

SUPPORTING INFORMATION

Acid-Controlled Access to β -Sulfenyl Ketones and α,β -Disulfonyl Ketones by Pummerer Reaction of β -Keto Sulfones and Sulfoxides

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X-ray crystallographic data of compound **2i** (CCDC 1903279)

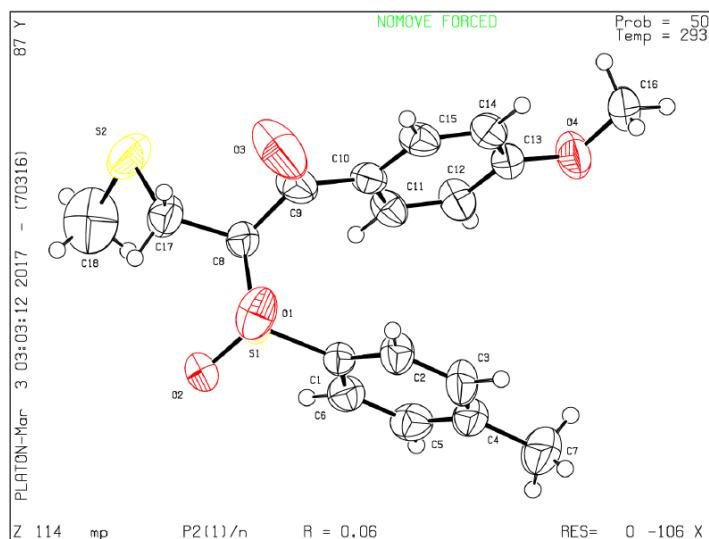


Figure S1. ORTEP drawing of **2i** showing thermal ellipsoid at the 50% probability level

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Bond precision: C-C = 0.0043 Å          Wavelength=0.71073

Cell:           a=5.6850(4)      b=15.5496(13)      c=20.7033(15)
                alpha=90          beta=91.102(1)       gamma=90
Temperature:   293 K

Calculated                               Reported
Volume          1829.8(2)            1829.8(2)
Space group     P 21/n              P2(1) /n
Hall group      -P 2yn             ?
Moietiy formula C18 H20 O4 S2        ?
Sum formula    C18 H20 O4 S2        C18 H20 O4 S2
Mr              364.46             364.46
Dx,g cm-3      1.323              1.323
Z               4                  4
Mu  (mm-1)      0.309              0.309
F000           768.0              768.0
F000'          769.33             6,18,24
h,k,lmax       6,18,24             6,18,24
Nref           3343              3340
Tmin,Tmax     0.931,0.940        0.932,0.941
Tmin'          0.931

Correction method= # Reported T Limits: Tmin=0.932 Tmax=0.941
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max) = 25.370
R(reflections)= 0.0578( 2804)    wR2(reflections)= 0.1709( 3340)
S = 1.055                      Npar= 220

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Crystallization: Crystals of compound **2i** suitable for X-ray analysis were grown from the solvent of ethyl acetate/hexane by slow evaporation method.

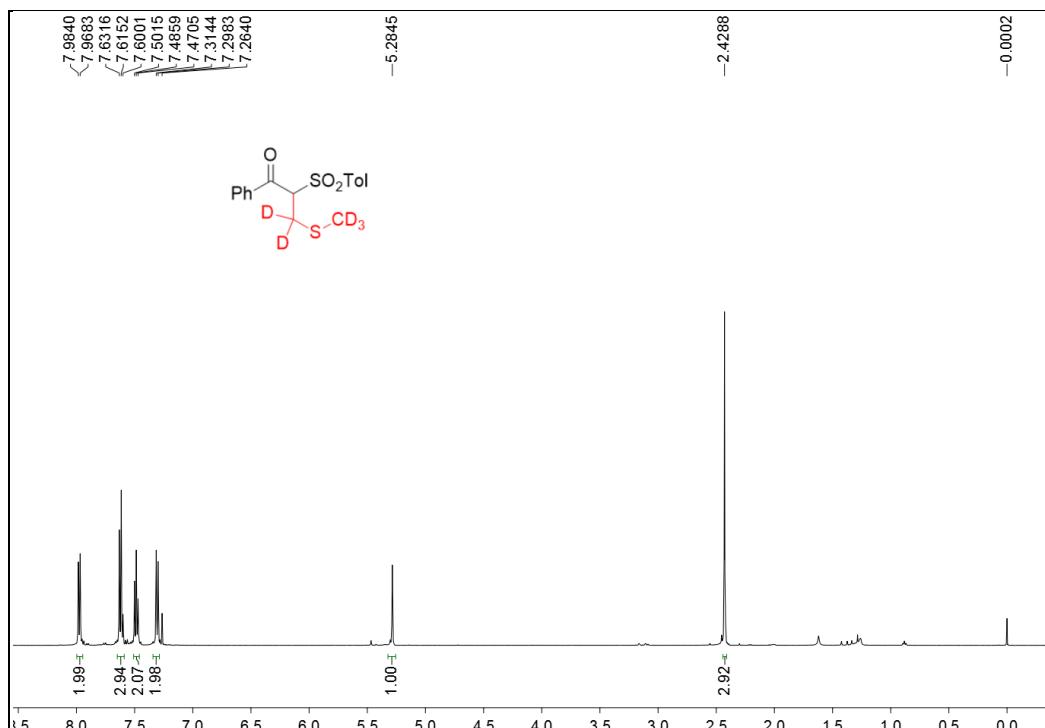
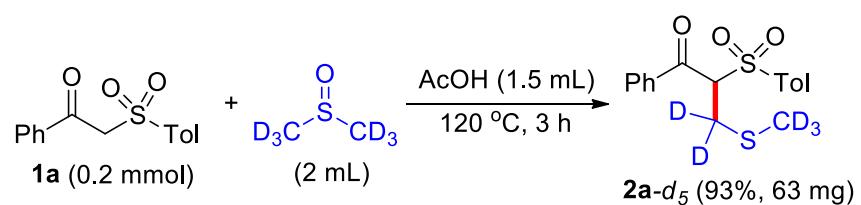
X-Ray Data Collection and structure Refinement Details:

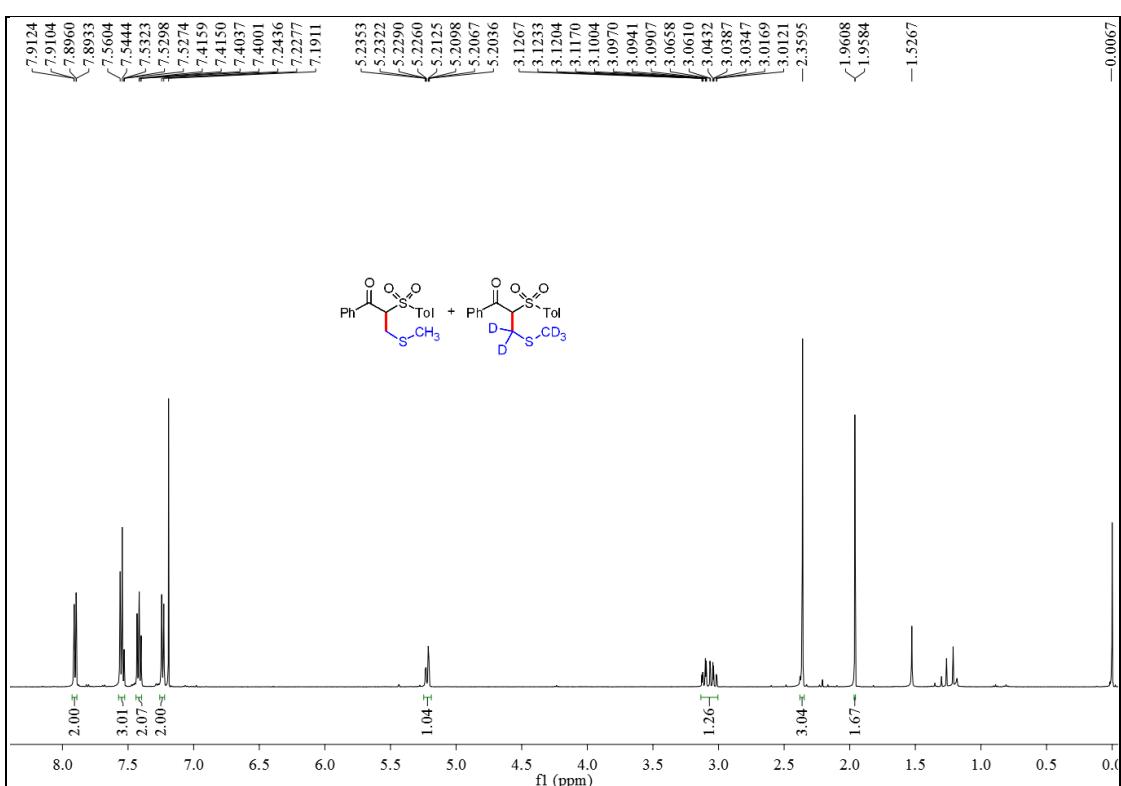
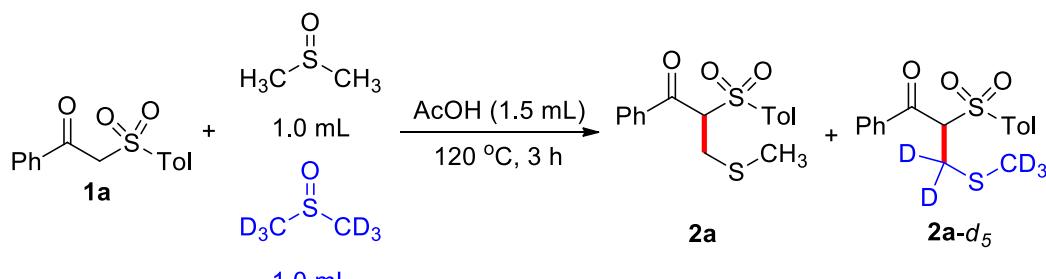
Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.¹ The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package.² The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.³ All crystal structural pictures drawn by IUCr web.

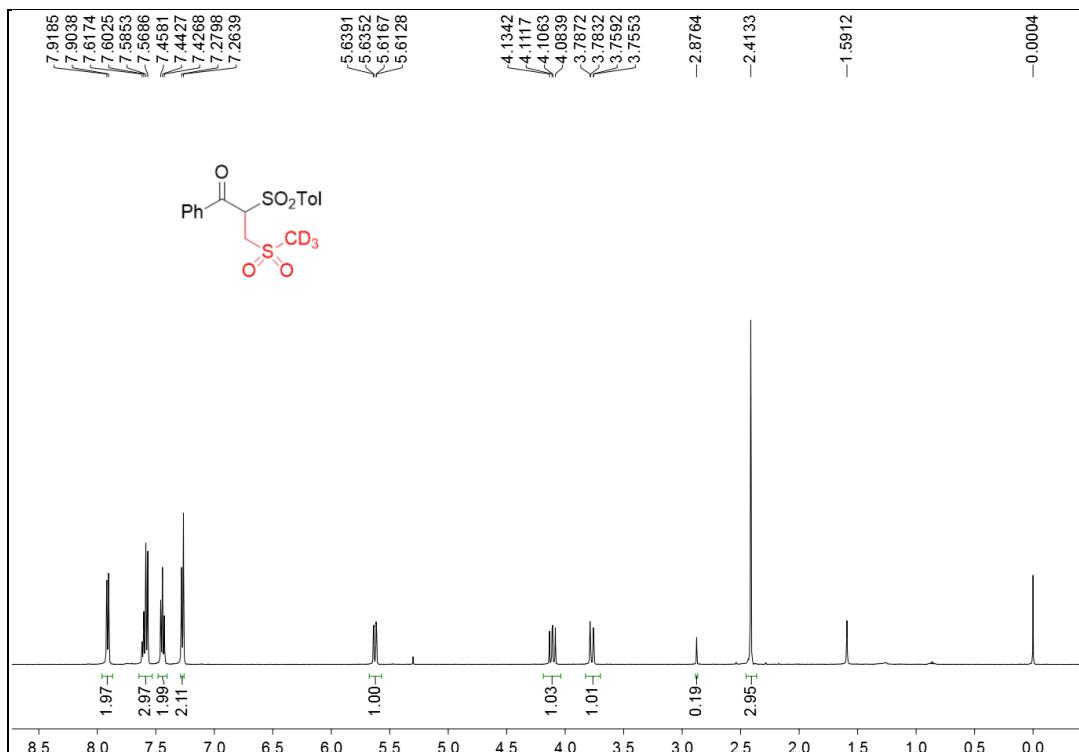
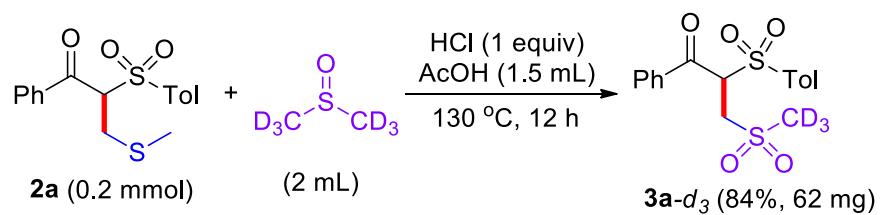
References

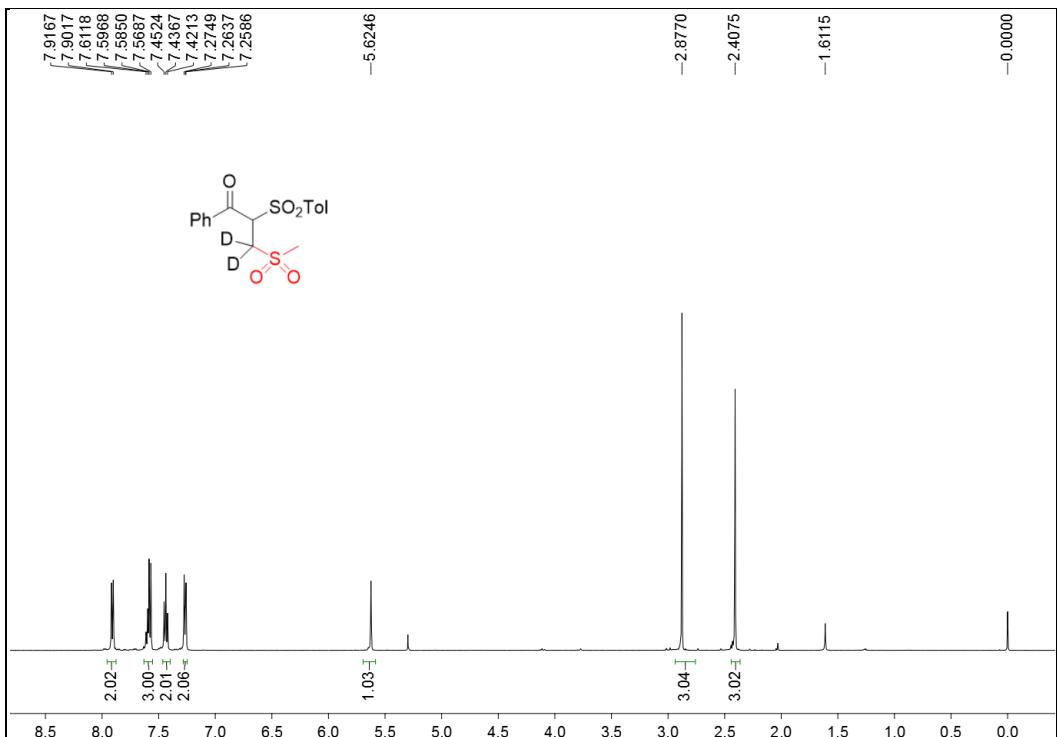
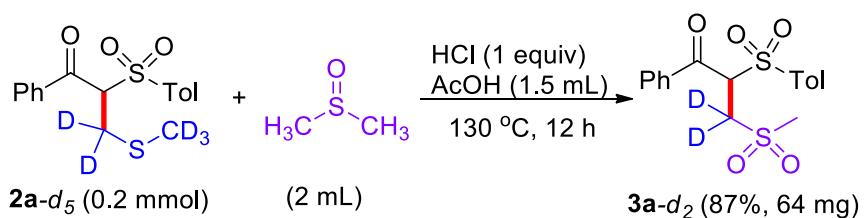
- [1] Sheldrick G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany, **1996**.
- [2] Sheldrick G. M. *Acta Cryst.* **2015**, *A71*, 3-8.
- [3] Spek A. L. *Acta Cryst.* **2015**, *C71*, 9-18.

Copies of ^1H NMR spectra of compounds **2a-d₅, **3a-d₃** and **3a-d₂****

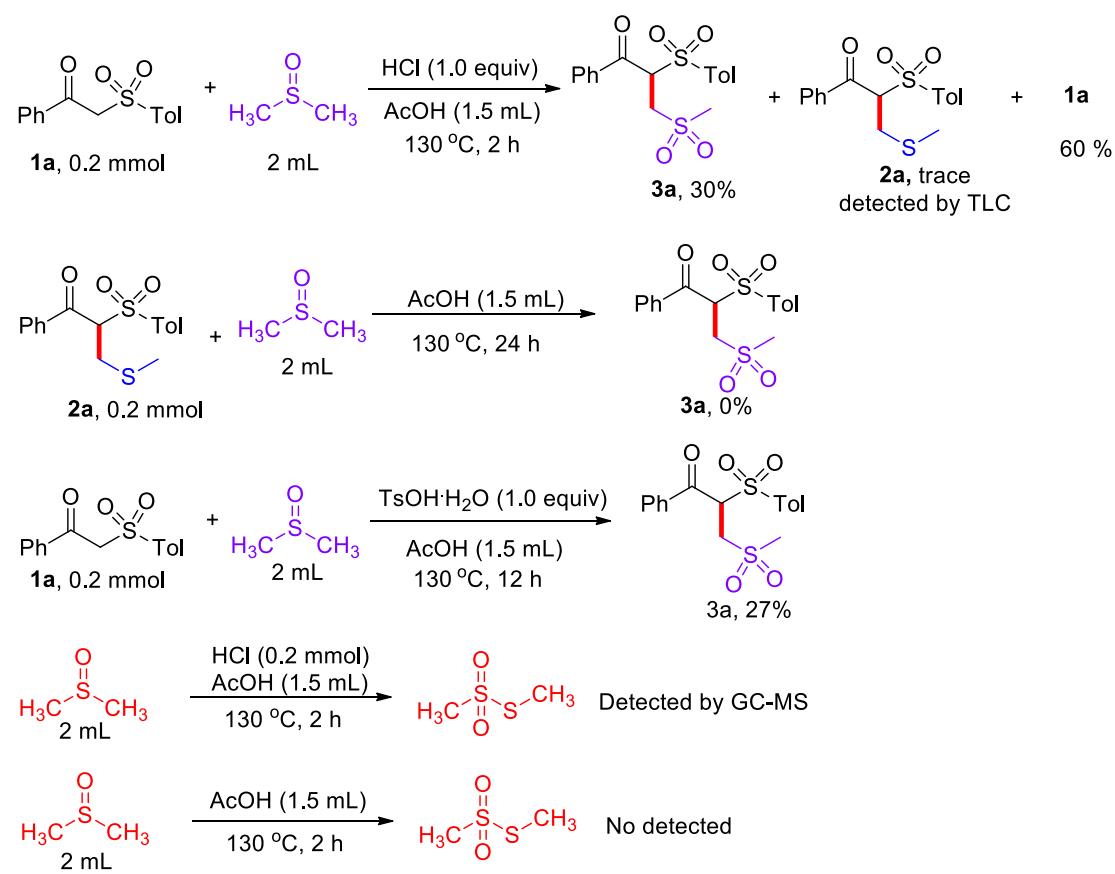






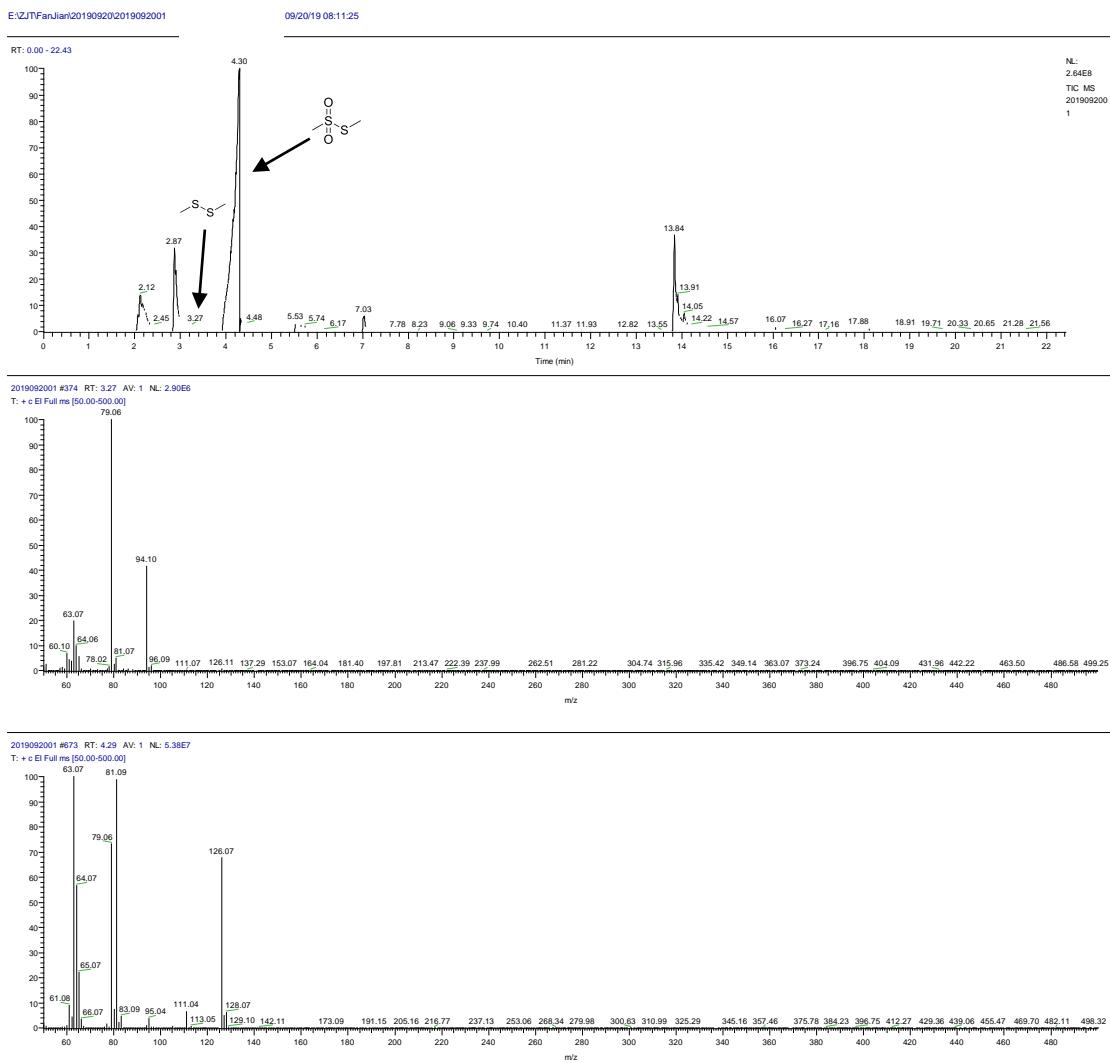


Role investigation of HCl



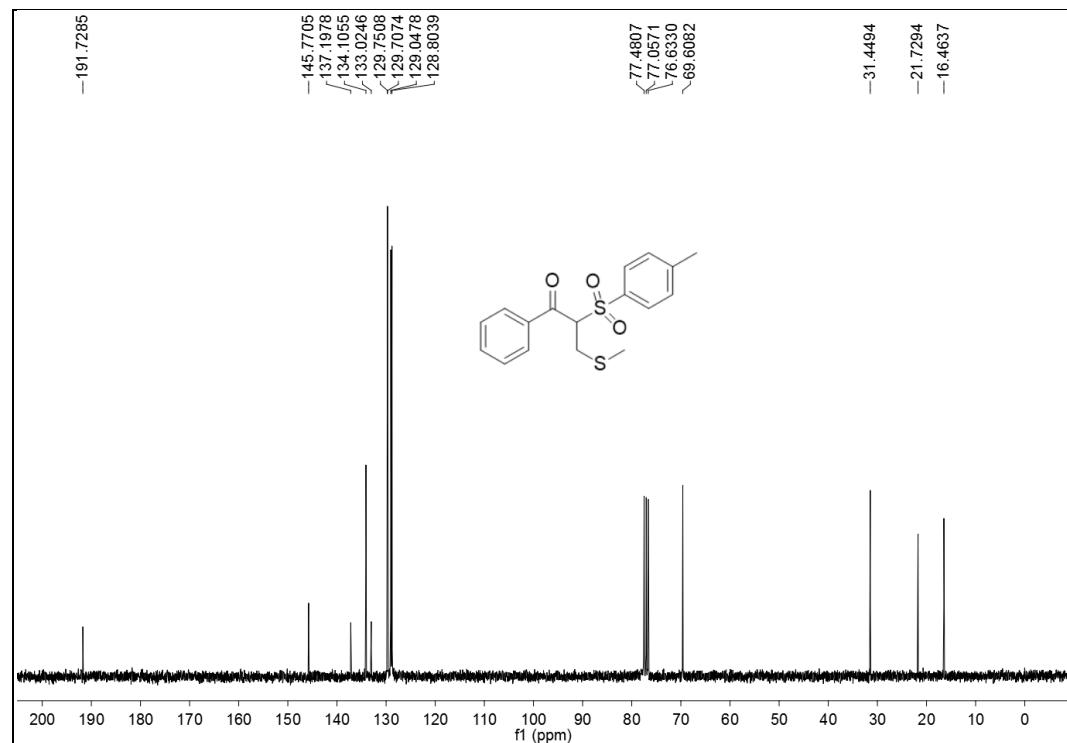
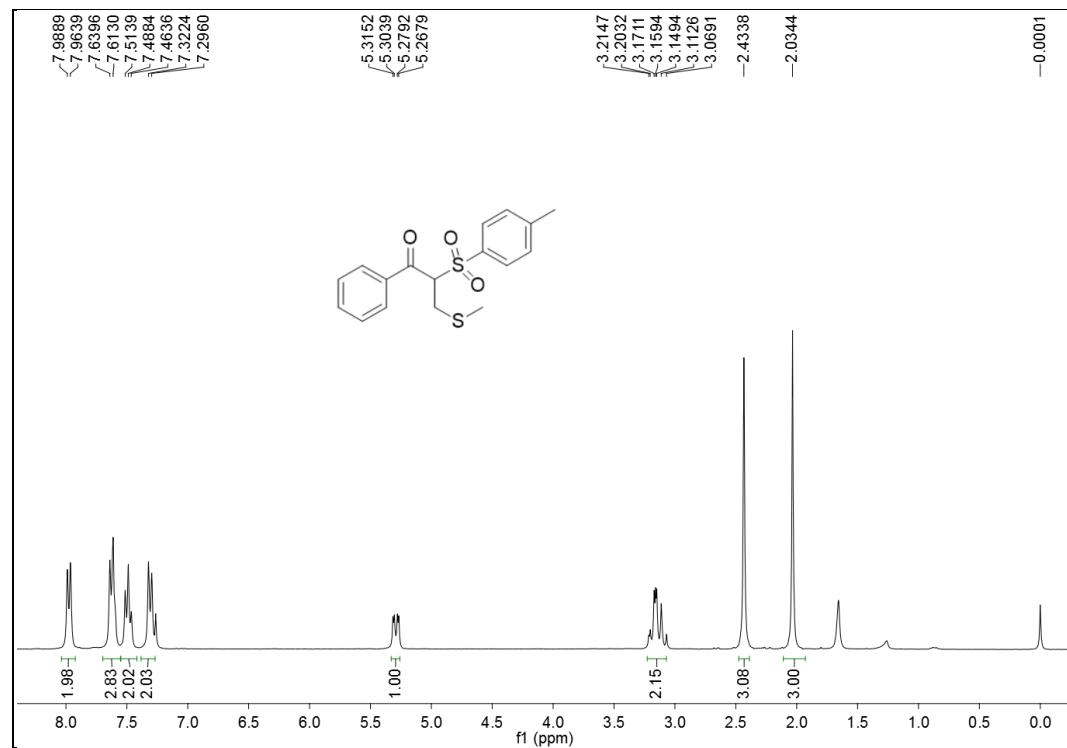
GC-MS Analysis for dimethyldisulfide and methyl methanethiosulfonate

To a stirring solution of 1-phenyl-2-tosylethanone (**1a**, 0.2 mmol) in DMSO (2 mL)/AcOH (1.5 mL) was added 0.2 mmol HCl (12 M aqueous solution, 17 μ L). The reaction mixture was stirred at 130 °C for 10 h. After the completion of the reaction, the reaction mixture was used directly for GC-MS analysis.

