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Supporting Information

Visible-Light-Induced Thiol Addition/Aerobic Oxidation Cascade Reactions of Epoxides and Thiols for Synthesis of β-Hydroxylsulfoxides

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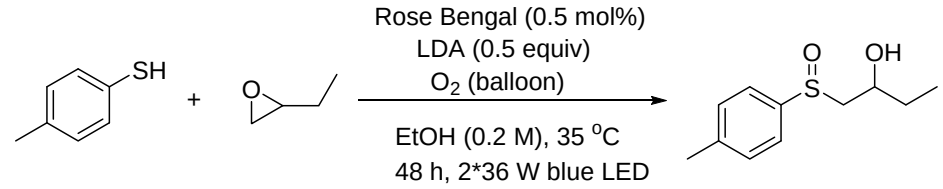
1. General information

Reactions via general procedure were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ or dimethyl sulfoxide-d_6 as solvent. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Stern-Volmer fluorescence quenching was obtained by American PTI corporation QM40 spectrophotometer. All reagents obtained from commercial suppliers were used without further purification.

2. General procedure for the aerobic oxidative coupling

General procedure: 1 (0.2 mmol), **2** (0.4 mmol), LDA (0.5 equiv), Rose Bengal (1 mol%) and EtOH (2.0 mL) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at room temperature under the irradiation by 36 W blue LED for 48 h. The reaction was monitored by TLC. The solvent was evaporated under vacuum, and the crude product was purified using column chromatography with silica gel (200-300 mesh) or thin layer chromatography with silica gel (GF254) to give product **3**.

Gram-scale reaction for the synthesis of 3a. 1a (4.8 mmol, 595.2 mg), **2a** (9.6 mmol, 0.84 mL), LDA (2.4 mmol, 0.3 mL), Rose Bengal (0.5 mol%, 24 mg) and EtOH (24 mL) were added into a 50 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at room temperature under the irradiation by 2*36 W blue LED for 48 h. The reaction was monitored by TLC. After completion, the solvent was evaporated under vacuum, and the crude product was purified using Column chromatography on silica gel (200-300 mesh) to obtain product **3a** in 60% yield (610.6 mg).



1a, 4.8 mmol **2a,** 9.6 mmol **3a**

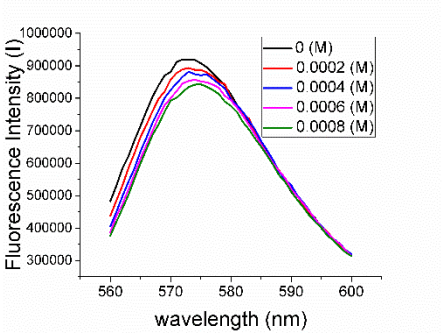
3. Stern-Volmer fluorescence quenching experiments

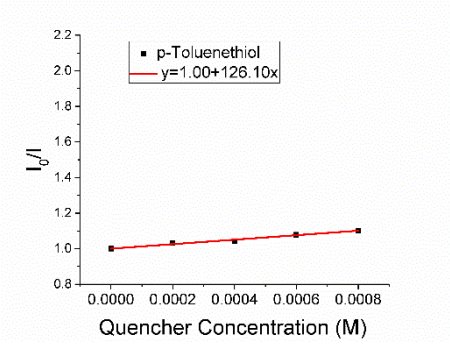
Formulation solution: 1a (6.2 mg) was dissolved in EtOH in a 5 mL volumetric flask to set the concentration to be 0.01 M. 1,2-buteneoxide (22 μL) was dissolved in EtOH in a 25 mL volumetric flask to set the concentration to be 0.01 M. 1-(p-tolylthio)butan-2-ol (9.8 mg) was dissolved in EtOH in a 5 mL volumetric flask to set the concentration to be 0.01 M. LDA (31 μL) was dissolved in EtOH in a 25 mL volumetric flask to set the concentration to be 0.01 M. Dissolve the photocatalyst Rose Bengal (2.5 mg) in EtOH in a 25 mL volumetric flask, shake well, take out 5 mL of the solution and make up to volume with EtOH in a 25 mL volumetric flask, setting the concentration to 0.02 mM.

Experimental procedure: The resulting 0.02 mM solution (20 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding EtOH to prepare a 0.2 μM solution. 40.0 μL of a 4-methylbenzenethiol solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 521 nm. Fluorescence emission spectra of 0 μL, 40.0 μL, 80.0 μL, 120.0 μL, 160.0 μL fluorescence intensity was recorded. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The solution was excited at λ= 521 nm.

We performed another Stern–Volmer fluorescence quenching experiment to investigate the influence of oxygen. In a typical experiment, 2.0 mL of solution of Rose Bengal in EtOH was bubbled with a stream of oxygen for several seconds. The solution was excited at λ= 521 nm.

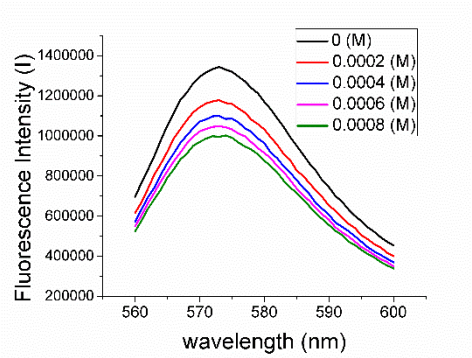
(a) Rose Bengal quenched by 4-methylbenzenethiol in EtOH.

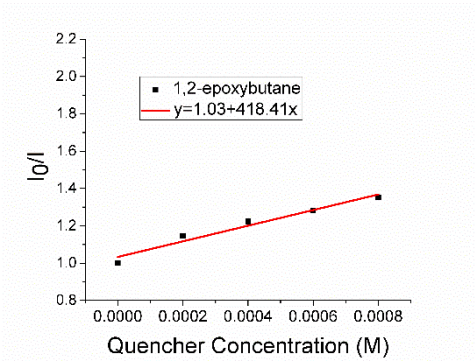




The emission intensity of the Rose Bengal catalyst solution affected by the gradual increase of the amount of 4-methylbenzenethiol.

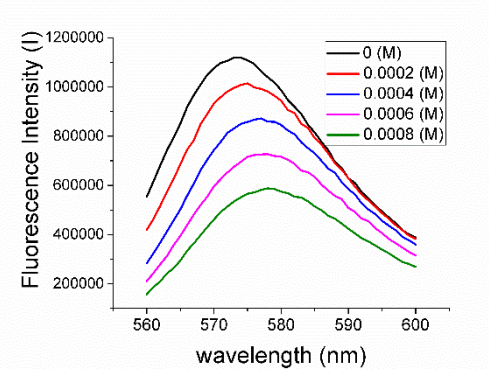
(b) Rose Bengal quenched by 1,2-buteneoxide in EtOH.

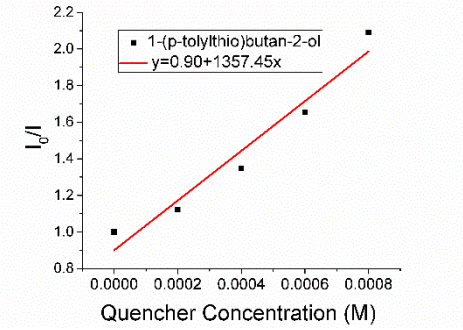




The emission intensity of the Rose Bengal catalyst solution affected by the gradual increase of the amount of 1,2-buteneoxide.

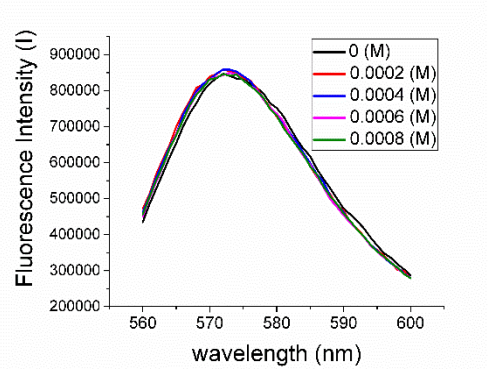
(c) Rose Bengal quenched by 1-(p-tolylthio)butan-2-ol in EtOH.

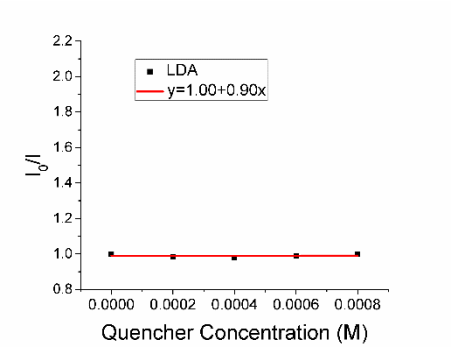




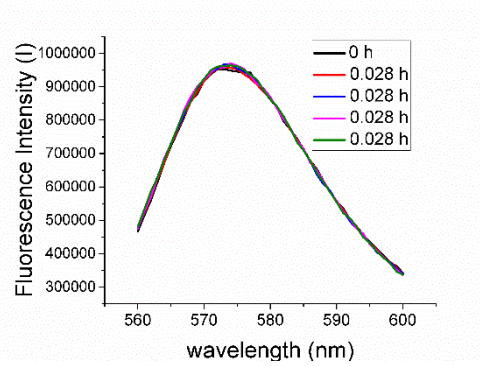
The emission intensity of the Rose Bengal catalyst solution affected by the gradual increase of the amount of 1-(p-tolylthio)butan-2-ol.

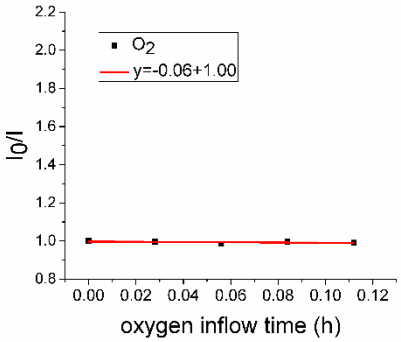
(d) Rose Bengal quenched by LDA in EtOH. Linear quenching is not observed.



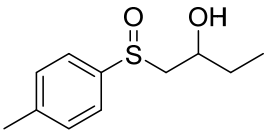


(e) Rose Bengal quenched by O_2 in EtOH. Linear quenching is not observed.





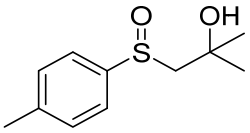
4. Characterization data of products



1-(p-tolylsulfinyl)butan-2-ol (3a)

3a was obtained as colorless liquid in 80% yield (33.9 mg), using EA /PE (1:1) as eluent (dr = 58:42).

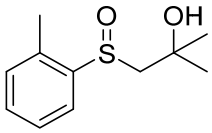
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.46 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.27 (brs, 0.58H), 4.13 – 4.08 (m, 1H), 3.99 (brs, 0.42H), 2.99 – 2.89 (m, 1H), 2.79 – 2.64 (m,1H), 2.39 (s, 3H), 1.61 – 1.49 (m, 2H), 0.97 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 141.9, 141.4, 140.4, 139.7, 130.1, 130.0, 124.0, 123.9, 69.7, 67.4, 62.5, 62.1, 30.0, 30.0, 21.4, 21.3, 9.5, 9.4. HRMS (ESI) m/z calcd for $C_{11}H_{16}NaO_2S^+$ $(M+Na)^+$ 235.0763, found 235.0769.



2-methyl-1-(p-tolylsulfinyl)propan-2-ol (3b)

3b was obtained as white solid (mp: 120-122 ^{o}C) in 72% yield (30.5 mg), using EA /PE (1:1) as eluent.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.20 (brs, 1H), 2.99 (d, *J* = 13.4 Hz, 1H), 2.70 (d, *J* = 13.3 Hz, 1H), 2.37 (s, 3H), 1.55 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 141.7, 140.5, 130.0, 123.8, 70.5, 68.6, 30.2, 28.9, 21.3. HRMS (ESI) m/z calcd for $C_{11}H_{16}NaO_2S^+$ $(M+Na)^+$ 235.0763, found 235.0776.

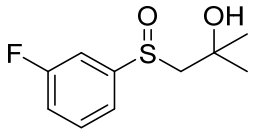


2-methyl-1-(o-tolylsulfinyl)propan-2-ol (3c)

3c was obtained as white solid (mp: 108-110 ^{o}C) in 68% yield (28.8 mg), using EA /PE (1:1) as eluent.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 4.12 (brs, 1H), 2.87 (d, *J* = 13.5 Hz, 1H), 2.77 (d, *J* = 13.4 Hz, 1H), 2.34 (s, 3H), 1.59 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.0,

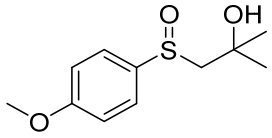
133.9, 130.9, 130.7, 127.5, 123.7, 70.7, 66.5, 30.4, 28.80, 18.1. HRMS (ESI) m/z calcd for $C_{11}H_{16}NaO_2S^+$ $(M+Na)^+$ 235.0763, found 235.0757.



1-((3-fluorophenyl)sulfinyl)butan-2-ol (3d)

3d was obtained as colorless liquid in 55% yield (23.8 mg), using EA /PE (1:1) as eluent.

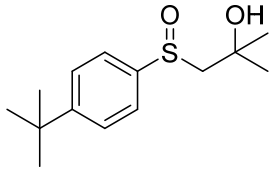
1H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.47 (m, 1H), 7.43 – 7.36 (m, 2H), 7.21 – 7.15 (m, 1H), 3.02 (d, *J* = 13.3 Hz, 1H), 2.78 (d, *J* = 13.3 Hz, 1H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 163.1 (d, *J* = 250.7Hz), 146.5 (d, *J* = 5.6 Hz), 131.1 (d, *J* = 7.9 Hz), 119.4 (d, *J* = 3.0 Hz), 118.3 (d, *J* = 21.3 Hz), 111.2 (d, *J* = 23.9 Hz), 70.7, 68.7, 30.3, 29.0. HRMS (ESI) m/z calcd for $C_{10}H_{13}FNaO_2S^+$ $(M+Na)^+$ 239.0512, found 239.0526.



1-((3-methoxyphenyl)sulfinyl)propan-2-ol (3e)

3e was obtained as colorless liquid in 65% yield (29.5 mg), using EA /PE (1:1) as eluent.

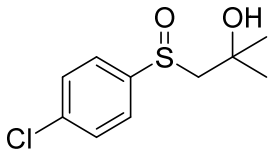
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.02 (d, *J* = 13.3 Hz, 2H), 2.68 (d, *J* = 13.3 Hz, 1H), 1.59 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2, 125.9, 114.9, 70.7, 67.9, 55.52, 30.60, 28.70. HRMS (ESI) m/z calcd for $C_{11}H_{16}NaO_3S^+$ $(M+Na)^+$ 251.0712, found 251.0725.



1-((4-(tert-butyl)phenyl)sulfinyl)-2-methylpropan-2-ol (3f)

3f was obtained as white solid (mp: 115-117 ^{o}C) in 71% yield (36.1 mg), using EA /PE (1:1) as eluent.

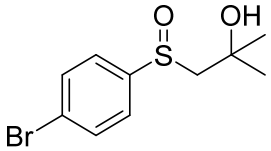
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 4.19 (brs, 1H), 3.01 (d, *J* = 13.4 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 1.55 (s, 3H), 1.34 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 126.5, 123.8, 70.7, 68.5, 35.0, 31.2, 30.5, 29.0. HRMS (ESI) m/z calcd for $C_{14}H_{22}NaO_2S^+$ $(M+Na)^+$ 277.1233, found 277.1247.



1-((4-chlorophenyl)sulfinyl)-2-methylpropan-2-ol (3g)

3g was obtained as white solid (mp: 133-135 ^{o}C) in 88% yield (40.8 mg), using EA /PE (1:1) as eluent.

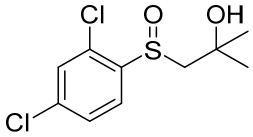
^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.53 (m, 2H), 7.49 – 7.43 (m, 2H), 4.04 (brs, 1H), 2.97 (d, *J* = 13.4 Hz, 1H), 2.75 (d, *J* = 13.4 Hz, 1H), 1.51 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (10 MHz, Chloroform-d) δ 142.7, 137.4, 129.7, 125.4, 70.5, 30.2, 29.3. HRMS (ESI) m/z calcd for $C_{10}H_{13}ClNaO_2S^+$ $(M+Na)^+$ 255.0217, found 255.0222.



1-((4-bromophenyl)sulfinyl)-2-methylpropan-2-ol (3h)

3h was obtained as colorless liquid in 65% yield (35.9 mg), using EA /PE (1:1) as eluent .

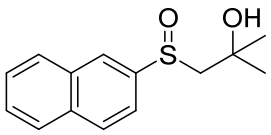
^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.00 (brs, 1H), 2.98 (d, *J* = 13.4 Hz, 1H), 2.74 (d, *J* = 13.4 Hz, 1H), 1.52 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.1, 132.6, 125.6, 125.5, 70.5, 69.1, 30.22, 29.2. HRMS (ESI) m/z calcd for $C_{10}H_{13}BrNaO_2S^+$ $(M+Na)^+$ 298.9712, found 298.9722.



1-((2,4-dichlorophenyl)sulfinyl)-2-methylpropan-2-ol (3i)

3i was obtained as white solid (mp: 130-132 ^{o}C) in 34% yield (18.1 mg), using EA /PE (1:1) as eluent.

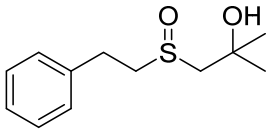
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 3.68 (brs, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 2.83 (d, *J* = 13.3 Hz, 1H), 1.62 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.5, 137.9, 130.1, 129.7, 128.7, 127.0, 70.8, 65.9, 30.5, 28.7. HRMS (ESI) m/z calcd for $C_{10}H_{13}Cl_2NaO_2S^+$ $(M+Na)^+$ 288.9827, found 288.9828.



2-methyl-1-(naphthalen-2-ylsulfinyl)propan-2-ol (3j)

3j was obtained as white solid (mp: 142-144 ^{o}C) in 47% yield (23.3 mg), using EA /PE (1:1) as eluent.

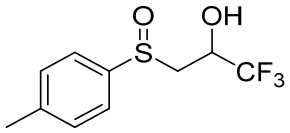
^{1}H NMR (400 MHz, Chloroform-d) δ 8.18 (s, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.89 (t, *J* = 9.4 Hz, 2H), 7.60 – 7.55 (m, 3H), 4.12 (s, 1H), 3.08 (d, *J* = 13.4 Hz, 1H), 2.82 (d, J = 13.4 Hz, 1H), 1.62 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 140.8, 134.4, 132.8, 129.7, 128.5, 128.0, 127.9, 127.4, 124.5, 70.8, 68.1, 30.5, 29.0. HRMS (ESI) m/z calcd for $C_{14}H_{16}NaO_2S^+$ $(M+Na)^+$ 271.0763, found 271.0772.



2-methyl-1-(phenethylsulfinyl)propan-2-ol (3k)

3k was obtained as colorless liquid in 57% yield (25.8 mg), using EA /PE (1:1) as eluent.

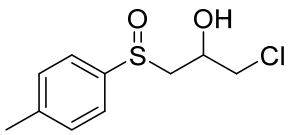
1H NMR (400 MHz, Chloroform-d) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (m, 3H), 3.91 (brs, 1H), 3.15 – 3.05 (m, 2H), 3.05 – 2.96 (m, 2H), 2.93 (d, *J* = 13.1 Hz, 1H), 2.68 (d, *J* = 13.0 Hz, 1H), 1.47 (s, 3H), 1.36 (s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 138.6, 128.9, 128.6, 126.9, 70.4, 63.0, 54.9, 30.4, 29.4, 28.6. HRMS (ESI) m/z calcd for $C_{12}H_{18}NaO_2S^+$ $(M+Na)^+$ 249.0920, found 249.0927.



