Electronic Supporting Information

# Demethyl oxidative halogenation of diacyl dimethylsulfonium methylides

**Duo Fu, Changmeng Xi and Jiaxi Xu***

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China. E-mail: jxxu@mail.buct.edu.cn

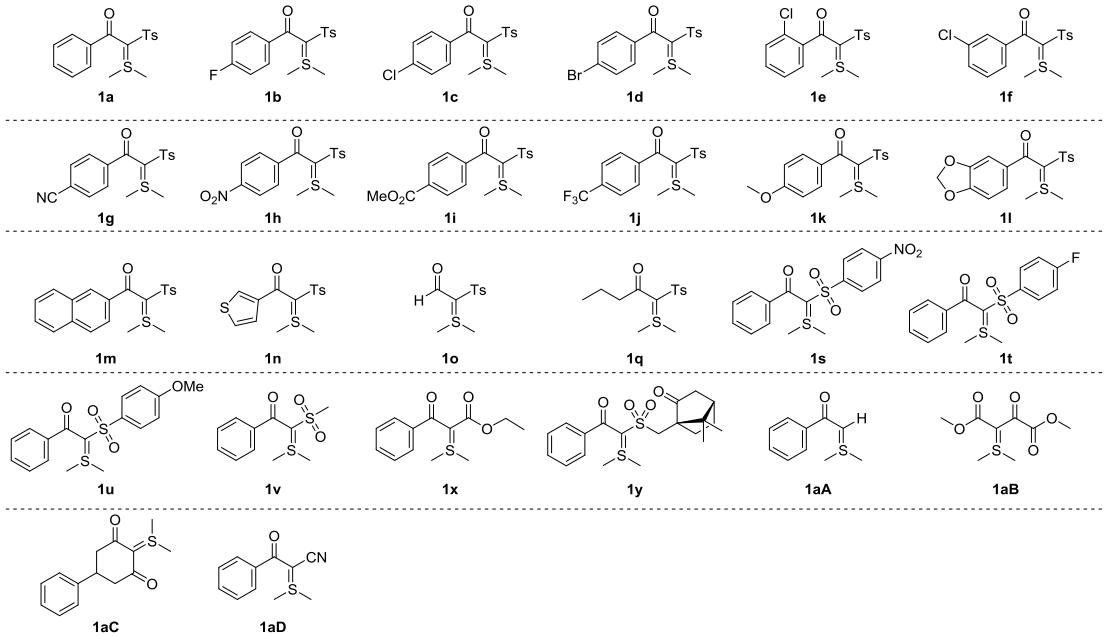
## Contents

# 1.Experimental

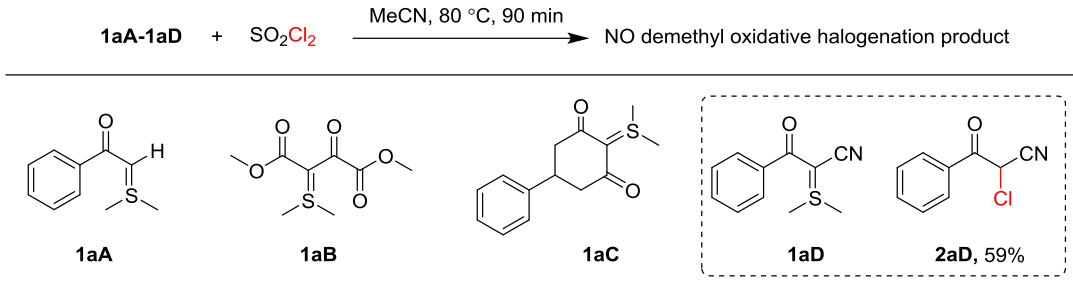
## 1.1 General information

Unless otherwise noted, all materials were purchased from commercial suppliers. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemicals. The thin layer chromatography (TLC) silica gel preparative plates were purchased from Anhui Liangchen Silicon Material Co. Ltd. Column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical, with petroleum ether (PE, 60−90 °C fraction) and ethyl acetate (EA). Reactions were monitored by thin-layer chromatography on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. $^{1}H$ (400 MHz), $^{13}C$ (101 MHz), and $^{19}F$ NMR (376 MHz) spectra were recorded on a Bruker 400 NMR spectrometer usually with TMS as an internal standard for $^{1}H$ NMR, the middle peak (77.16 ppm) of $CDCl_3$ for $^{13}C$ NMR, and $CF_3CO_2H$ as an external standard (-76.55) for $^{19}F$ NMR in $CDCl_3$ solution and the chemical shifts ($\delta$) were reported in parts per million (ppm). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected.