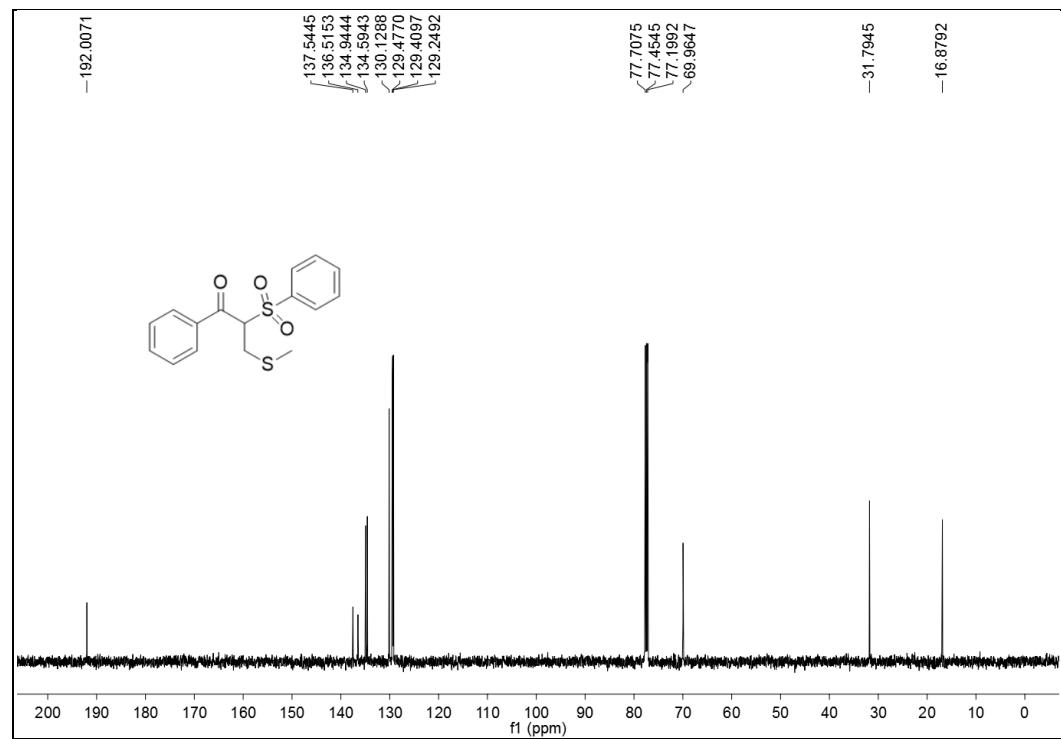
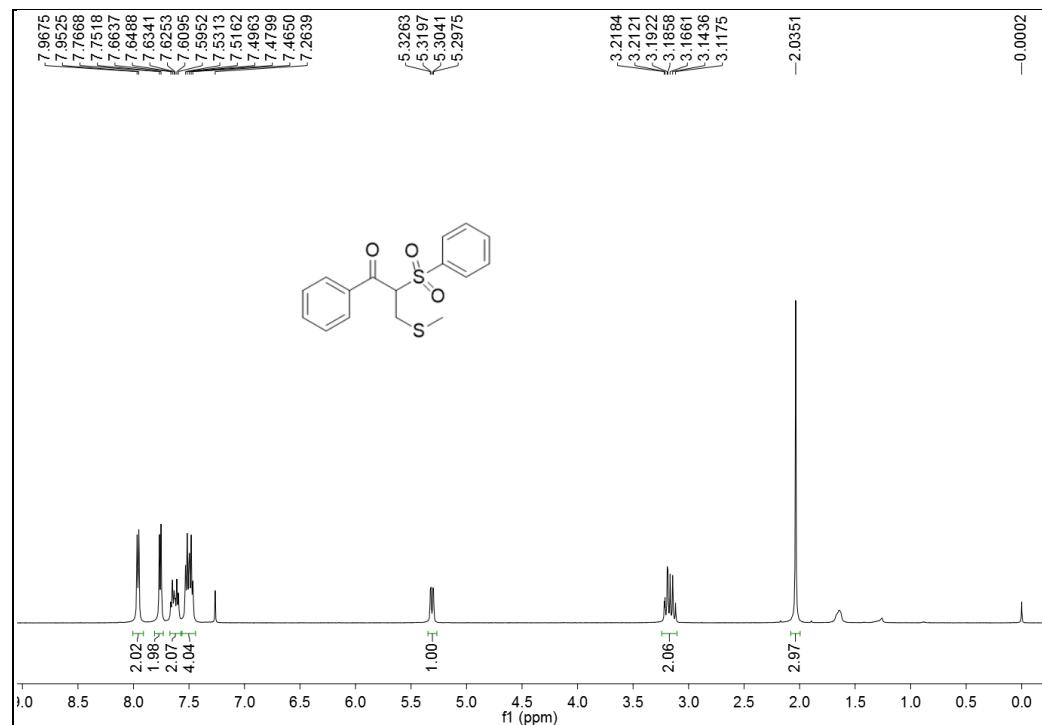


Copies of ^1H NMR and ^{13}C NMR spectra of compounds 2

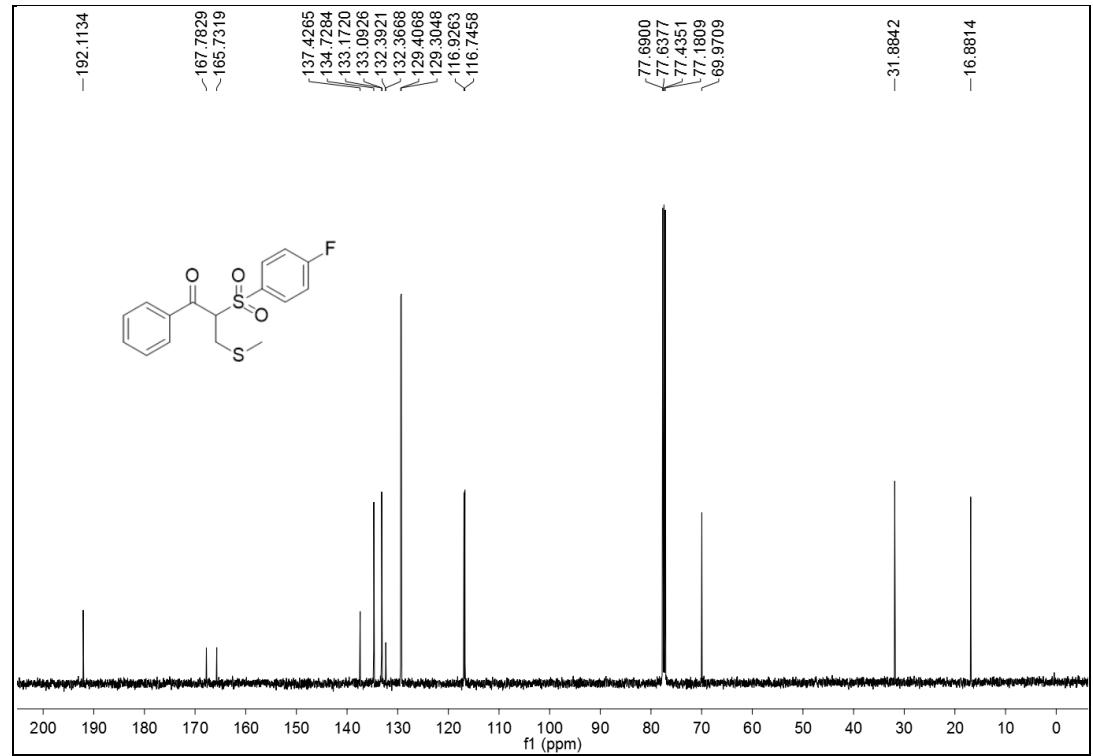
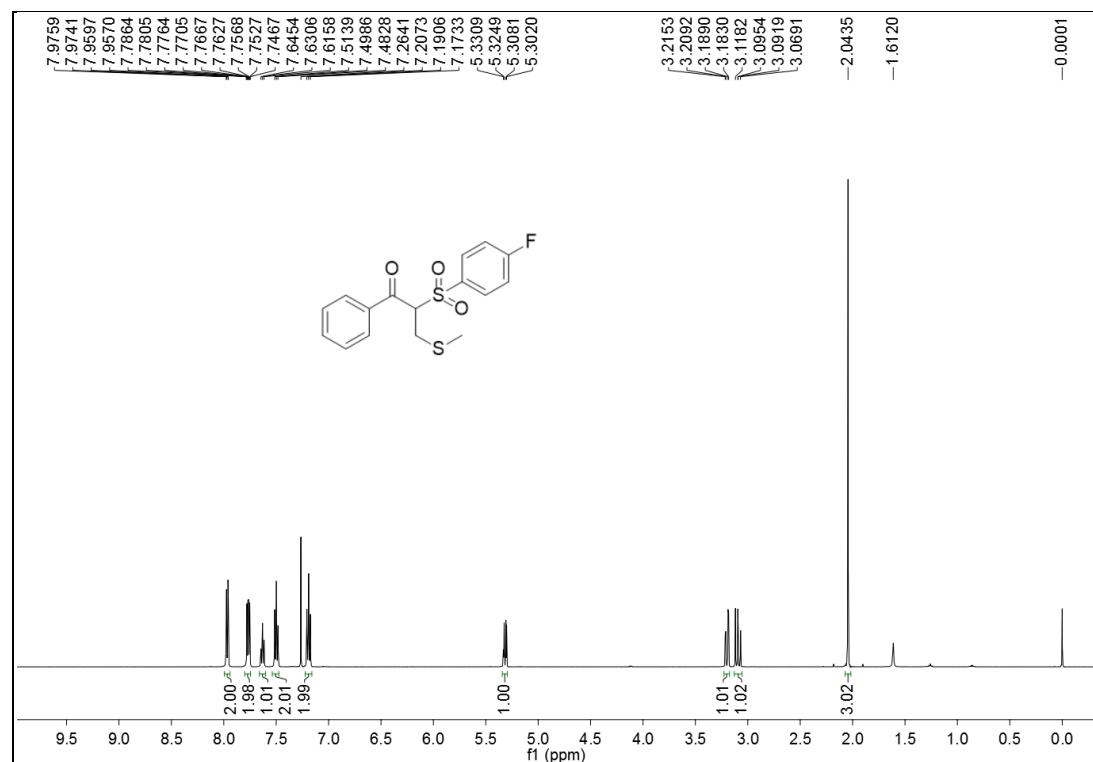
3-(methylthio)-1-phenyl-2-tosylpropan-1-one (2a)



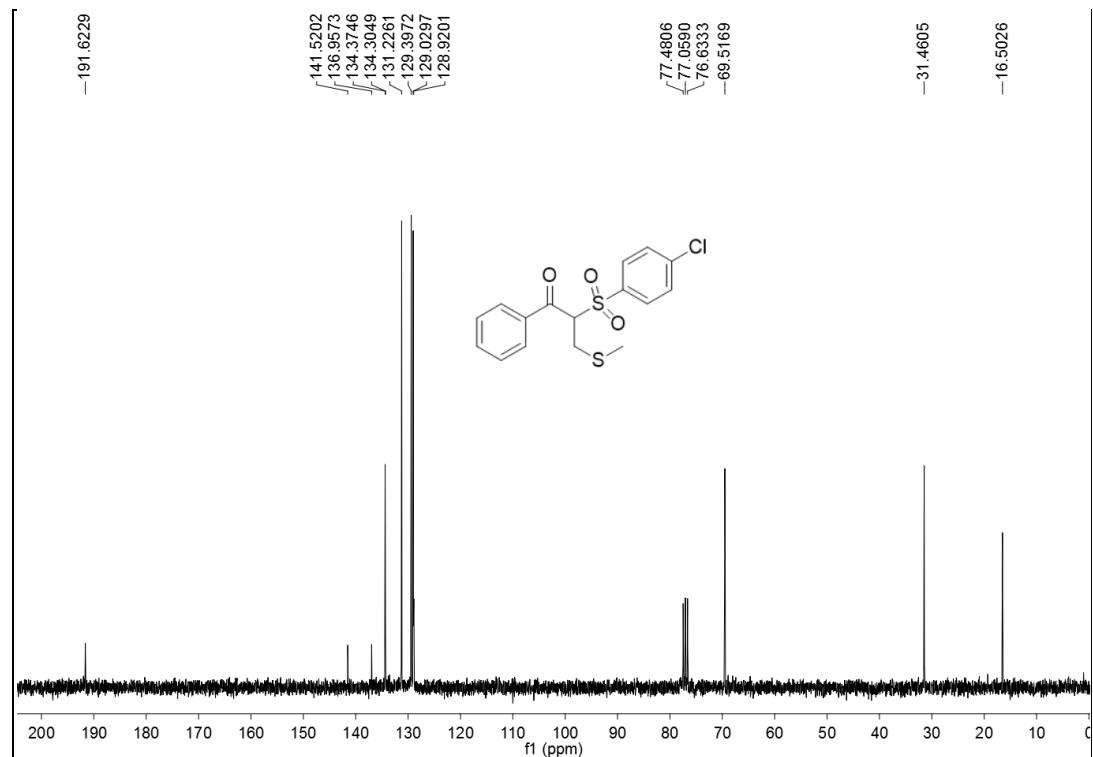
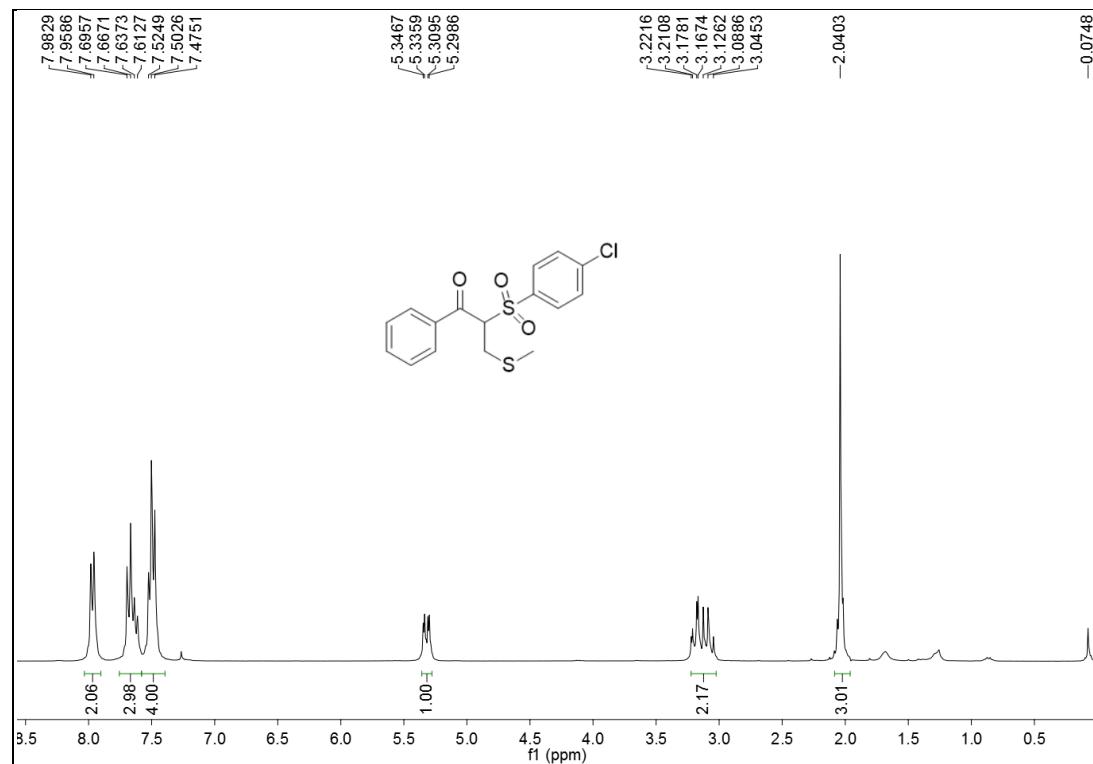
3-(methylthio)-1-phenyl-2-(phenylsulfonyl)propan-1-one(2b)



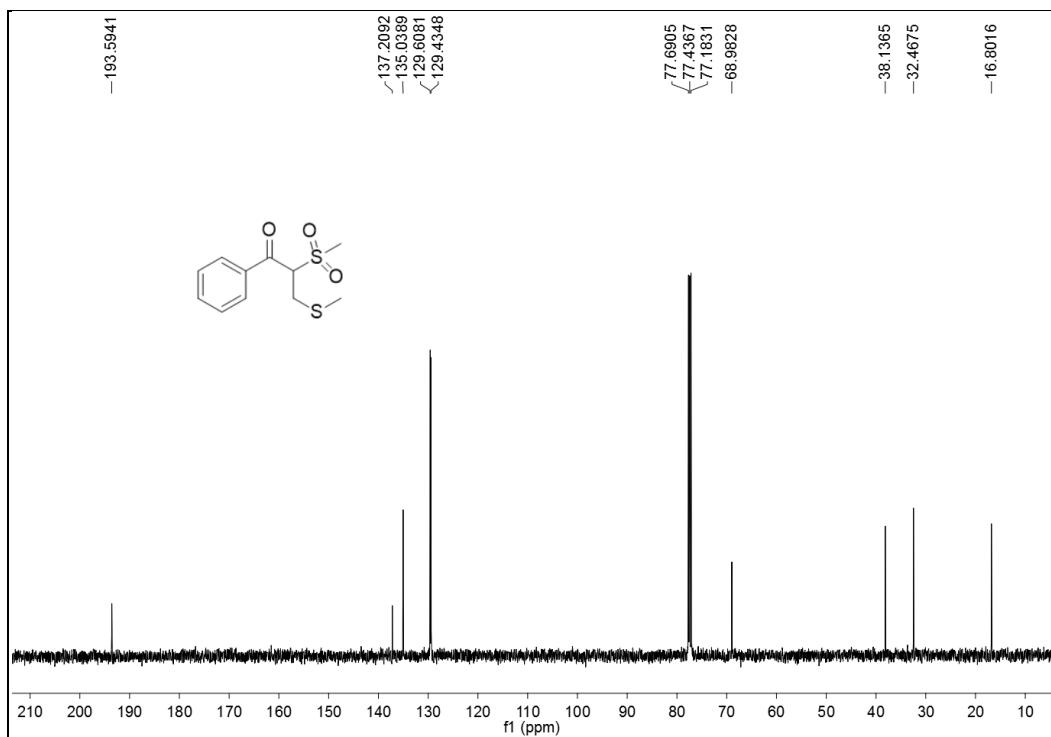
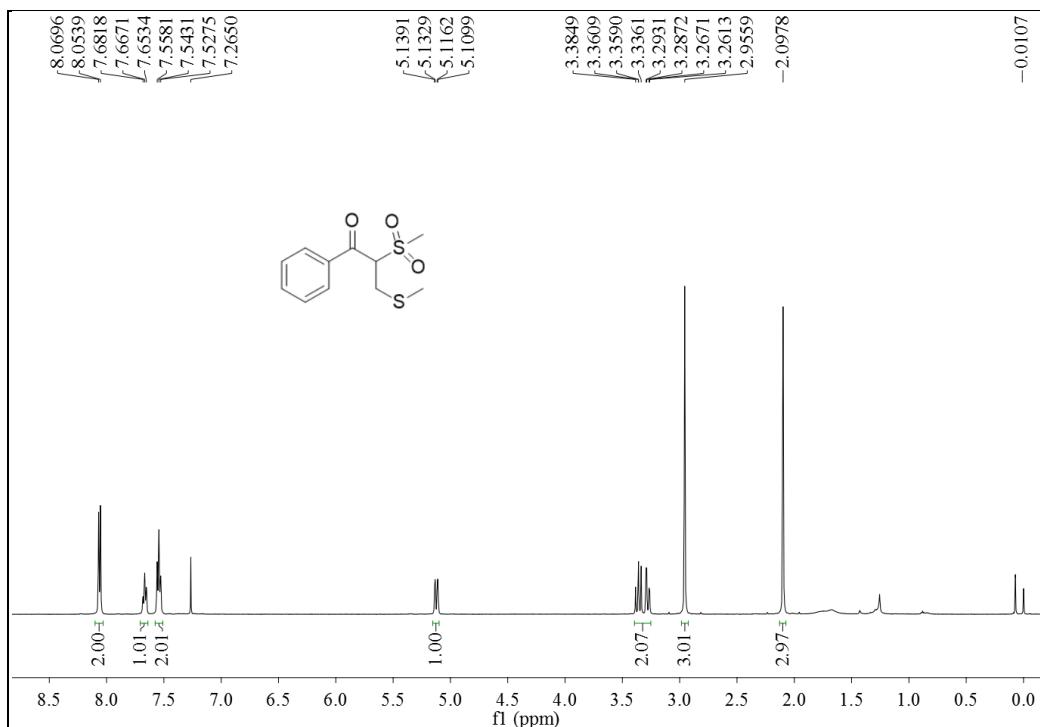
2-((4-fluorophenyl)sulfonyl)-3-(methylthio)-1-phenylpropan-1-one (2c)



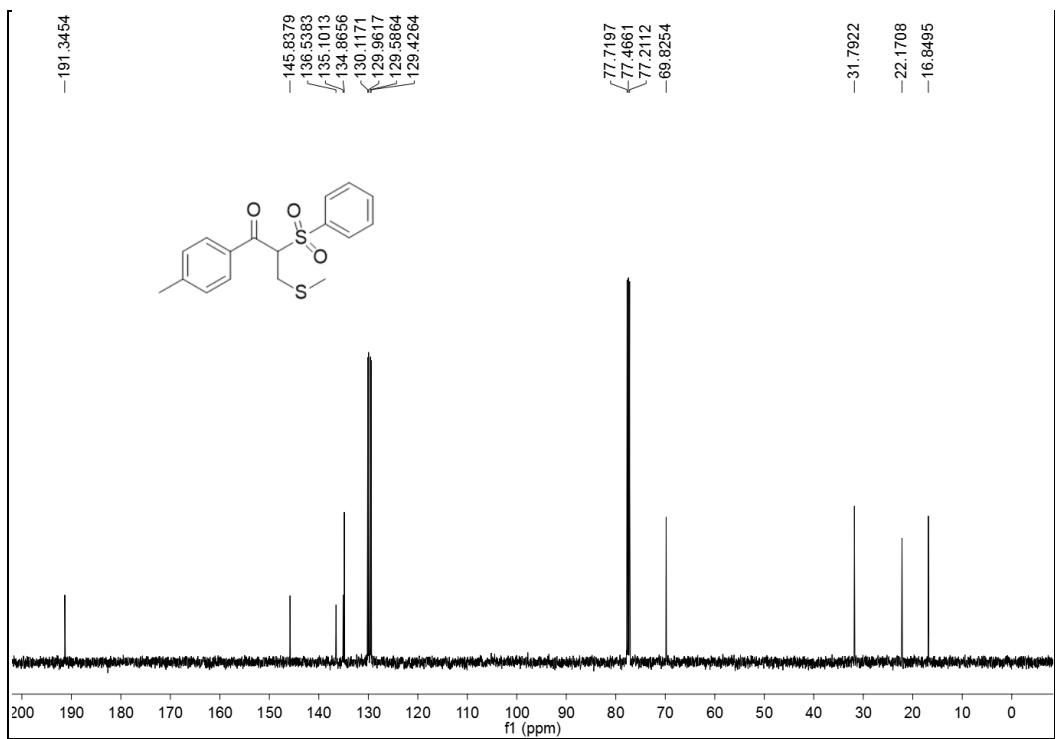
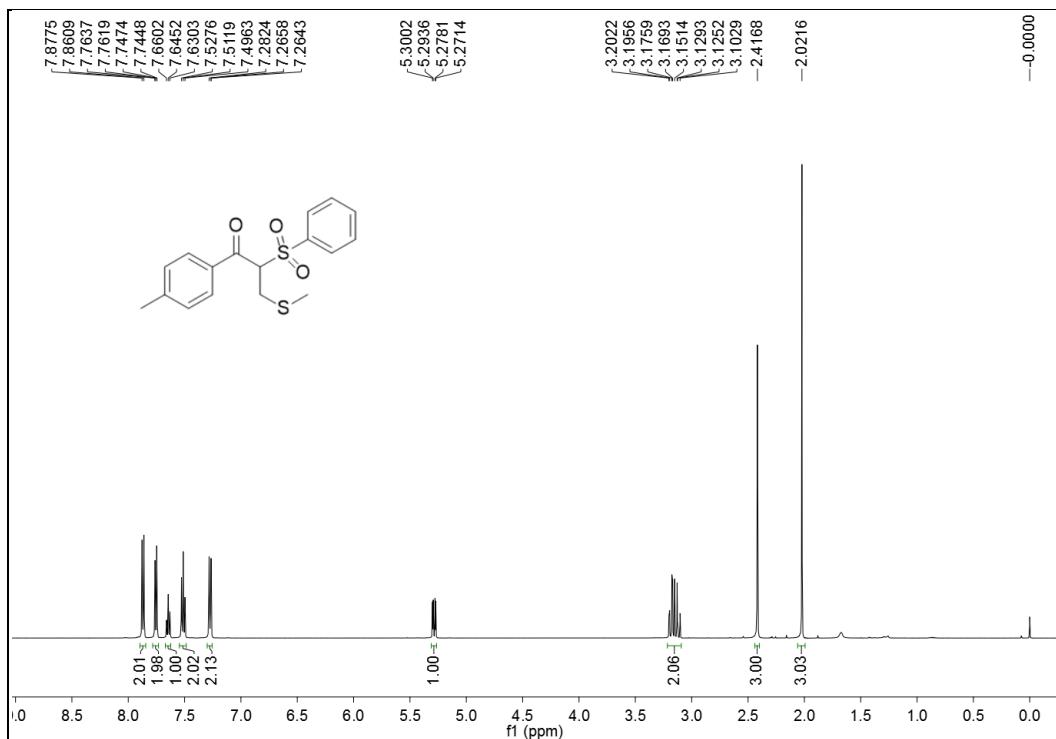
2-((4-chlorophenyl)sulfonyl)-3-(methylthio)-1-phenylpropan-1-one (2d)



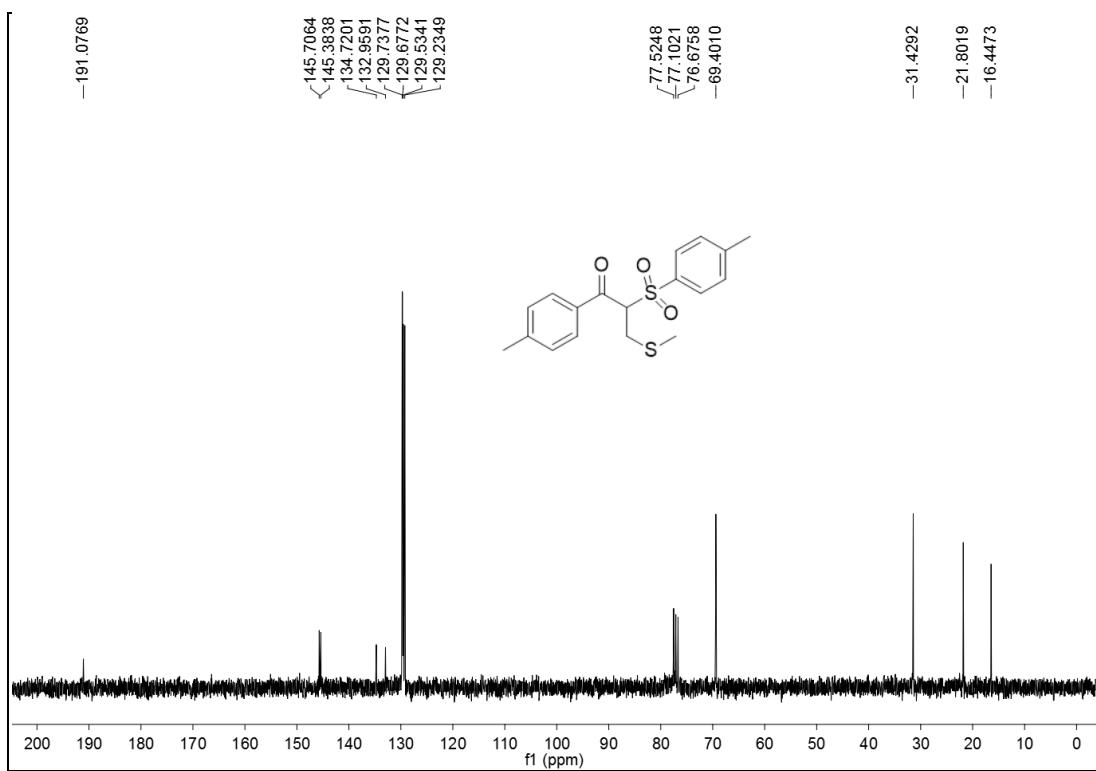
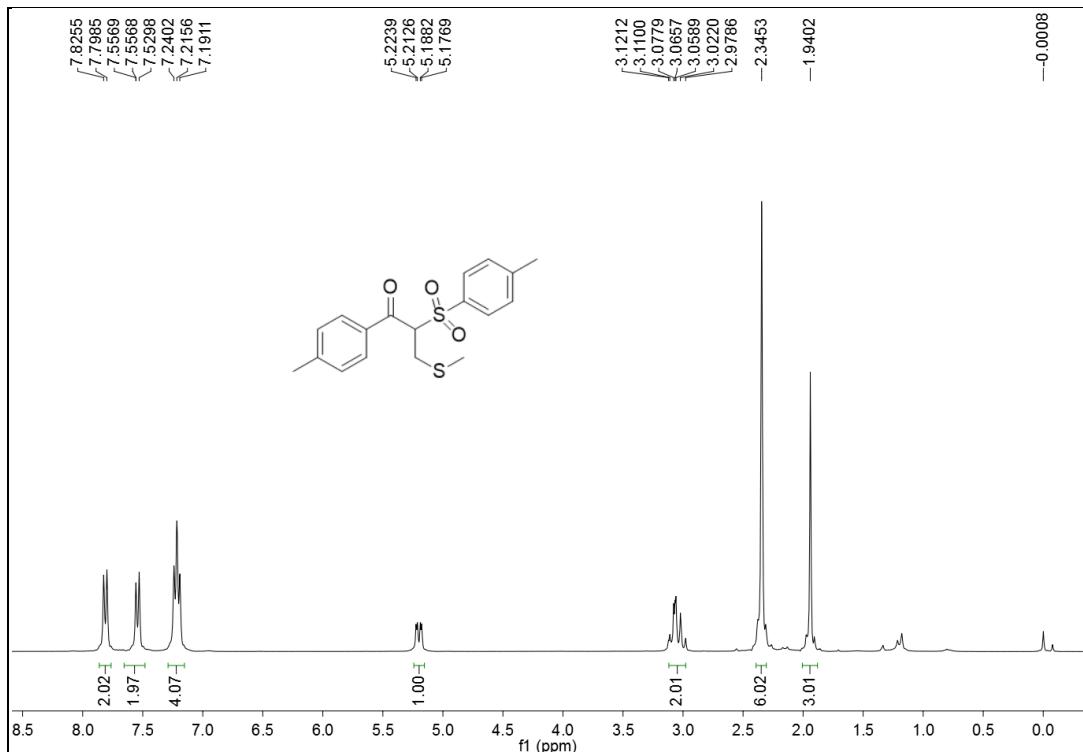
2-(methylsulfonyl)-3-(methylthio)-1-phenylpropan-1-one(2e)



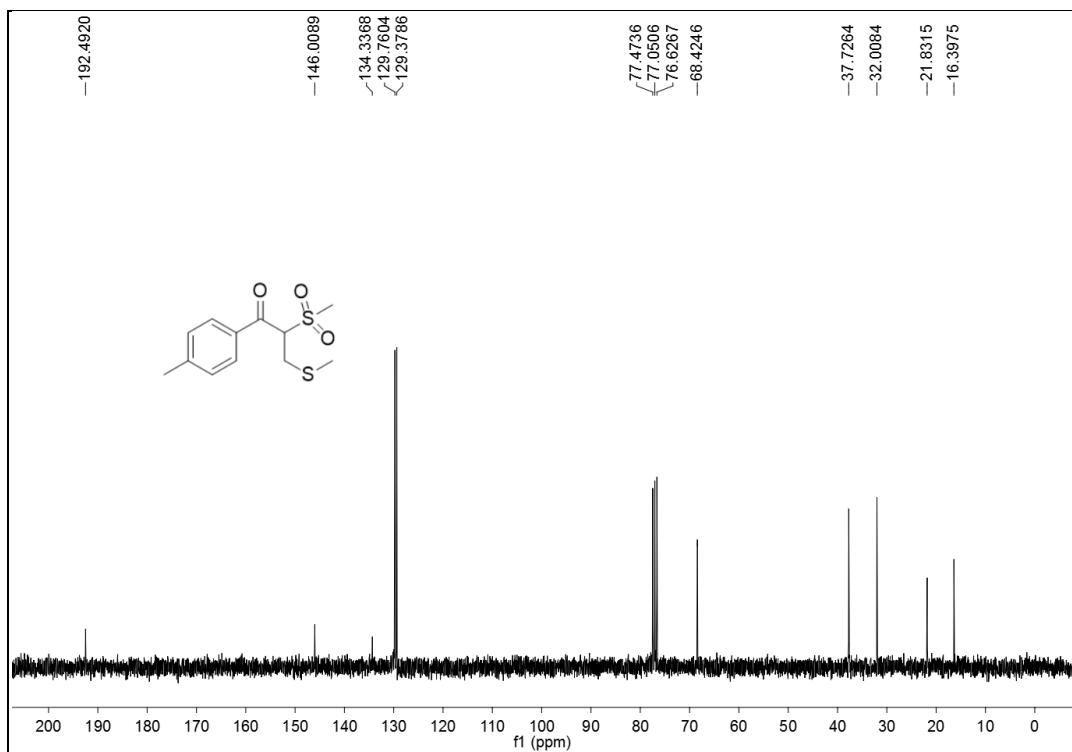
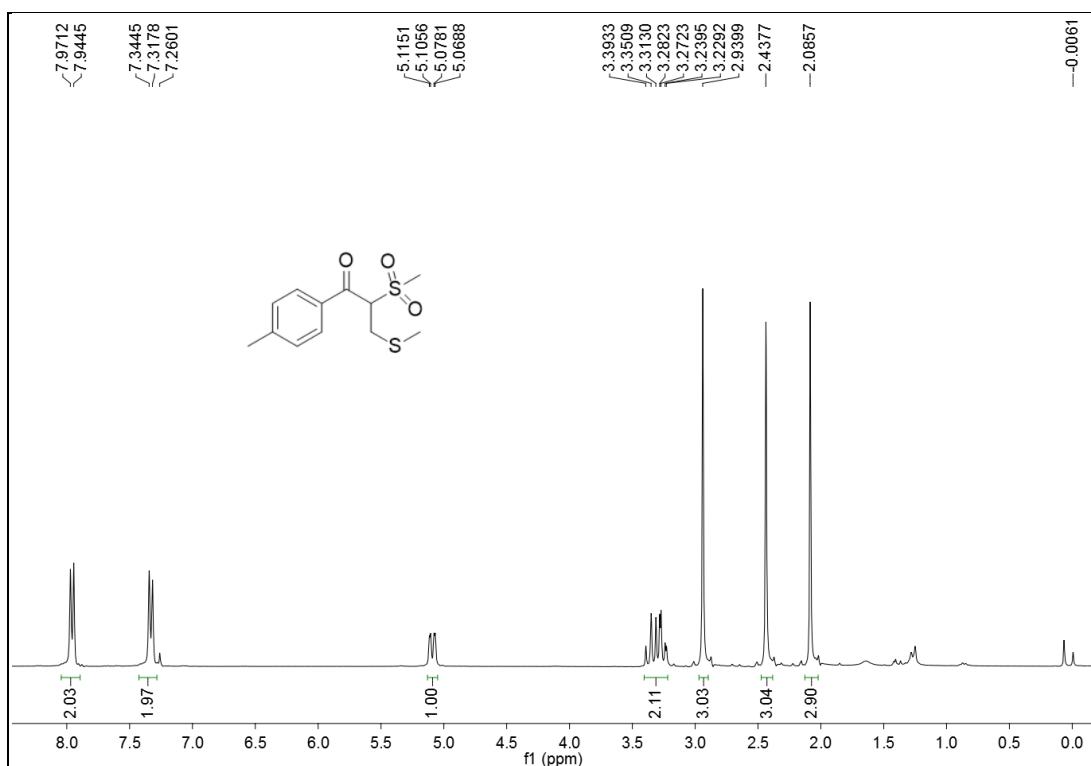
3-(methylthio)-2-(phenylsulfonyl)-1-(p-tolyl)propan-1-one(2f)