1,1,1-trifluoro-3-(p-tolylsulfinyl)propan-2-ol (3l)

3l was obtained as white solid (mp: 82-84 ^{o}C) in 58% yield (29.2 mg), using EA /PE (1:1) as eluent (dr = 1:1).

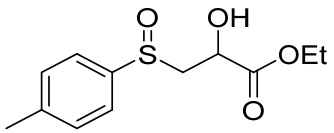
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.25 (brs, 0.64H), 5.53 (brs, 0.36H), 4.58 (brs, 0.64H), 4.47 (brs, 0.36H), 3.25 – 3.18 (m, 0.36H), 3.06 – 2.94 (m, 1.64H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.8, 142.5, 138.8, 138.3, 130.3, 126.9 (q, *J* = 280 Hz), 124.4 (q, *J* = 280 Hz), 124.2, 124.0, 66.7 (q, *J* = 32.9 Hz), 64.9 (q, *J* = 32.8 Hz), 57.4, 56.3, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{10}H_{11}F_3NaO_2S^+$ $(M+Na)^+$ 275.0324, found 275.0337.



1-chloro-3-(p-tolylsulfinyl)propan-2-ol (3m)

3m was obtained as white solid (mp: 105-107 ^{o}C) in 55% yield (25.5 mg), using EA /PE (1:1) as eluent (dr = 1:1).

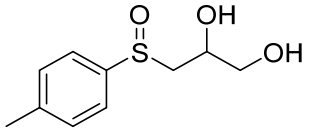
^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.58 (d, *J* = 4.2 Hz, 1H), 4.45 – 4.37 (m, 1H), 3.61 – 3.50 (m, 2H), 3.13 – 3.03 (m, 1H), 2.88 – 2.82 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.3, 141.9, 139.8, 139.1, 130.2, 130.2, 124.0, 123.9, 68.2, 66.3, 60.0, 59.9, 48.1, 48.0, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{10}H_{13}ClNaO_2S^+$ $(M+Na)^+$ 255.0217, found 255.0232.



ethyl 3-hydroxy-4-(p-tolylsulfinyl)butanoate (3n)

3n was obtained as colorless liquid in 45% yield (23.0 mg), using EA /PE (1:1) as eluent (dr = 60:40).

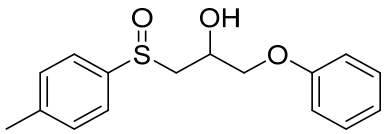
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.74 (d, *J* = 11.8 Hz, 0.6H), 4.51 – 4.47 (m, 0.4H), 4.32 – 4.11 (m , 3H), 3.30 – 3.23 (m, 0.4H), 3.19 – 3.11 (m, 1H), 3.03 – 2.96 (m, 0.6H), 2.40 (s, 3H), 1.32 – 1.19 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 172.4, 172.2, 142.0, 141.9, 139.8, 139.8, 130.1, 130.1, 124.2, 123.9, 66.6, 65.9, 62.3, 62.1, 61.1, 60.4, 21.4, 21.4, 14.1, 14.0. HRMS (ESI) m/z calcd for $C_{12}H_{16}NaO_4S^+$ $(M+Na)^+$ 279.0662, found 279.0682.



3-(p-tolylsulfinyl)propane-1,2-diol (3o)

3o was obtained as colorless liquid in 65% yield (27.8 mg), using EA /PE (1:1) as eluent (dr = 55:45).

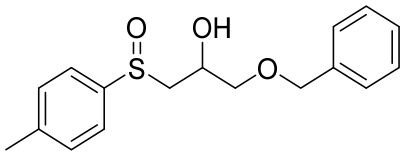
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 – 7.49(m, 2H), 7.37 – 7.33 (m, 2H), 5.28 (d, *J* = 5.6 Hz, 0.55H), 5.08 (d, *J* = 5.2 Hz, 0.45H), 4.75 – 4.68 (m, 1H), 3.93 – 3.84 (m, 0.55H), 3.58 – 3.49(m, 0.45H), 3.36 – 3.24 (m, 2H), 2.91 (t, *J* = 6.1 Hz, 0.9H), 2.82 – 2.74 (m, 0.55H), 2.71 – 2.63 (m, 0.55H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.6, 141.7, 141.3, 141.0, 130.2, 130.2, 124.7, 124.1, 67.6, 66.2, 65.6, 65.2, 63.0, 61.8, 21.3, 21.3. HRMS (ESI) m/z calcd for $C_1H_{14}NaO_3S^+$ $(M+Na)^+$ 237.0556, found 237.0556.



1-phenoxy-3-(p-tolylsulfinyl)propan-2-ol (3p)

3p was obtained as colorless liquid in 70% yield (40.6 mg), using EA /PE (1:1) as eluent (dr = 55:45).

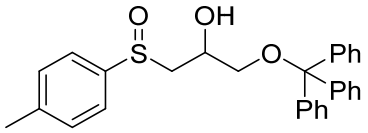
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.20 (m, 2H), 6.97 – 6.90 (m, 1H), 6.89 – 6.81 (m, 2H), 4.59 (t, *J* = 34.8 Hz, 1.55H), 4.26 (brs, 0.45H), 4.14 – 4.08 (m, 0.45H), 4.02 – 3.9 (m, 1.55H), 3.2 – 3.0 (m, 1.45H), 2.96 (d, *J* = 12.4 Hz, 0.55H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 158.2, 142.1, 141.7, 140.0, 139.5, 130.1, 130.1, 129.5, 129.4, 124.1, 124.0, 121.2, 121.1, 114.5, 70.8, 70.4, 67.0, 65.0, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{16}H_{18}NaO_3S^+$ $(M+Na)^+$ 313.0869, found 313.0885.



1-(benzyloxy)-3-(p-tolylsulfinyl)propan-2-ol (3q)

3q was obtained as white solid (mp: 82-84 ^{o}C) in 62% yield (37.7 mg), using EA /PE (1:1) as eluent (dr = 60:40).

1H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.48 (m, 2H), 7.32 – 7.22 (m, 7H), 4.52 – 4.44 (m, 2H), 4.38 (d, *J* = 5.3 Hz, 0.60H), 4.32 – 4.25 (m, 0.40H), 4.16 (d, *J* = 5.3 Hz, 0.60H), 3.86 (d, *J* = 2.4 Hz, 0.40H), 3.61 – 3.56 (m, 0.40H), 3.53 – 3.41 (m, 1.60H), 3.08 – 2.9 (m, 1.40H), 2.81 –2.75(m, 0.60H), 2.39(s, 3H). 13C NMR (100 MHz, Chloroform-d) δ 141.9, 141.6, 140.2, 139.8, 137.7, 137.6, 130.4, 130.0, 128.4, 128.4, 127.8, 127.8, 127.8, 127.7, 73.5, 73.3, 73.2, 72.9, 67.3, 67.3, 65.5, 65.4, 60.2, 60.1, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{17}H_{20}NaO_3S^+$ $(M+Na)^+$ 327.1025, found 327.1037.

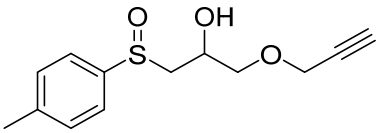


4,4,4-triphenyl-1-(p-tolylsulfinyl)butan-2-ol (3r)

3r was obtained as colorless liquid in 70% yield (63.8 mg), using EA /PE (1:1) as eluent (dr = 60:40).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.43 – 7.26 (m, 14H), 7.25 – 7.10 (m, 3H), 4.39 (brs, 0.60H), 4.28 (brs, 0.40H), 3.87 (brs, 0.60H), 3.70 (brs, 0.40H), 3.34 – 3.28 (m, 0.40H), 3.20 – 3.11 (m, 1.60H), 3.07 – 2.91 (m, 1.40H), 2.77(d, *J* = 13.6 Hz, 0.60H), 2.42(s,

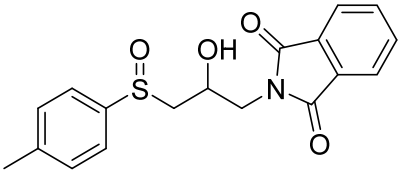
3H).[13]C NMR (100 MHz, Chloroform-d) δ 143.5, 143.5, 142.0, 141.5, 140.3, 139.7, 130.1, 130.0, 128.5, 128.5, 127.9, 127.8, 127.1, 127.1, 124.1, 124.0, 86.8, 86.7, 67.8, 66.6, 66.5, 66.1, 60.2, 59.4, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{10}H_{11}F_3NaO_2S^+$ $(M+Na)^+$ 479.1651, found 479.1665.



1-(ethynyloxy)-3-(p-tolylsulfinyl)propan-2-ol (3s)

3s was obtained as colorless liquid in 44% yield (22.1 mg), using EA /PE (1:1) as eluent (dr = 60:40).

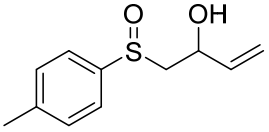
[1]H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.39 – 4.31 (m, 1H), 4.17 –4.13(m, 2.6H), 3.86 (brs, 0.4H), 3.67 – 3.63 (m, 0.4H), 3.60 – 3.48 (m, 1.6H), 3.07 – 3.00 (m, 1H), 2.96 – 2.91 (m, 0.4H), 2.80 – 2.76 (m, 0.6H), 2.44 – 2.41 (m, 1H), 2.39 (s, 3H). [13]C NMR (100 MHz, Chloroform-d) δ142.1, 141.7, 140.3, 139.7, 130.2, 130.1, 124.1, 124.0, 79.2, 75.1, 75.0, 72.9, 72.6, 67.4, 65.5, 60.0, 59.7, 58.7, 58.6, 21.5, 21.4. HRMS (ESI) m/z calcd for $C_{13}H_{16}NaO_3S^+$ $(M+Na)^+$ 275.0712, found 275.0718.



2-(2-hydroxy-3-(p-tolylsulfinyl)propyl)isoindoline-1,3-dione (3t)

3t was obtained as white solid (mp: 179-181 ^oC) in 54% yield (37.0 mg), using EA /PE (1:1) as eluent (dr = 60:40).

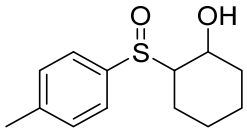
[1]H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.75 (m, 2H), 7.69 – 7.66 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 0.60H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.20 (m, 2.40H), 4.79 (s, 0.60H), 4.55 – 4.40 (m, 1H), 4.32 (brs, 0.40H), 3.91 – 3.78 (m, 2H), 3.08 – 3.01 (m, 0.4H), 2.98 –2.87 (m, 1H), 2.80 (d, *J* = 13.3 Hz, 0.6), 2.36(d, *J* = 5.5 Hz, 3H). [13]C NMR (100 MHz, Chloroform-*d*) δ 168.56, 168.47, 141.61, 139.55, 134.20, 134.07, 131.94, 131.84, 130.18, 130.08, 124.17, 123.95, 123.49, 123.42, 66.68, 64.64, 61.04, 60.72, 43.28, 43.16, 21.50, 21.45. HRMS (ESI) m/z calcd for $C_{18}H_{17}NNaO_4S^+$ $(M+Na)^+$ 366.0770, found 366.0783.



1-(p-tolylsulfinyl)but-3-en-2-ol (3u)

3u was obtained as white solid (mp: 78-80 ^{o}C) in 48% yield (20.2 mg), using EA /PE (1:1) as eluent (dr = 60:40).

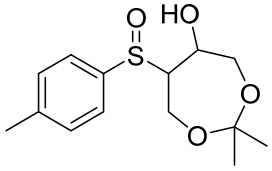
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.90 – 5.77 (m, 1H), 5.39 – 5.30 (m, 1H), 5.16 (t, *J* = 11.6 Hz, 1H), 4.69 (brs, 1H), 4.35 (brs, 0.6H), 4.06 (brs, 0.40H), 3.09 – 3.02 (m, 0.40H), 2.99 – 2.92 (m, 0.60H), 2.84 – 2.75 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.1, 141.7, 140.1, 139.4, 138.1, 137.9, 130.1, 130.1, 124.0, 124.0, 116.3, 116.0, 69.4, 67.3, 62. 5, 61.90, 21.4, 21.4. HRMS (ESI) m/z calcd for $C_{11}H_{14}NaO_2S^+$ $(M+Na)^+$ 233.0607, found 233.0617.



2-(p-tolylsulfinyl)cyclohexan-1-ol (3v)

3v was obtained as white solid (mp: 112-114 ^{o}C) in 53% yield (25.2 mg), using EA /PE (1:1) as eluent (dr = 1:1).

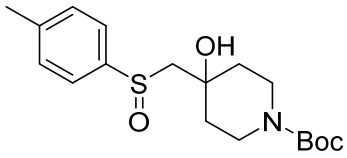
^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.18 (s, 1H), 4.11 – 4.04 (m, 1H), 2.74 – 2.66 (m, 1H), 2.41 (s, 3H), 2.10 (d, *J* = 8.3 Hz, 1H), 1.70 (t, *J* = 15.6 Hz, 2H), 1.42 – 1.01 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-d) δ 141.3, 136.2, 129.7, 125.0, 69.0, 67.2, 35.4, 24.7, 23.6, 21.4, 20.8. HRMS (ESI) m/z calcd for $C_{13}H_{18}NaO_2S^+$ $(M+Na)^+$ 261.0920, found 261.0931.



2,2-dimethyl-6-(p-tolylsulfinyl)-1,3-dioxepan-5-ol (3w)

3w was obtained as colorless liquid in 43% yield (24.4 mg), using EA /PE (1:1) as eluent (dr = 60:40).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 0.6H), 7.35 – 7.30 (m, 2H), 4.47 (brs, 0.40H), 4.33 (brs, 0.60H), 4.22 (brs, 0.60H), 3.97 (d, *J* = 10.2 Hz, 1H), 3.78 – 3.42 (m, 3.40H), 2.90 – 2.83 (m, 1H), 2.40 (d, *J* = 2.8 Hz, 3H), 1.32 – 1.22 (m, 6.40H). ^{13}C NMR (100 MHz, Chloroform-d) δ 142.8, 142.0, 138.4, 130.1, 130.0, 125.4, 124.8, 101.9, 71.0, 68.9, 67.8, 67.6, 64.1, 63.4, 55.6, 54.9, 24.4, 24.3, 24.2, 24.2, 21.5, 21.4. HRMS (ESI) m/z calcd for $C_{14}H_{20}F_3NaO_4S^+$ $(M+Na)^+$ 307.0975, found 307.0987.



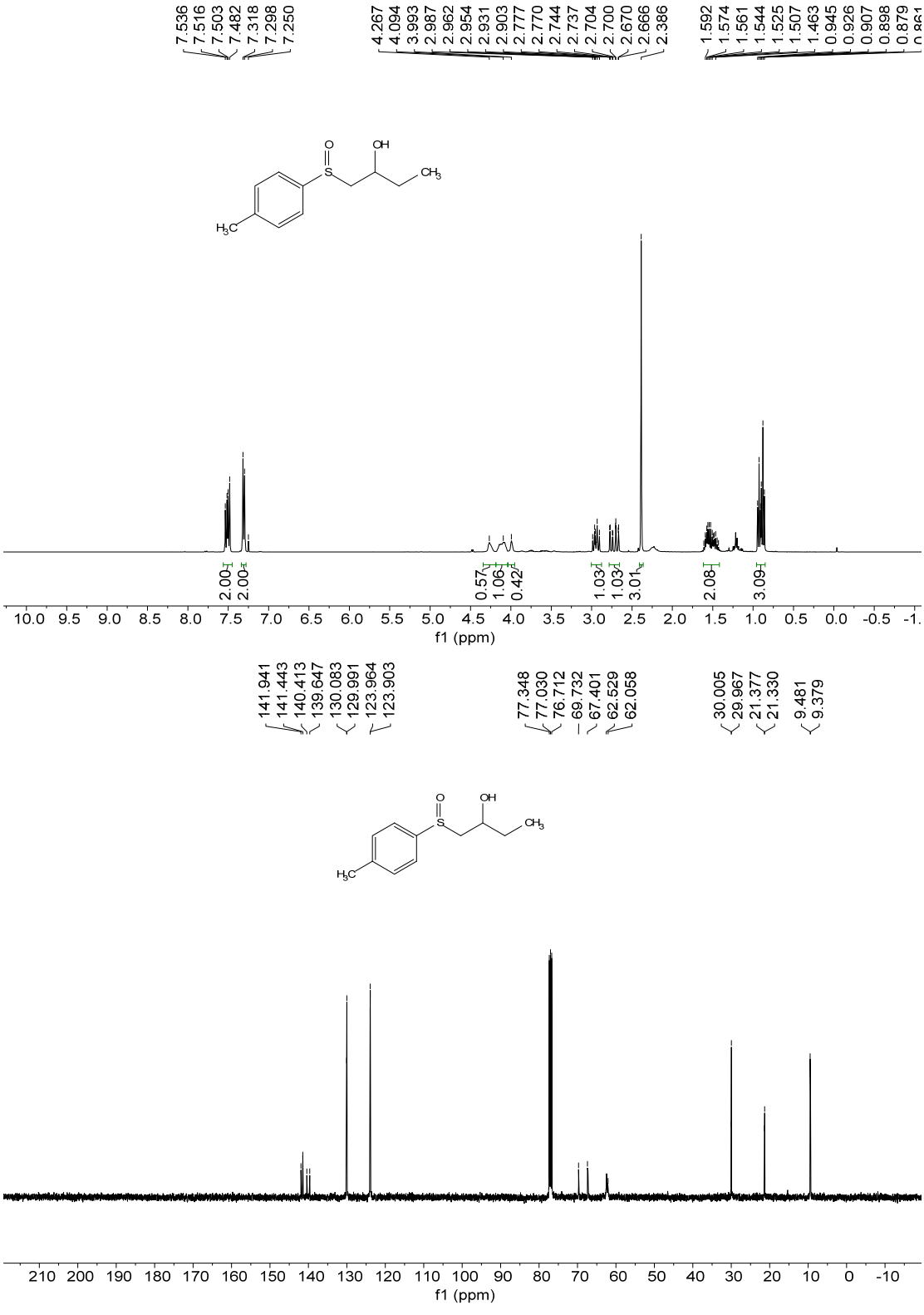
tert-butyl 4-hydroxy-4-(p-tolylsulfinyl)piperidine-1-carboxylate (3x)

3x was obtained as white solid (mp: 186-188 ^{o}C) in 64% yield (45.2 mg), using EA /PE (1:1) as eluent.