Diacyl dimethylsulfonium methylides **1a–1h**,[1] **1i**,[2] **1j–1n**,[1] **1o**[2], **1q**,[1] **1s**,[1] **1t**,[1] **1u**,[2] **1v**,[1] **1x**,[3] **1y**,[2] **1aA**,[4] **1aB**,[1] **1aC**,[2] and **1aD**[2] were reported in our previous work.

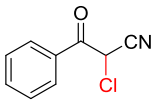


## 1.2 Other attempted (di)acyl dimethylsulfonium methylides 1




**Scheme S1.** Reaction of dimethylsulfonium ylides **1aA-1aD** with sulfuryl chloride.

***Procedure:*** A 10 mL reaction tube was charged with diacyl dimethylsulfonium methylides **1** (0.15 mmol), acetonitrile (3.0 mL), and sulfury chloride (0.24 mmol, 14.6 μL) without inert atmosphere (Sealed after addition). The reaction vessel was sealed and stirred at 60 °C for 90 min. After cooling, the mixture was acidified with acetic acid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/v) as eluent to afford corresponding product.



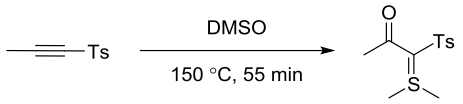
2-Chloro-3-oxo-3-phenylpropanenitrile (**2aD**)[5]

Colorless oil; yield: 16 mg (59%); $R_f$ = 0.10 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09–7.96 (m, 2H), 7.71 (tt, $J$ = 7.6, 1.5 Hz, 1H), 7.56 (m, 2H), 5.70 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 183.4, 135.5, 131.5, 129.7, 128.1, 113.2, 43.7.

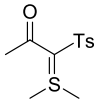
# 1.3 Synthesis of diacyl dimethylsulfonium methylides 1p, 1r, and 1w.

### 1.3.1 Synthesis of diacyl dimethylsulfonium methylide 1p




**1p**

1-Methyl-4-(prop-1-yn-1-ylsulfonyl)benzene (1.94 g, 10.0 mmol, prepared by referring literature[6]) was dissolved in anhydrous DMSO (25.0 mL) in a 35 mL pressure tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 150 °C for 55 min. After cooling and addition of water (60 mL), the mixture was extracted with DCM (3 × 50 mL), and the combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (2:1, *v*/v) to dichloromethane and methanol (40/1, *v*/*v*) as eluent to afford product **1p**.

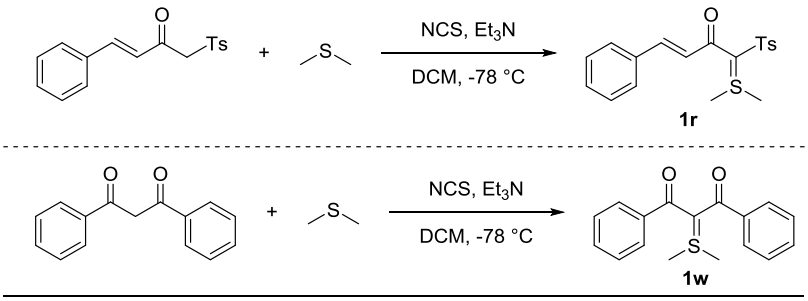



1-(Dimethyl-$\lambda^4$-sulfaneylidene)-1-tosylpropan-2-one (**1p**)

Colorless crystals; yield: 2.23 g (82%); M.p. 120–122 °C; $R_f$ = 0.32 (DCM/MeOH 25:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 (d, $J$ = 7.8 Hz, 2H), 7.28 (d, $J$ = 8.3 Hz, 2H), 2.99 (s, 6H), 2.40 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.9, 143.0, 142.3, 129.6, 125.6, 78.8, 28.5, 27.6, 21.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{17}O_3S_2^+$ 273.0614, found 273.0618.

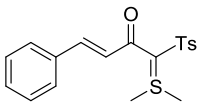
### 1.3.2 Synthesis of diacyl dimethylsulfonium methylides 1r and 1w.




