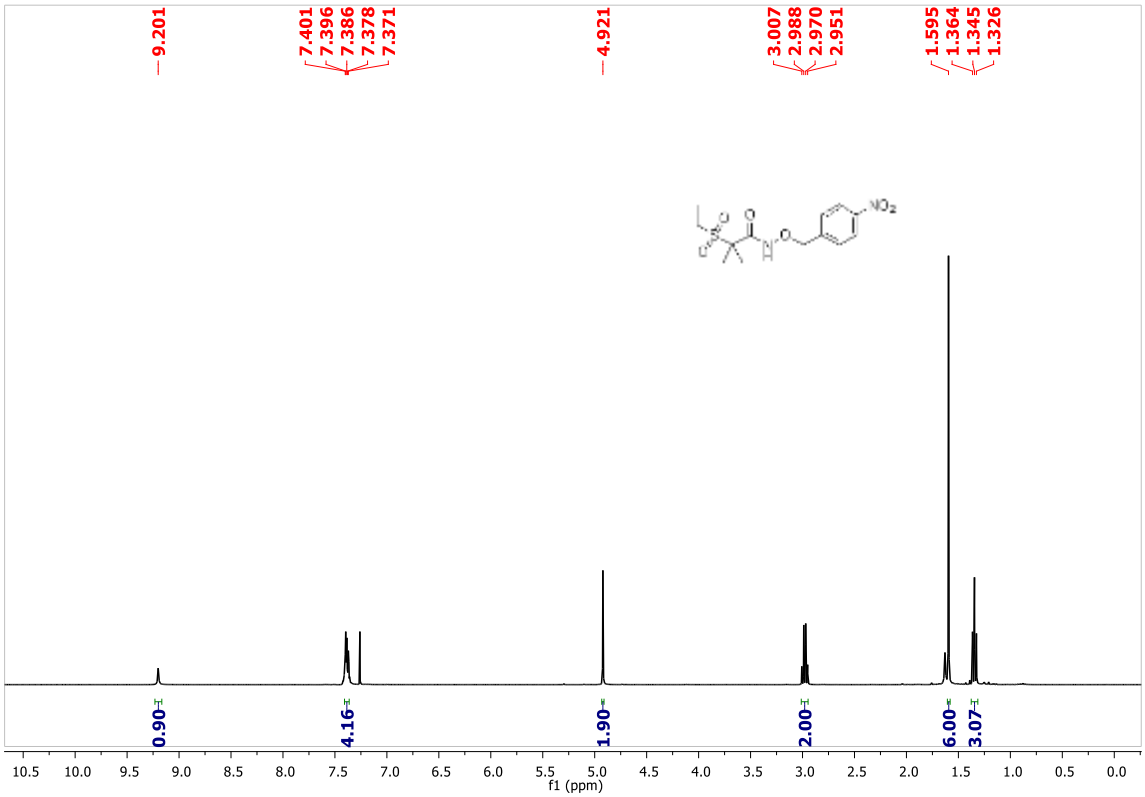
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3x