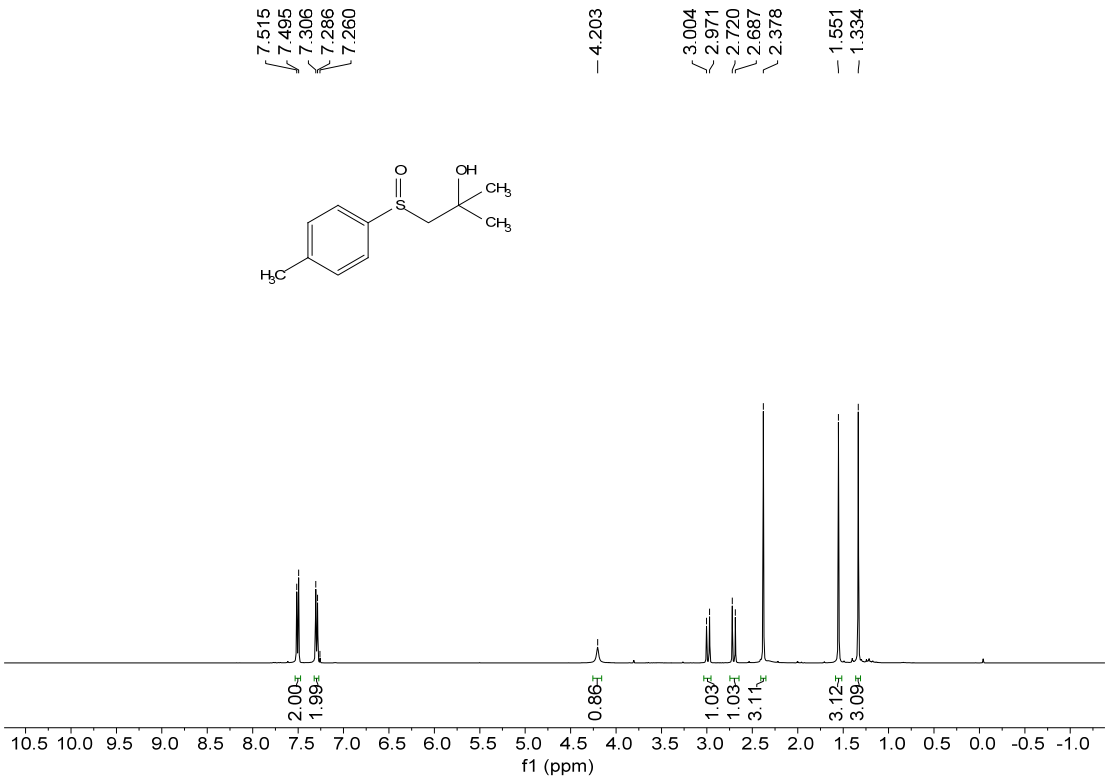
^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.28 (s, 1H), 3.88 (d, *J* = 47.1 Hz, 2H), 3.31 − 3.17 (m, 2H), 3.02 (d, *J* = 13.4 Hz, 1H), 2.64 (d, *J* = 13.3 Hz, 1H), 2.41 (s, 3H), 2.13 (d, *J* = 2.6 Hz, 1H), 1.84 − 1.76 (m, 2H), 1.69 − 1.64 (m, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-d) δ 154.8, 142.2, 140.2, 130.3, 124.0, 70.2, 66.7, 38.1, 36.2, 28.5 21.5. HRMS (ESI) m/z calcd for $C_{18}H_{27}NNaO_4S^+$ $(M+Na)^+$ 376.1553, found 366.1564.