β-Keto sulfone for the preparation of **1r** was prepared by referring literature.[7]

To a suspension of *N*-chlorosuccinimide (1.3 equiv.) in anhydrous dichloromethane (60 mL) was added dimethyl sulfide (1.845 equiv.) dropwise at -78 °C under $N_2$. The resulting mixture was stirred at the same temperature for 1 h. Then, a solution of an active methylene compound (1.0 eq) was added at the same temperature. After 1 h, triethylamine (1.515 equiv.) was added into the mixture, and the mixture was stirred at the same temperature for additional 1 h. After addition of cold brine (60 mL), the mixture was extracted with DCM (3 × 50 mL), and the combined organic layer was washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo*. The resulting residue was purified by silica gel column

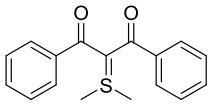
chromatography with a mixture of petroleum ether (60–90 °C) and ethyl acetate (1:1, *v*/v) to dichloromethane and methanol 40/1, *v*/*v*) as eluent to afford products **1r** and **1w**.[8]




(*E*)-1-(Dimethyl-λ$^4$-sulfaneylidene)-4-phenyl-1-tosylbut-3-en-2-one (**1r**)

Prepared on a 5 mmol scale. Colorless crystals; yield: 920 mg (53%); M.p. 159–160 °C; $R_f$ = 0.42 (DCM/MeOH 25:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.76 (m, 3H), 7.55–7.52 (m, 2H), 7.48 (d, $J$ = 15.5 Hz, 1H), 7.42–7.31 (m, 3H), 7.24 (d, $J$ = 8.0 Hz, 2H), 3.03 (s, 6H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 180.9, 143.4, 142.4, 138.9, 135.6, 129.7, 129.4, 128.7, 128.1, 125.6, 124.6, 80.6, 27.6, 21.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{21}O_3S_2^+$ 361.0927, found 361.0928.

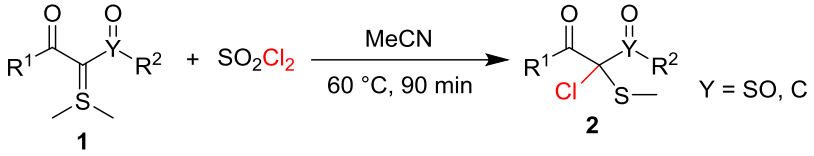



2-(Dimethyl-λ$^4$-sulfaneylidene)-1,3-diphenylpropane-1,3-dione (**1w**)[8]

Prepared on a 5 mmol scale. Colorless crystals; yield: 1.58 g (56%); M.p. 208–210 °C; $R_f$ = 0.28 (DCM/MeOH 25:1, *v*/*v*).

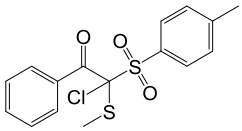
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.33–7.20 (m, 4H), 7.11–7.04 (m, 2H), 7.04–6.97 (m, 4H), 3.81–2.21 (m, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 191.0, 142.0, 129.8, 128.6, 127.4, 88.1, 26.9.

## 1.4 General procedure for the synthesis of chlorinated products 2




Diacyl dimethylsulfonium methylide **1** (0.15 mmol) and sulfuryl chloride (0.18 mmol, 14.6 μL) were dissolved in MeCN (3.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 60 °C for 90 min. After cooling, the mixture was acidified with acetic acid and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (**Silica gel was acidified with 2% acetic acid**) with petroleum ether (60 – 90 °C) and ethyl acetate (15:1, *v*/v) as eluent (**Acidified with 0.25% acetic acid**) to afford **2**.

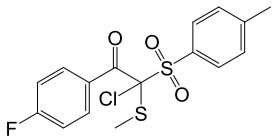
### 1.4.1 Analytic date for products 2



2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**)

Colorless crystals; yield: 52 mg (98%); M.p. 59–60 °C; $R_f$ = 0.59 (PE/EA 3:1, *v*/*v*).

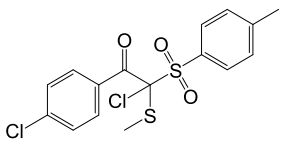
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.24–8.08 (m, 2H), 7.92 (d, $J$ = 8.4 Hz, 2H), 7.63–7.49 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.43 (t, $J$ = 8.0 Hz, 2H), 7.33 (d, $J$ = 7.9 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.5, 146.1, 133.9, 133.9, 132.2, 131.4, 130.6, 129.2, 128.2, 92.6, 21.9, 16.6. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{16}H_{19}ClNO_3S_2^+$ 372.0489, found 372.0487.