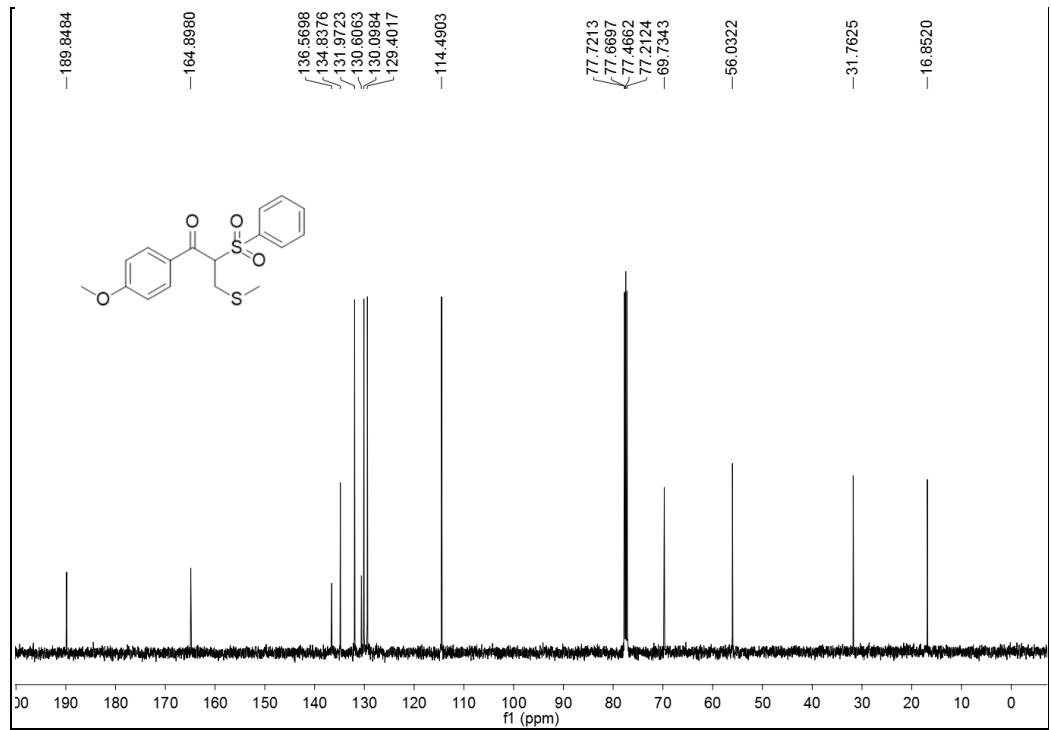
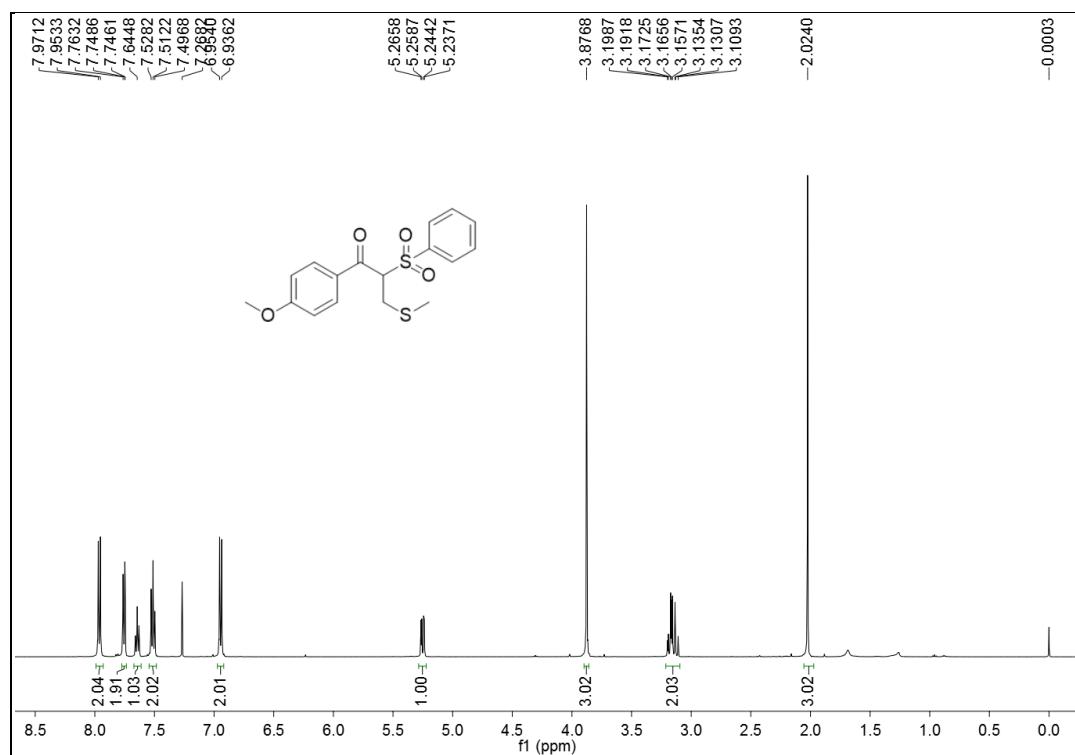
3-(methylthio)-1-(p-tolyl)-2-tosylpropan-1-one(2g)



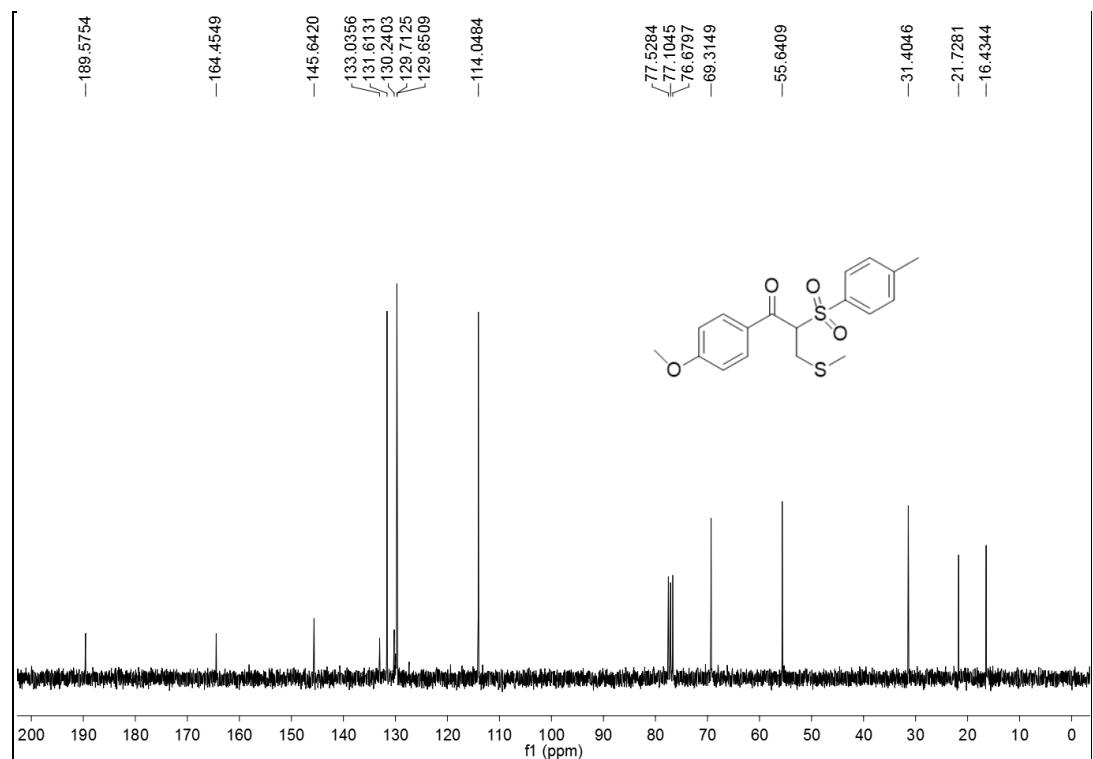
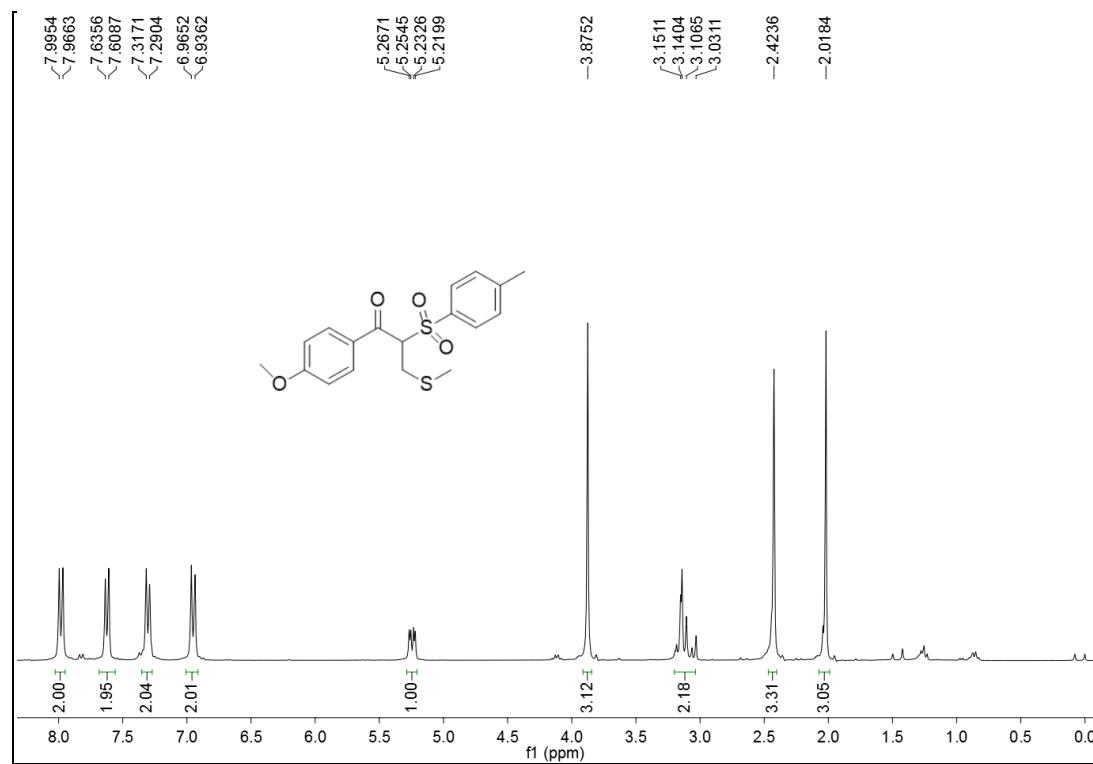
2-(methylsulfonyl)-3-(methylthio)-1-(p-tolyl)propan-1-one(2h)



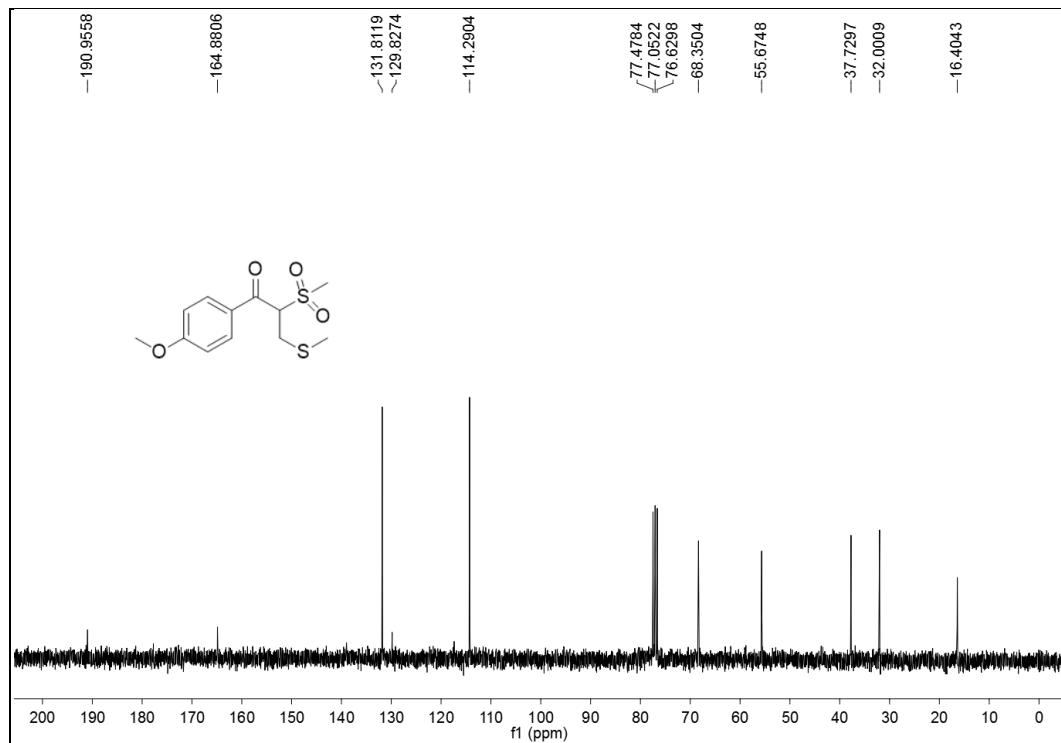
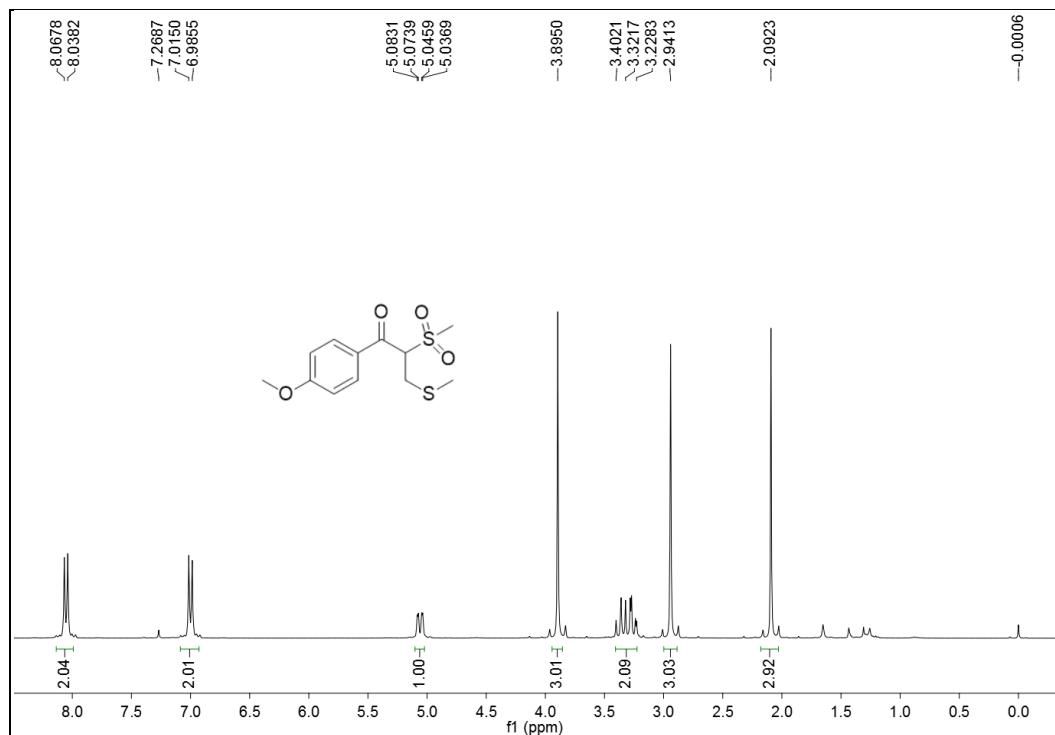
1-(4-methoxyphenyl)-3-(methylthio)-2-(phenylsulfonyl)propan-1-one(2i)



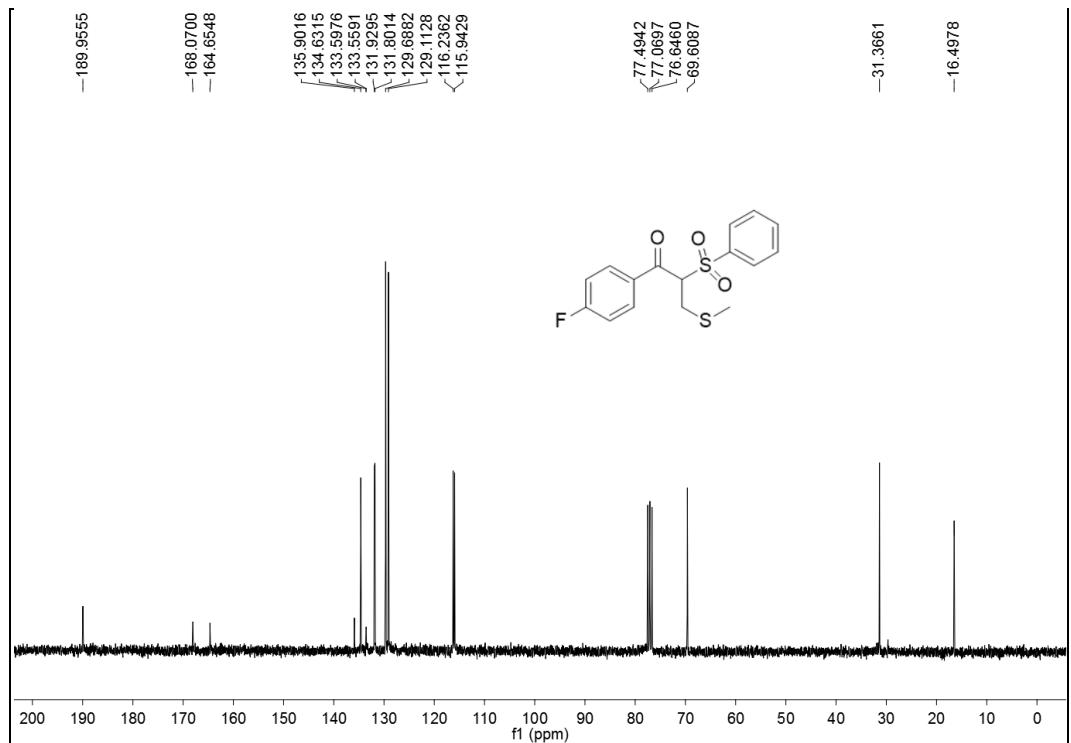
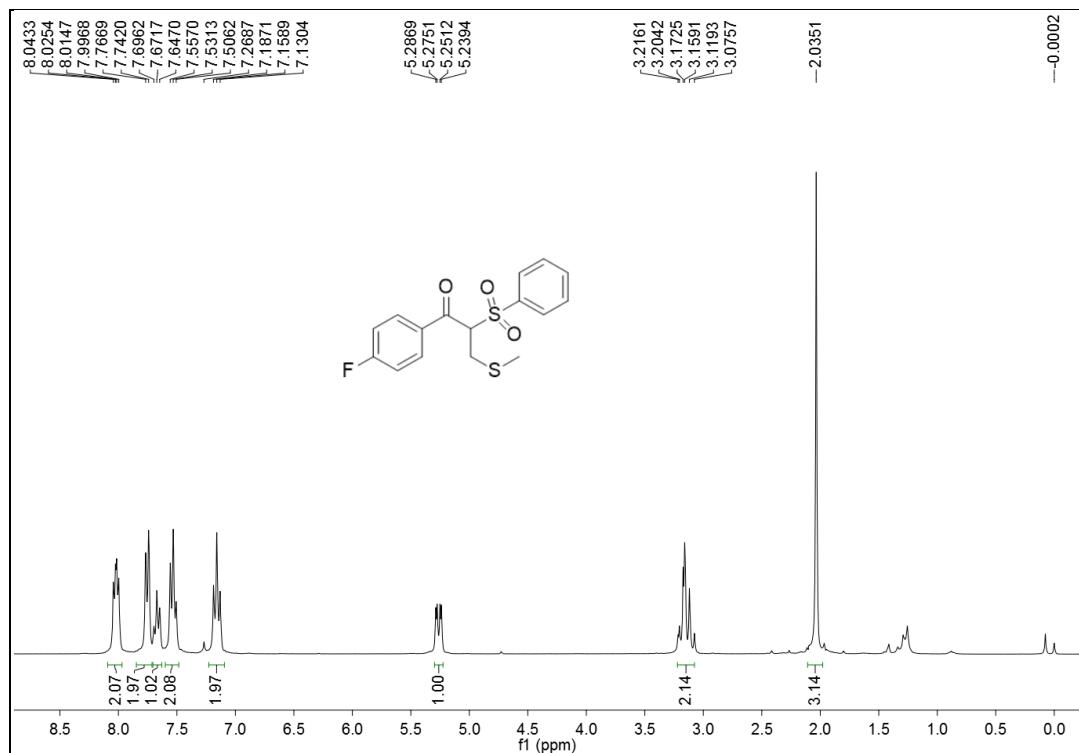
1-(4-methoxyphenyl)-3-(methylthio)-2-tosylpropan-1-one(2j)



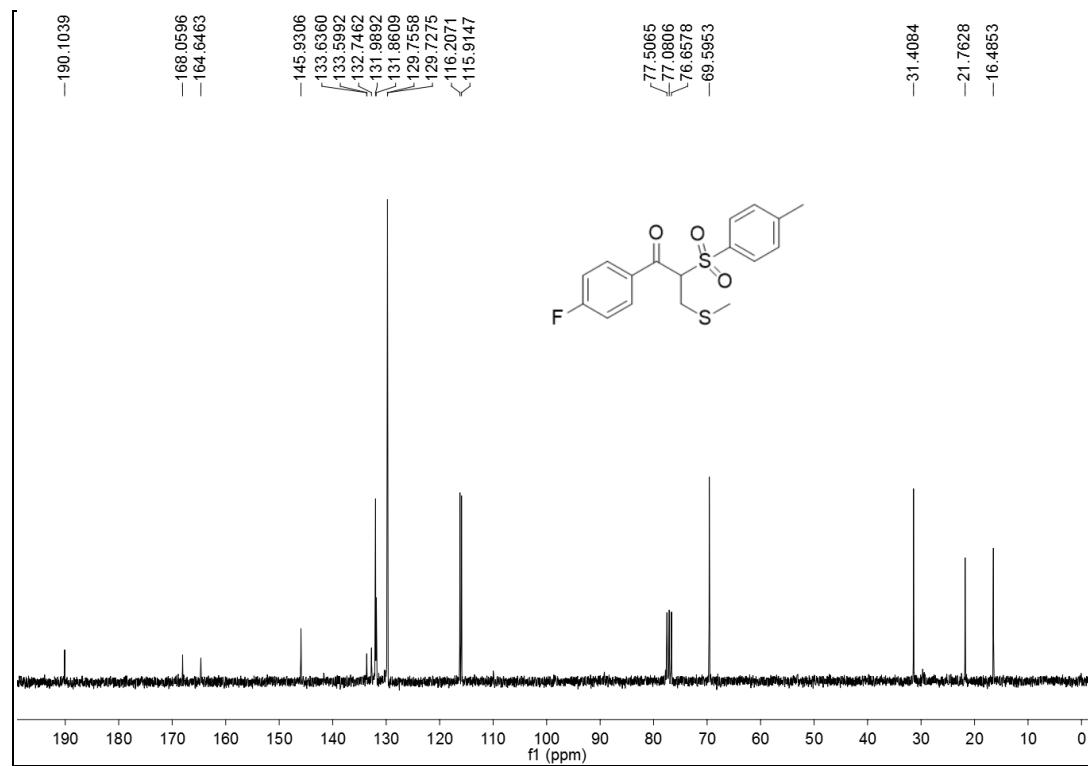
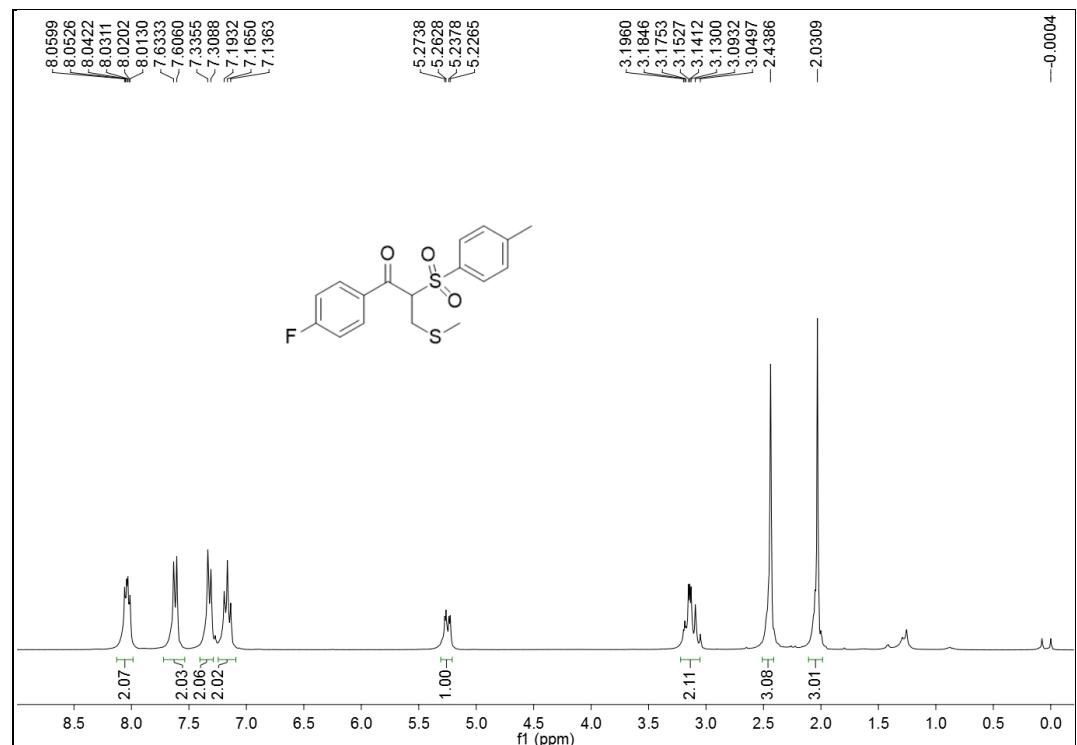
1-(4-methoxyphenyl)-2-(methylsulfonyl)-3-(methylthio)propan-1-one(2k)



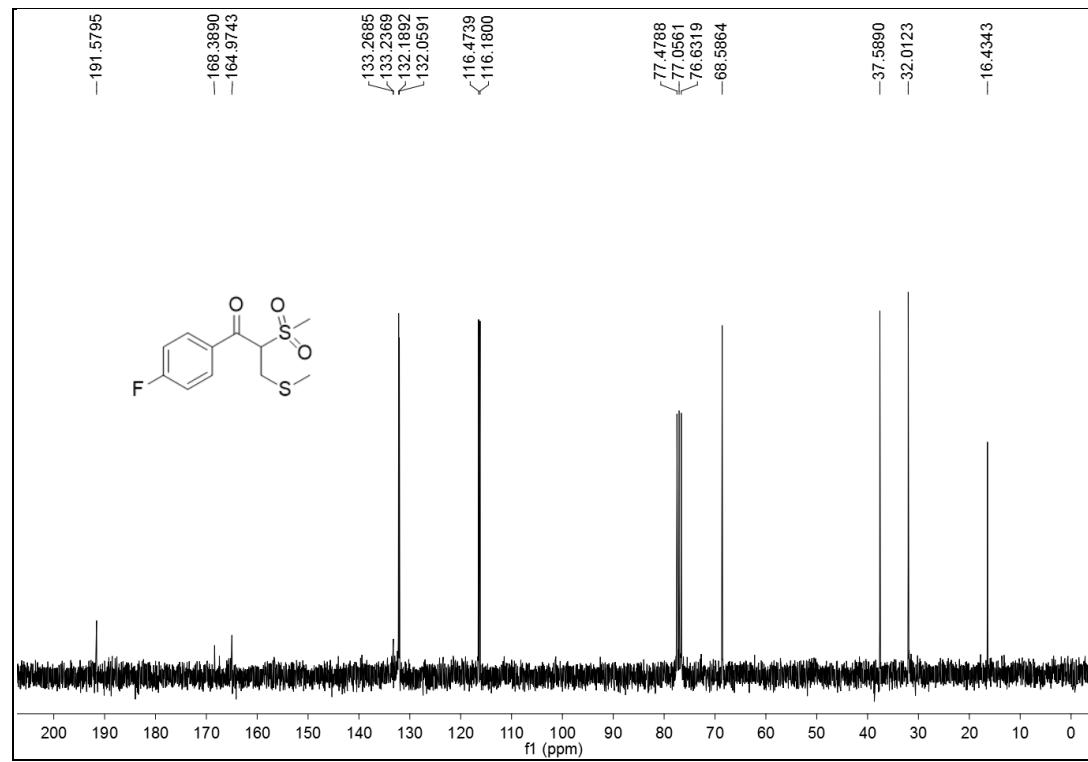
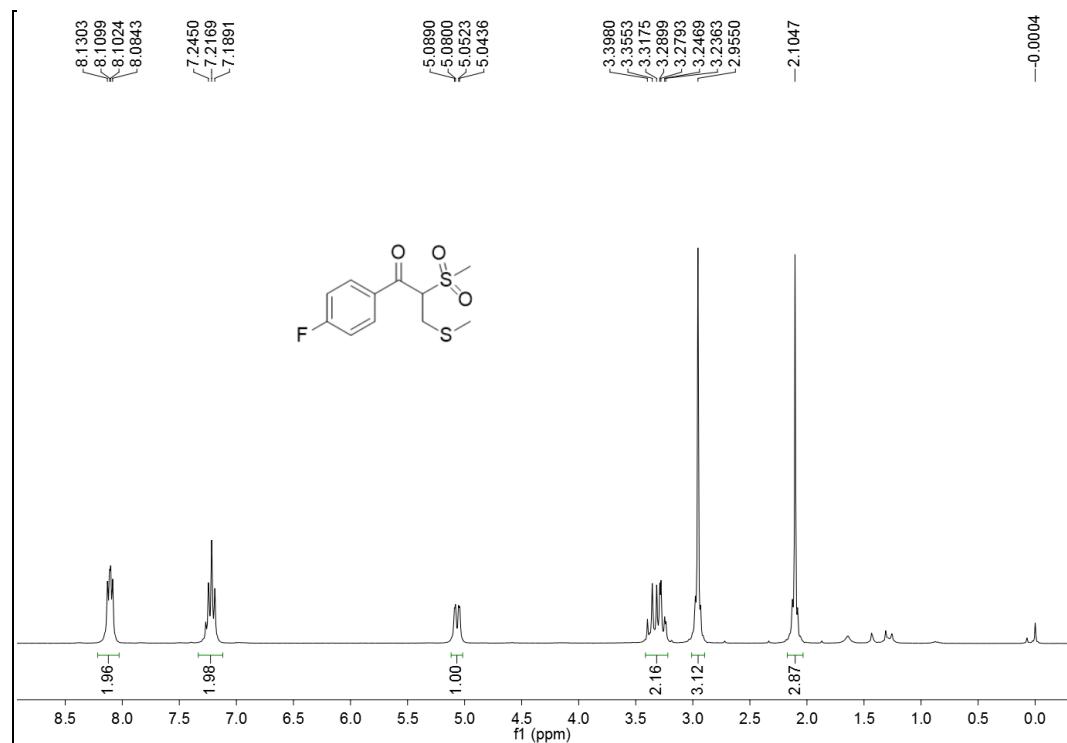
1-(4-fluorophenyl)-3-(methylthio)-2-(phenylsulfonyl)propan-1-one(2l)