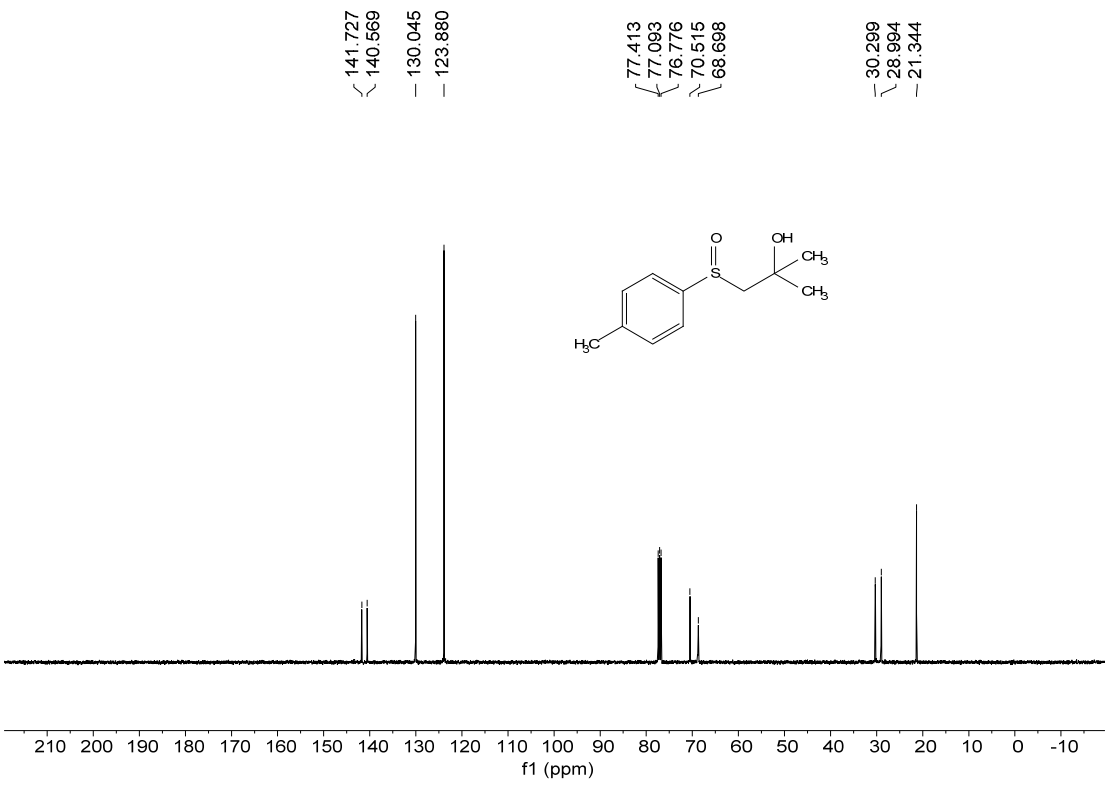
5. Copies of NMR spectra

^{1}H and ^{13}C NMR spectra of **3a**

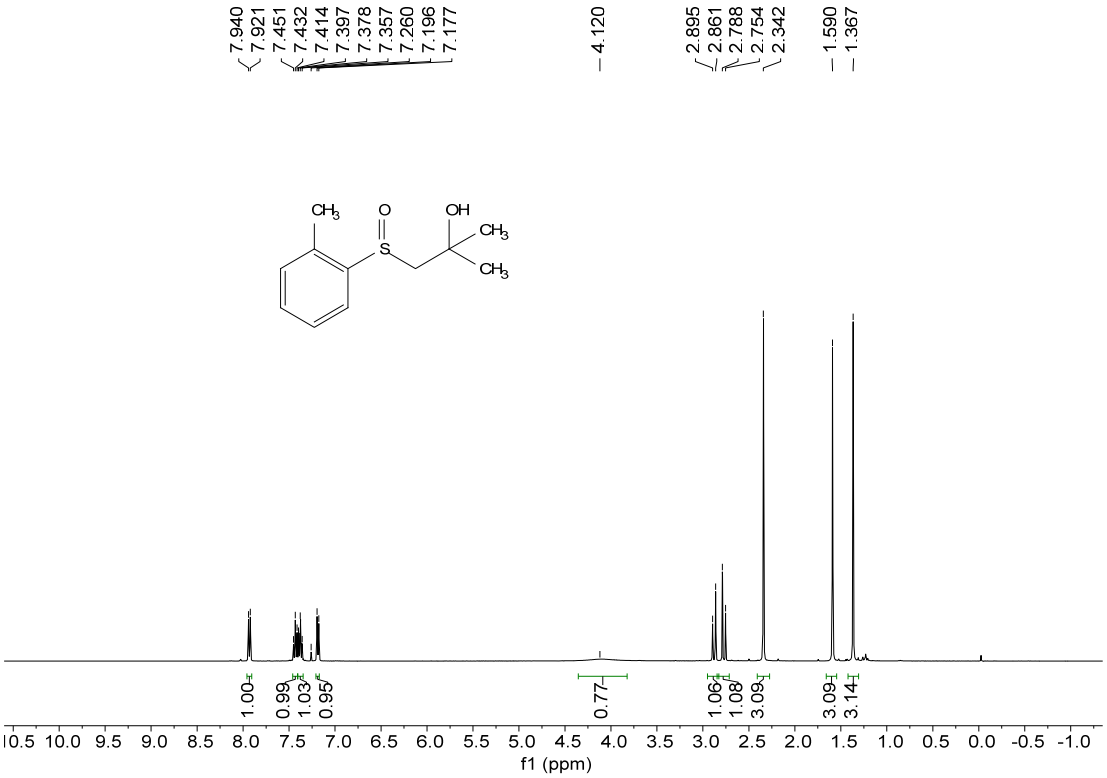


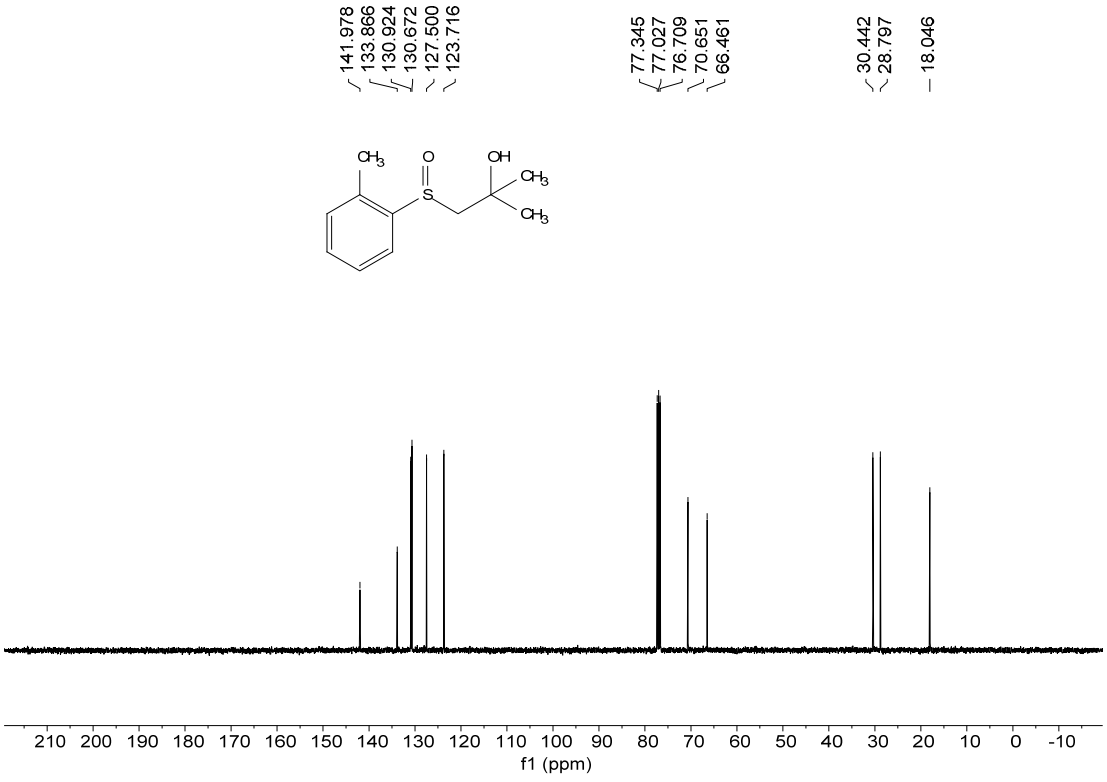
^{1}H and ^{13}C NMR spectra of **3b**



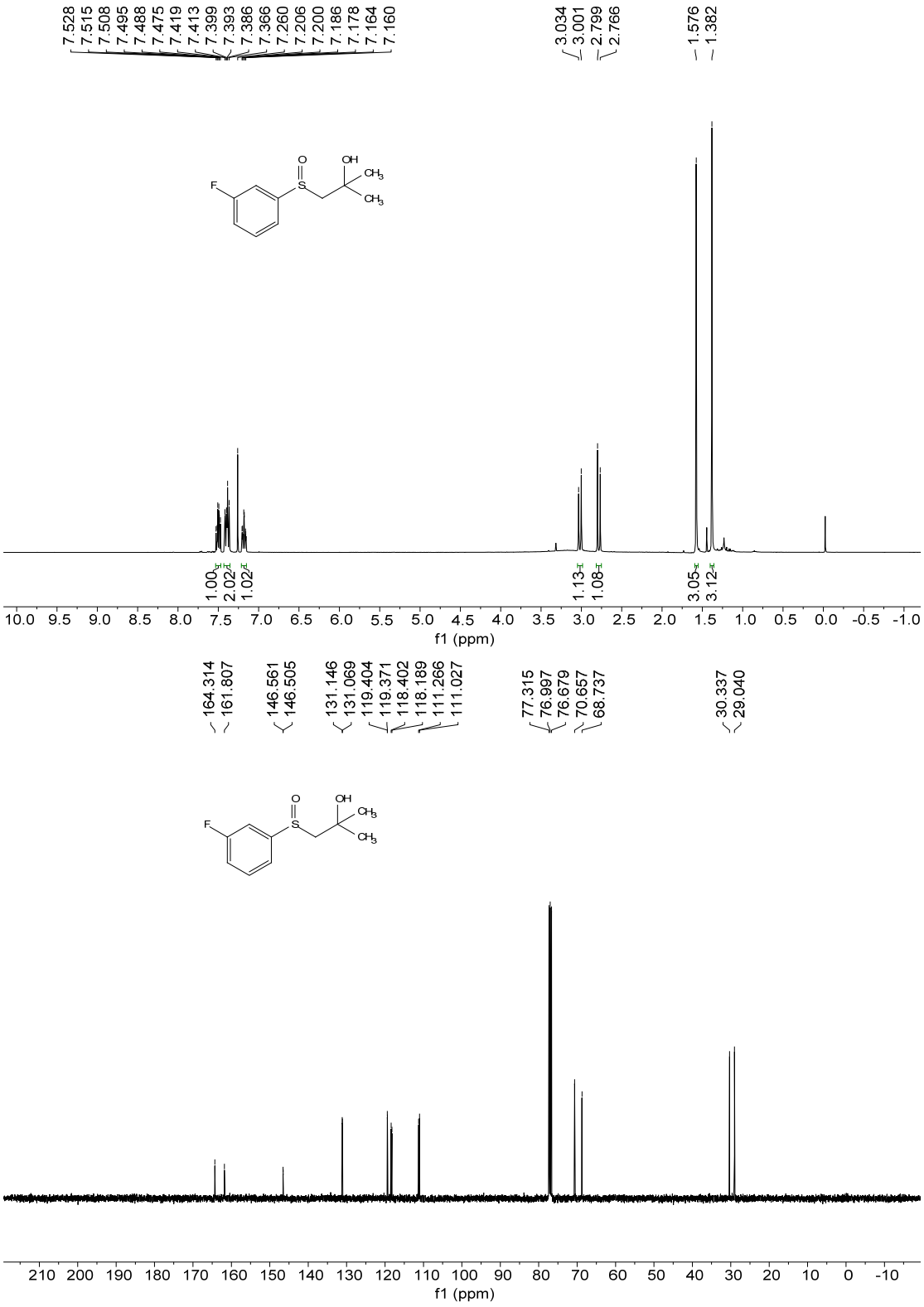


^{1}H and ^{13}C NMR spectra of **3c**

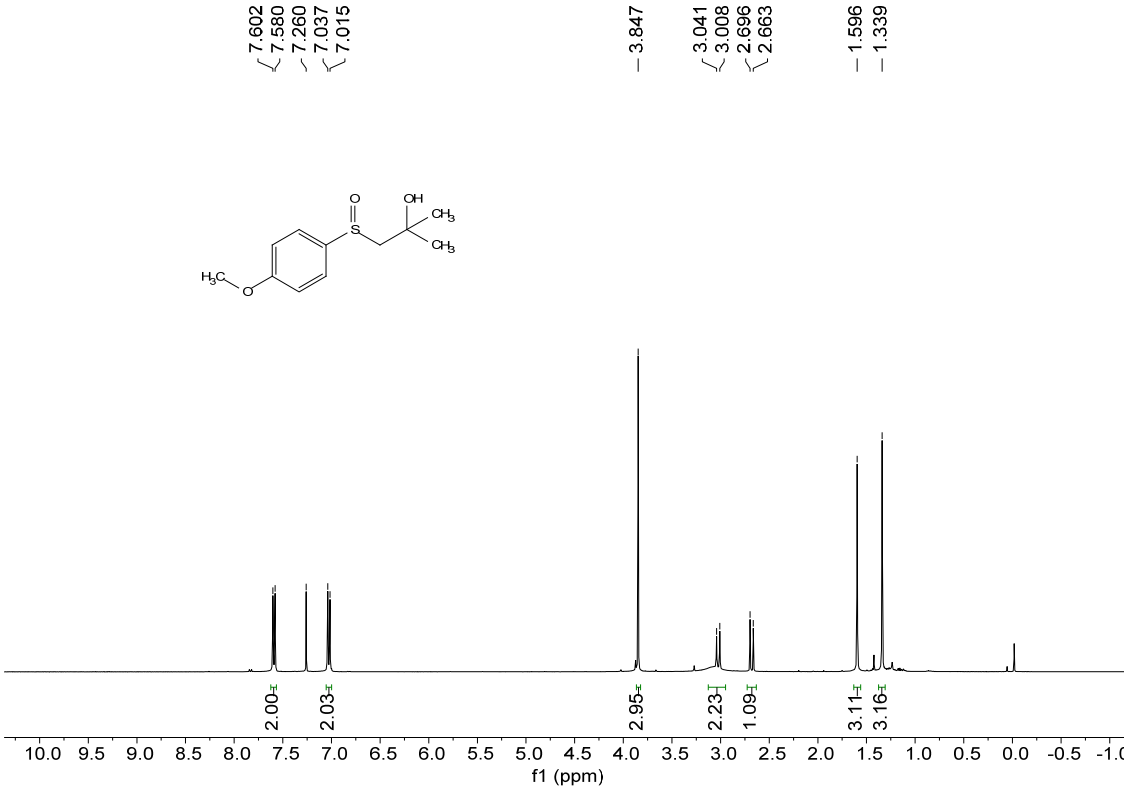


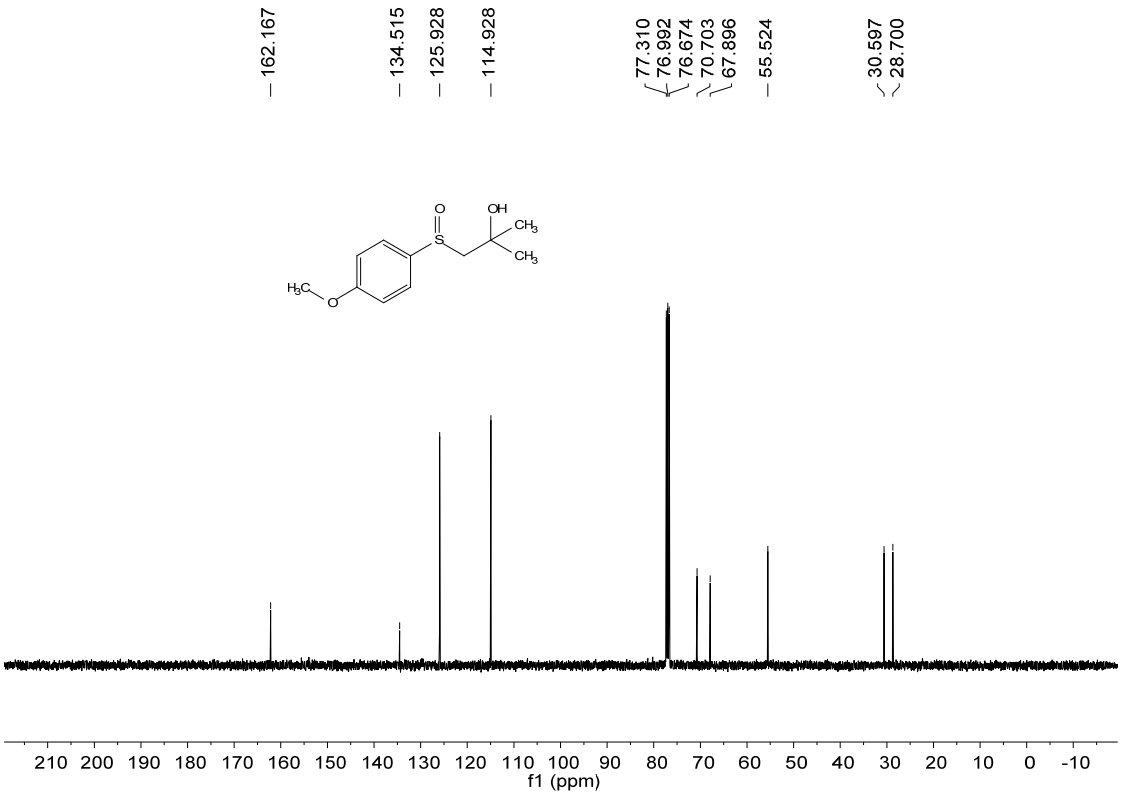


^{1}H and ^{13}C NMR spectra of **3d**

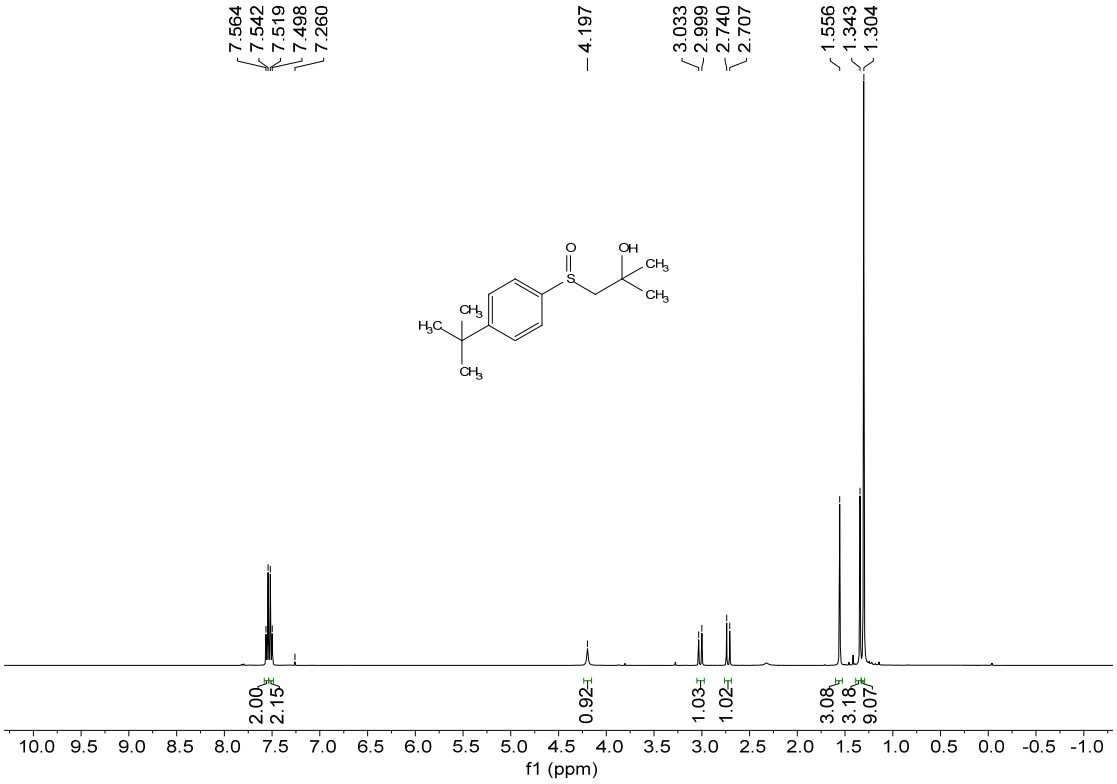


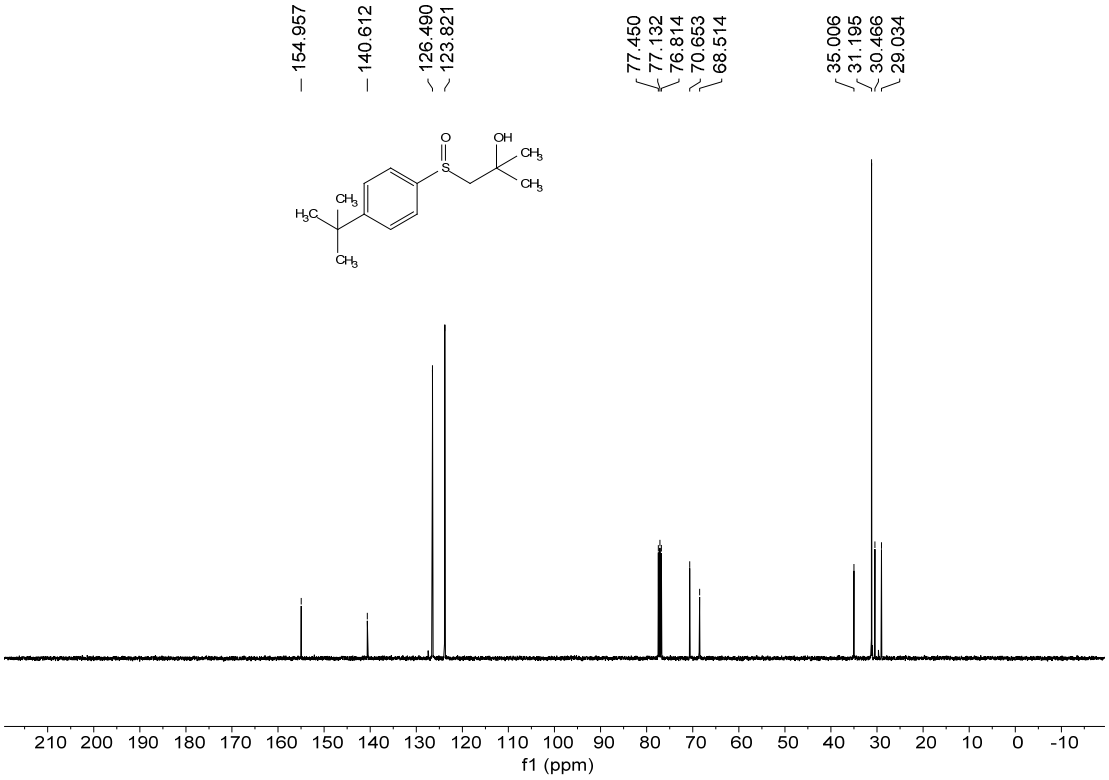
^{1}H and ^{13}C NMR spectra of **3e**