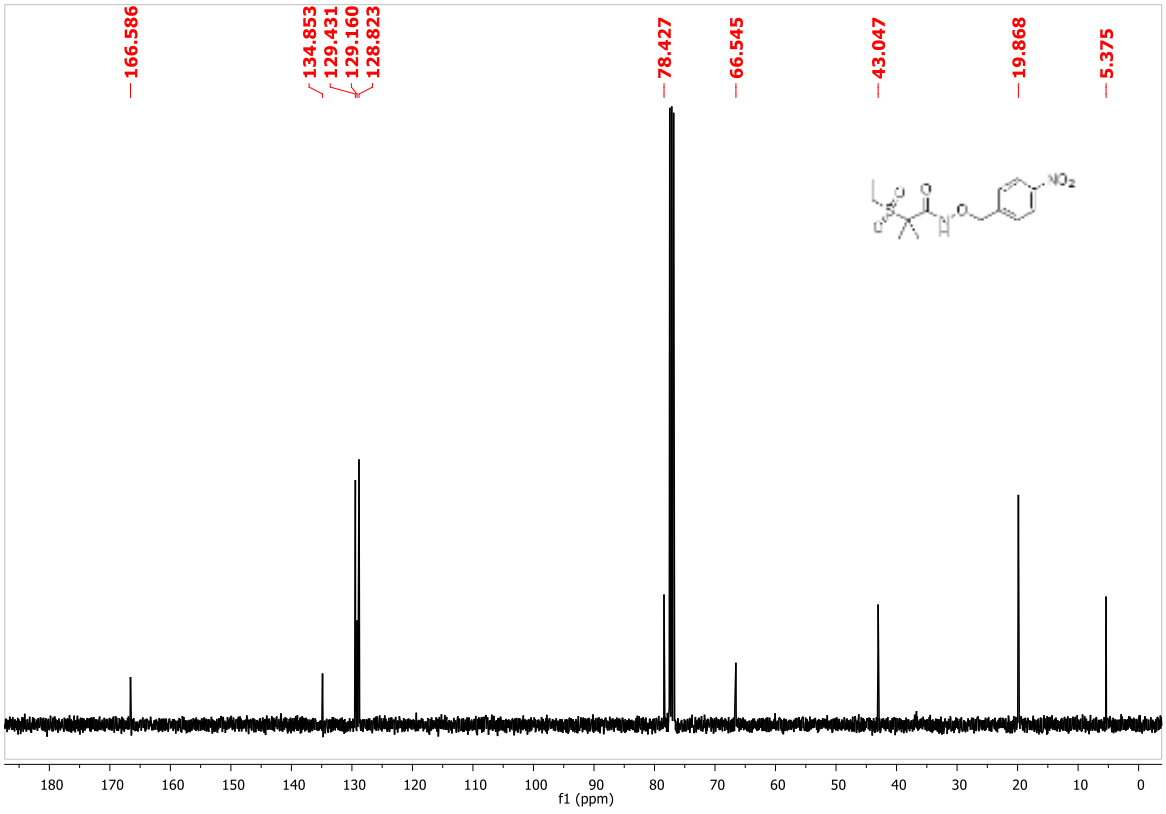

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3x