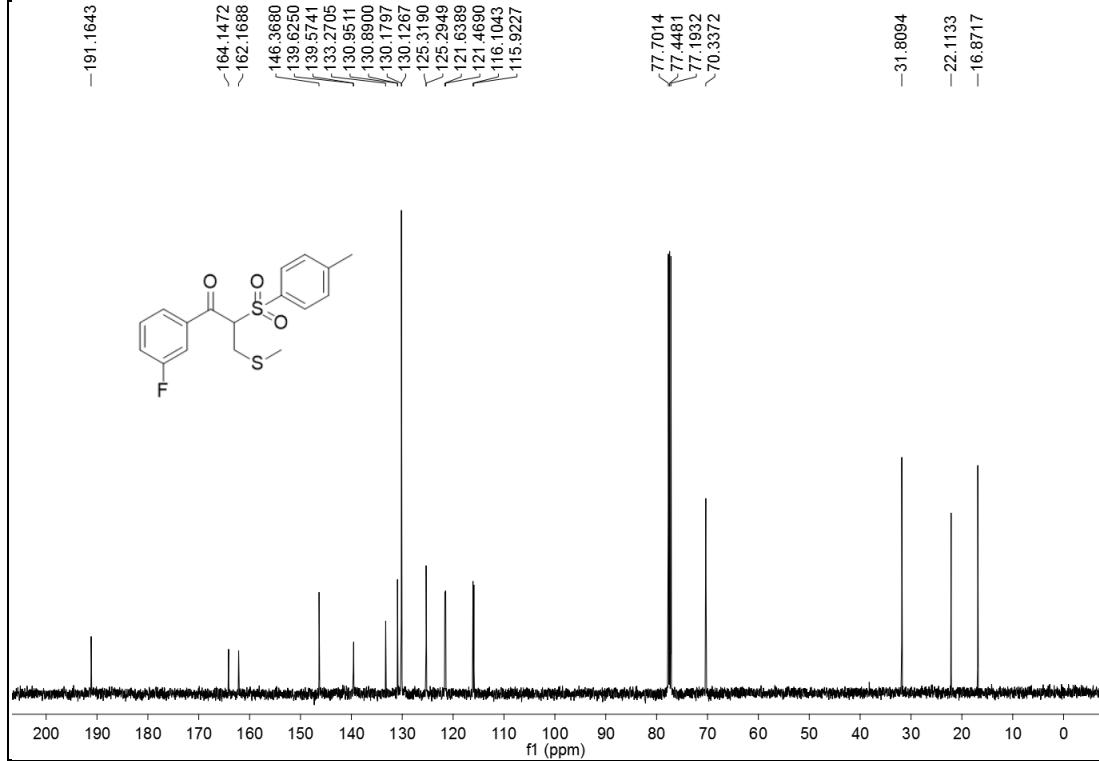
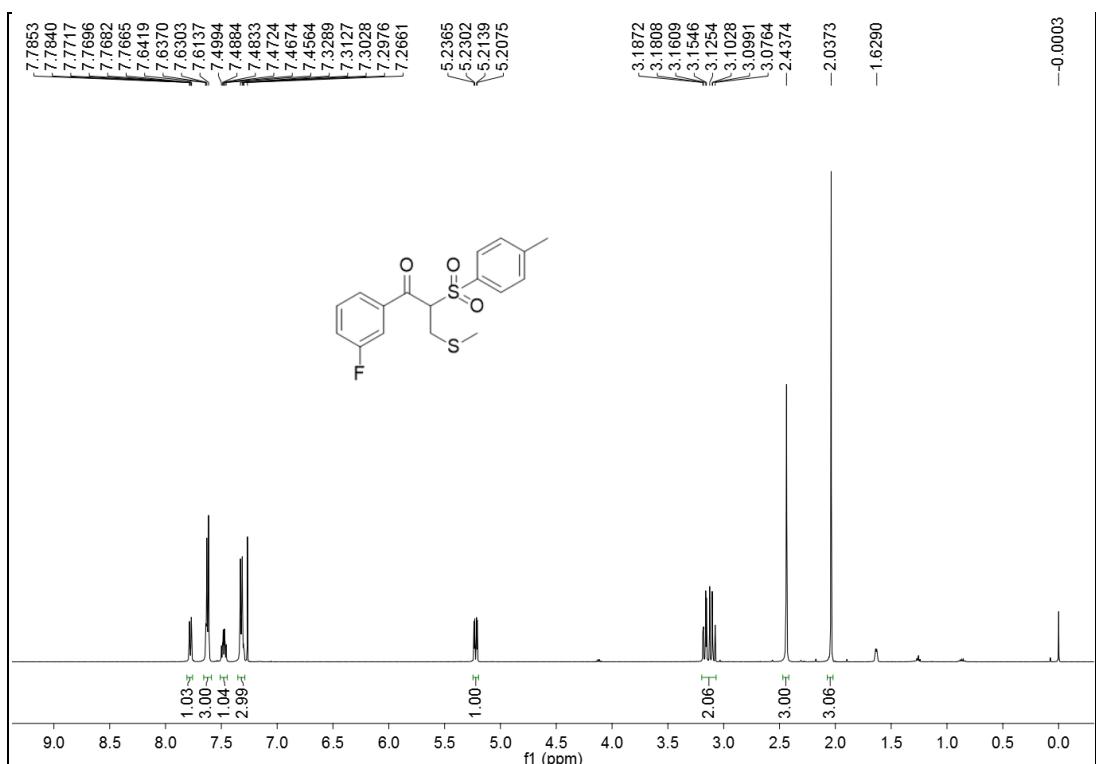
1-(4-fluorophenyl)-3-(methylthio)-2-tosylpropan-1-one (2m)



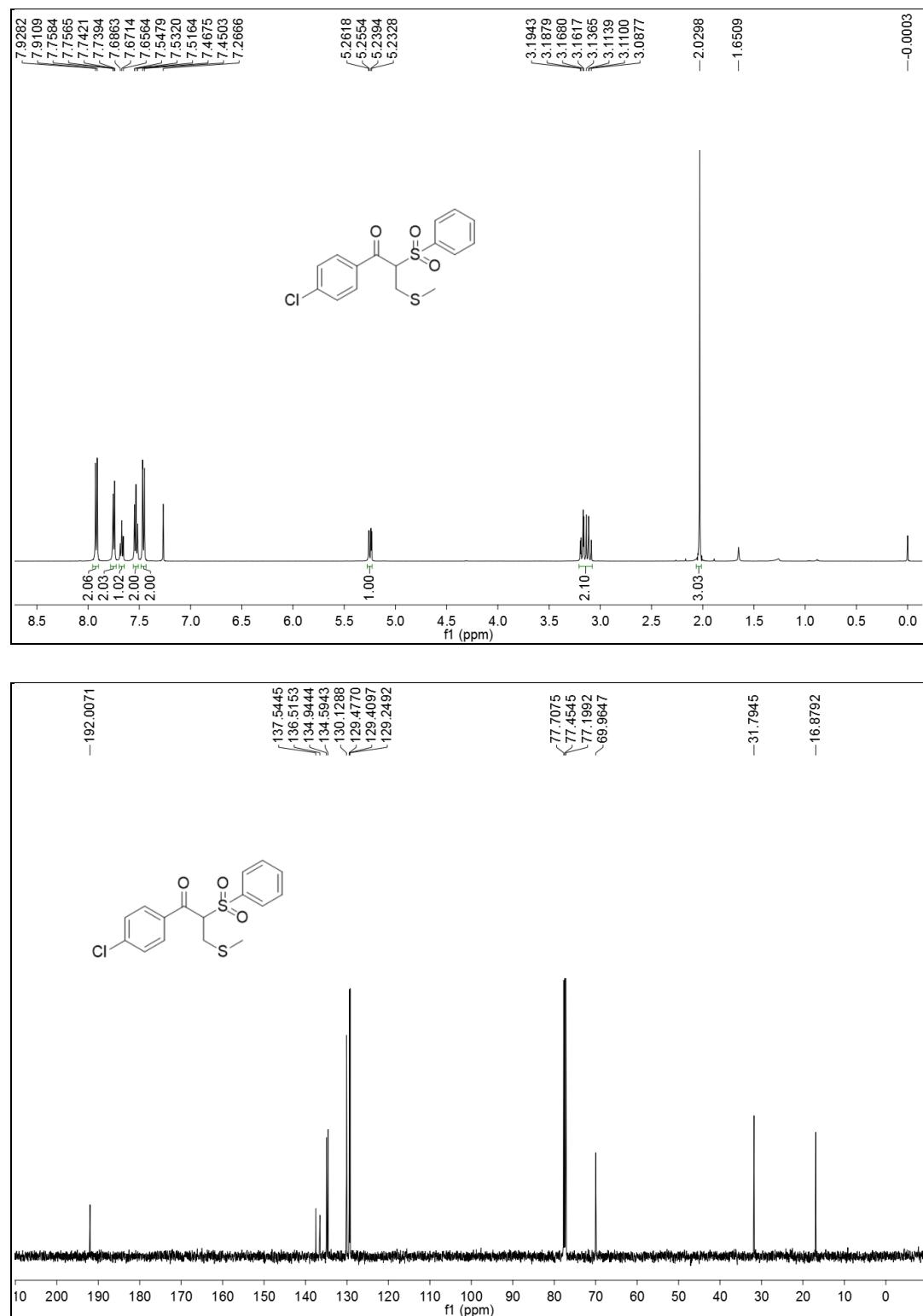
1-(4-fluorophenyl)-2-(methylsulfonyl)-3-(methylthio)propan-1-one(2n)



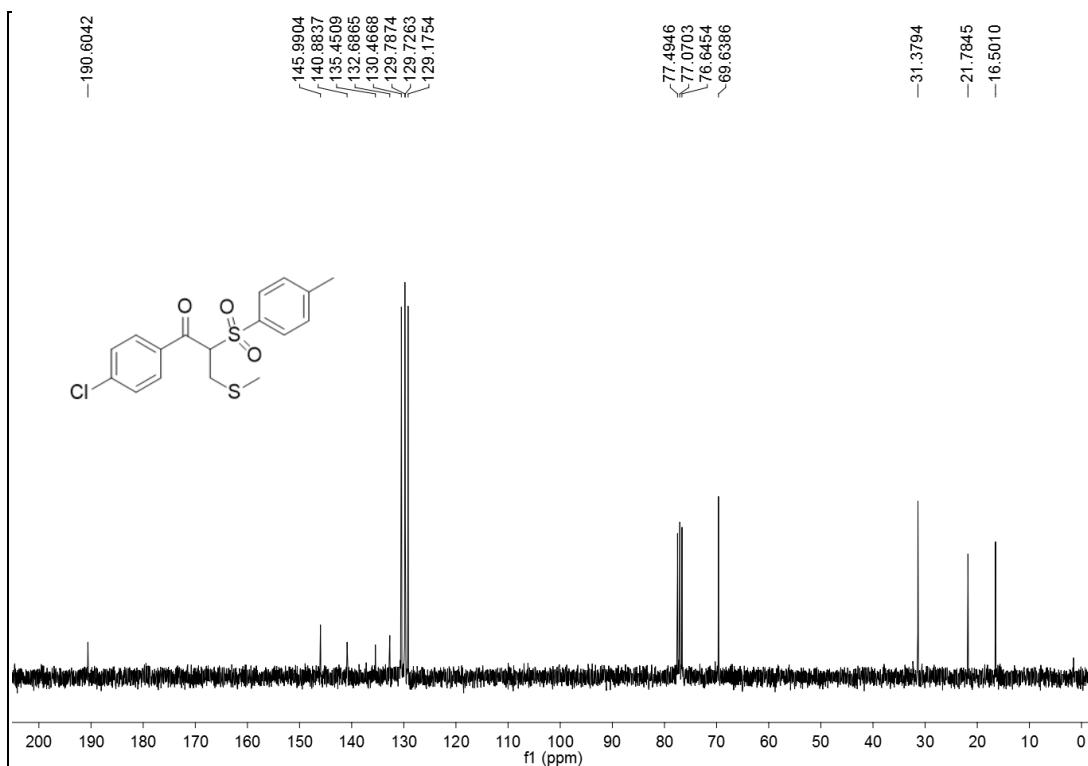
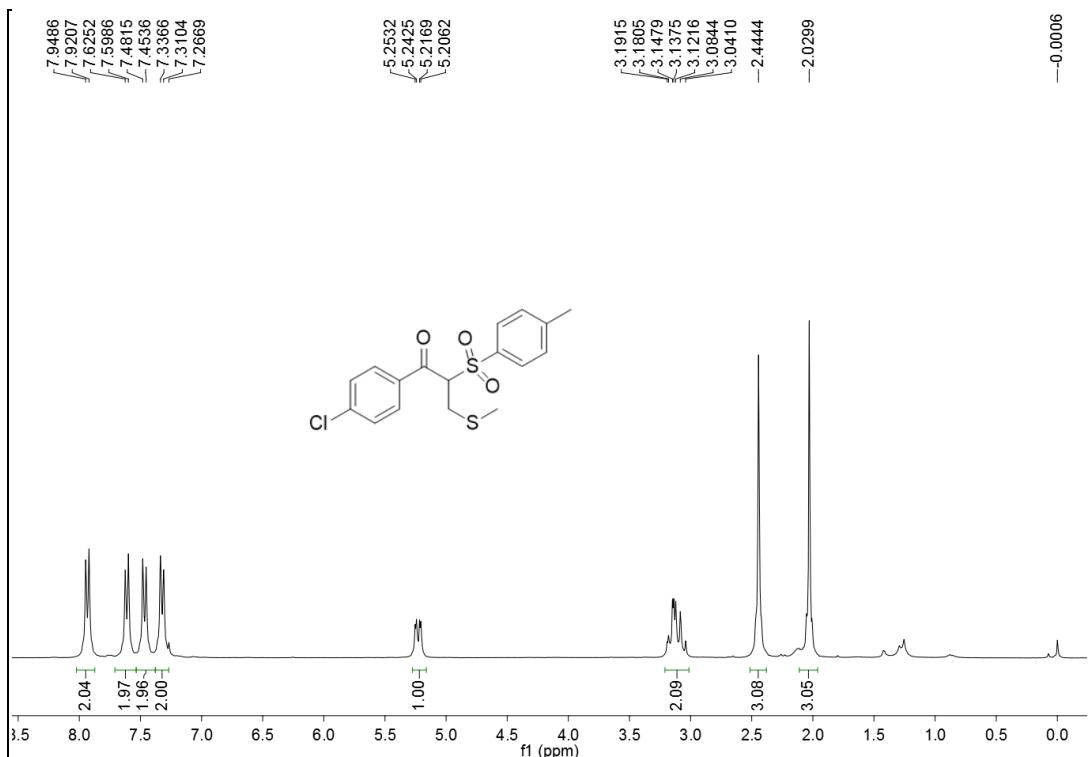
1-(3-fluorophenyl)-3-(methylthio)-2-tosylpropan-1-one (2o)



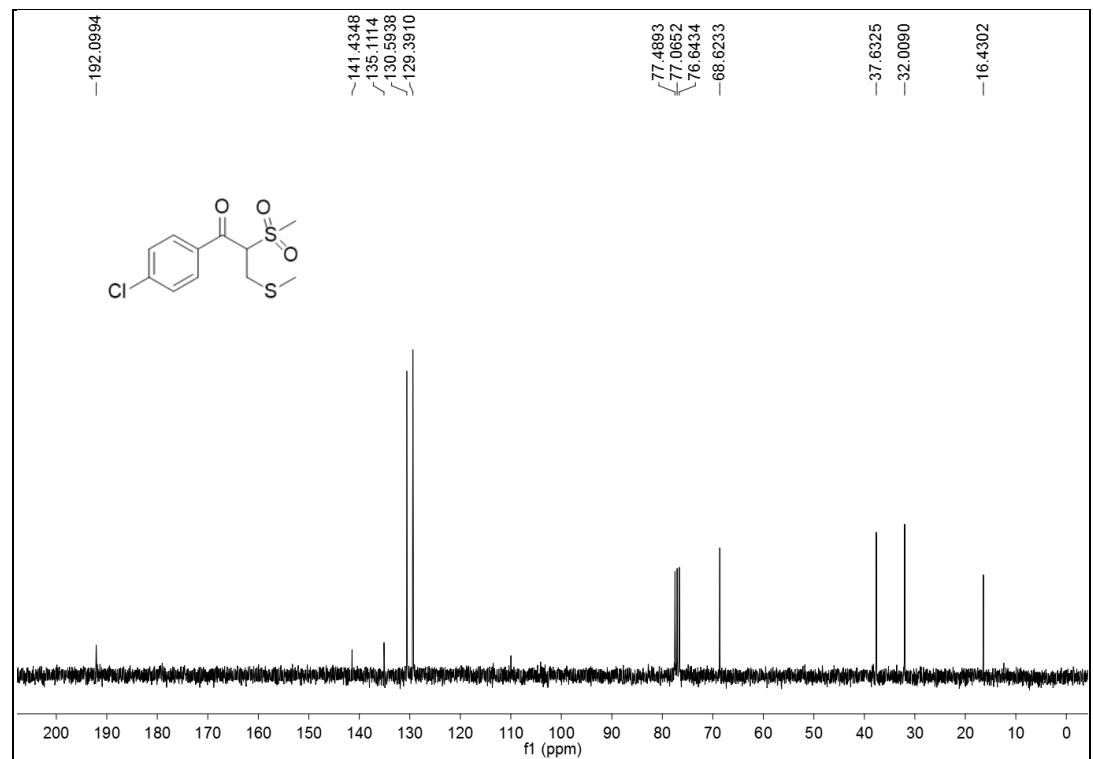
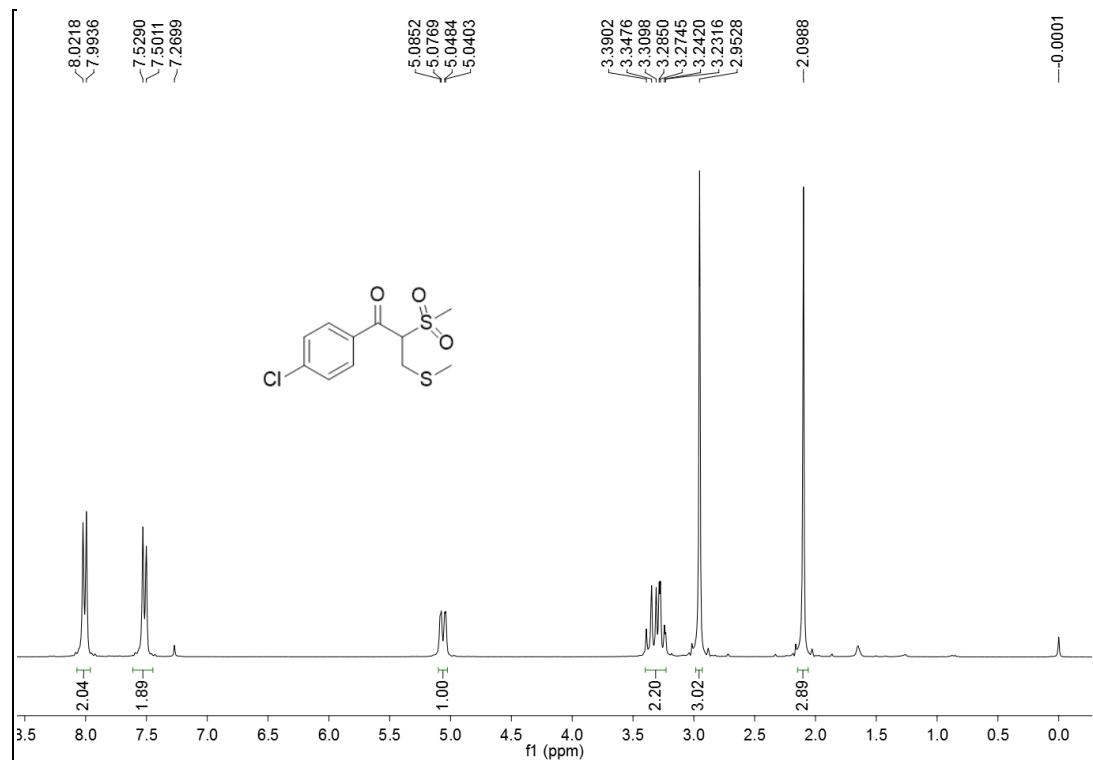
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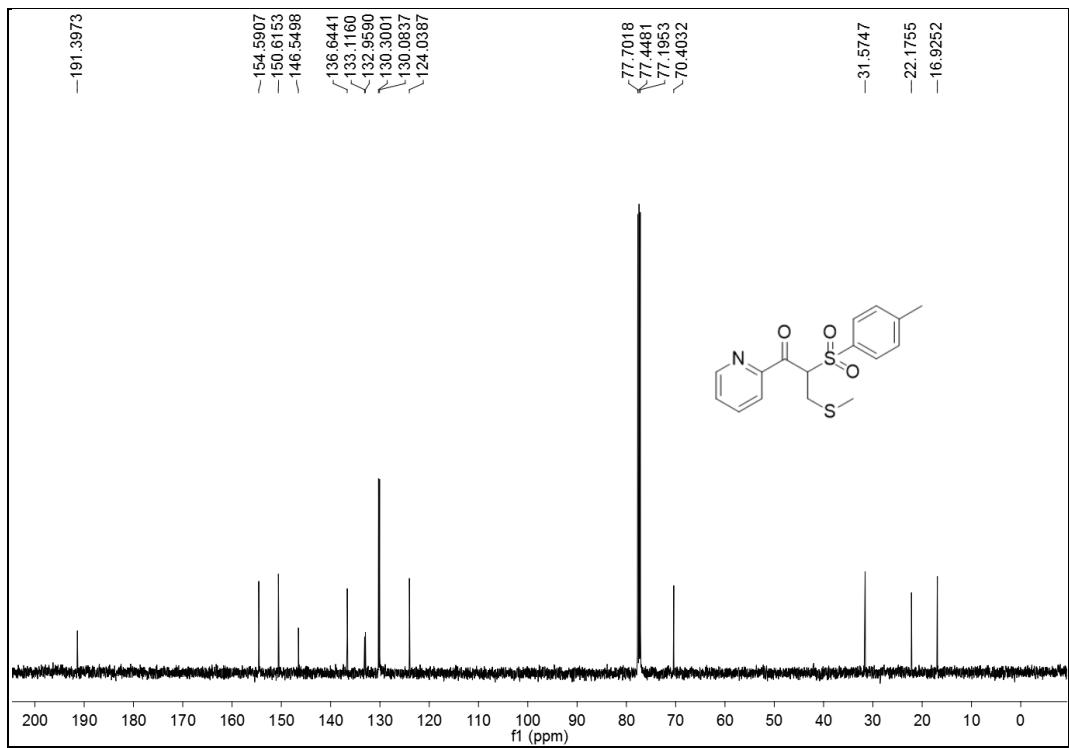
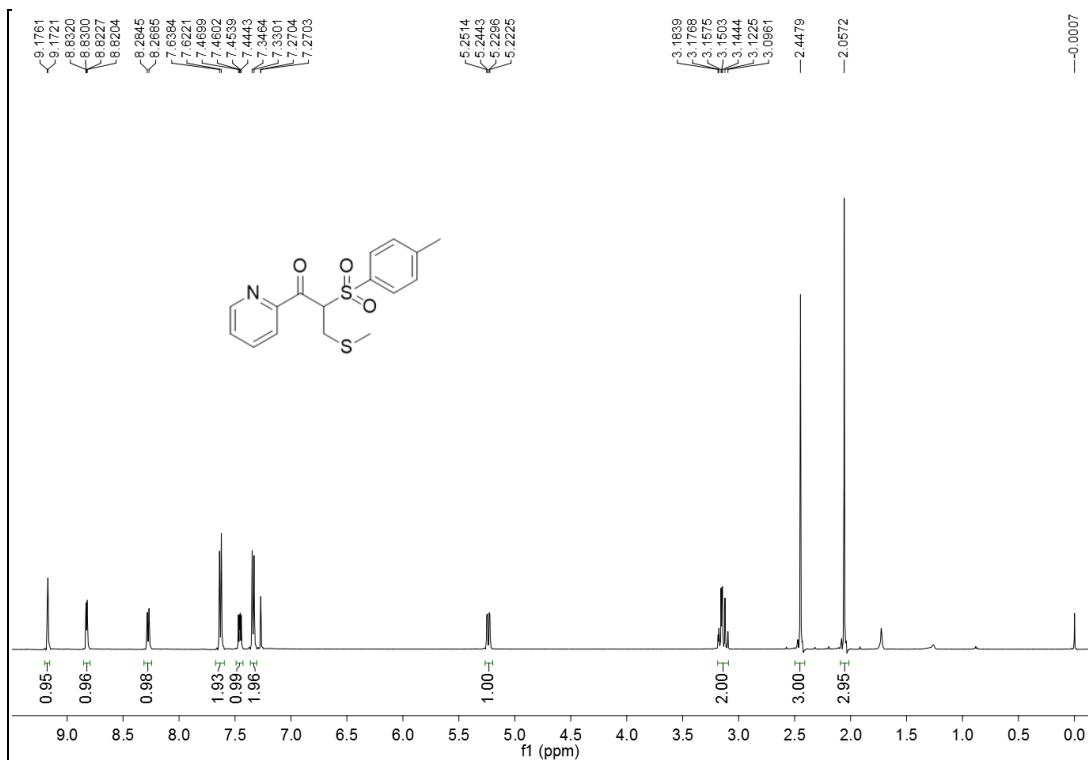
1-(4-chlorophenyl)-3-(methylthio)-2-tosylpropan-1-one(2q)