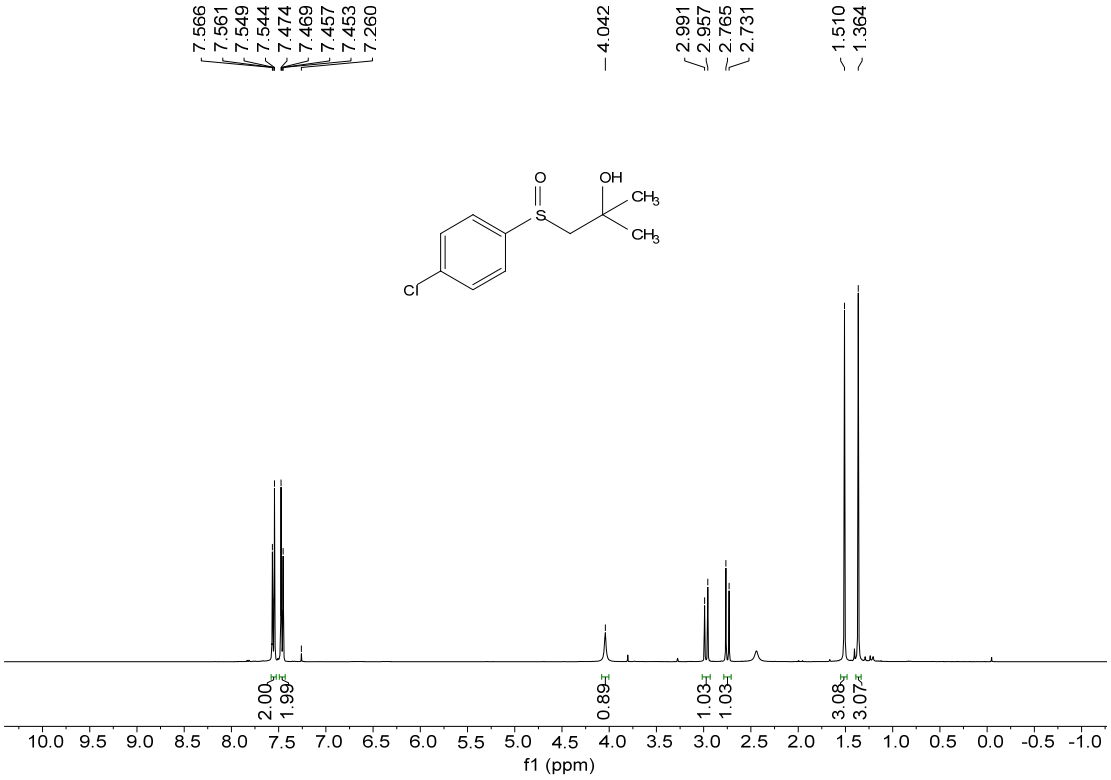


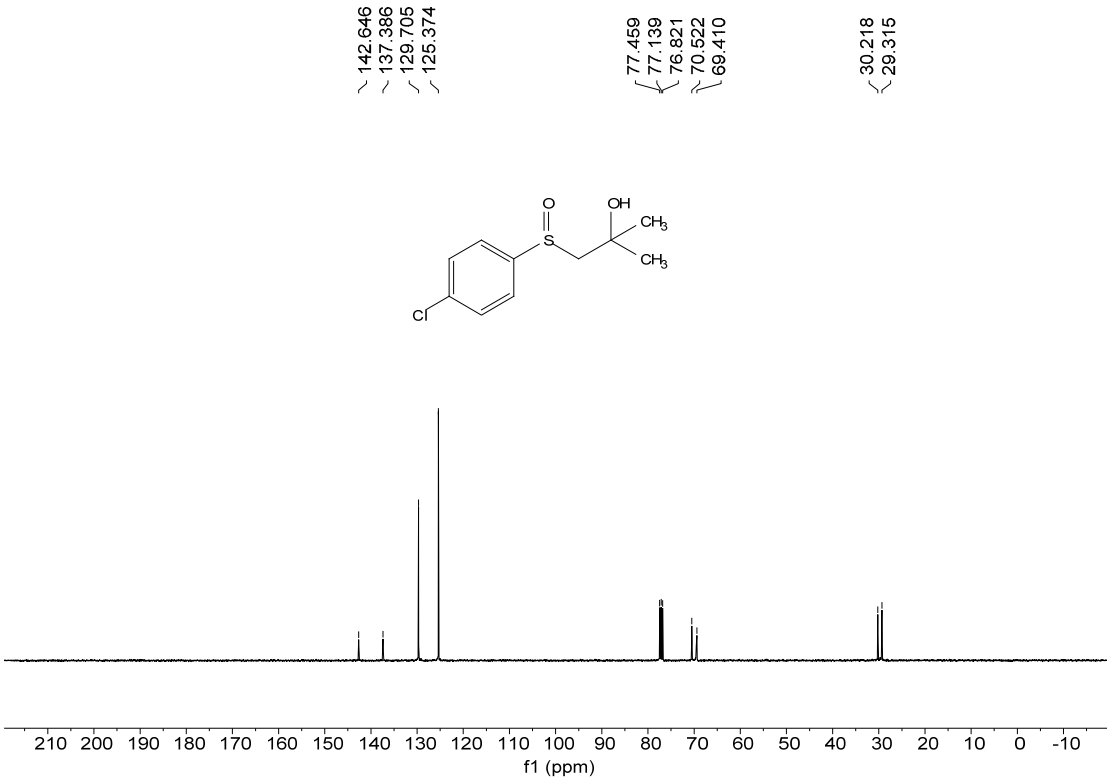
^{1}H and ^{13}C NMR spectra of **3f**



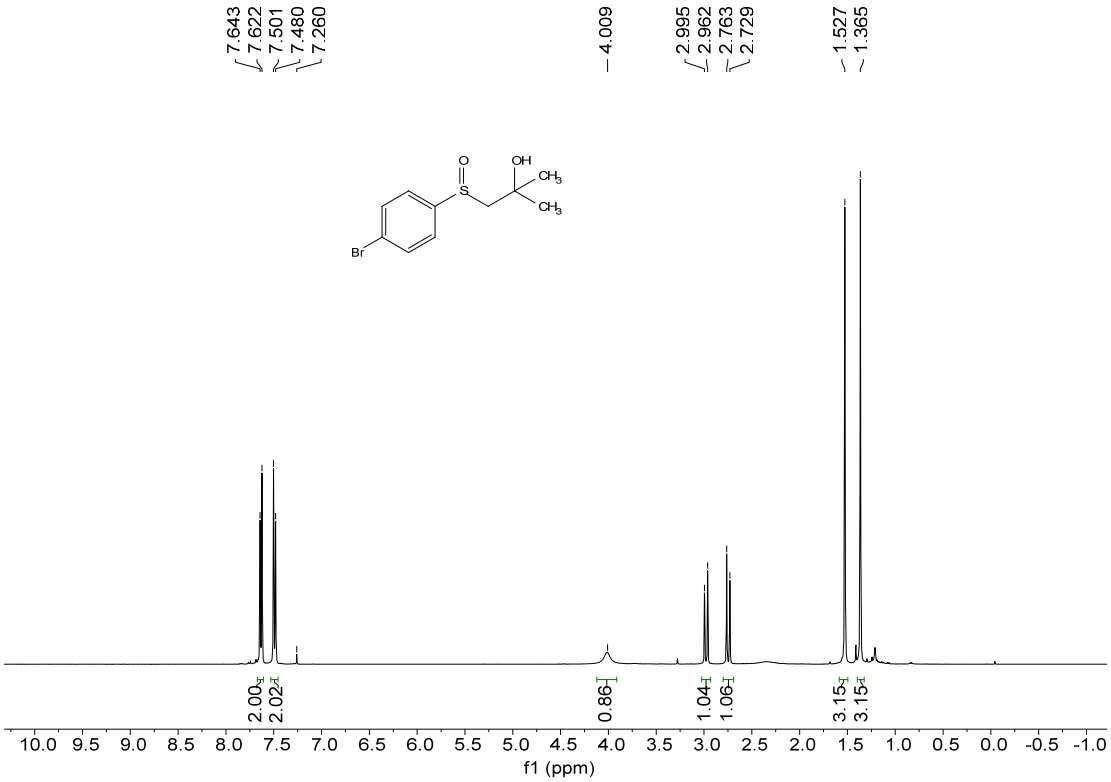


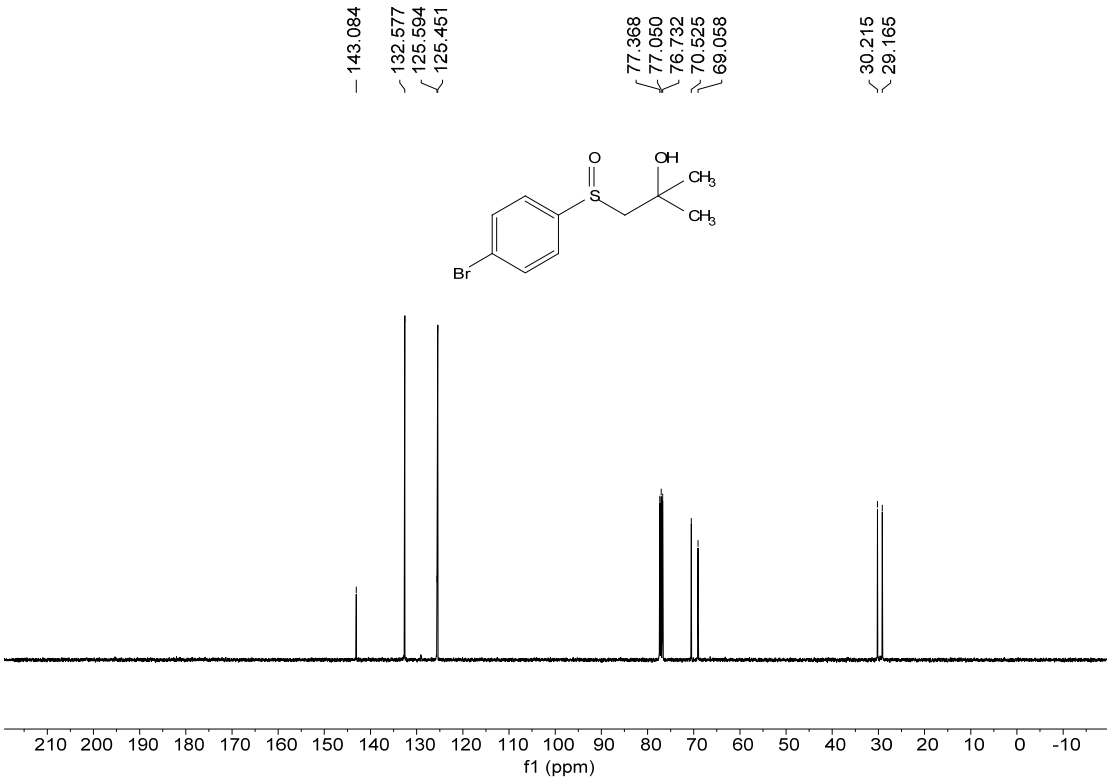
^{1}H and ^{13}C NMR spectra of **3g**



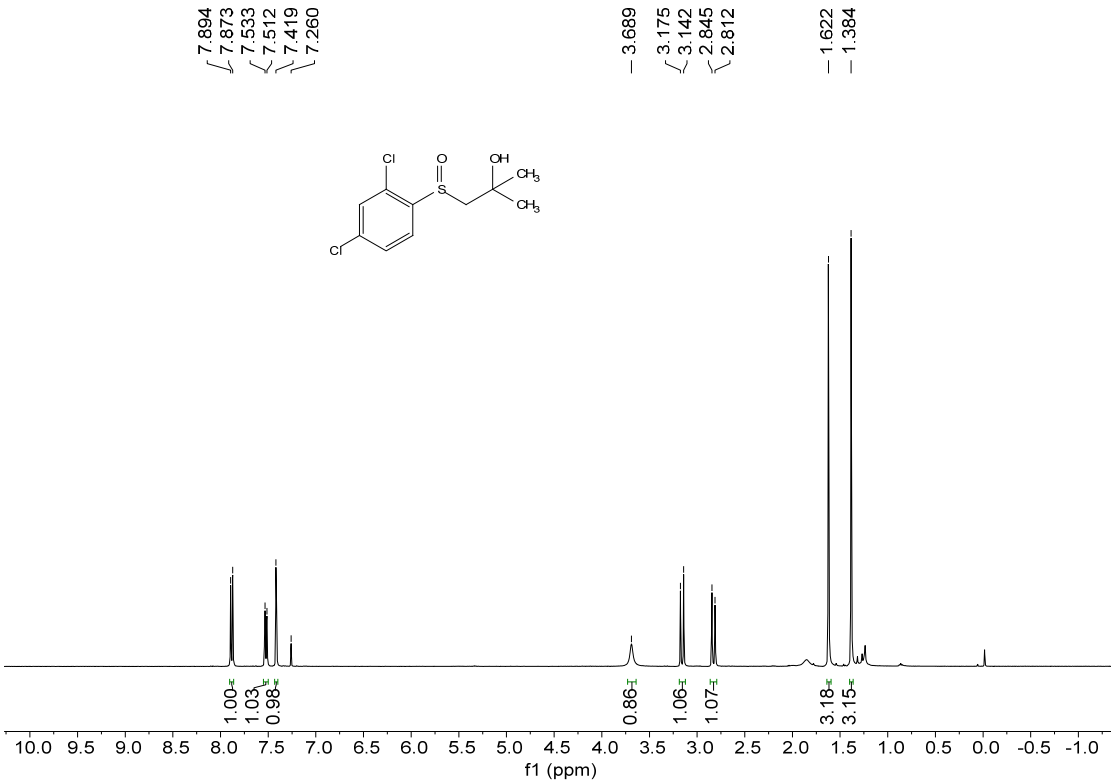


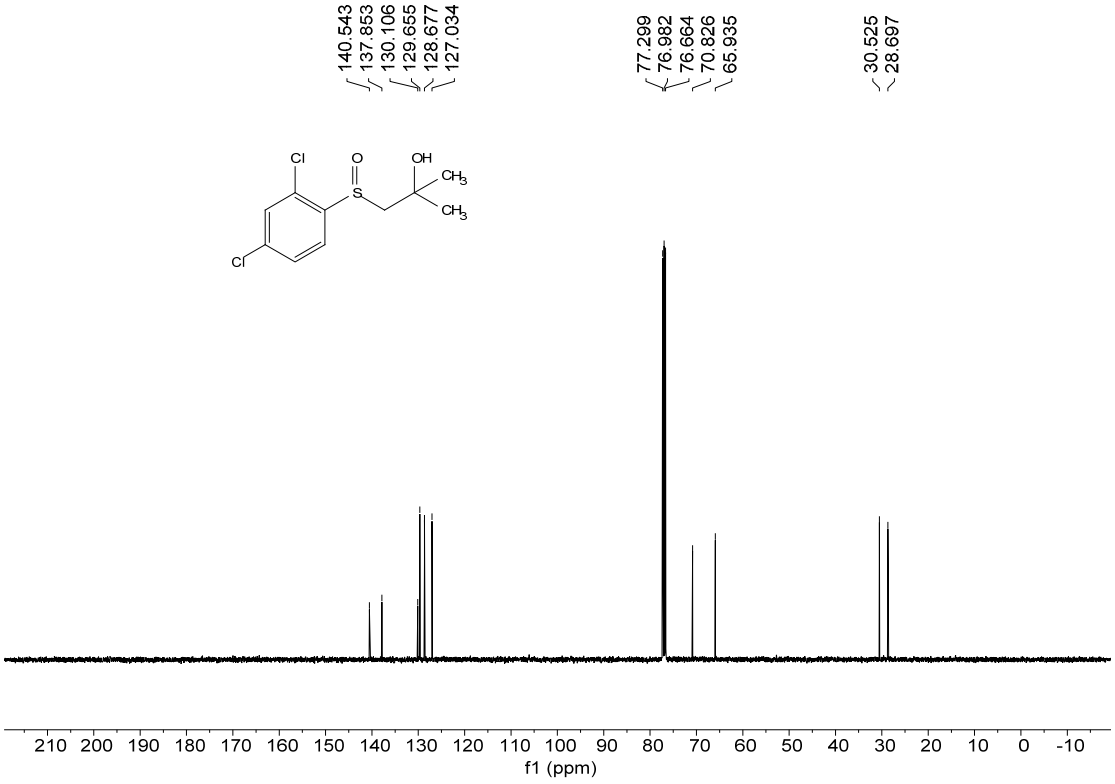
^{1}H and ^{13}C NMR spectra of **3h**



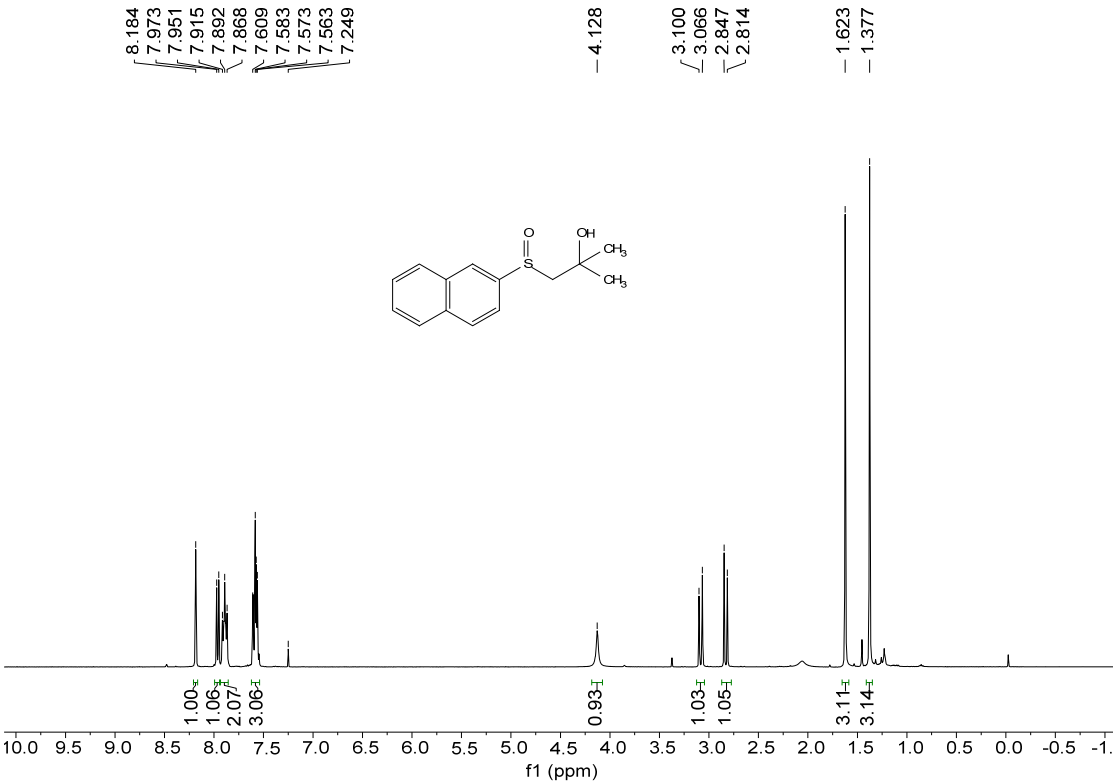


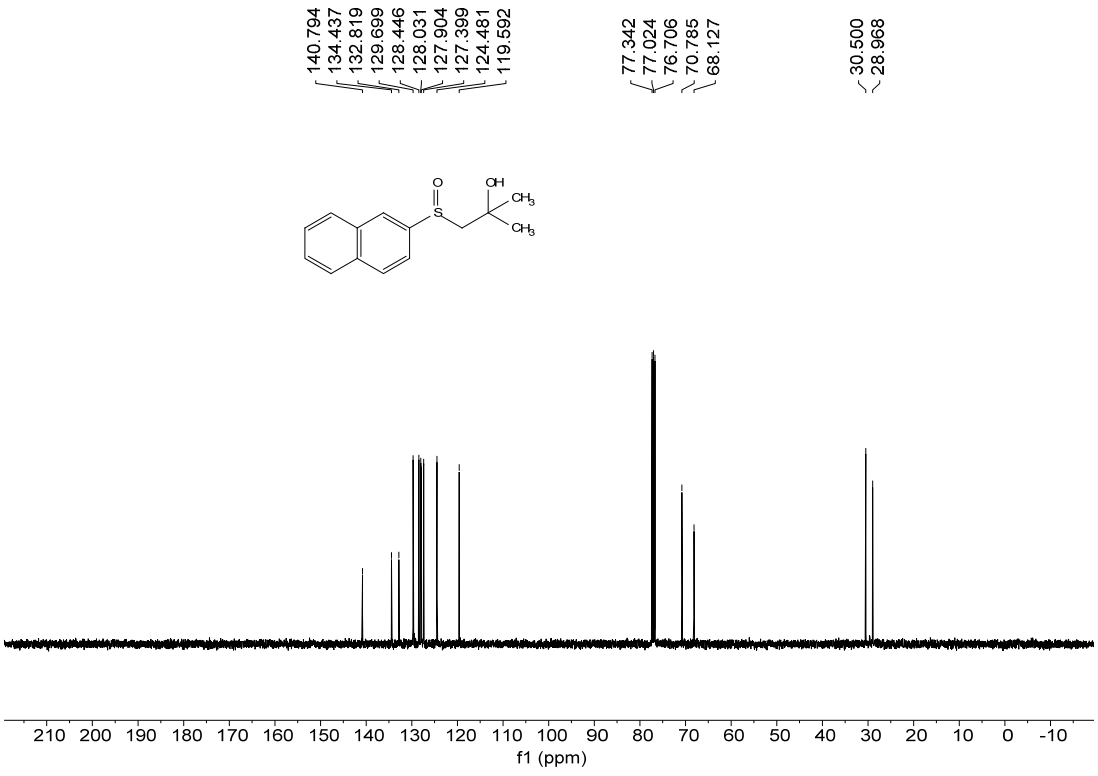
^{1}H and ^{13}C NMR spectra of **3i**



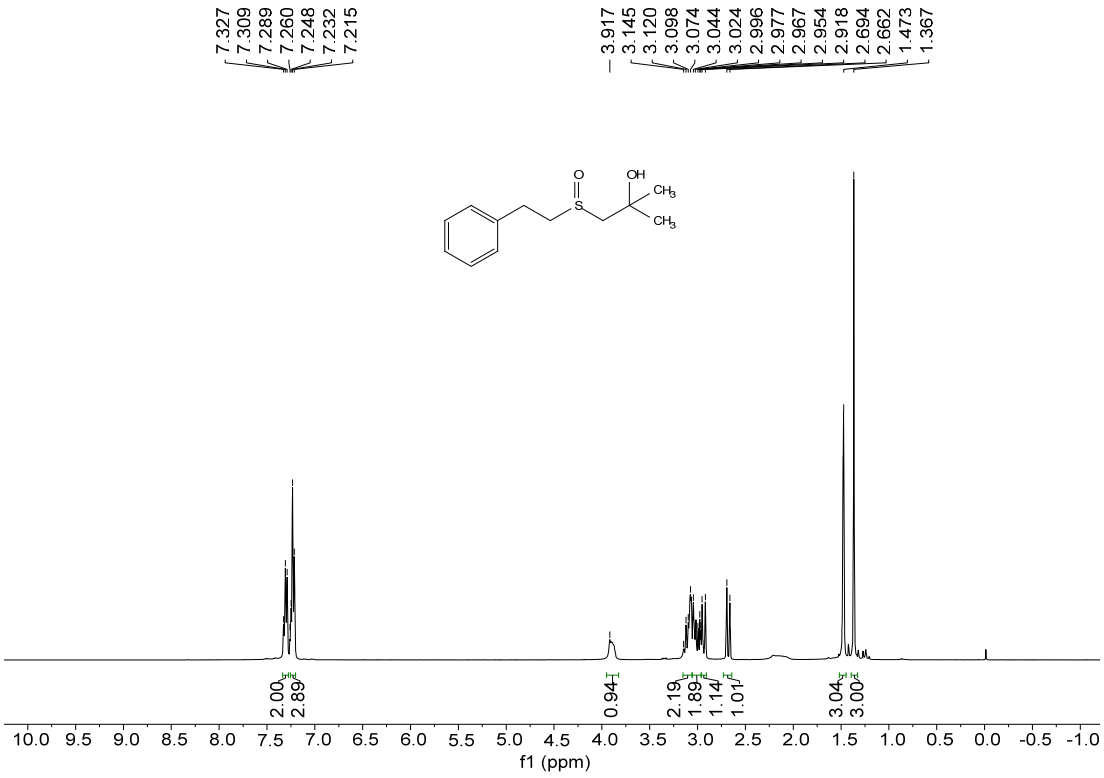