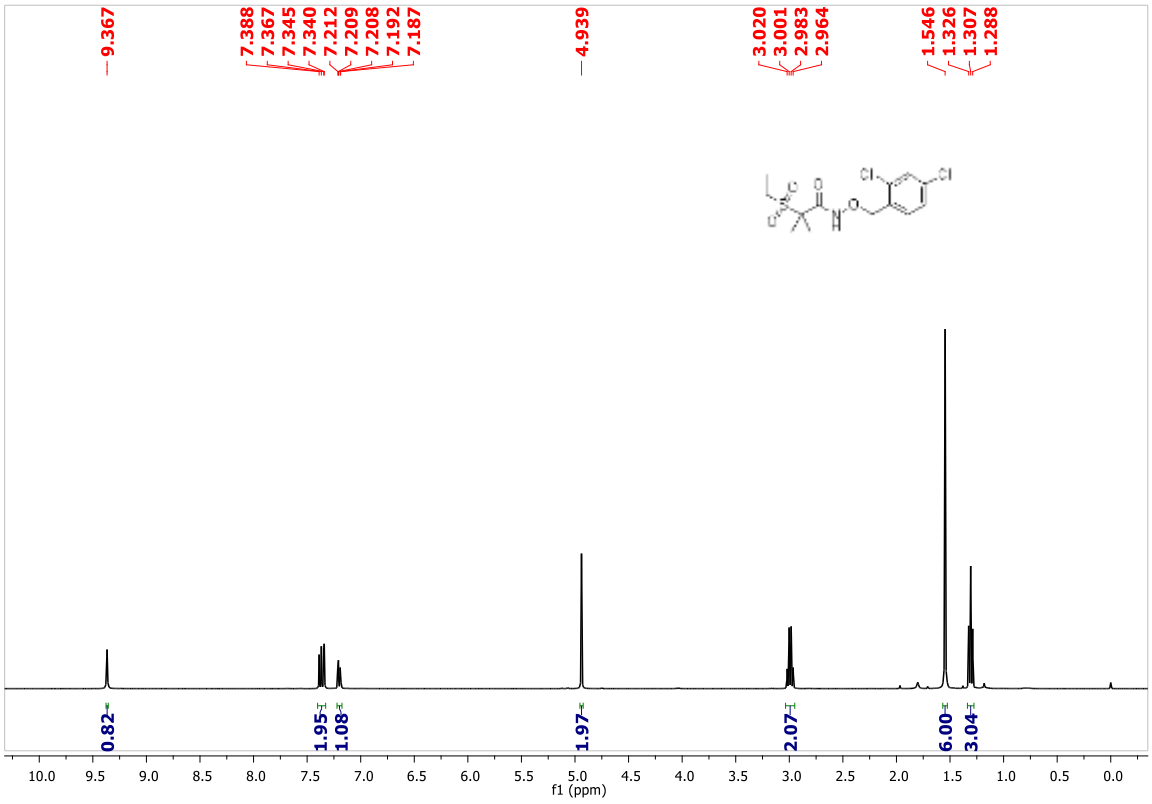
**$^{1}$H NMR (400 MHz, $CDCl_3$) of 3y**