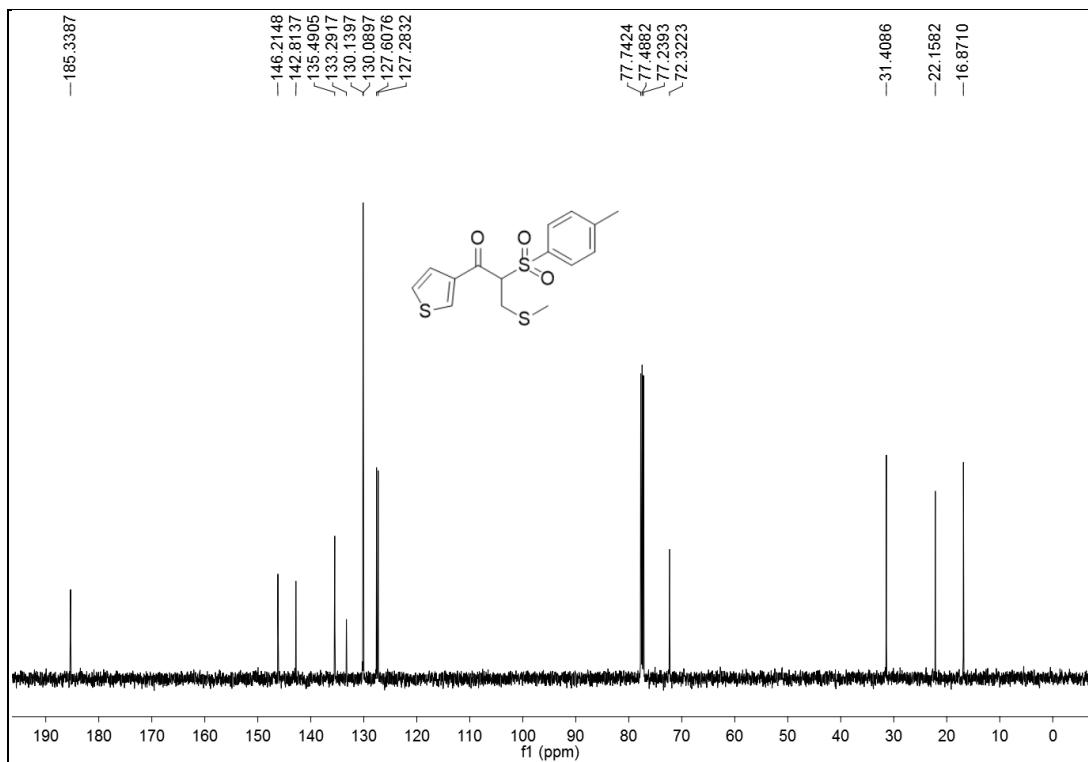
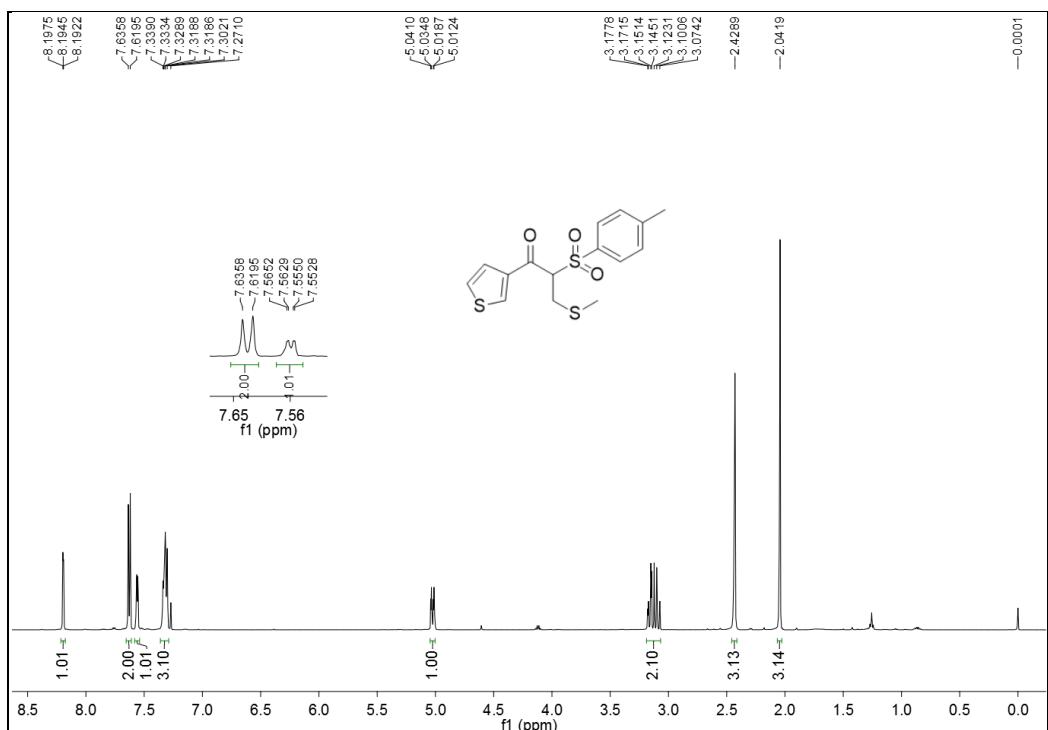
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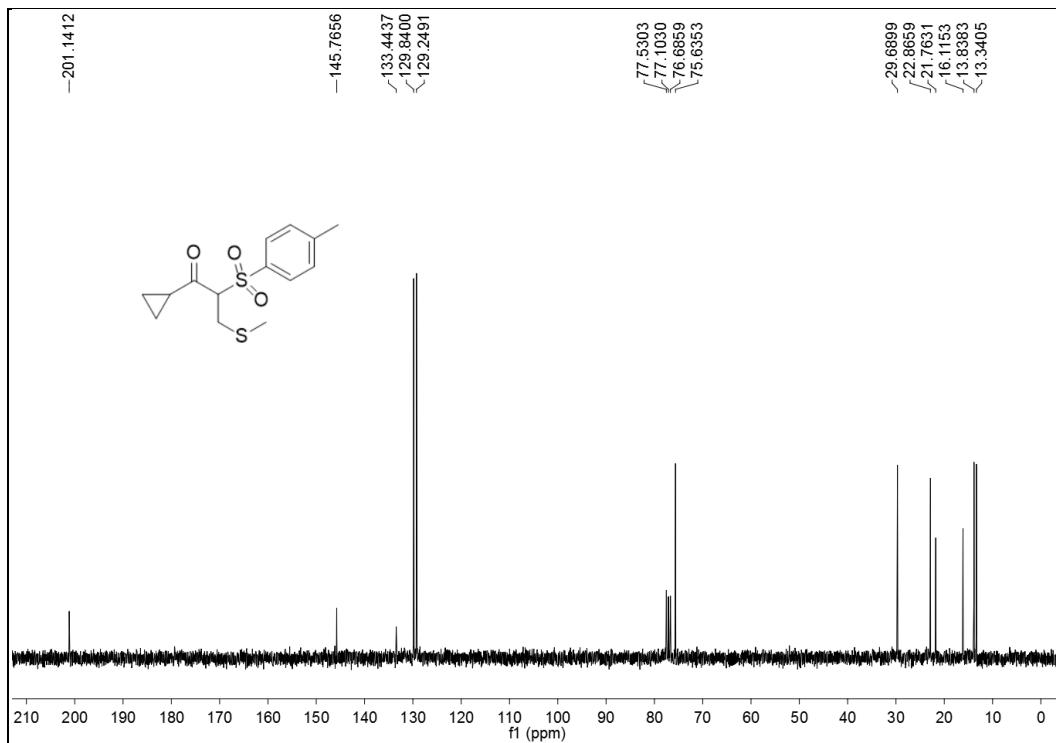
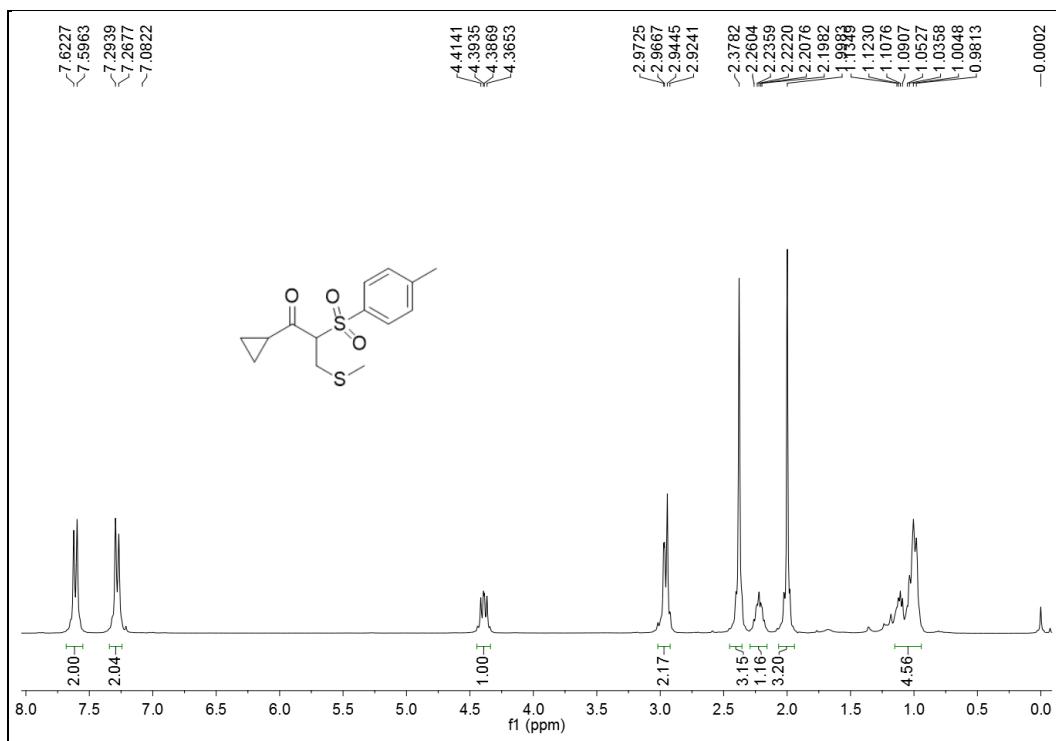
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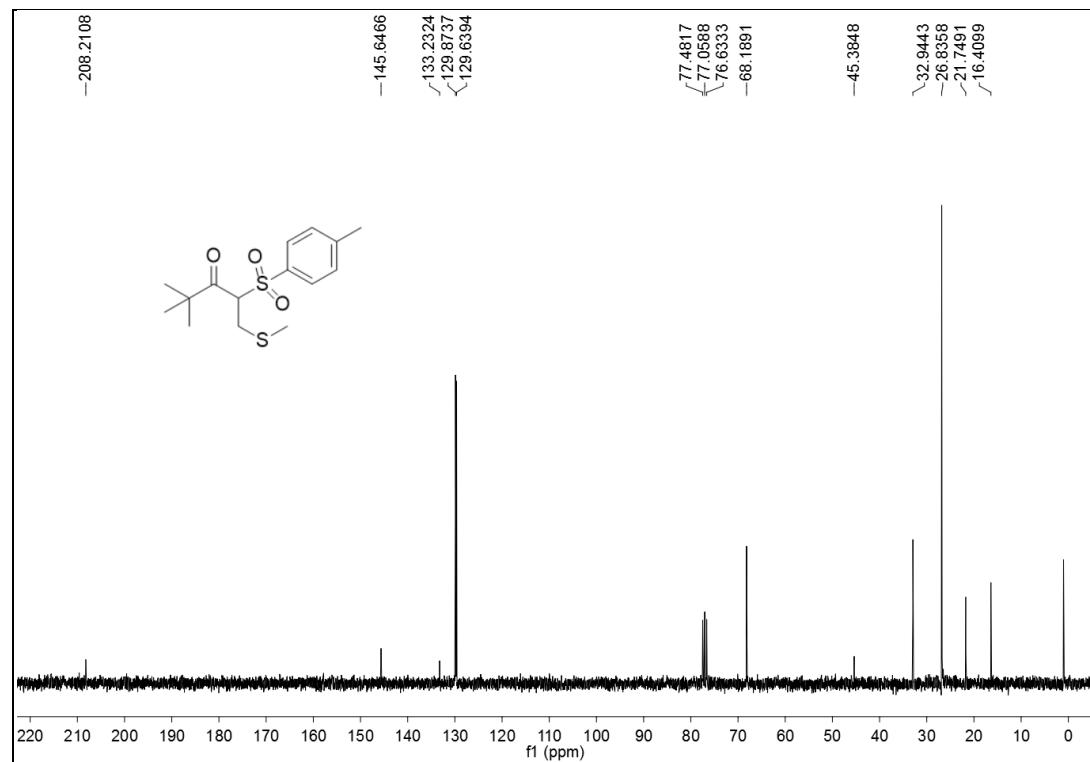
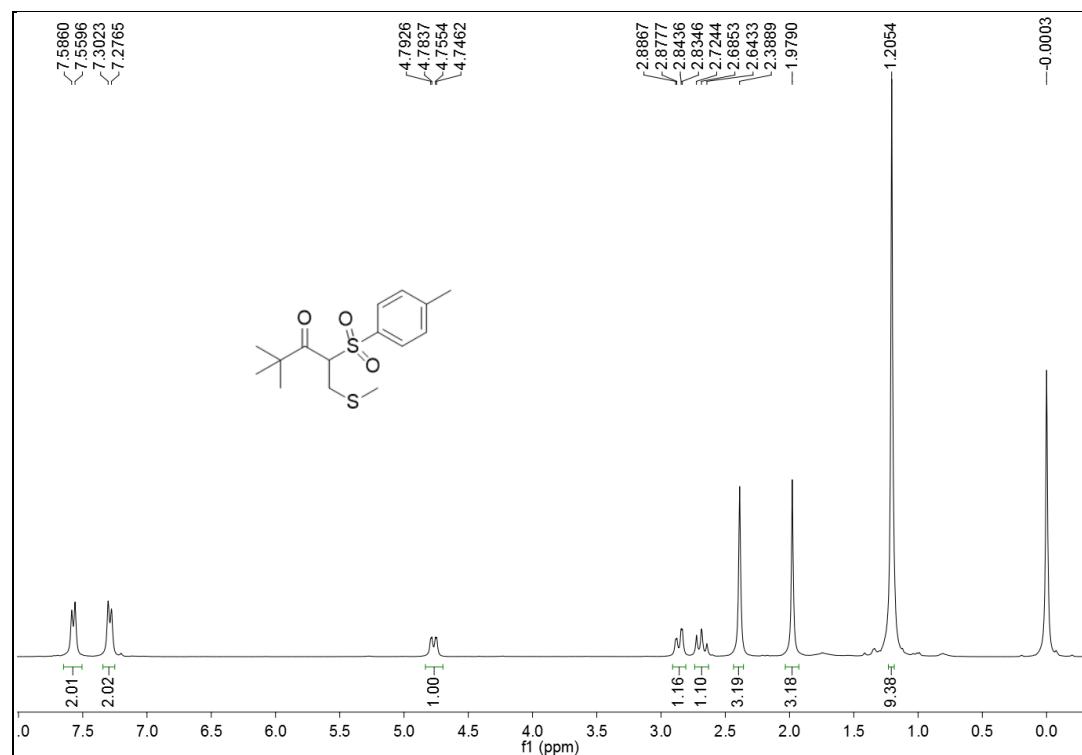
3-(methylthio)-1-(thiophen-3-yl)-2-tosylpropan-1-one(2t)



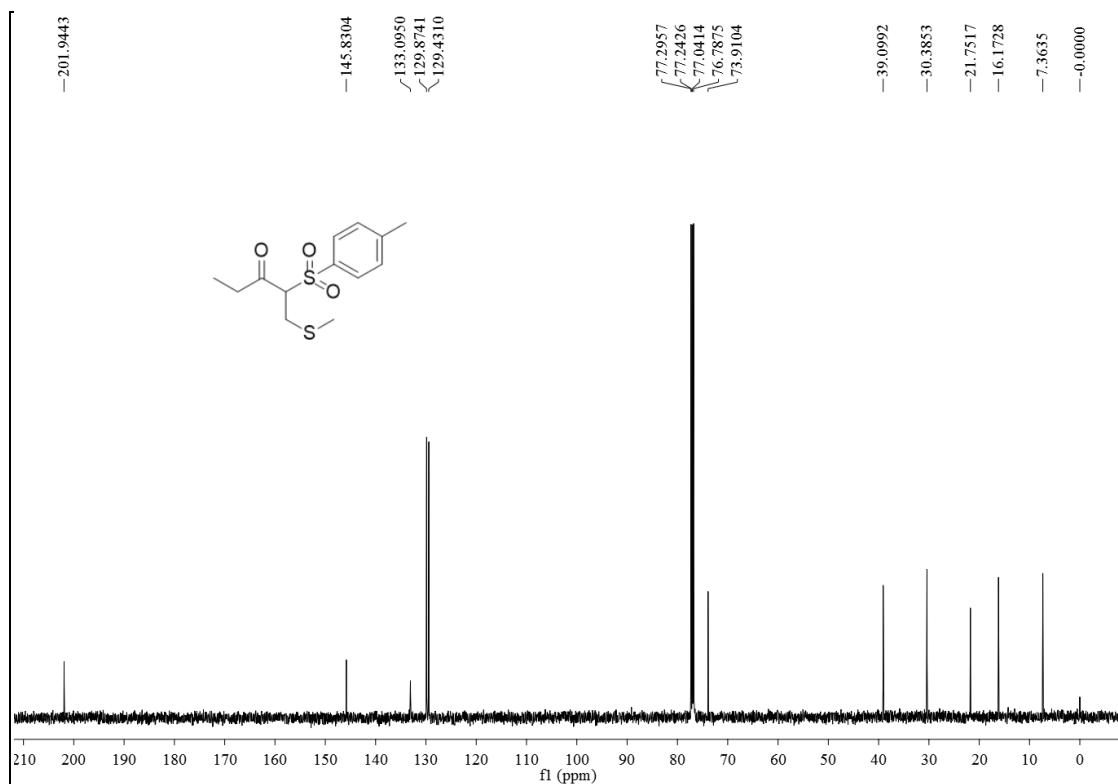
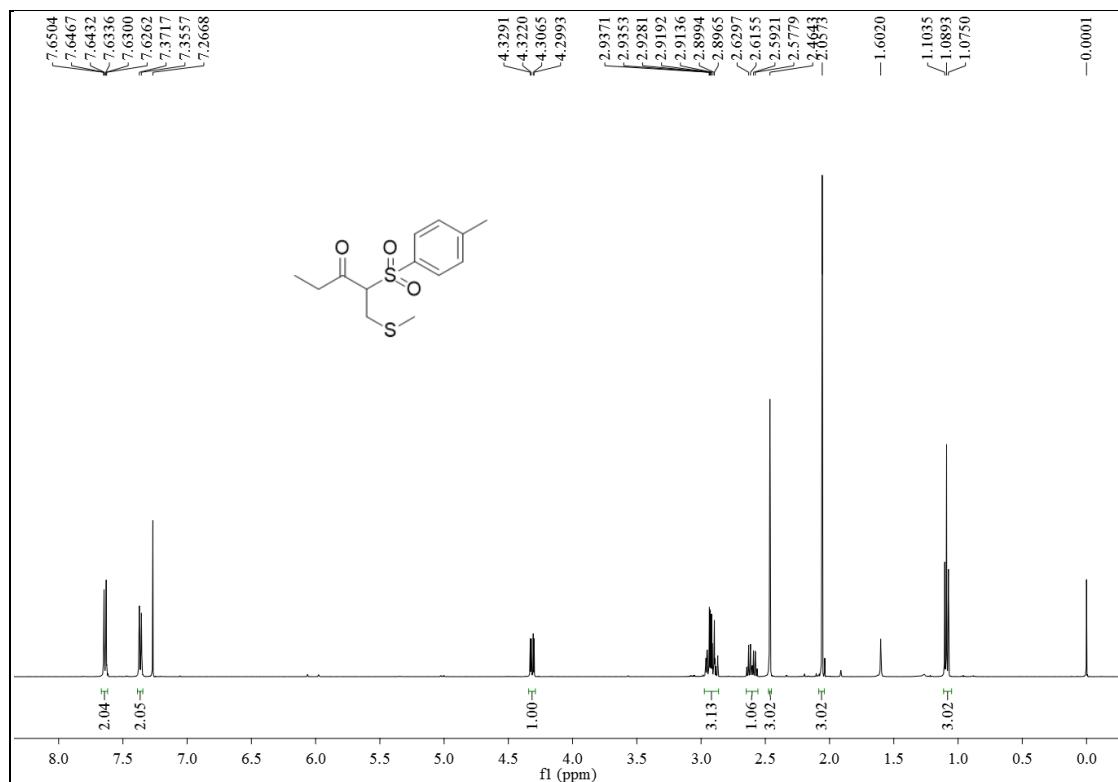
1-cyclopropyl-3-(methylthio)-2-tosylpropan-1-one (2u)



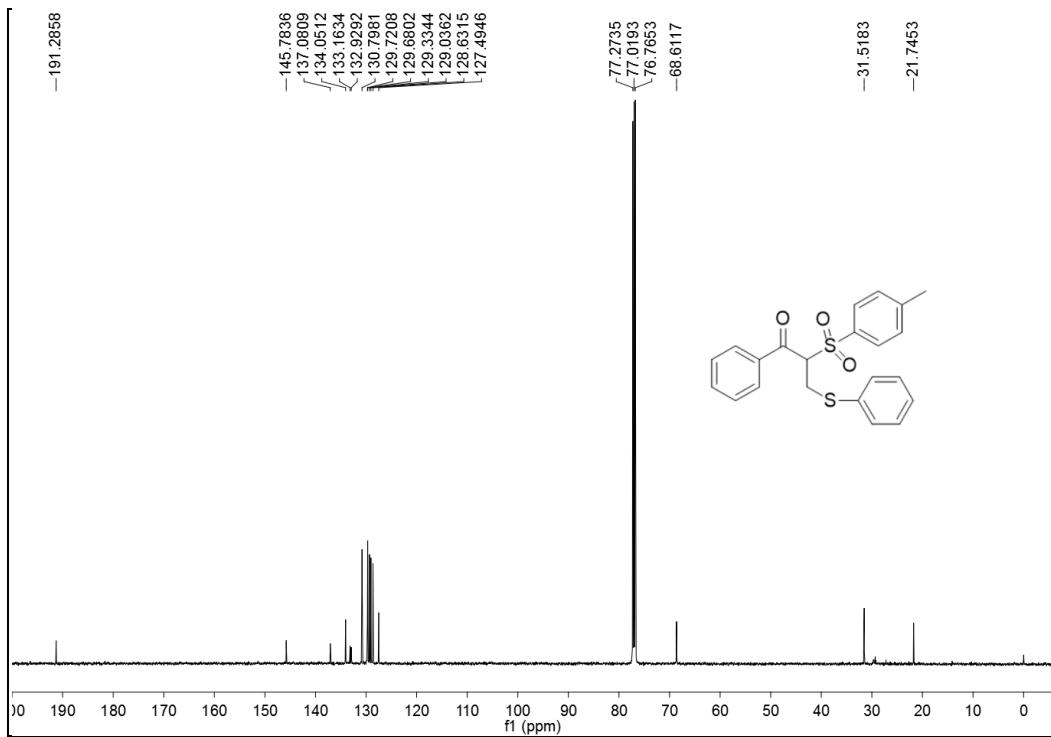
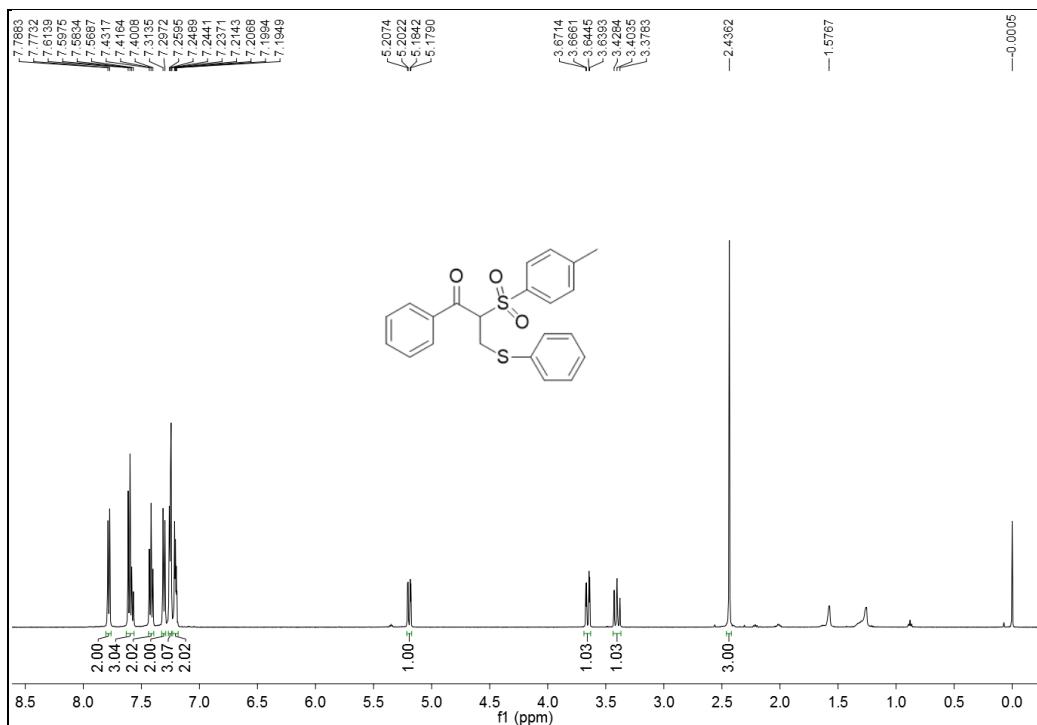
4,4-dimethyl-1-(methylthio)-2-tosylpentan-3-one (2v)



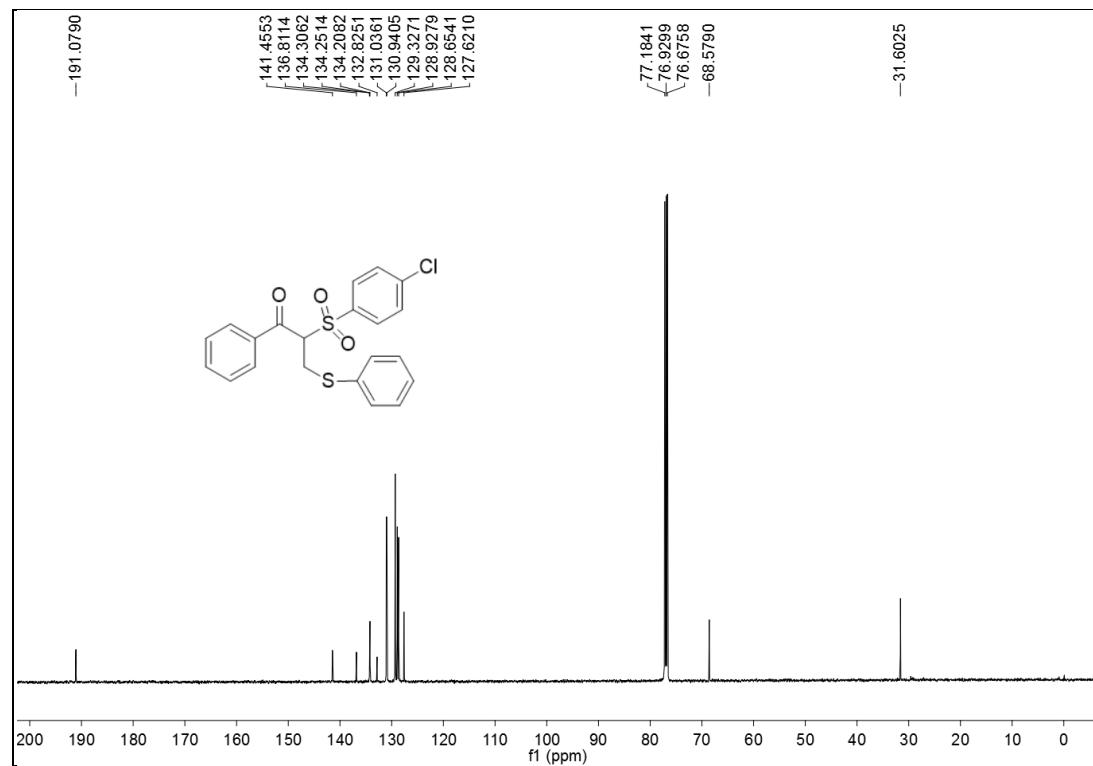
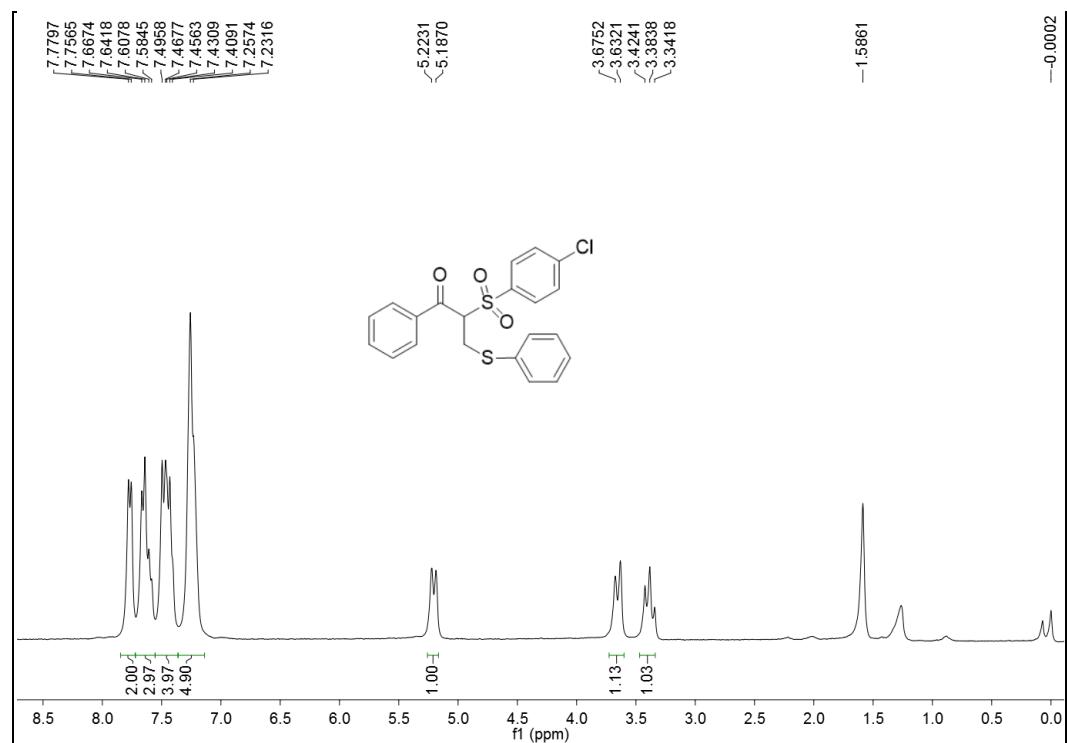
1-(methylthio)-2-tosylpentan-3-one (2w)



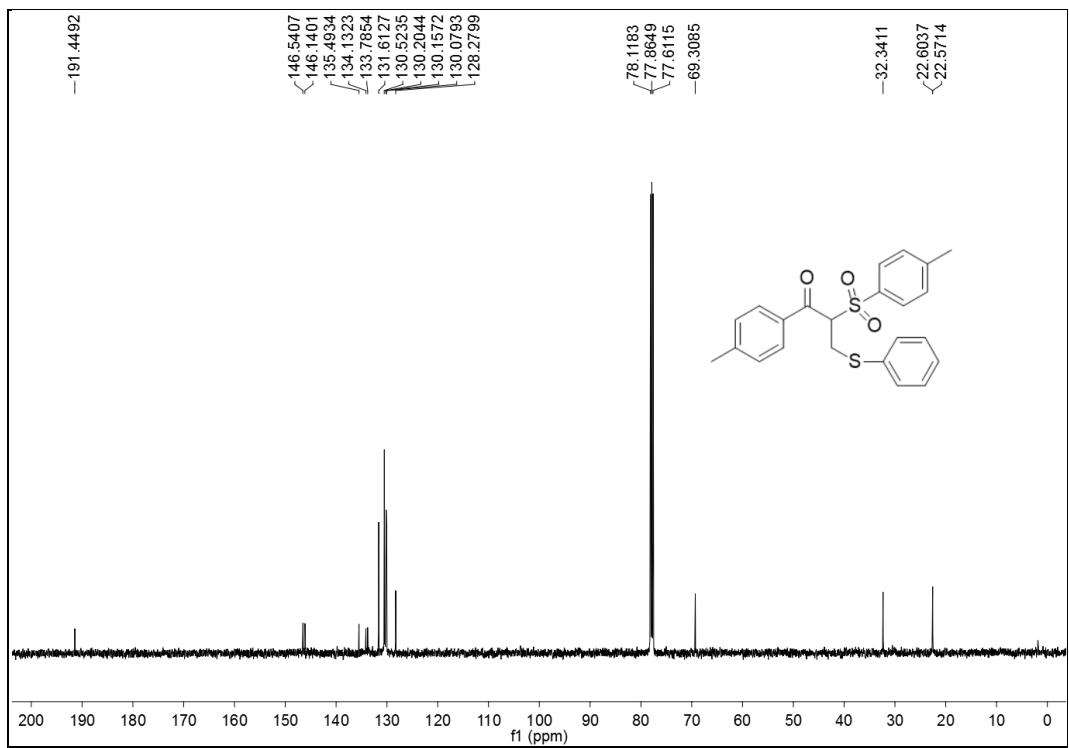
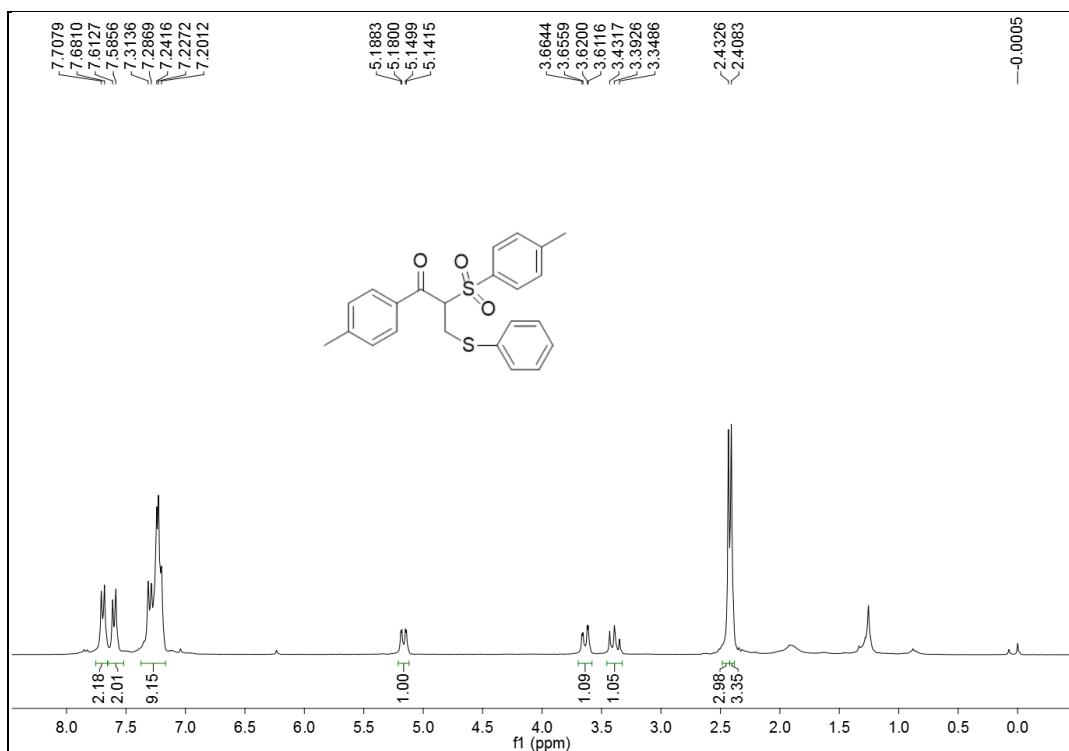
1-phenyl-3-(phenylthio)-2-tosylpropan-1-one(2aa)