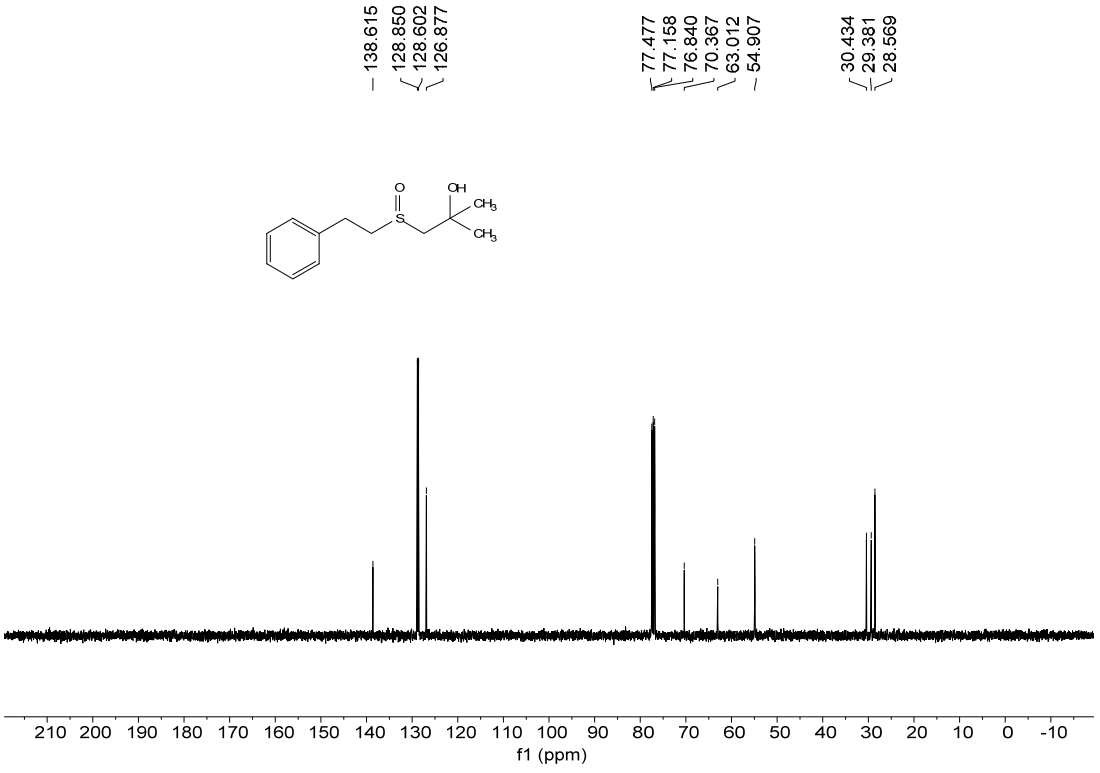
^{1}H and ^{13}C NMR spectra of **3j**



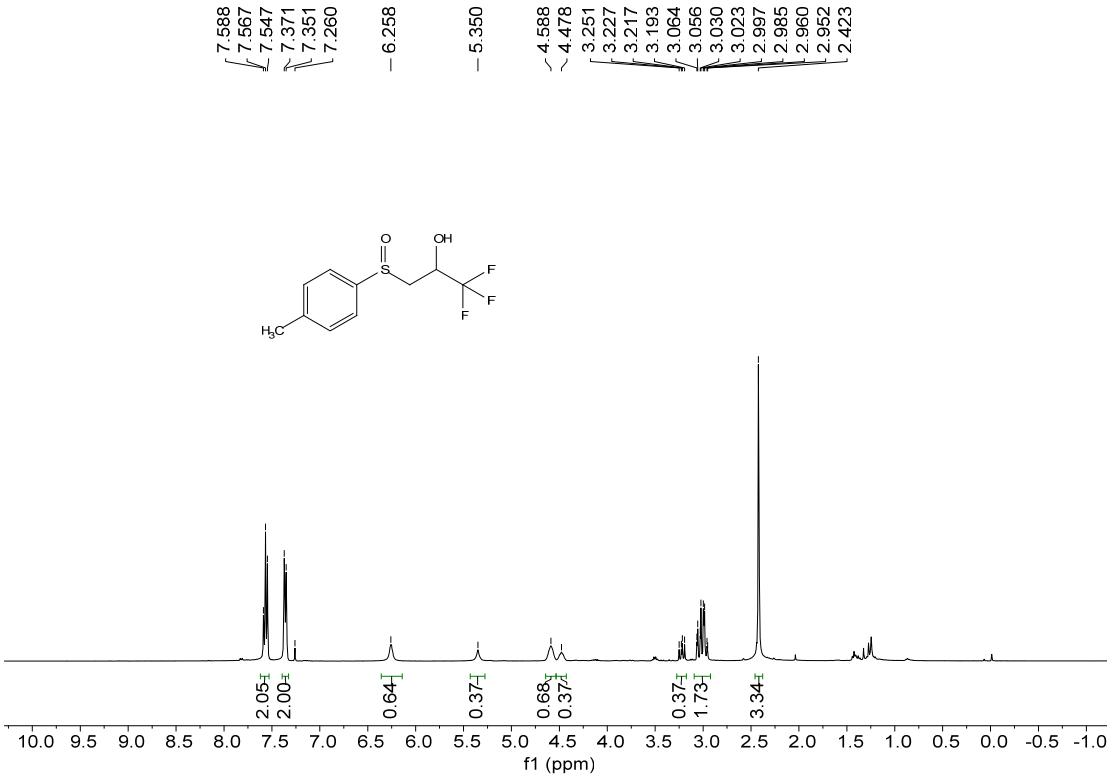


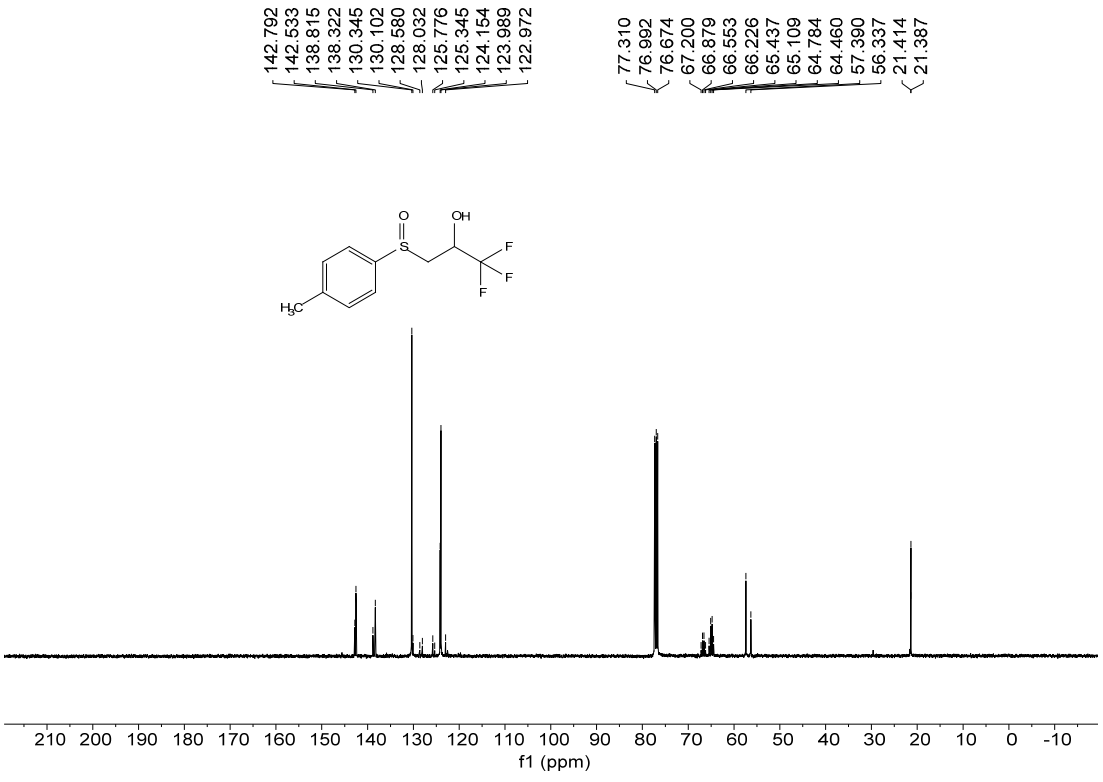
^{1}H and ^{13}C NMR spectra of **3k**



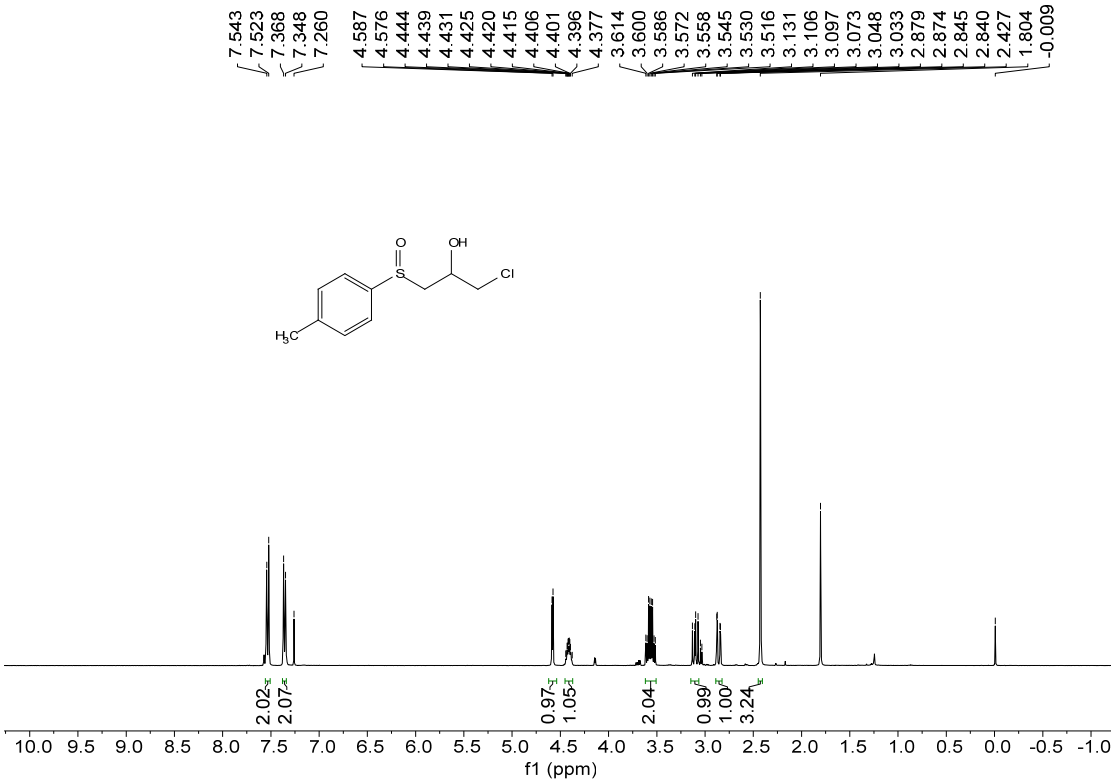


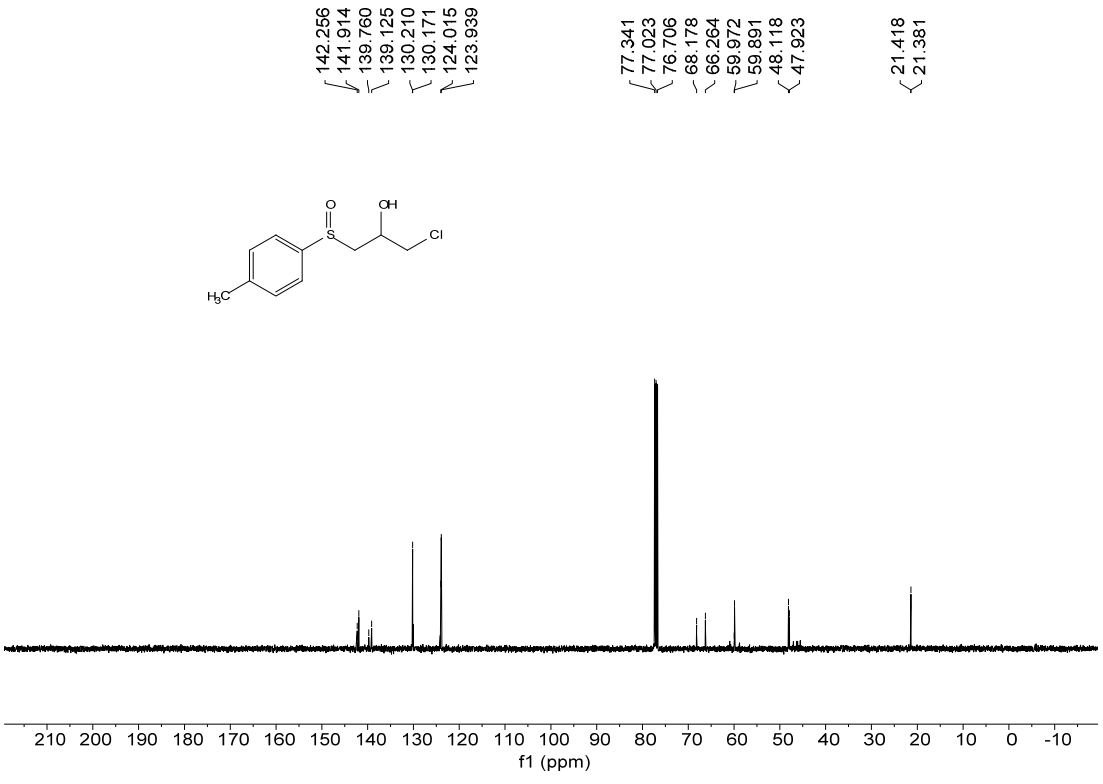
^{1}H and ^{13}C NMR spectra of **3l**



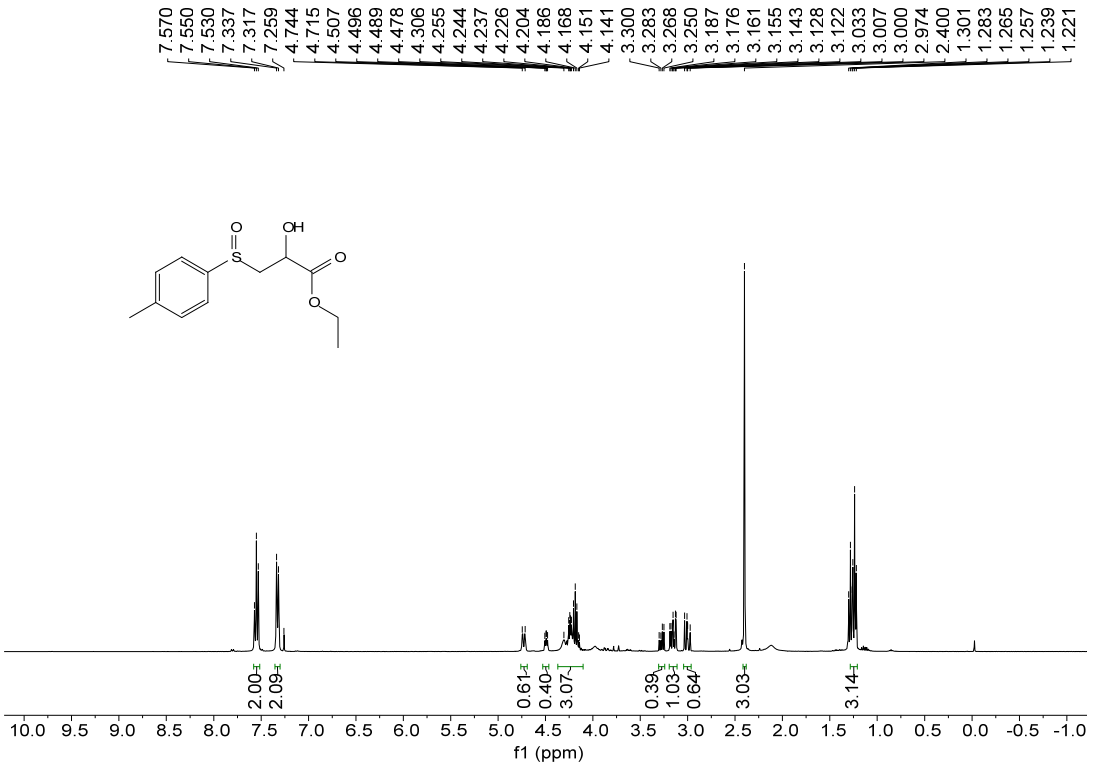


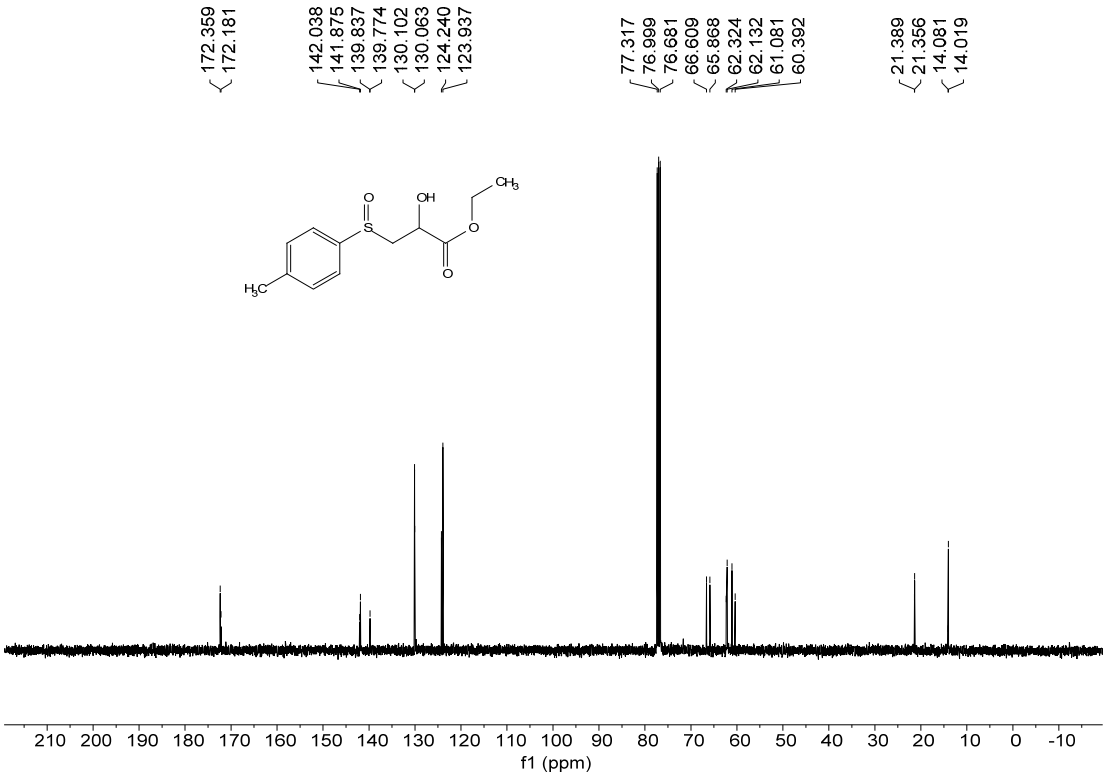
^{1}H and ^{13}C NMR spectra of **3m**



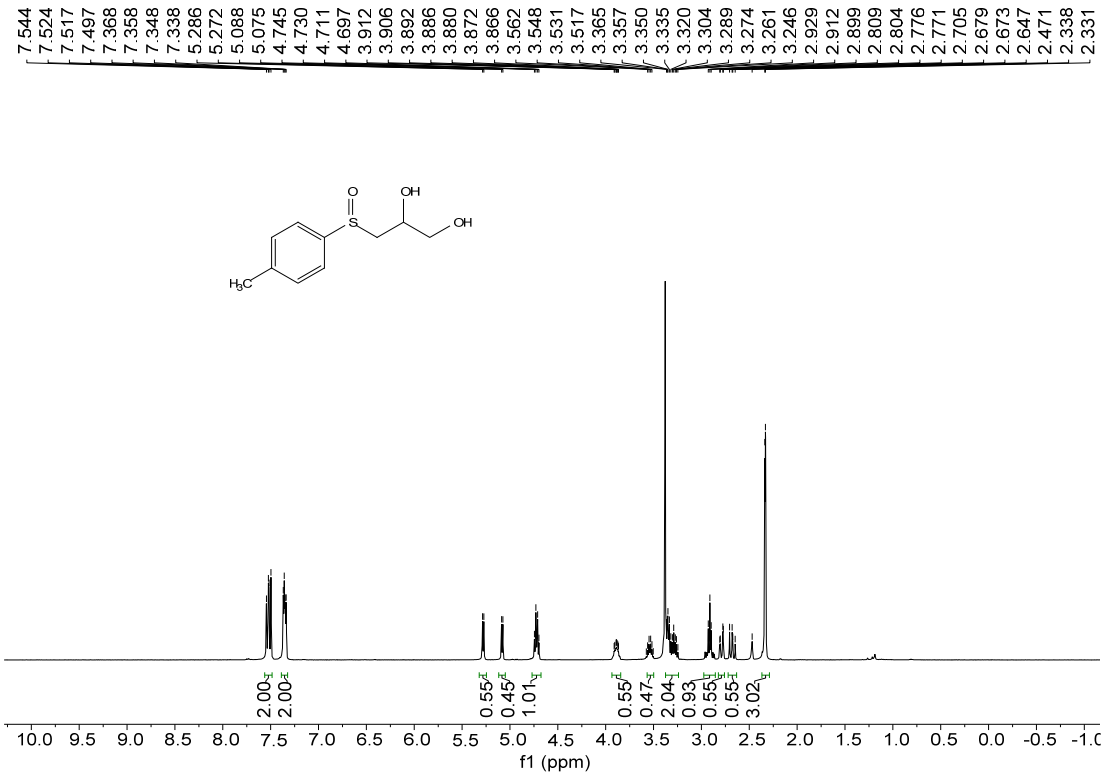


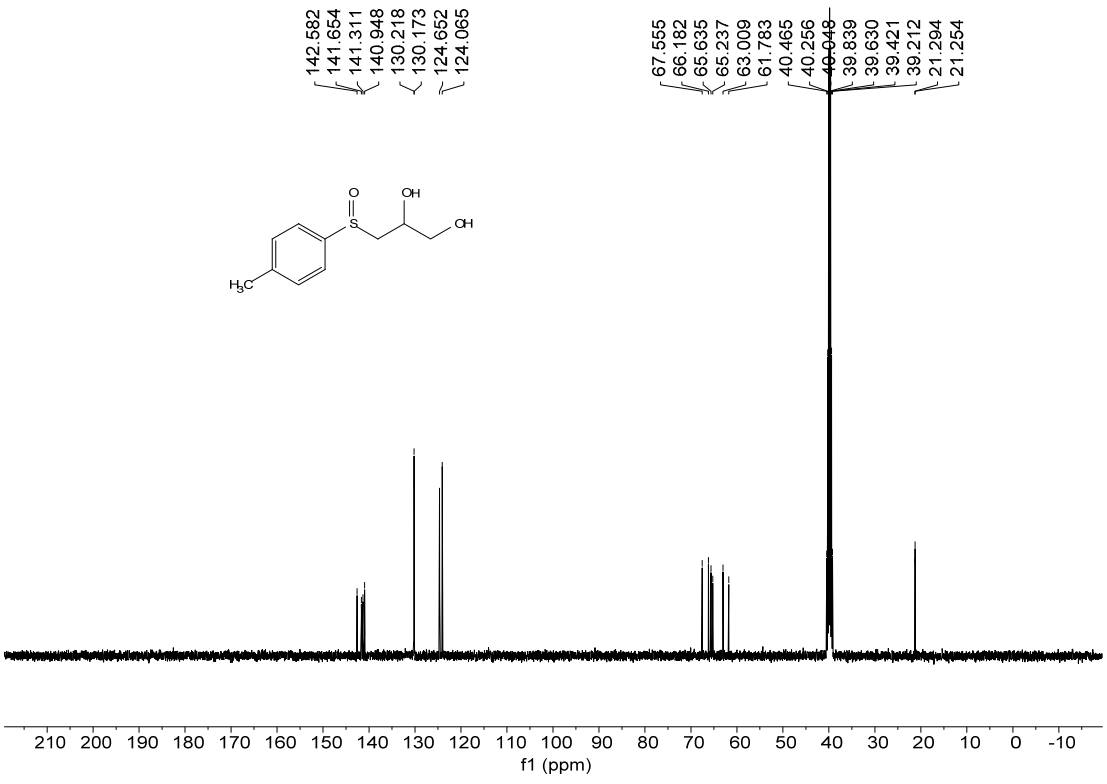