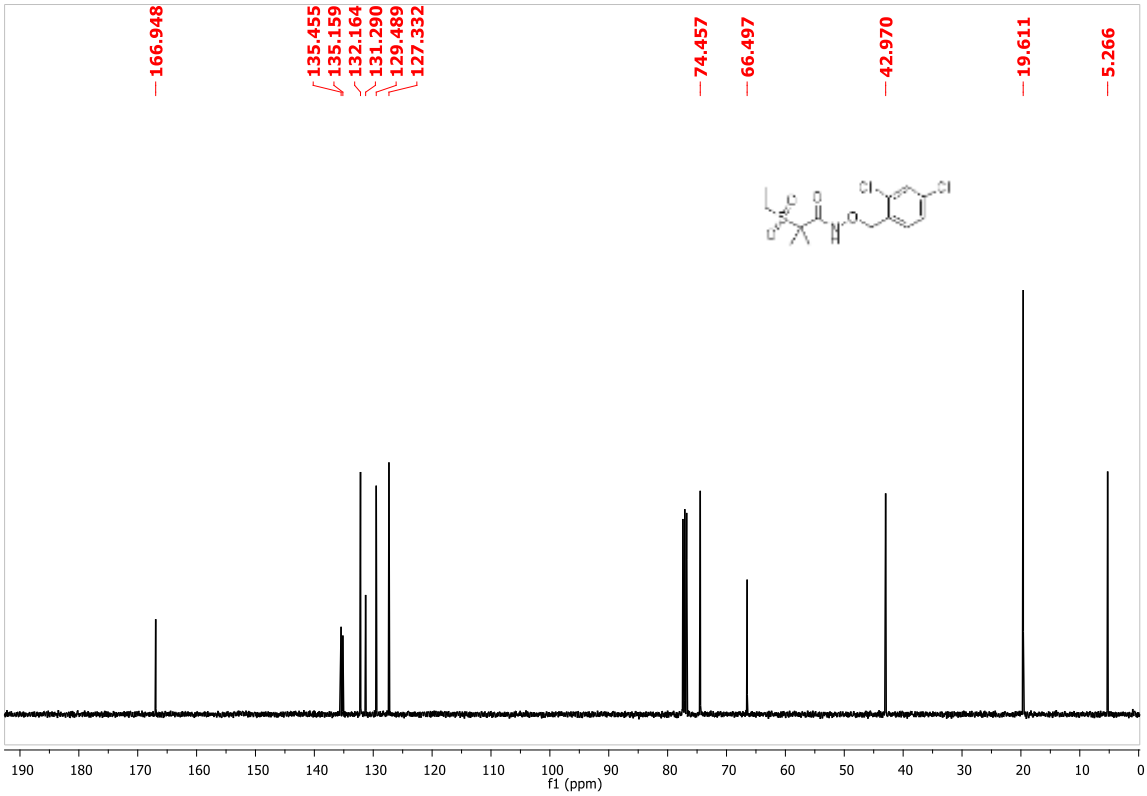

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3y**



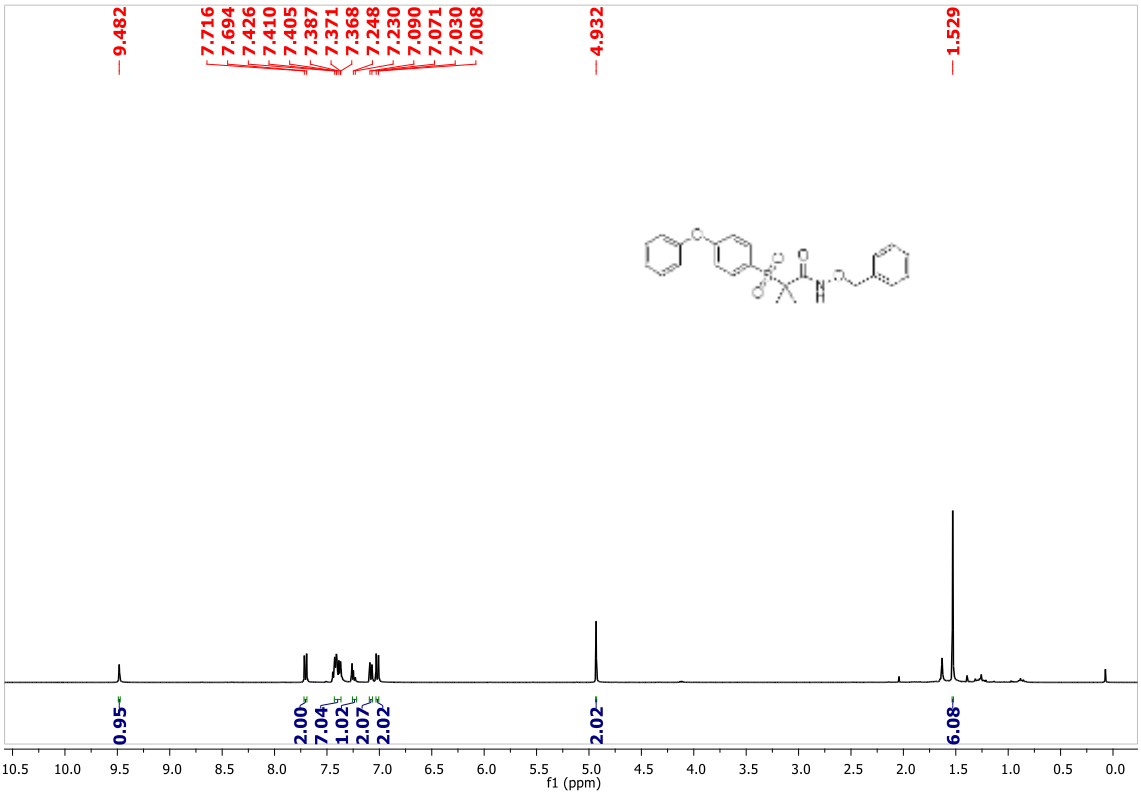
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3z