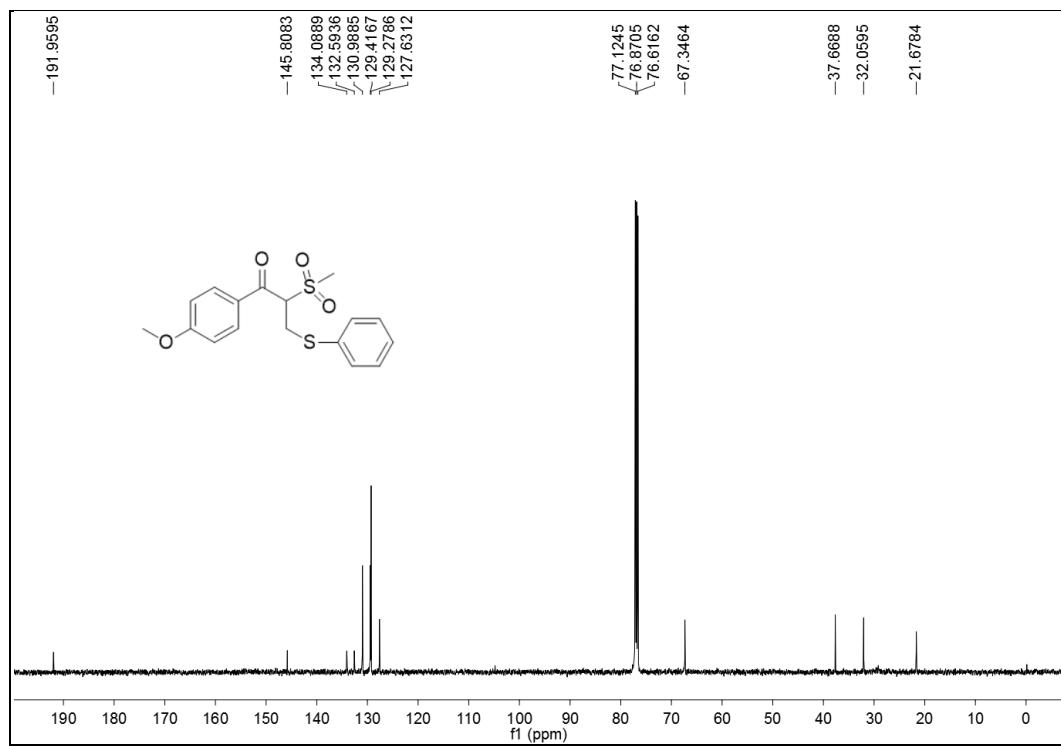
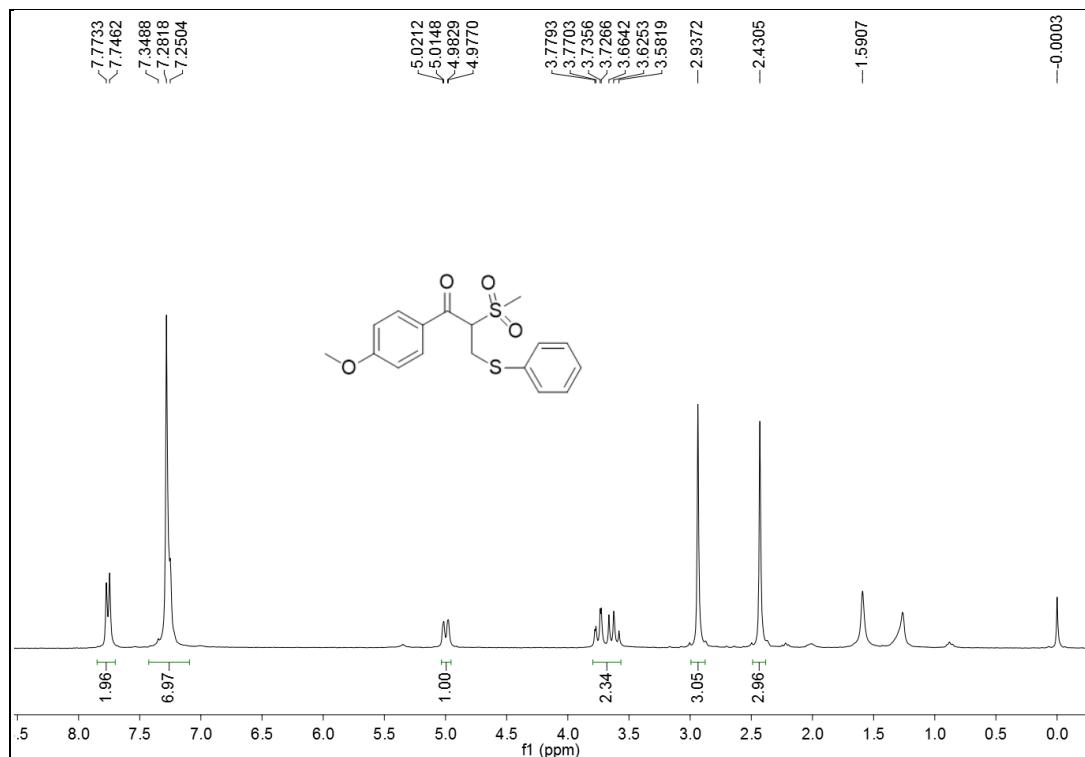
2-((4-chlorophenyl)sulfonyl)-1-phenyl-3-(phenylthio)propan-1-one(2ab)



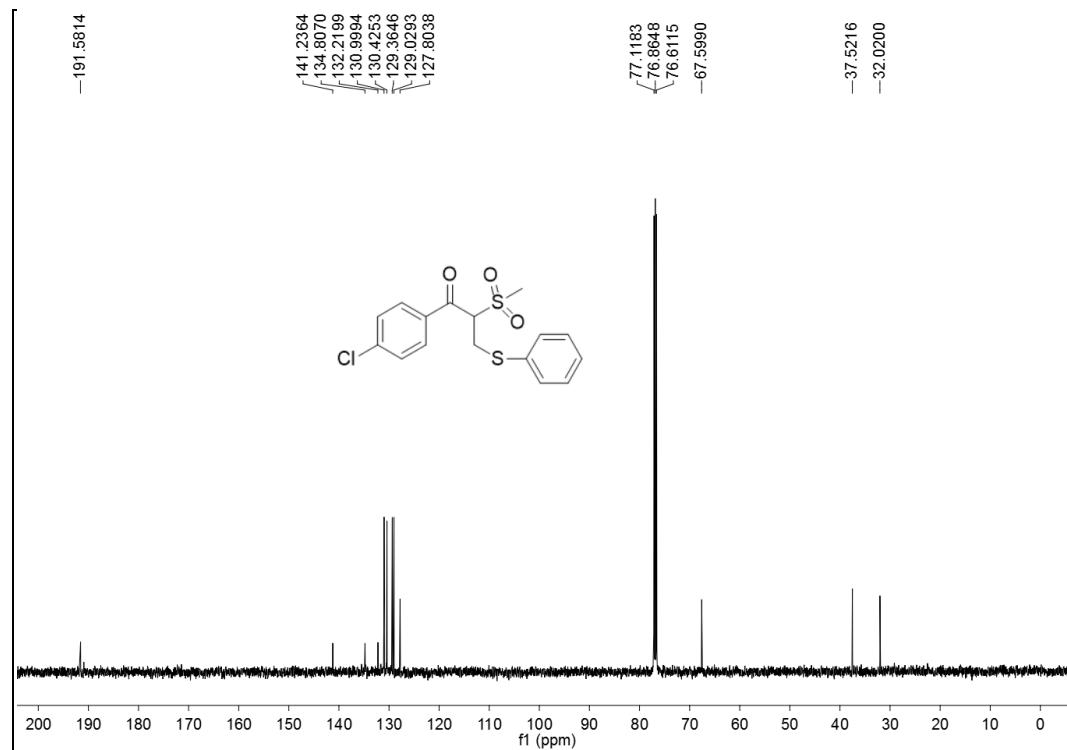
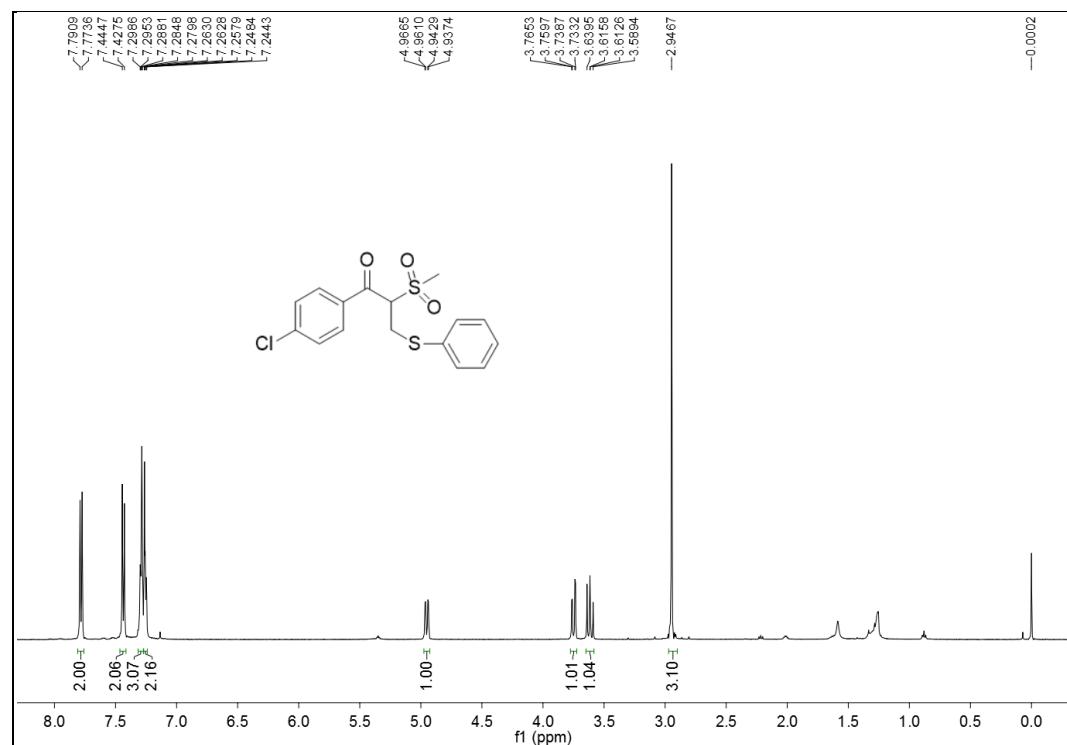
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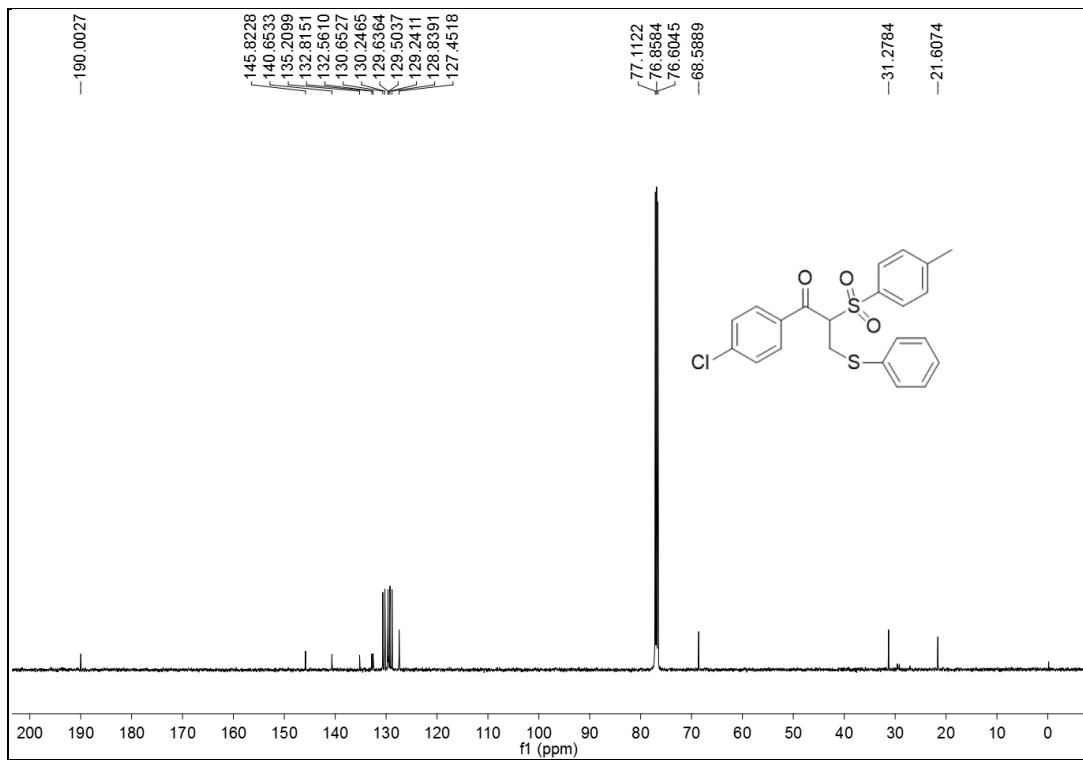
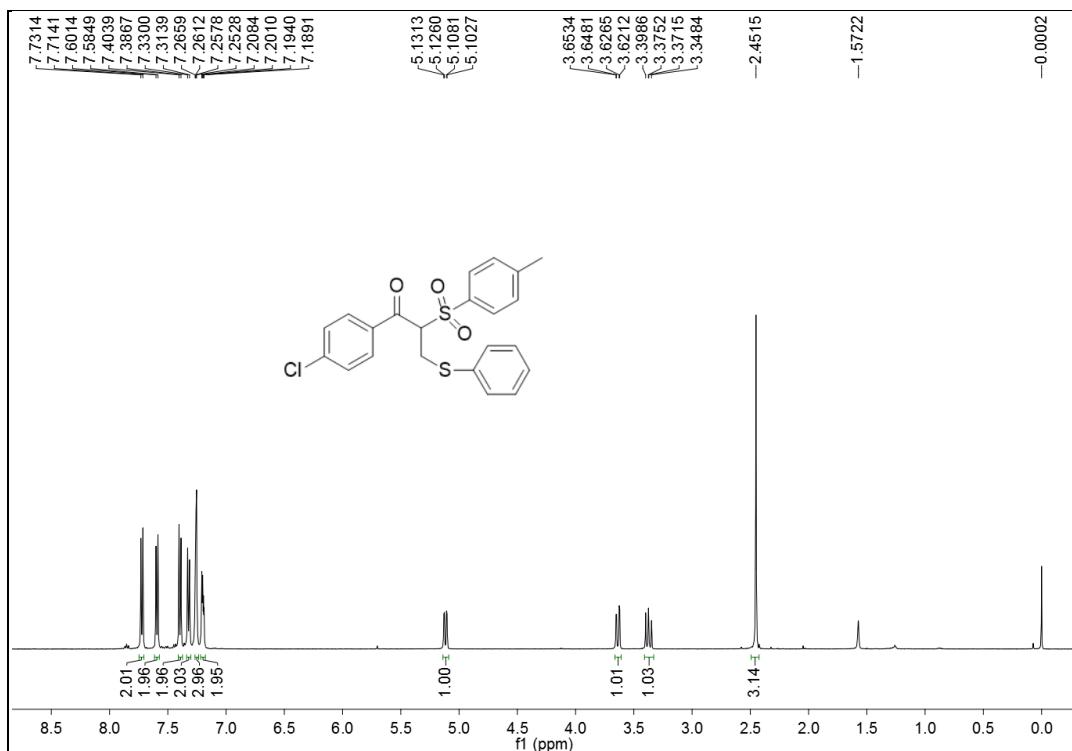
1-(4-methoxyphenyl)-2-(methylsulfonyl)-3-(phenylthio)propan-1-one(2ad)



1-(4-chlorophenyl)-2-(methylsulfonyl)-3-(phenylthio)propan-1-one(2ae)

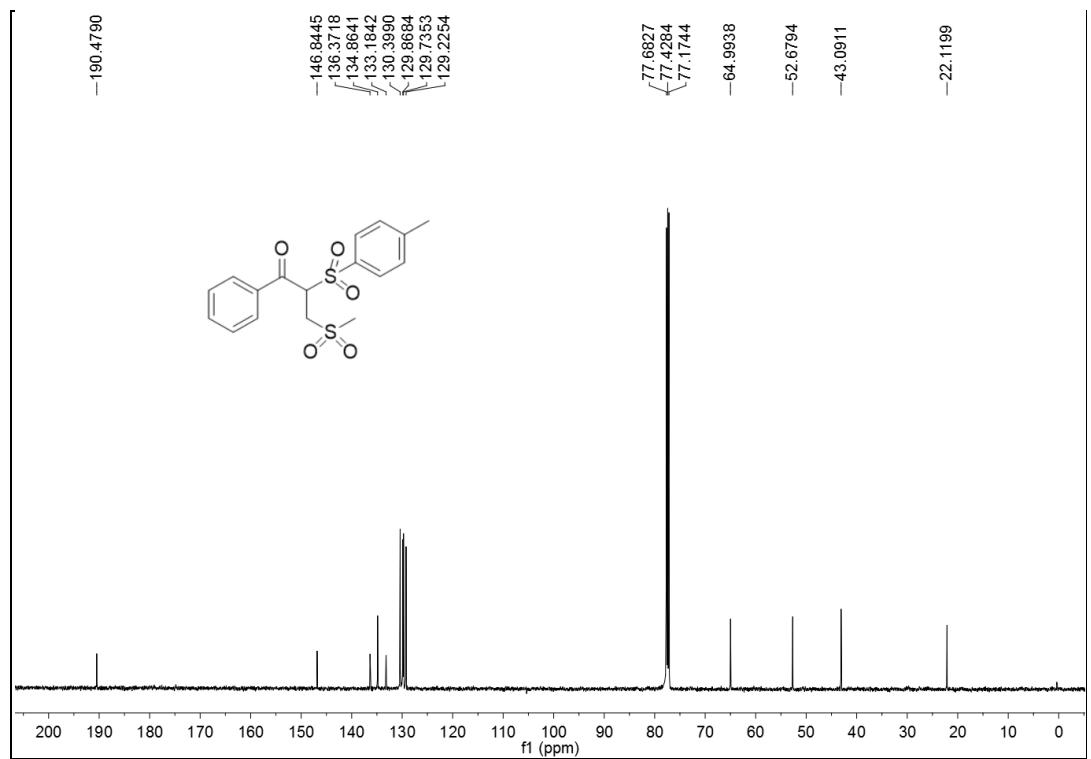
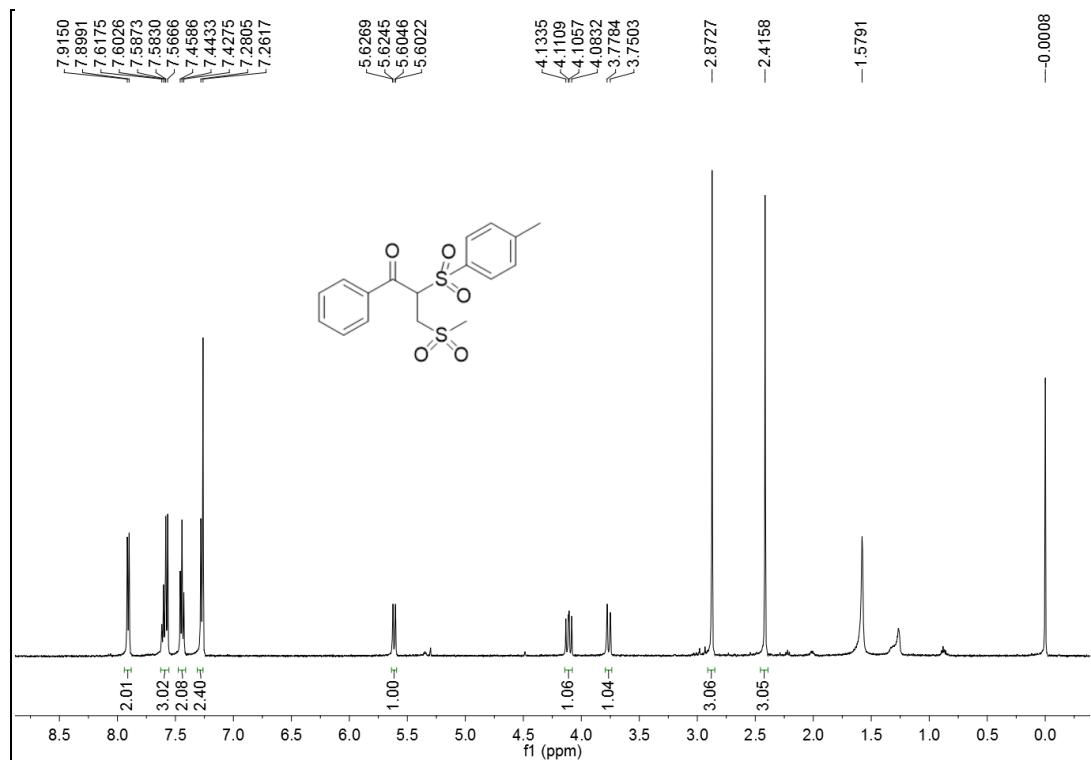


1-(4-chlorophenyl)-3-(phenylthio)-2-tosylpropan-1-one(2af)

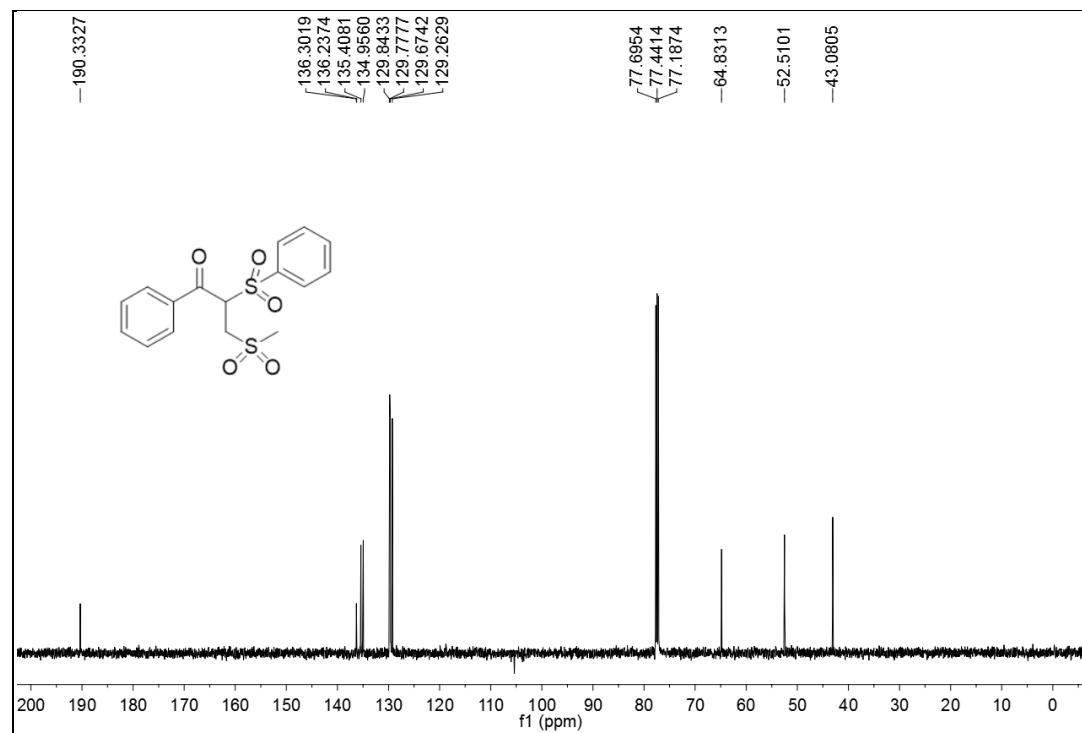
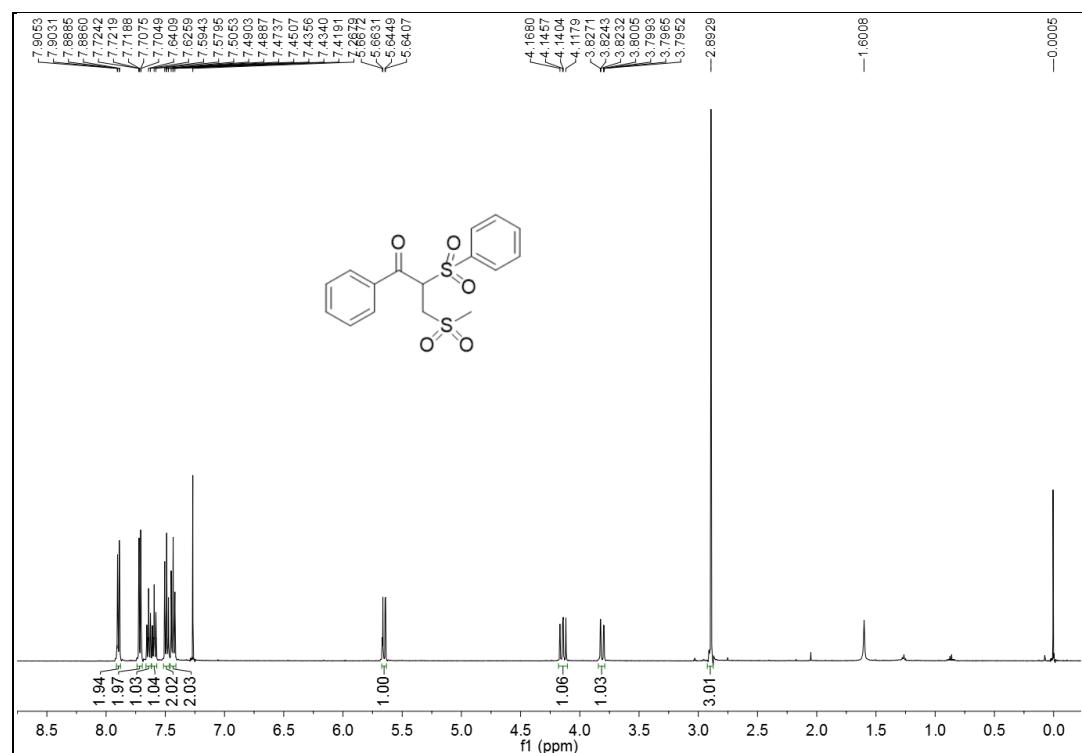


Copies of ^1H NMR and ^{13}C NMR spectra of compounds 3

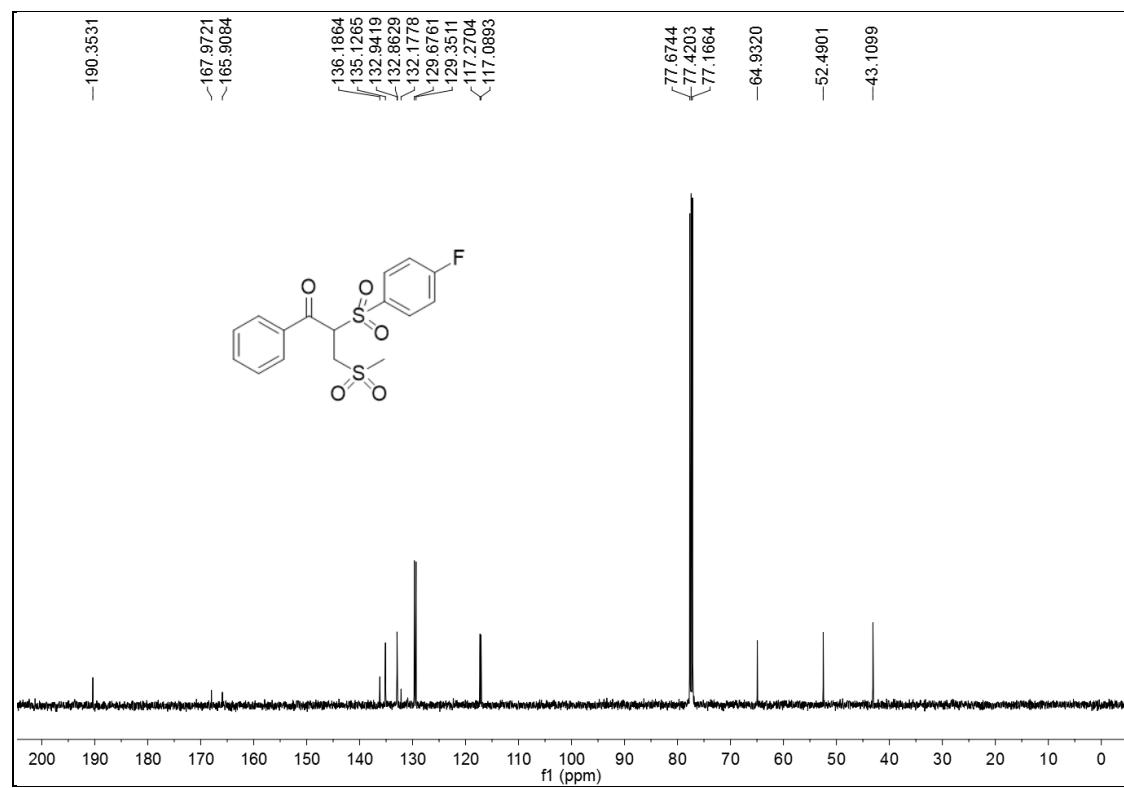
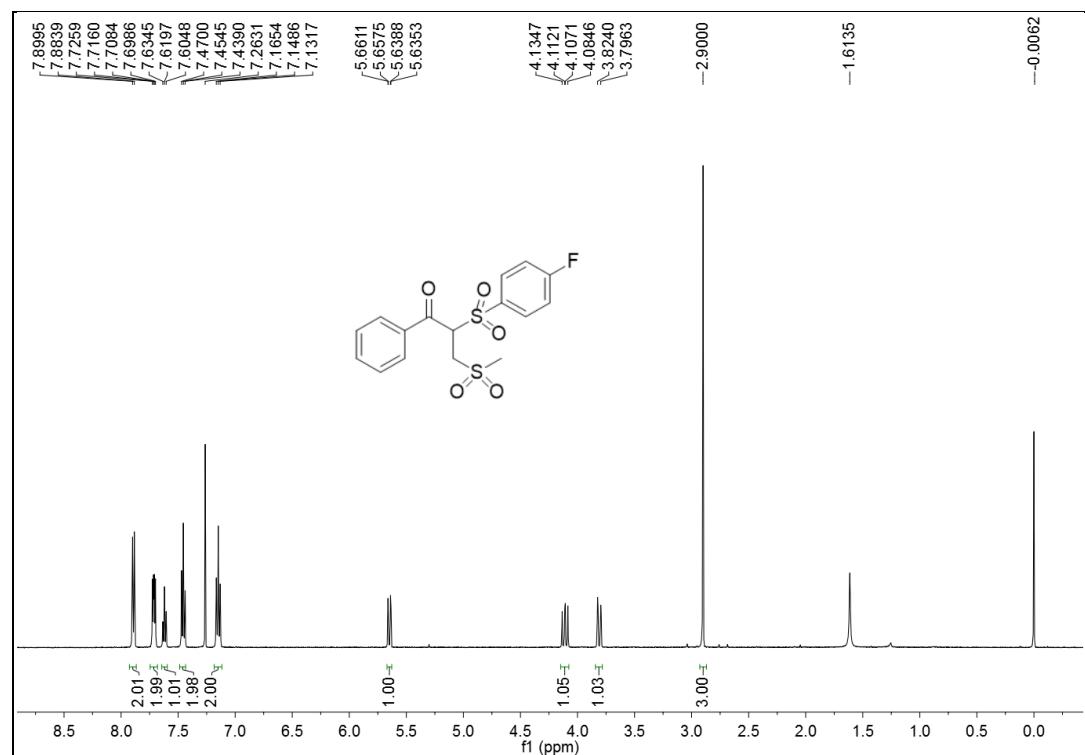
3-(methylsulfonyl)-1-phenyl-2-tosylpropan-1-one (3a)