^{1}H and ^{13}C NMR spectra of **3n**



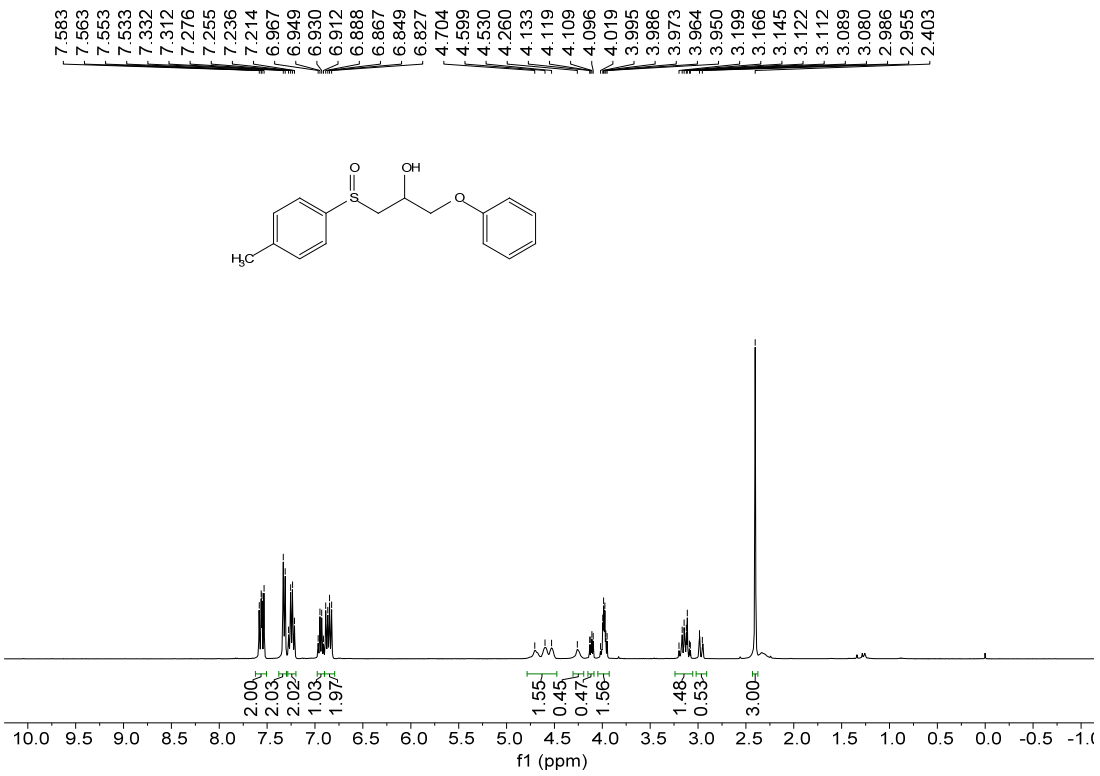


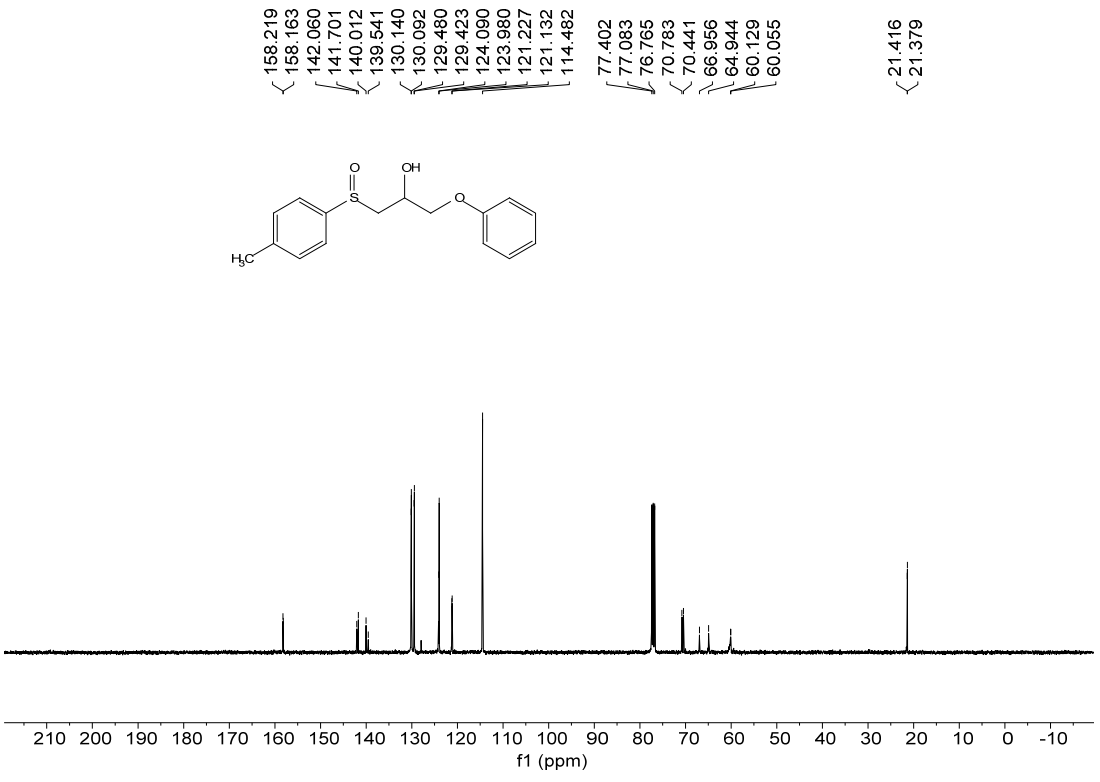
^{1}H and ^{13}C NMR spectra of **3o**



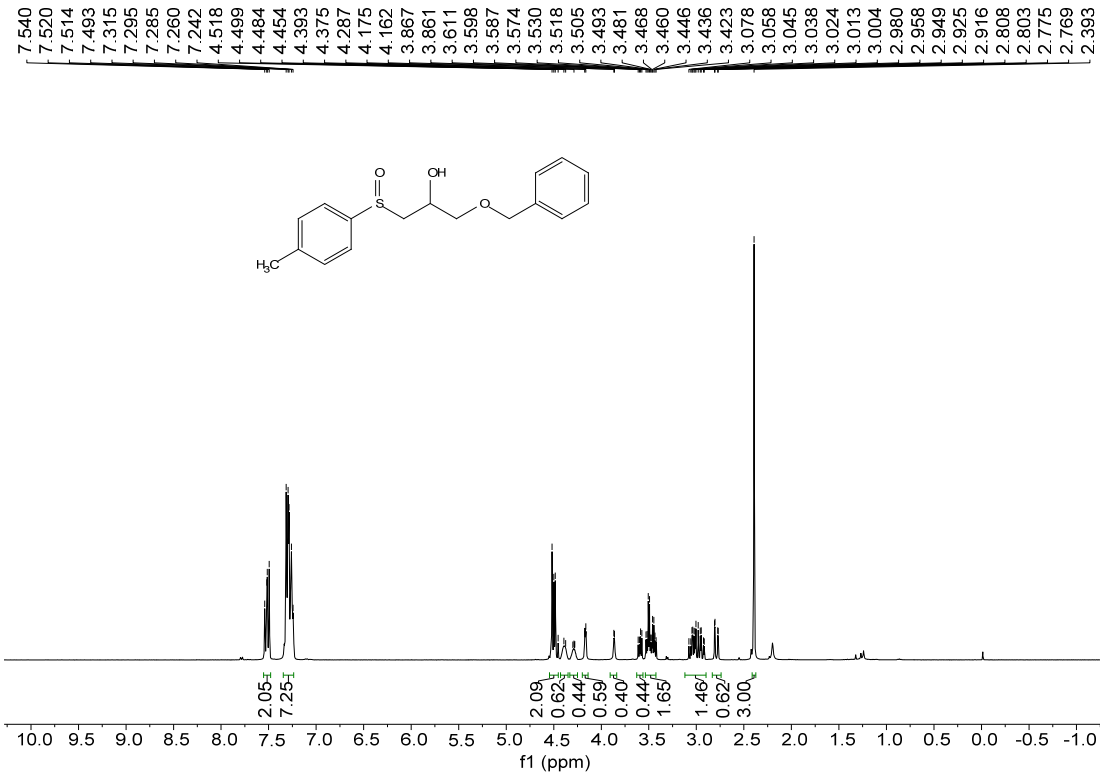


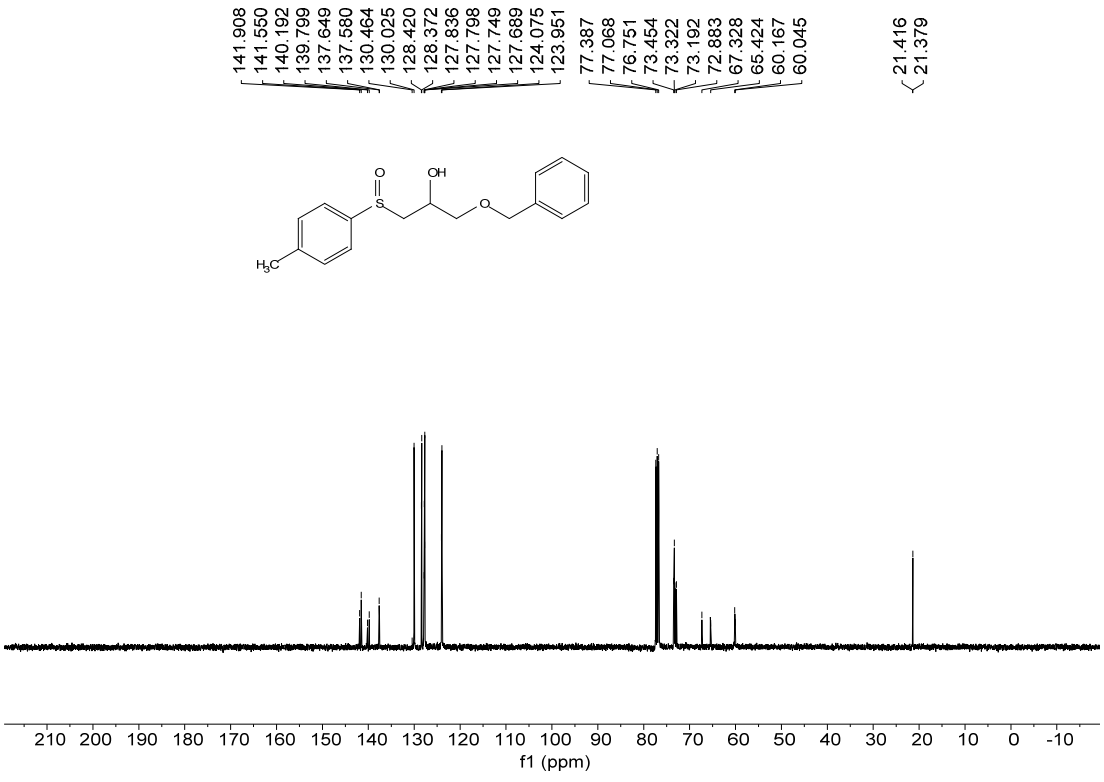
^{1}H and ^{13}C NMR spectra of **3p**



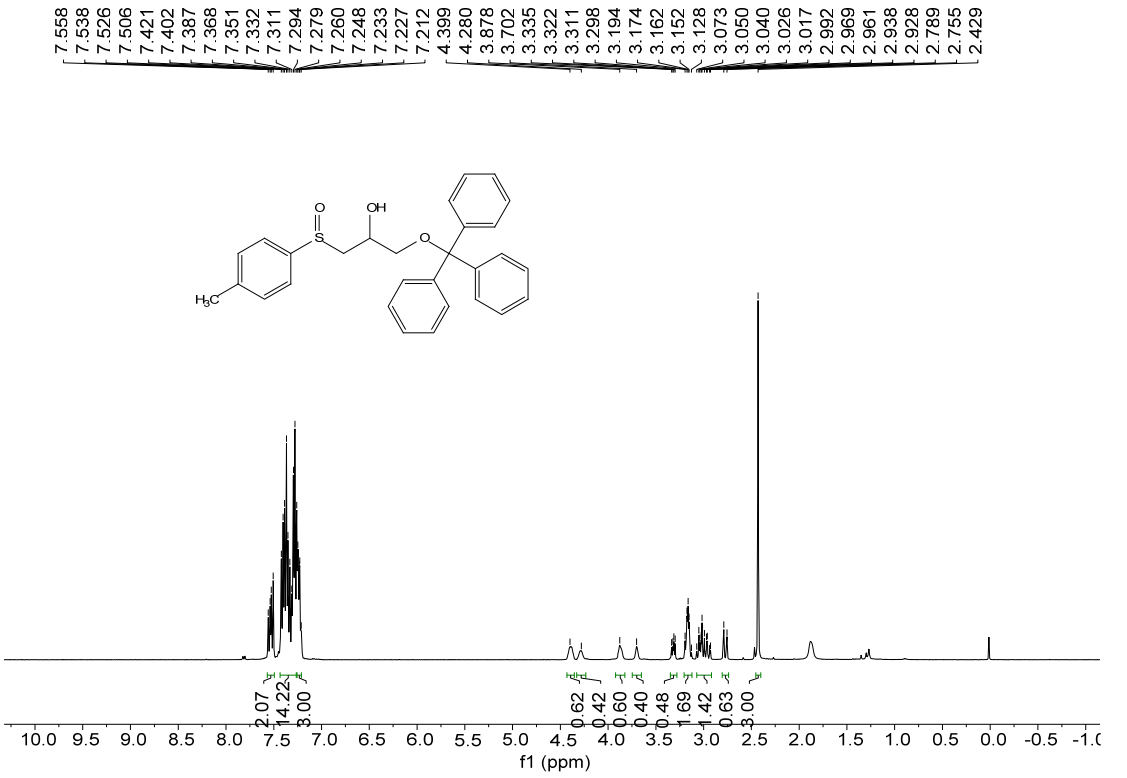


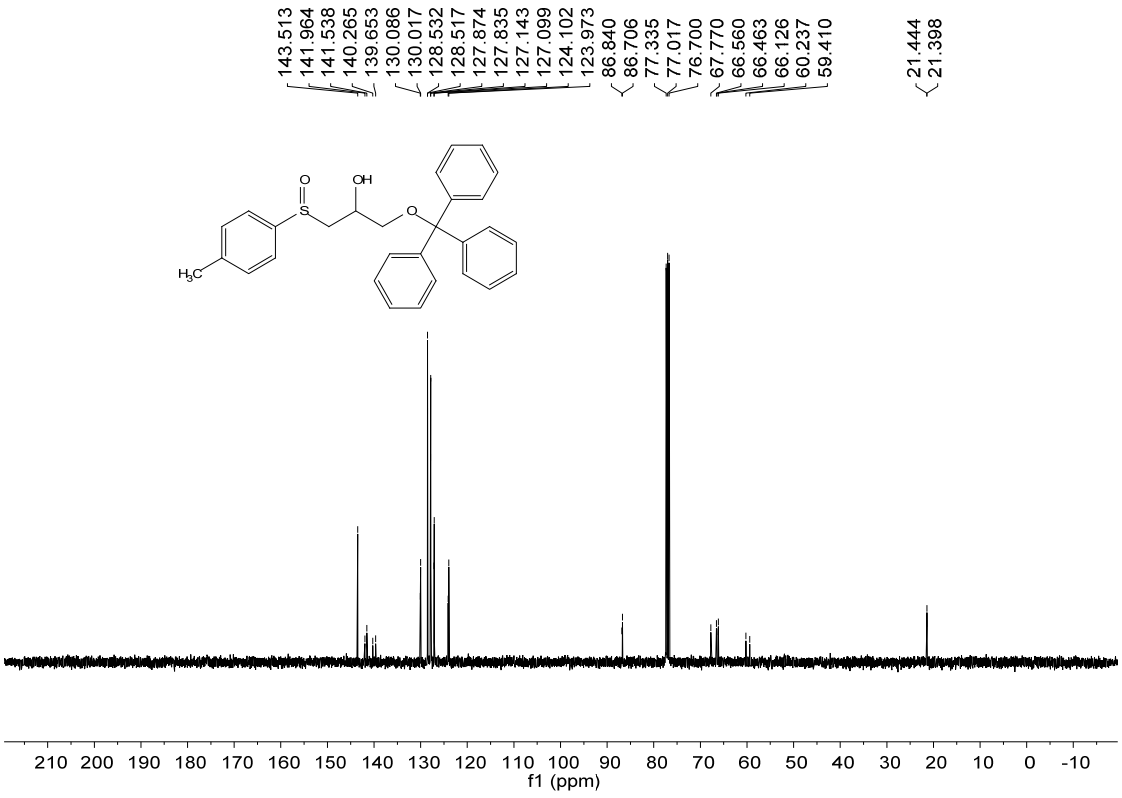
^{1}H and ^{13}C NMR spectra of **3q**



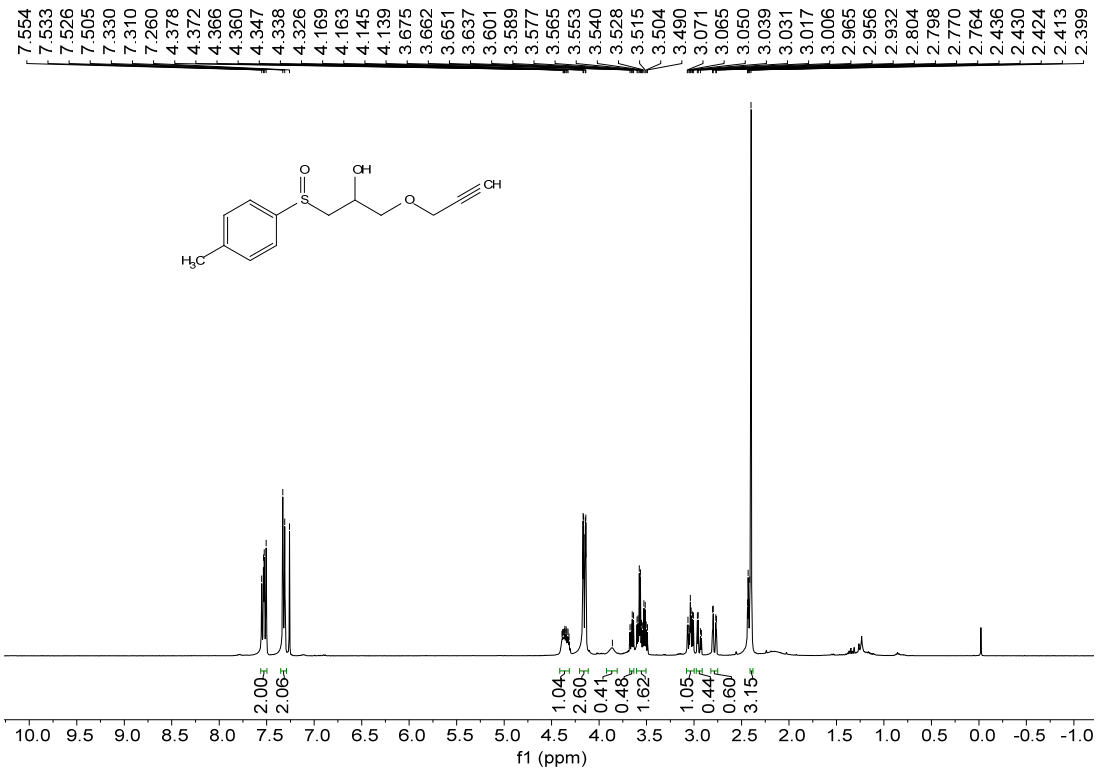


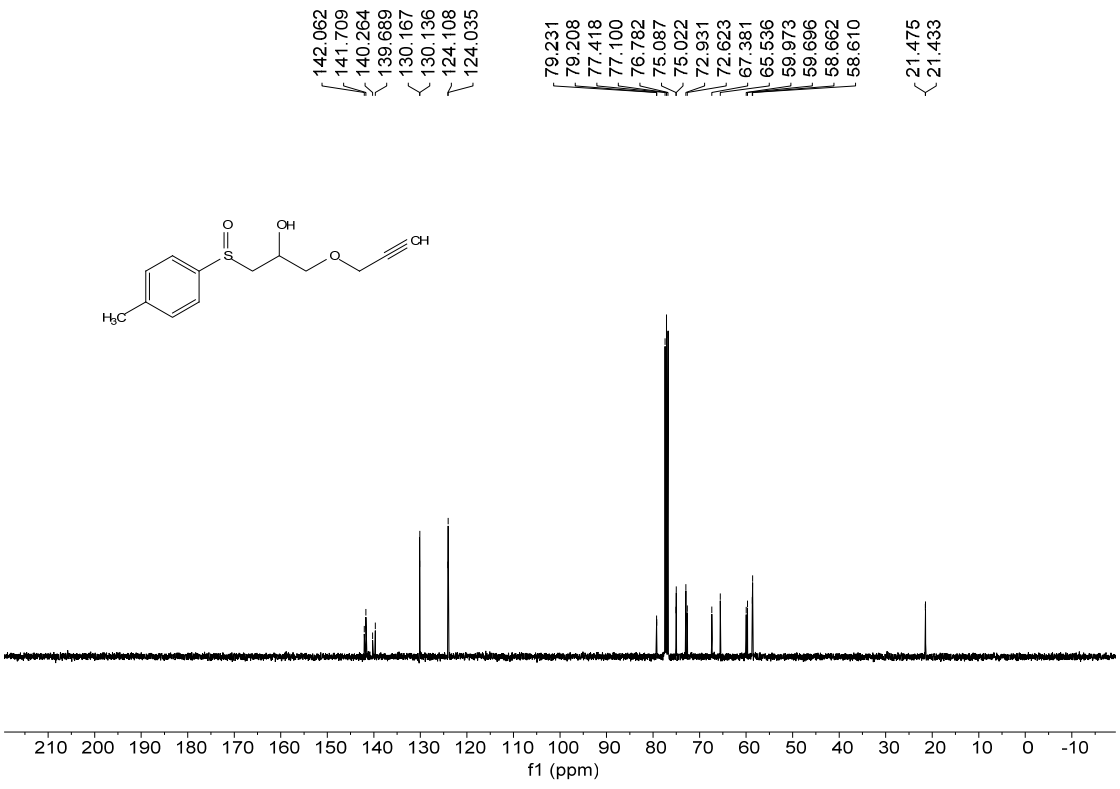
^{1}H and ^{13}C NMR spectra of **3r**