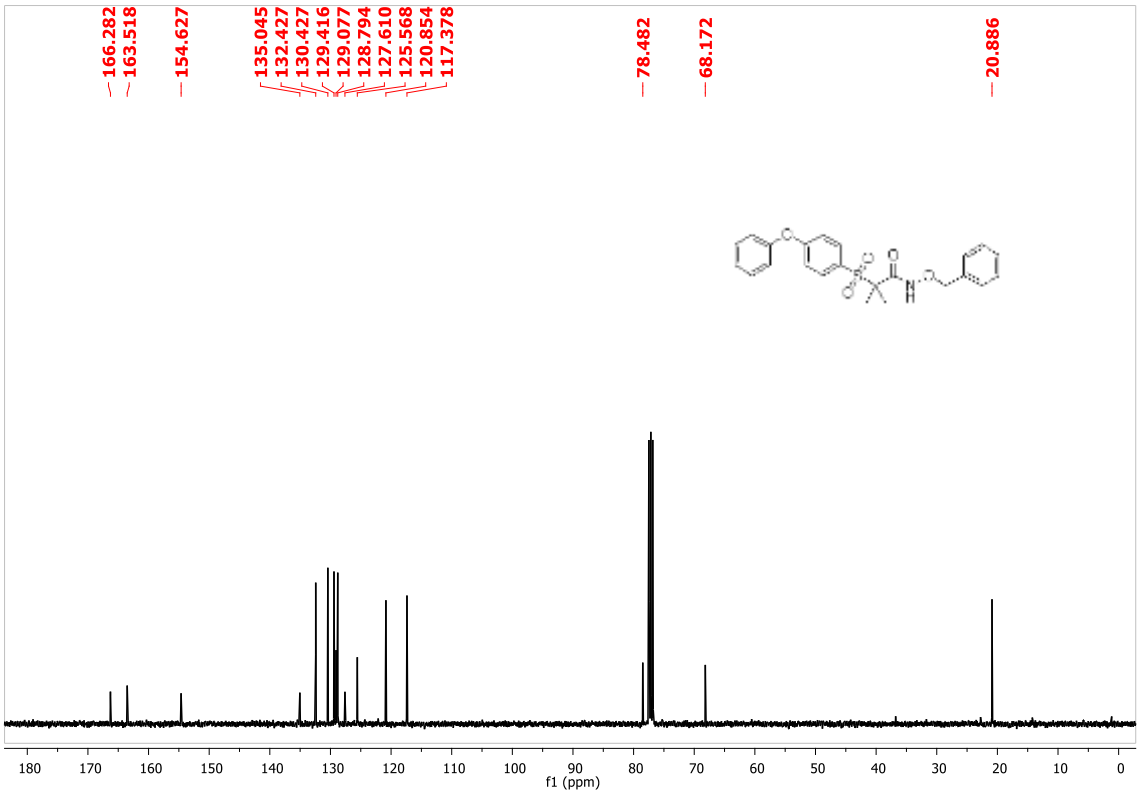

## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 3z



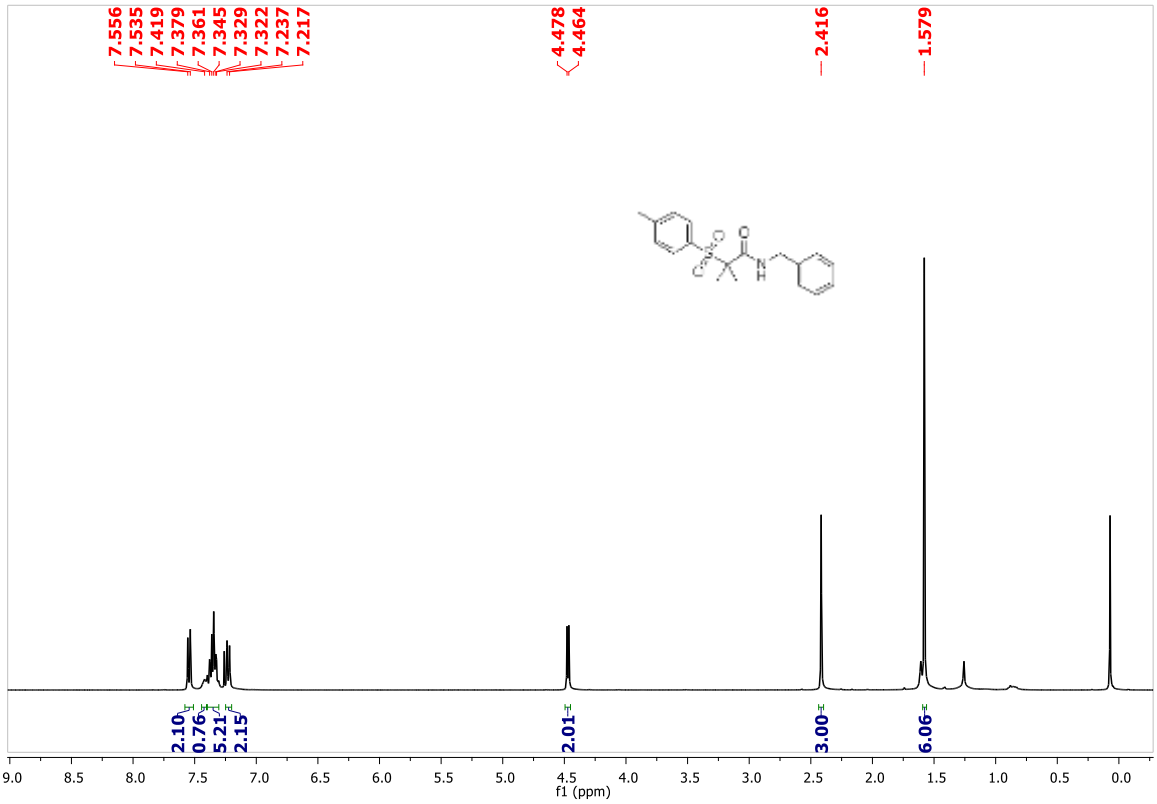
## $^{1}$H NMR (400 MHz, $CDCl_3$) of 3aa




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



## $^{1}$H NMR (400 MHz, $CDCl_3$) of 4a




## $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$) of 4a