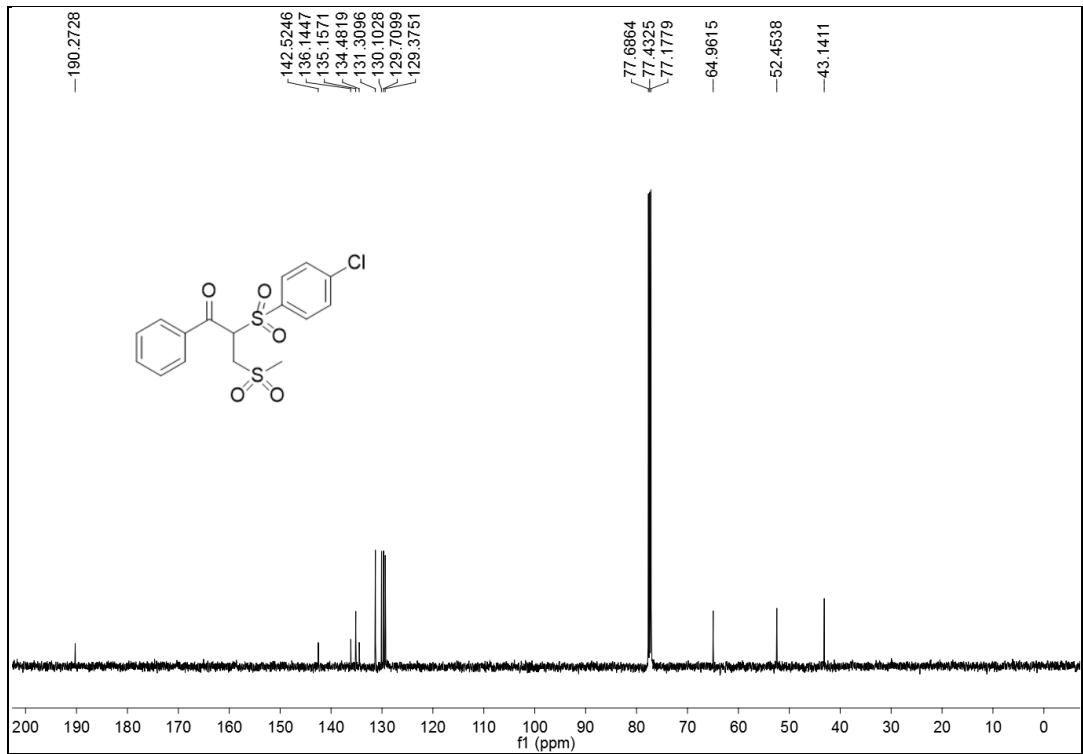
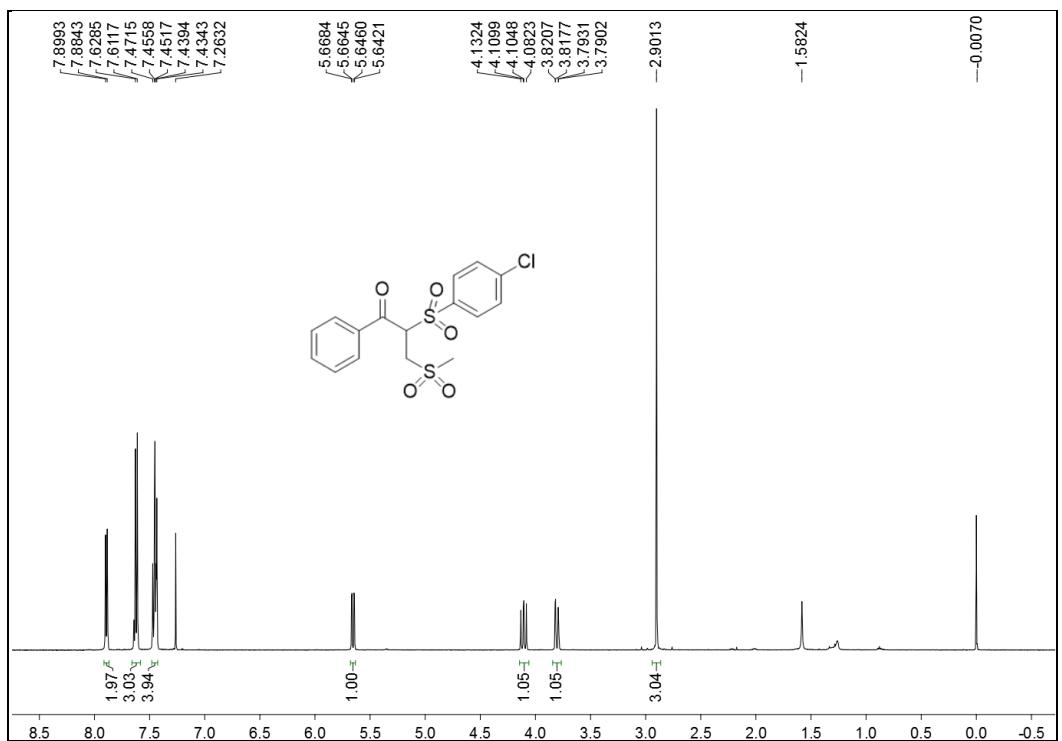
3-(methylsulfonyl)-1-phenyl-2-(phenylsulfonyl)propan-1-one (3b)



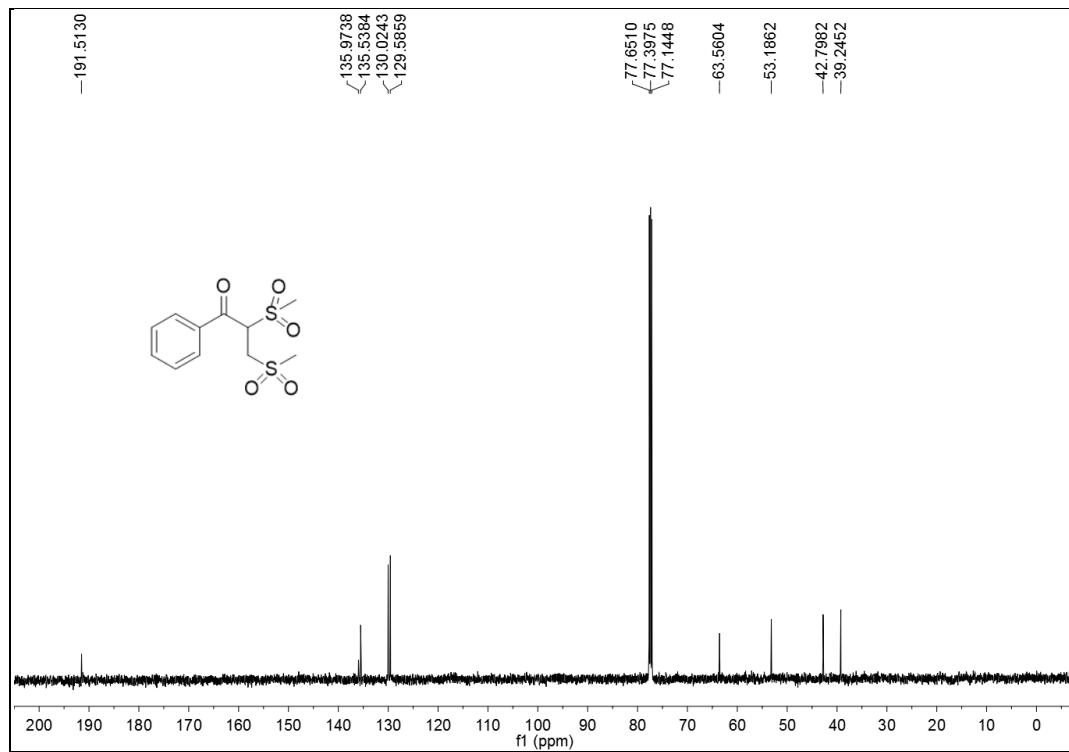
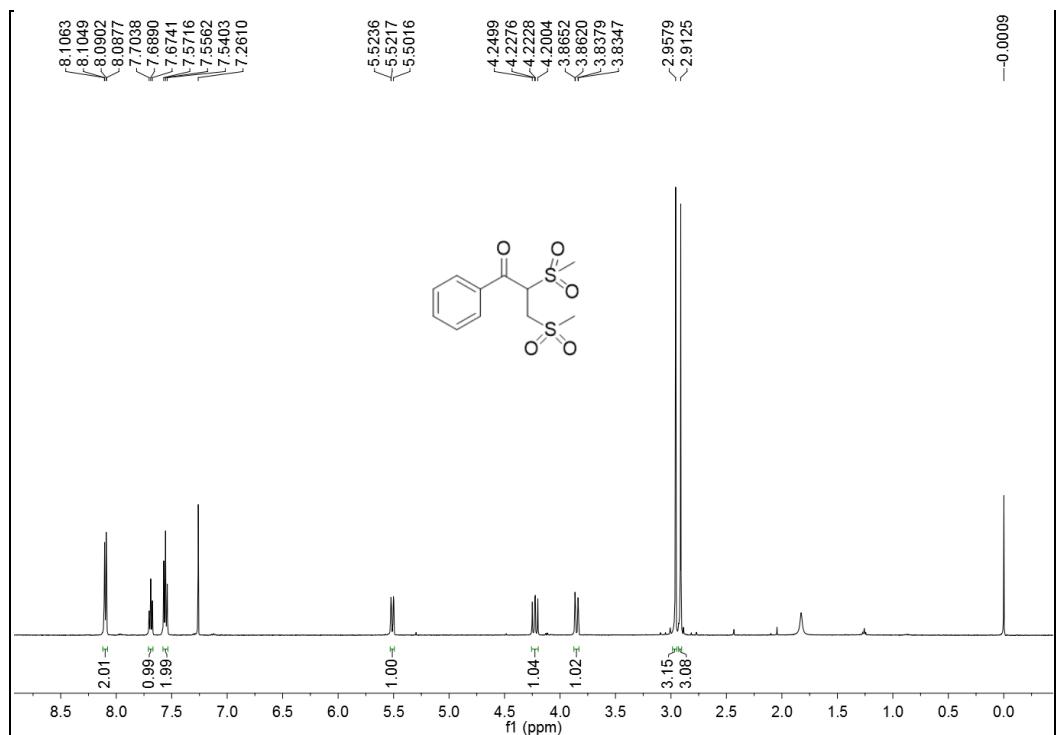
2-((4-fluorophenyl)sulfonyl)-3-(methylsulfonyl)-1-phenylpropan-1-one (3c)



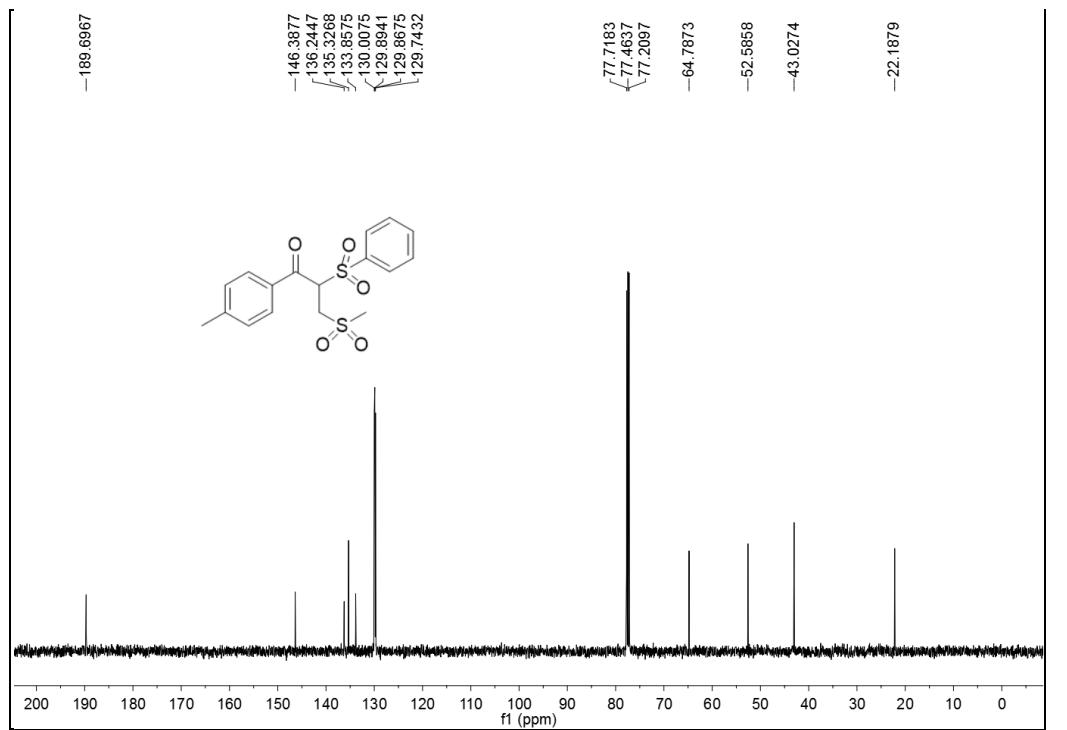
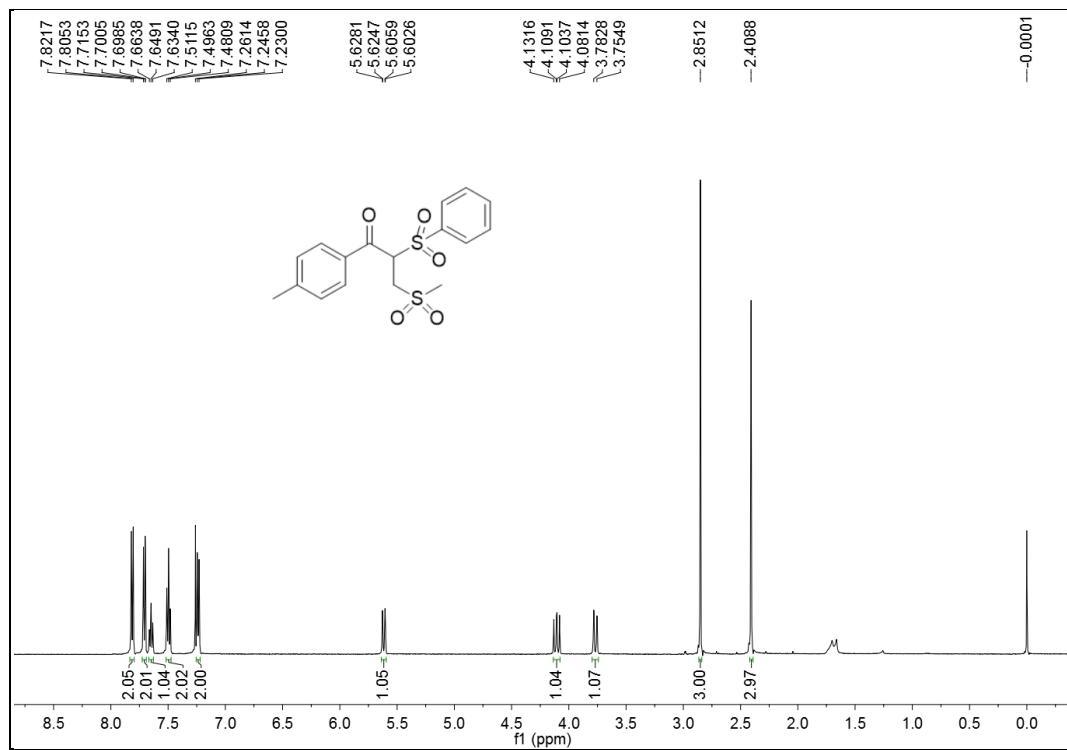
2-((4-chlorophenyl)sulfonyl)-3-(methylsulfonyl)-1-phenylpropan-1-one (3d)



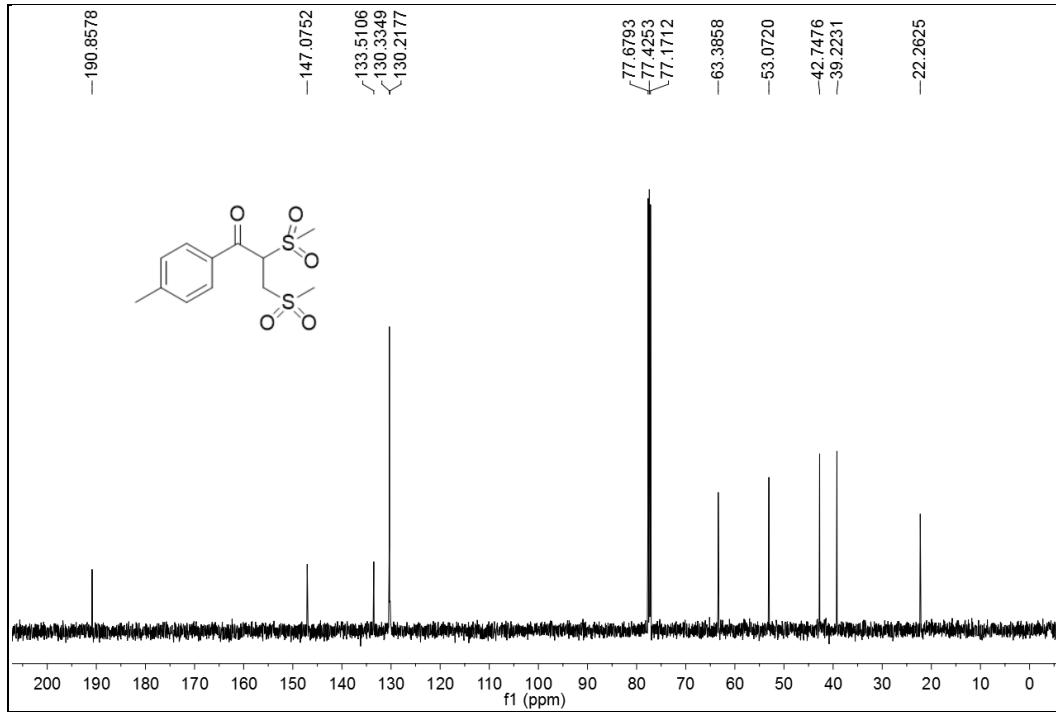
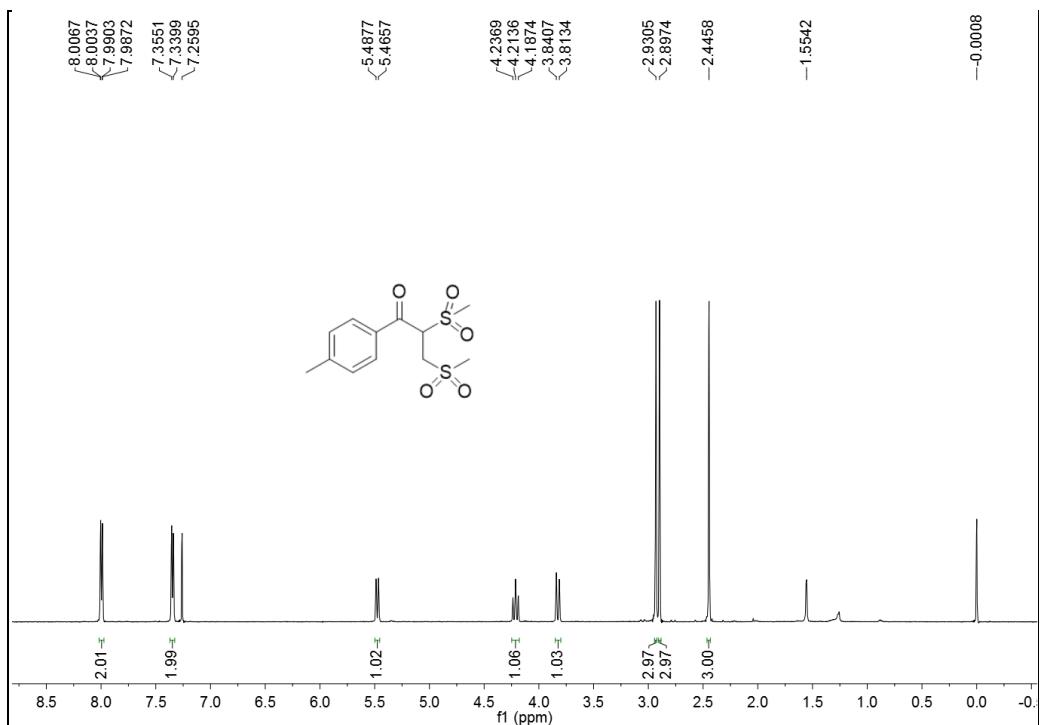
2,3-bis(methylsulfonyl)-1-phenylpropan-1-one (3e)



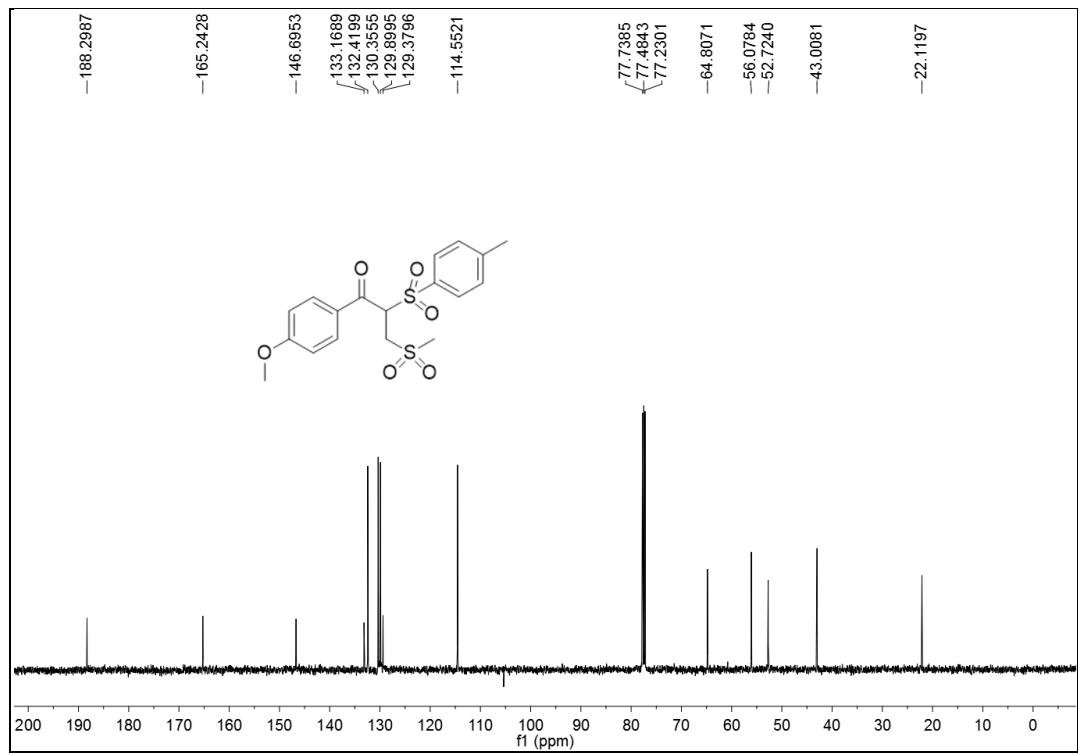
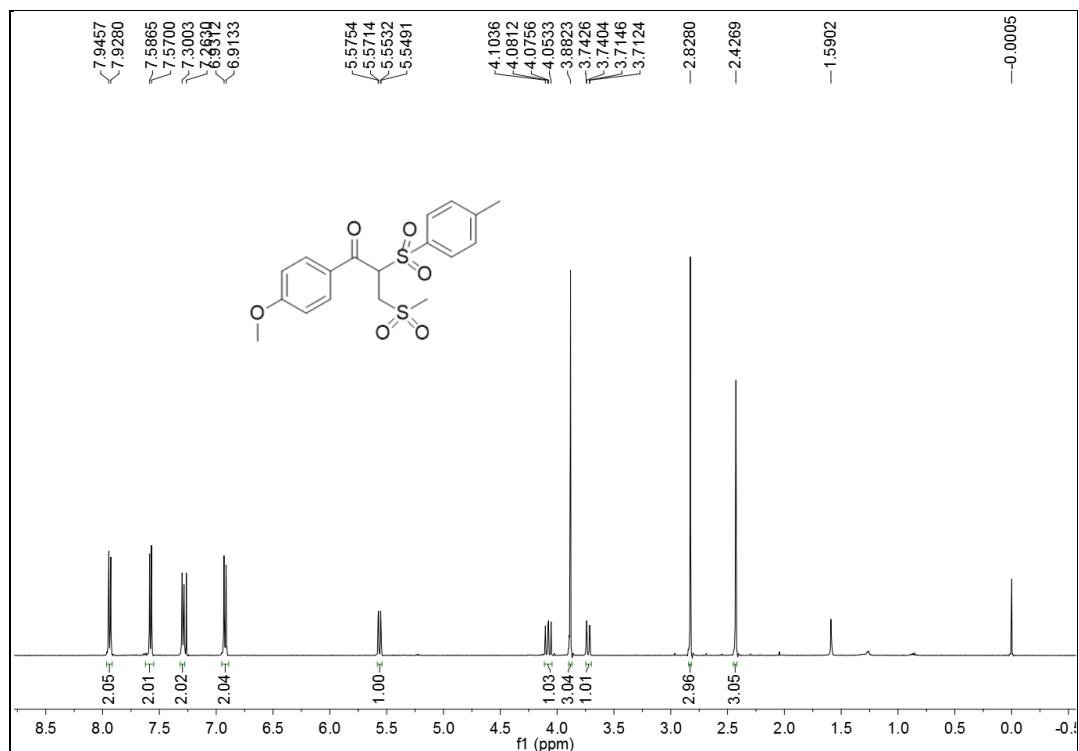
3-(methylsulfonyl)-2-(phenylsulfonyl)-1-(p-tolyl)propan-1-one (3f)



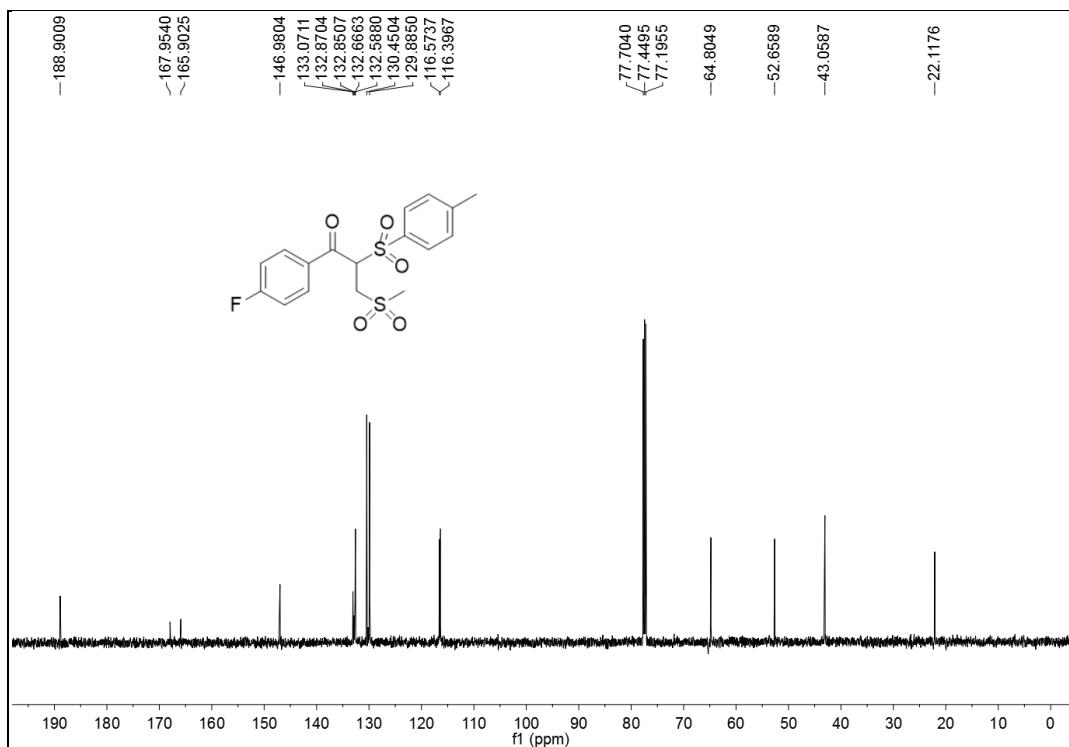
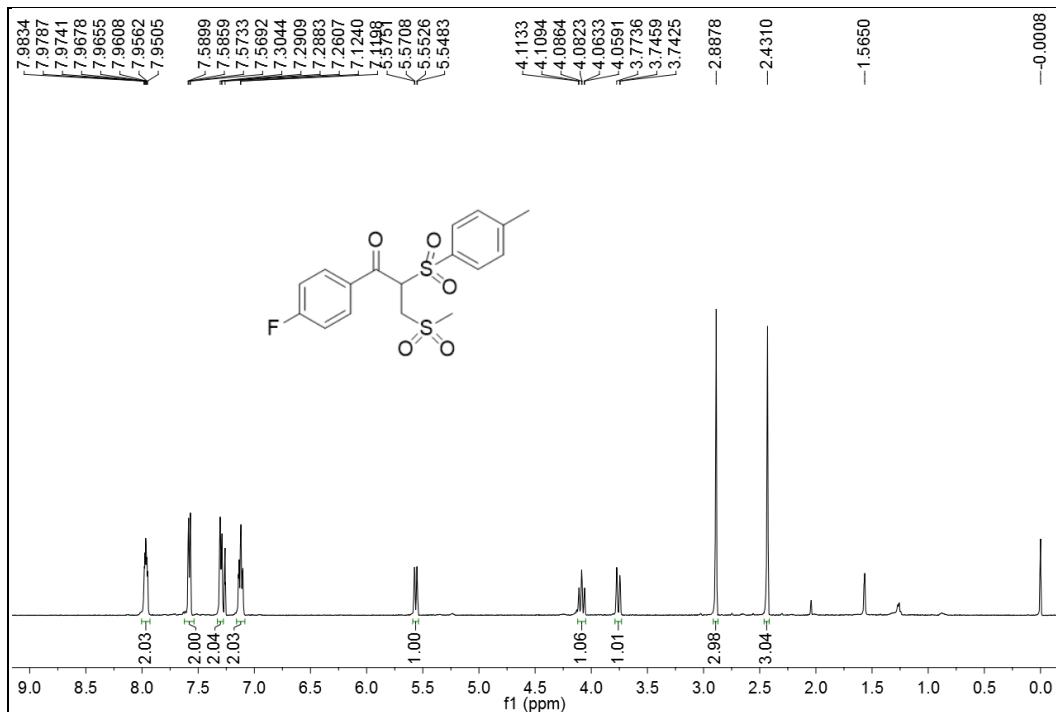
2,3-bis(methylsulfonyl)-1-(p-tolyl)propan-1-one (3g)



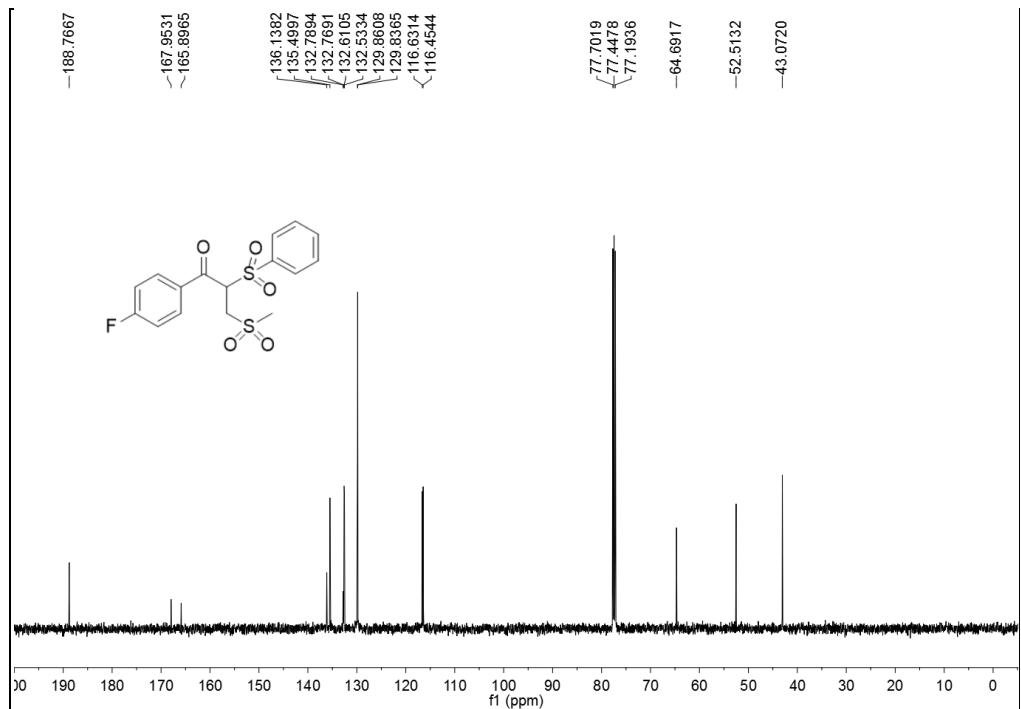
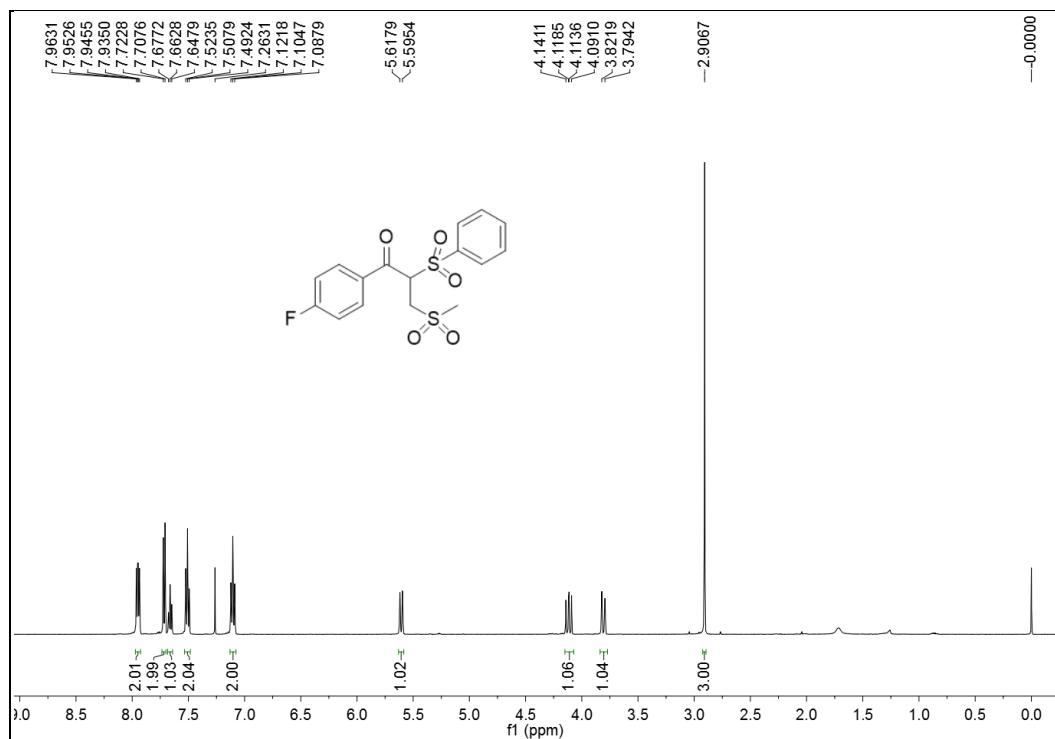
1-(4-methoxyphenyl)-3-(methylsulfonyl)-2-tosylpropan-1-one (3h)