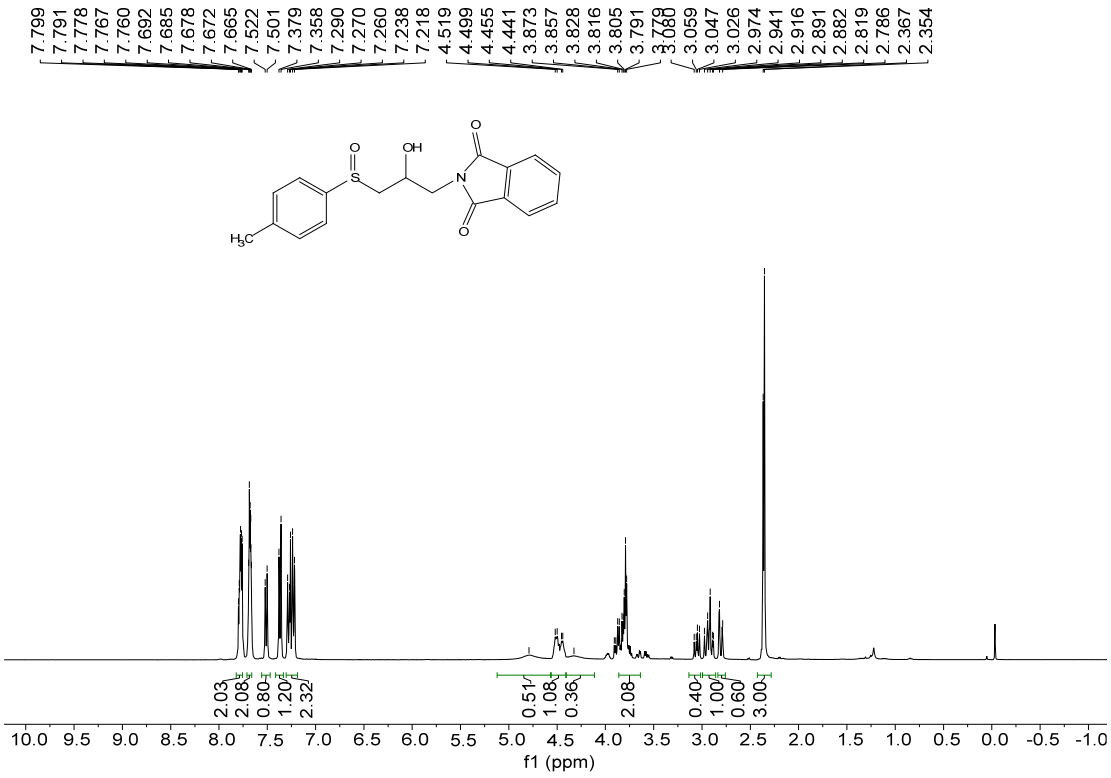


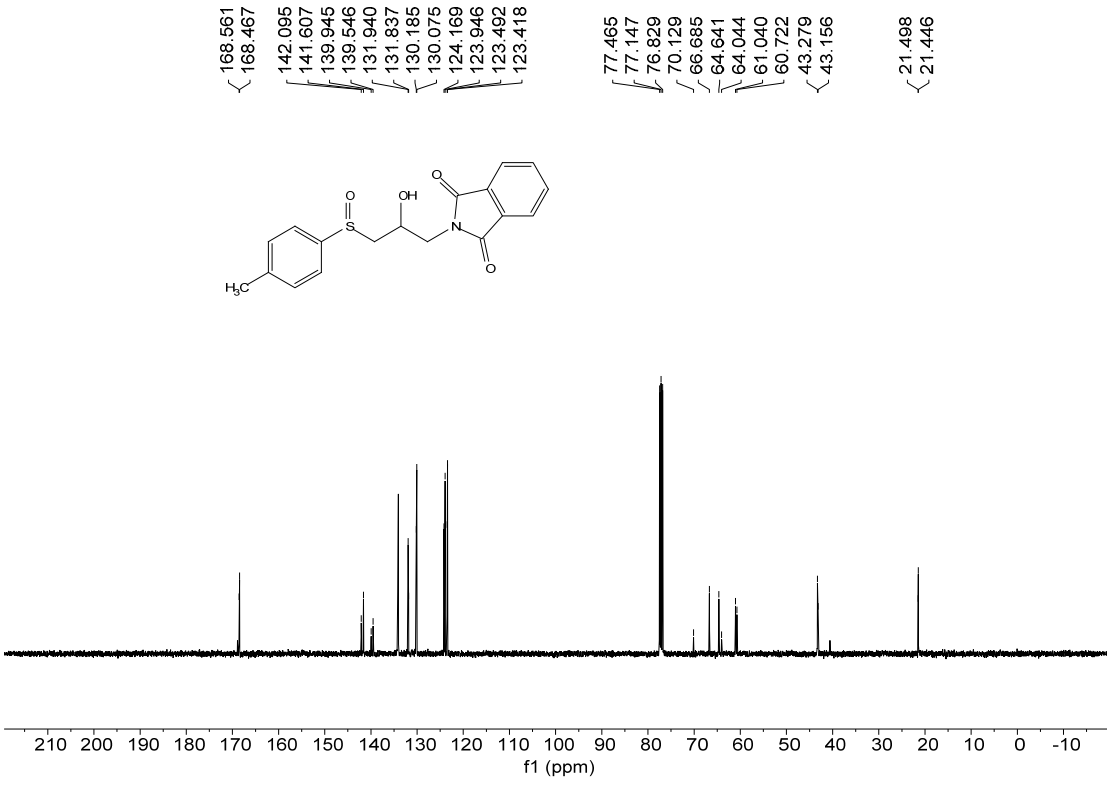
^{1}H and ^{13}C NMR spectra of **3s**



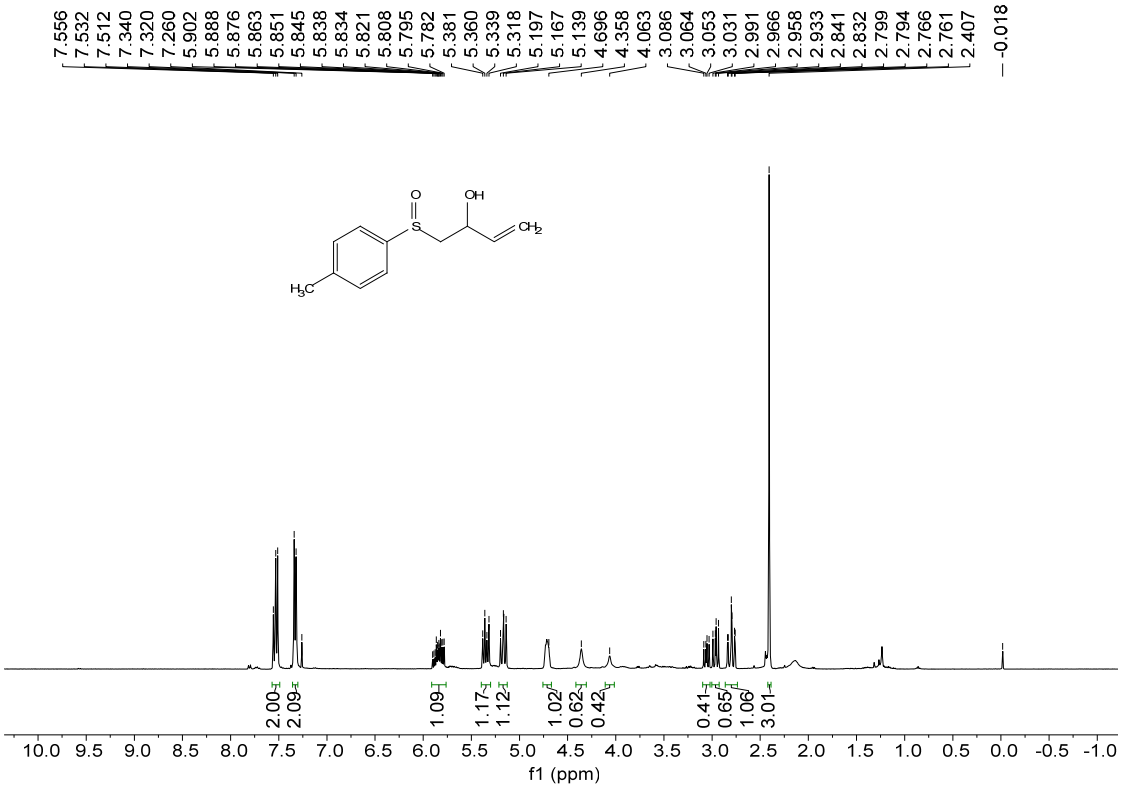


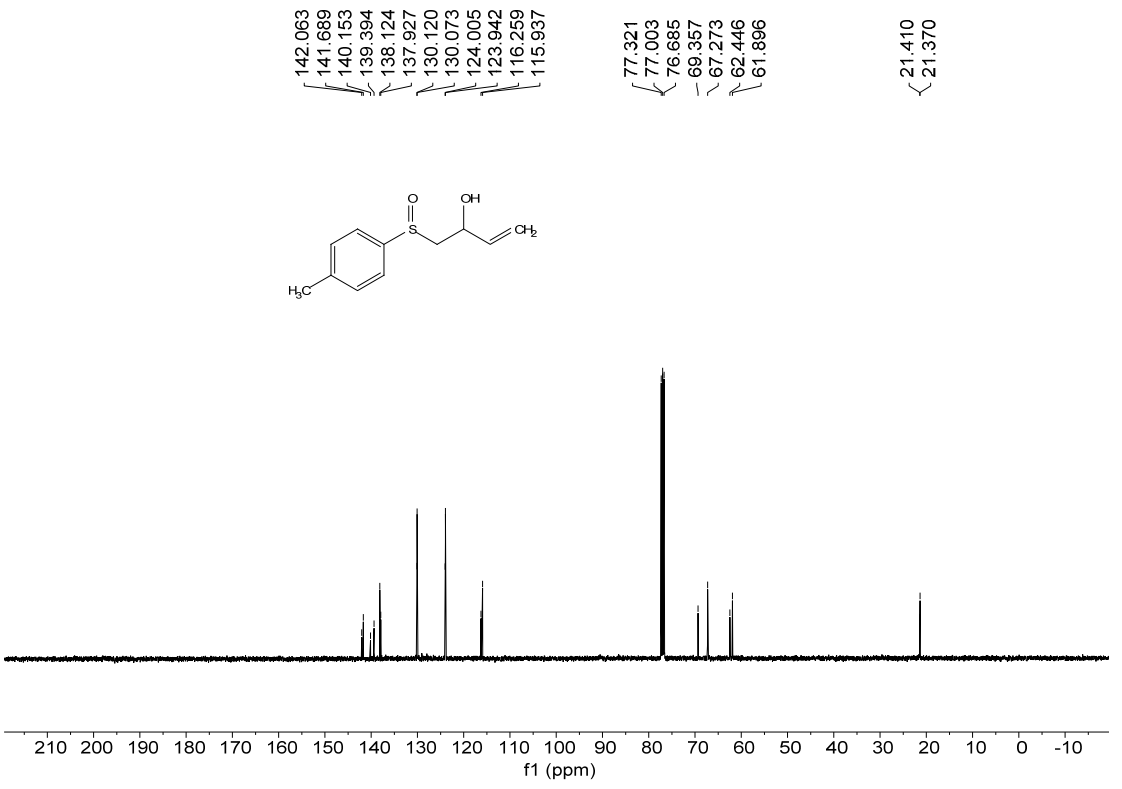
^{1}H and ^{13}C NMR spectra of **3t**



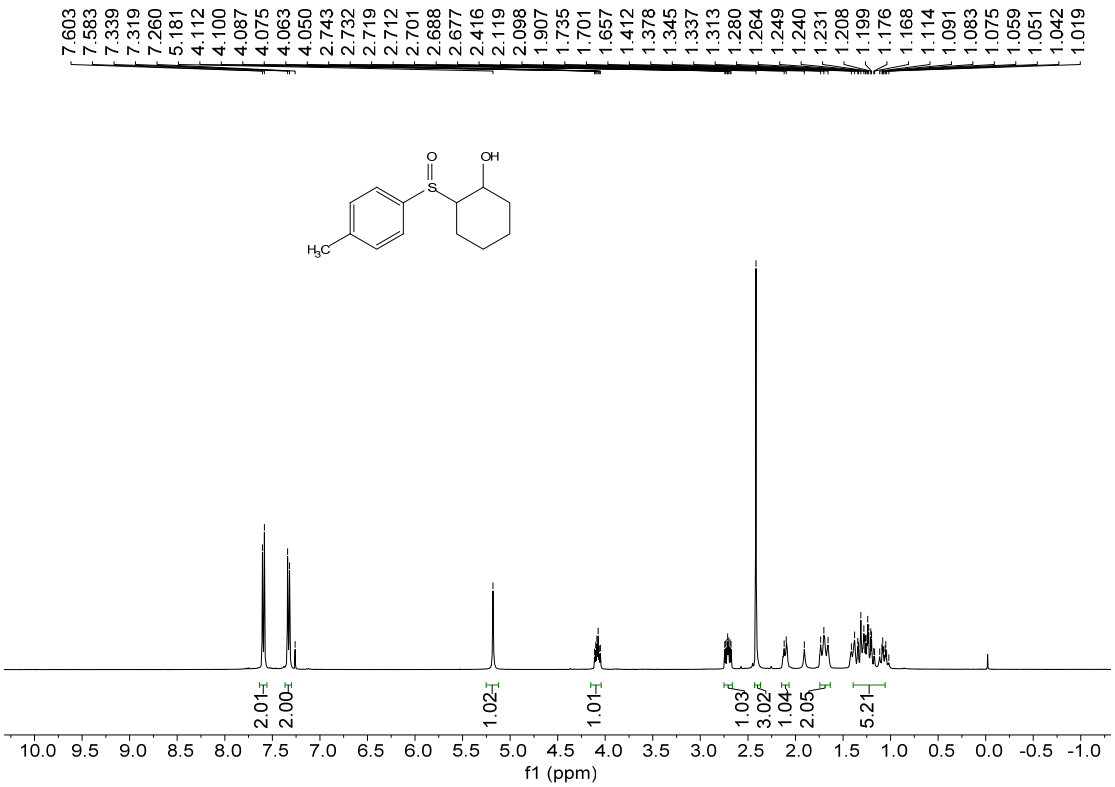


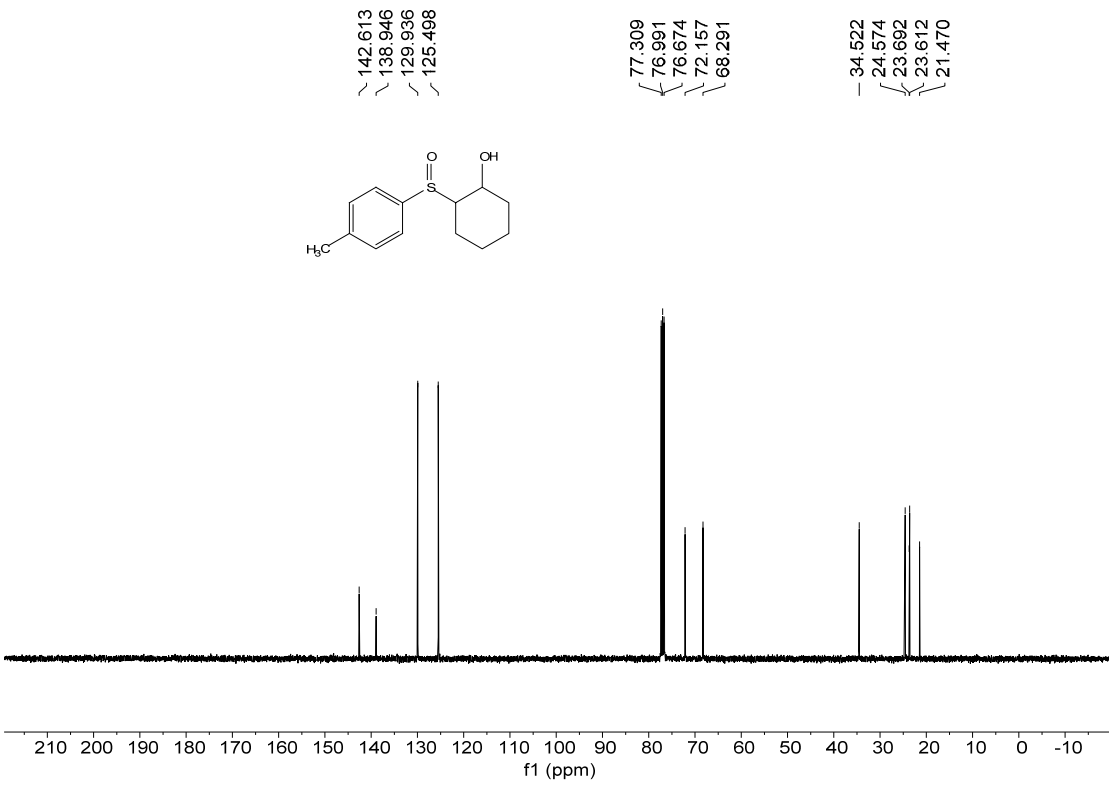
^{1}H and ^{13}C NMR spectra of **3u**



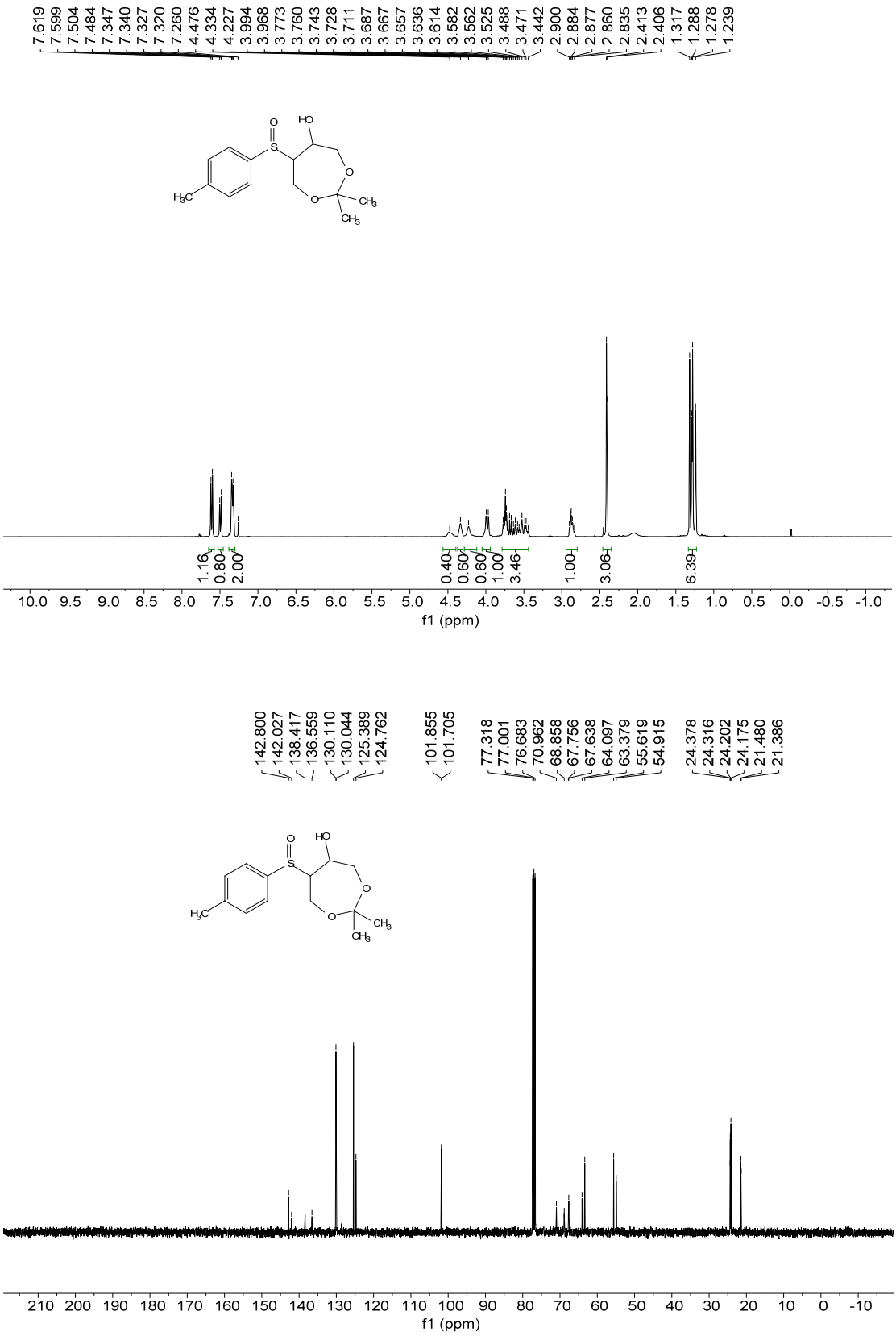


^{1}H and ^{13}C NMR spectra of **3v**





^{1}H and ^{13}C NMR spectra of **3w**



^{1}H and ^{13}C NMR spectra of **3x**