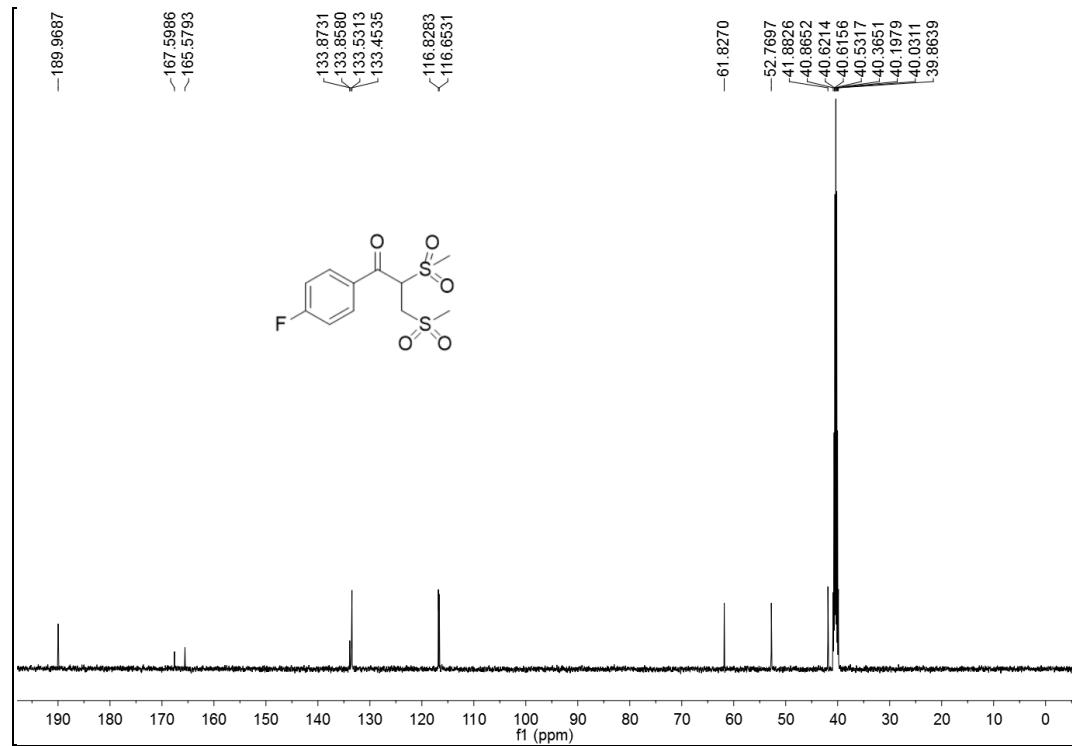
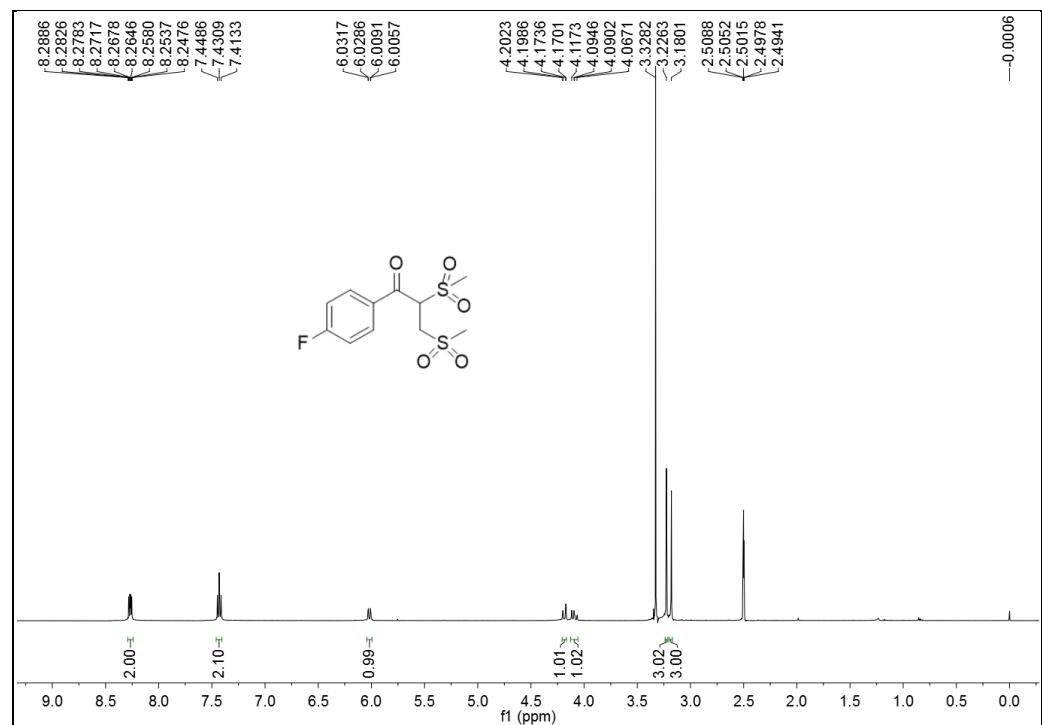
1-(4-fluorophenyl)-3-(methylsulfonyl)-2-tosylpropan-1-one (3i)



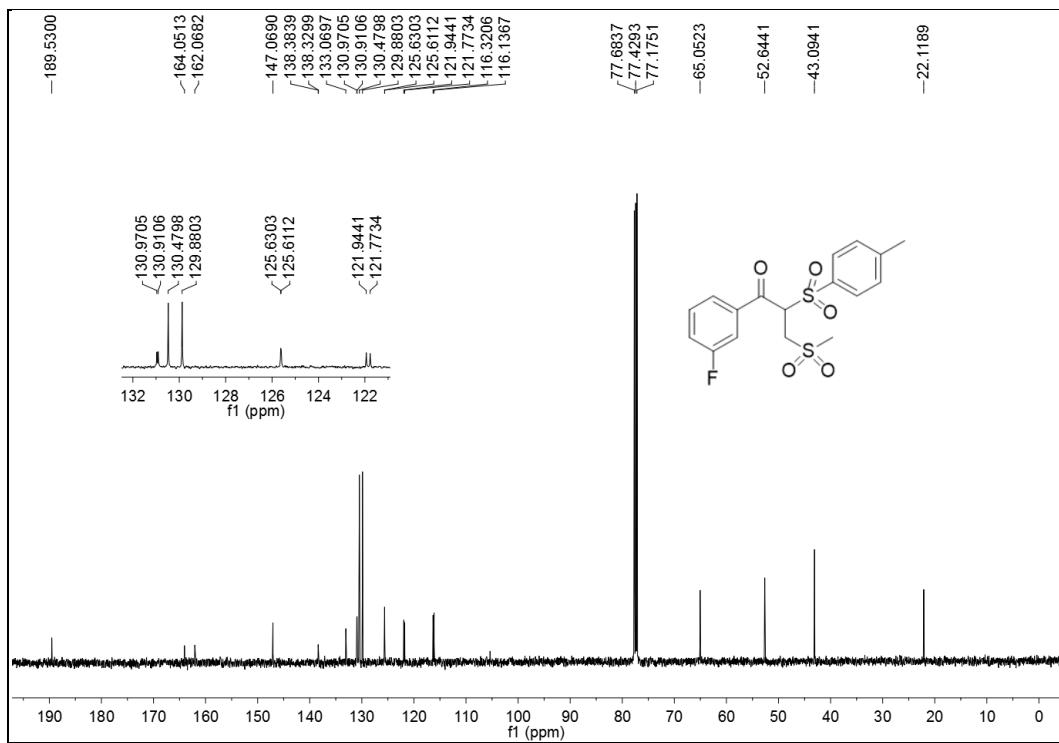
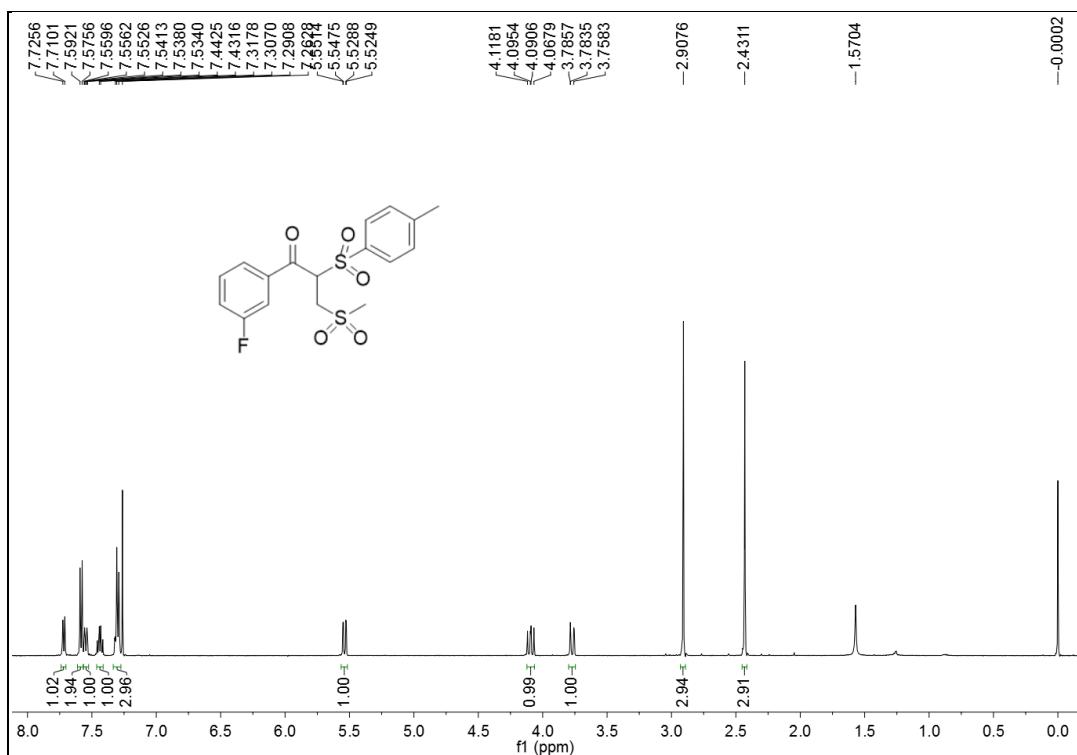
1-(4-fluorophenyl)-3-(methylsulfonyl)-2-(phenylsulfonyl)propan-1-one (3j)



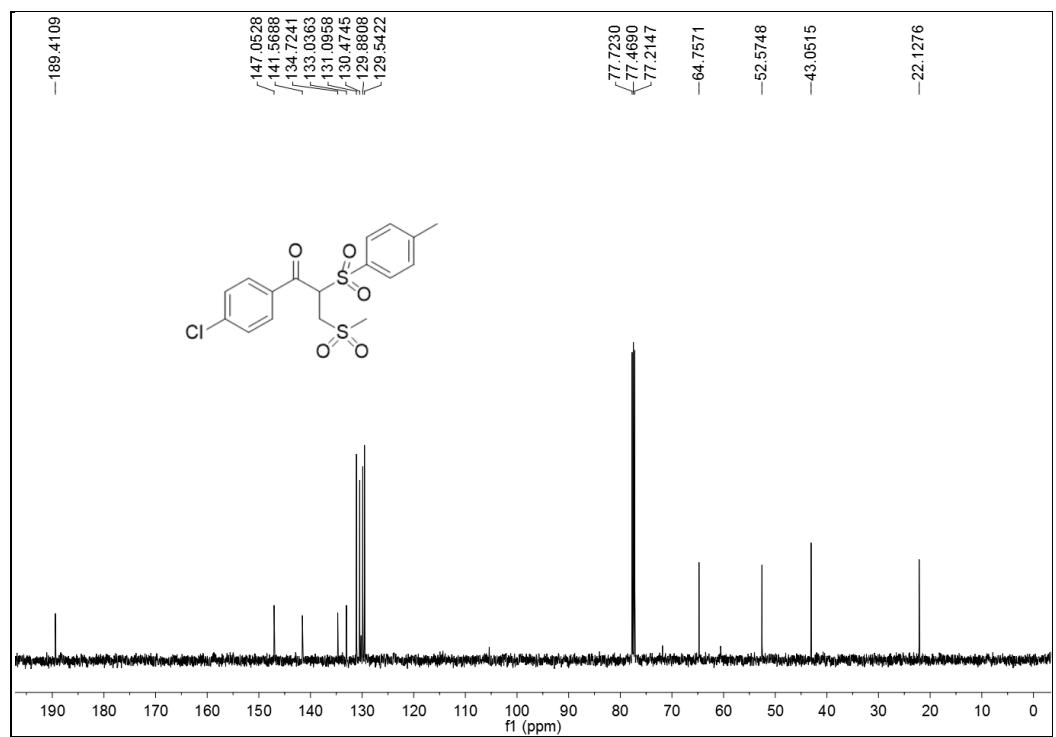
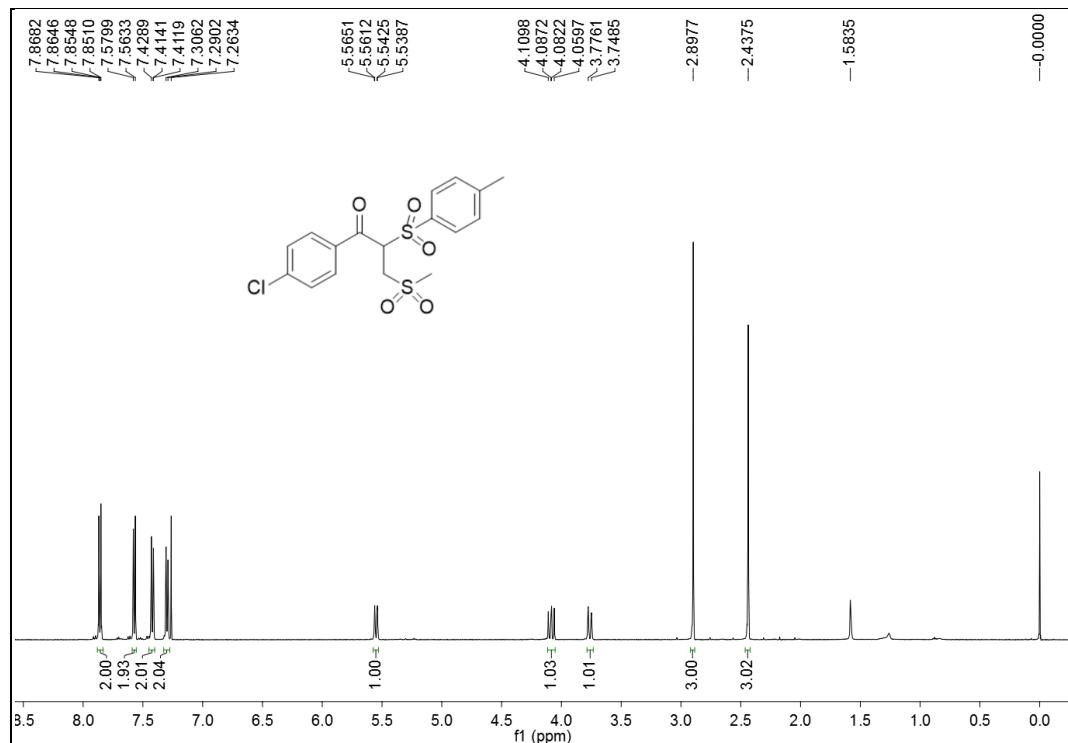
1-(4-fluorophenyl)-2,3-bis(methylsulfonyl)propan-1-one (3k)



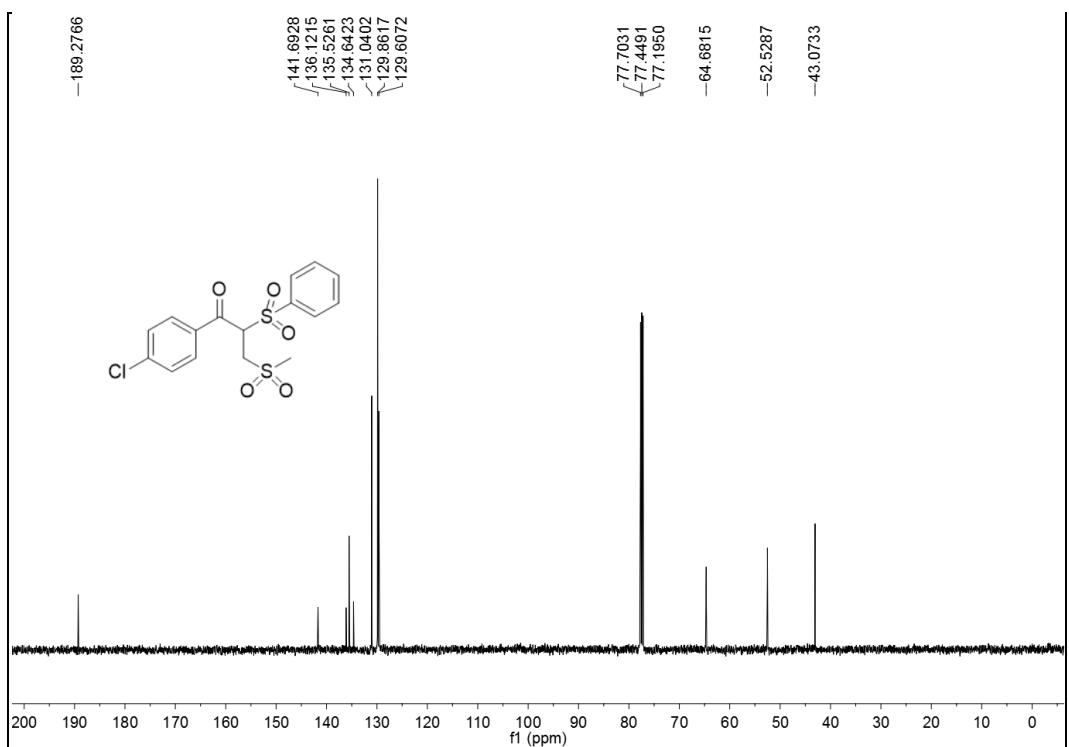
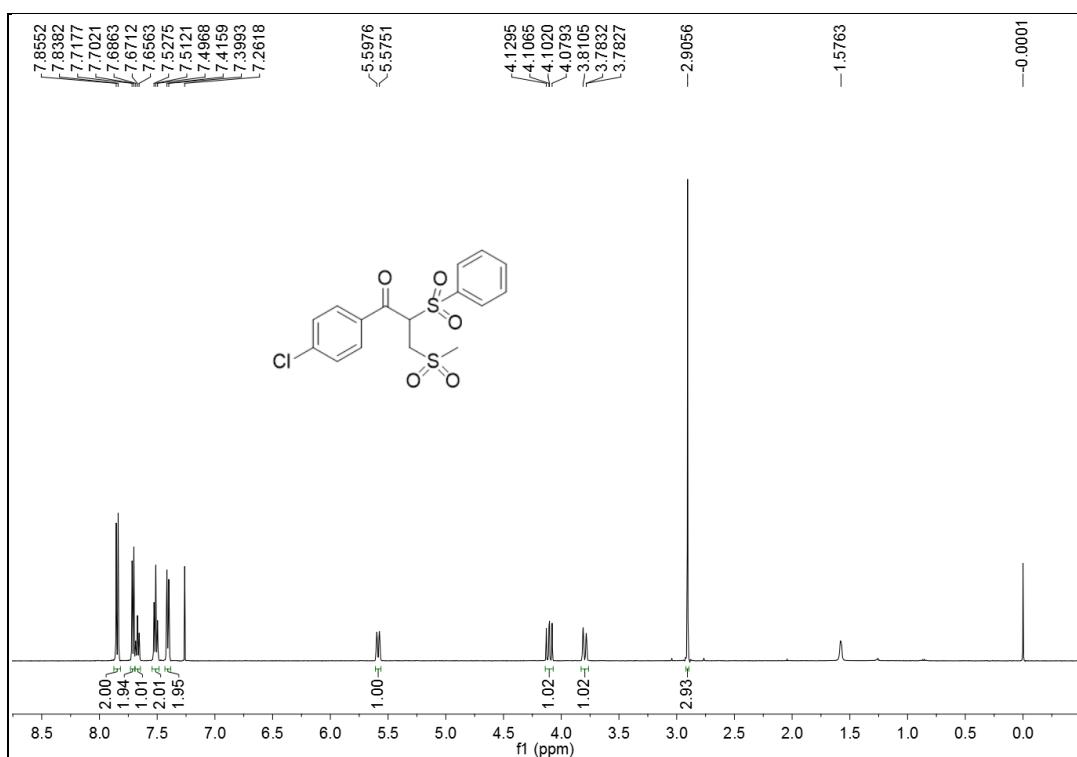
1-(3-fluorophenyl)-3-(methylsulfonyl)-2-tosylpropan-1-one (3l)



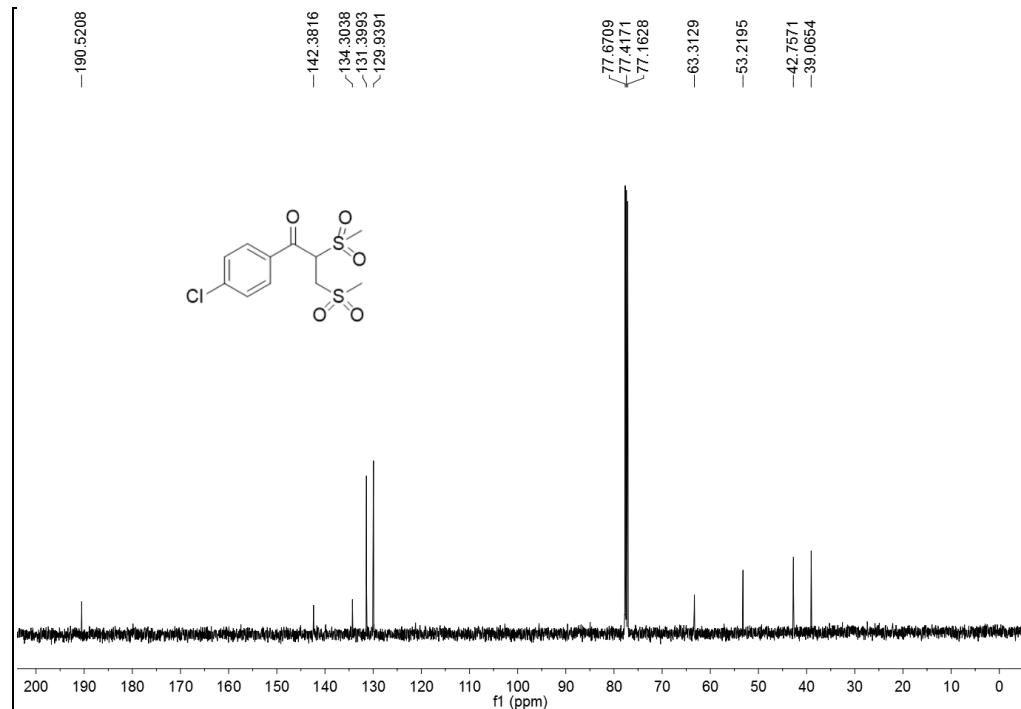
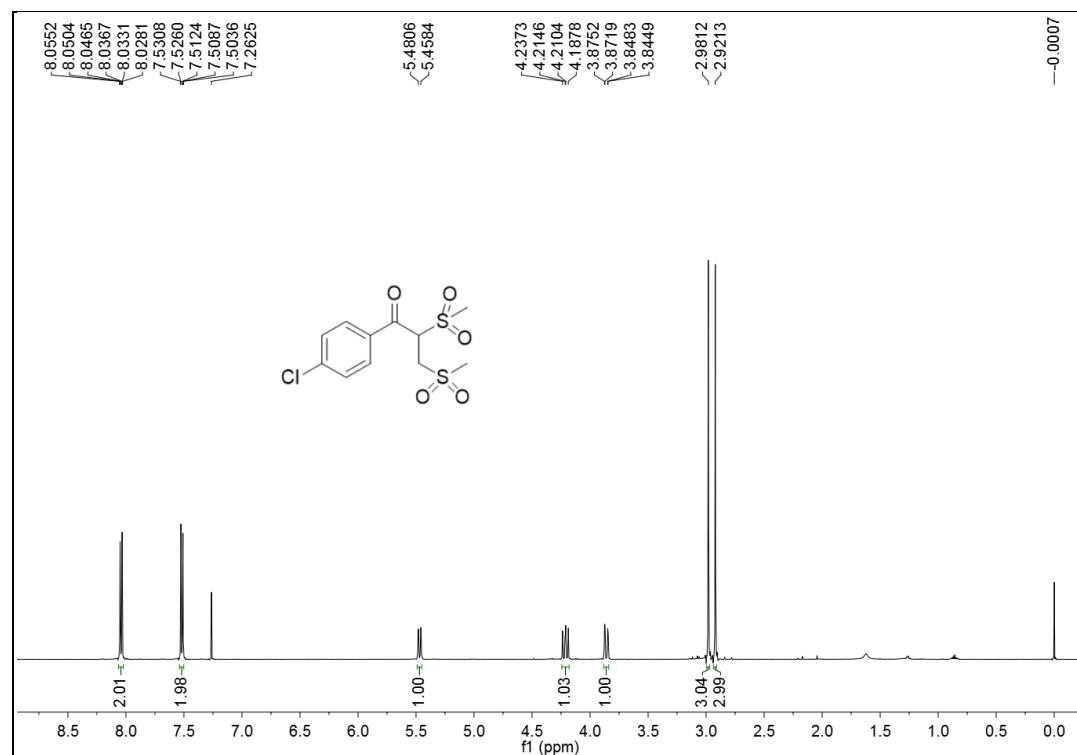
1-(4-chlorophenyl)-3-(methylsulfonyl)-2-tosylpropan-1-one (3m)



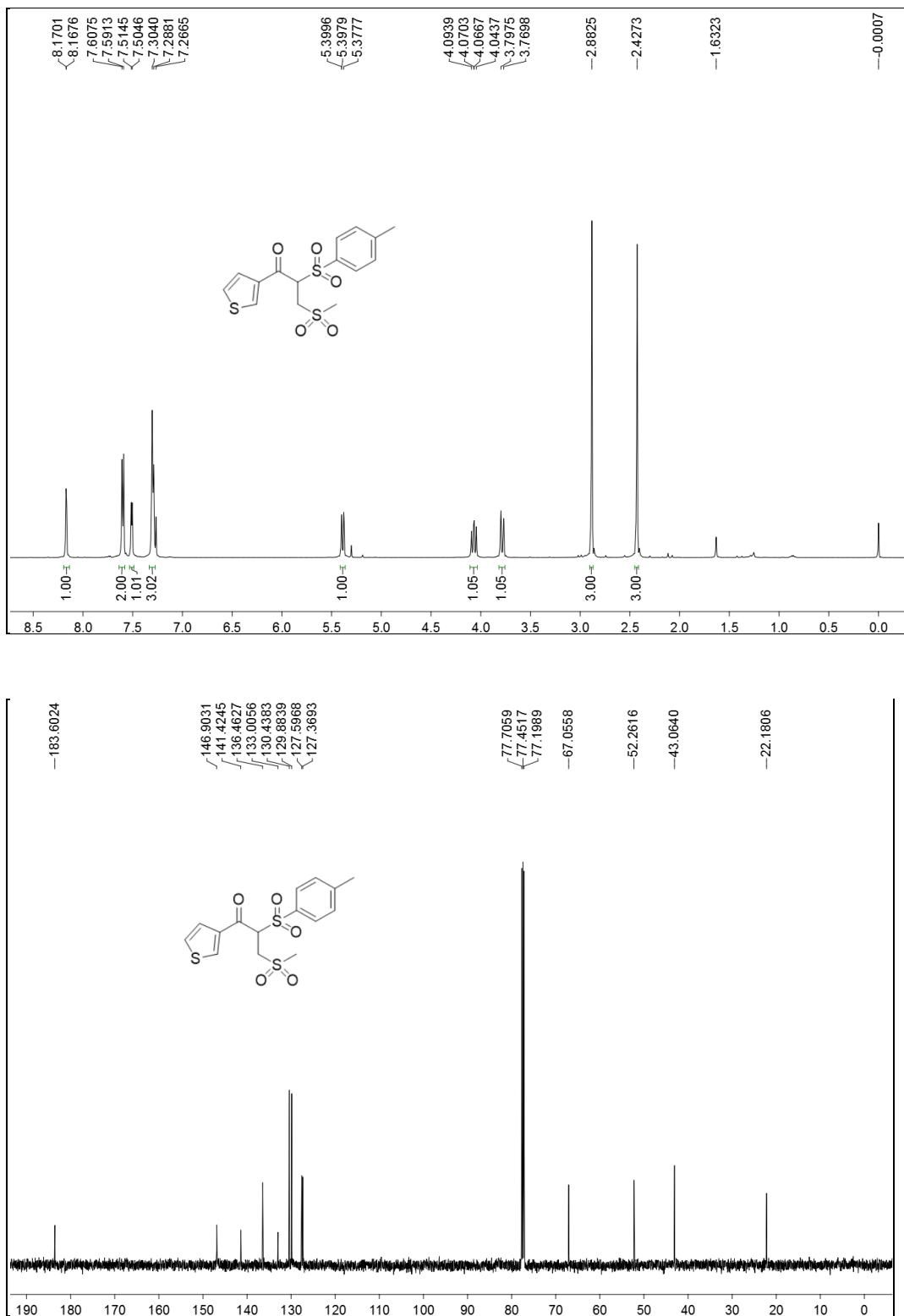
1-(4-chlorophenyl)-3-(methylsulfonyl)-2-(phenylsulfonyl)propan-1-one (3n)



1-(4-chlorophenyl)-2,3-bis(methylsulfonyl)propan-1-one (3o)



3-(methylsulfonyl)-1-(thiophen-3-yl)-2-tosylpropan-1-one(3p)



4,4-dimethyl-1-(methylsulfonyl)-2-tosylpentan-3-one (3q)