2-Chloro-1-(4-fluorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2b**)

Colorless oil; yield: 50 mg (89%); $R_f$ = 0.36 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.29 (dd, $J$ = 9.0, 5.3 Hz, 2H), 7.90 (d, $J$ = 8.3 Hz, 2H), 7.34 (d, $J$ = 8.3 Hz, 2H), 7.11 (t, $J$ = 8.6 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 186.7, 166.0 (d, $J$ = 257.4 Hz), 146.2, 133.7 (d, $J$ = 9.4 Hz), 132.0, 131.2, 129.9 (d, $J$ = 3.2 Hz), 129.2, 115.4 (d, $J$ = 22.0 Hz), 92.7, 21.8, 16.4. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -102.7. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{16}H_{18}ClFNO_3S_2^+$ 390.0395, found 390.0394.

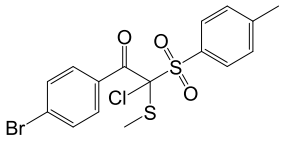


2-Chloro-1-(4-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2c**)

Colorless crystals; yield: 55 mg (94%); M.p. 80–81 °C; $R_f$ = 0.42 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.17 (d, $J$ = 8.7 Hz, 2H), 7.89 (d, $J$ = 8.3 Hz, 2H), 7.41 (d, $J$ = 8.7 Hz,

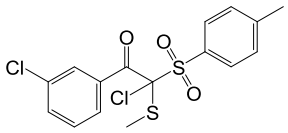
2H), 7.34 (d, $J$ = 8.3 Hz, 2H), 2.49 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.4, 146.3, 140.6, 132.2, 132.22, 132.16, 131.13, 129.3, 128.6, 92.8, 21.9, 16.5. HRMS (ESI-TOF) $m/z$: $[M + NH_4]^+$ calcd for $C_{16}H_{18}Cl_2NO_3S_2^+$ 406.0100, found 406.0089.




1-(4-Bromophenyl)-2-chloro-2-(methylthio)-2-tosylethan-1-one (**2d**)

Colorless crystals; yield: 56 mg (86%); M.p. 94–95 °C; $R_f$ = 0.42 (PE/EA 10:1, v/v).

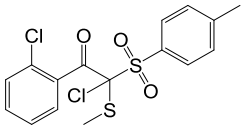
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 (d, $J$ = 8.7 Hz, 2H), 7.89 (d, $J$ = 8.4 Hz, 2H), 7.58 (d, $J$ = 8.7 Hz, 2H), 7.34 (d, $J$ = 8.2 Hz, 2H), 2.49 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.6, 146.3, 132.6, 132.2, 132.1, 131.6, 131.2, 129.4, 129.3, 92.8, 21.9, 16.5. HRMS (ESI-TOF) $m/z$: $[M + NH_4]^+$ calcd for $C_{16}H_{18}BrClNO_3S_2^+$ 449.9595, found 449.9592.




2-Chloro-1-(3-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2e**)

Light yellow oil; yield: 52 mg (89%); $R_f$ = 0.49 (PE/EA 10:1, $v/v$).

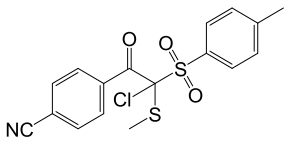
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (dt, $J$ = 7.9, 1.2 Hz, 1H), 8.08 (t, $J$ = 2.0 Hz, 1H), 7.90 (d, $J$ = 8.0 Hz, 2H), 7.54 (ddd, $J$ = 8.0, 2.0, 1.2 Hz, 1H), 7.38 (t, $J$ = 7.9 Hz, 1H), 7.35 (d, $J$ = 8.1 Hz, 2H), 2.50 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.6, 146.4, 135.5, 134.4, 133.8, 132.1, 131.2, 130.3, 129.5, 129.3, 128.7, 92.6, 21.9, 16.5. HRMS (ESI-TOF) $m/z$: $[M + NH_4]^+$ calcd for $C_{16}H_{18}Cl_2NO_3S_2^+$ 406.0100, found 406.0092.




2-Chloro-1-(2-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2f**)

Colorless crystals; yield: 36 mg (62%); M.p. 124–125 °C; $R_f$ = 0.40 (PE/EA 10:1, $v/v$).

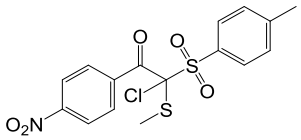
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.89 (d, $J$ = 8.4 Hz, 2H), 7.76 (d, $J$ = 7.4 Hz, 1H), 7.40–7.37 (m, 4H), 7.35–7.29 (m, 1H), 2.55 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 191.5, 146.5, 136.5, 132.0, 131.7, 131.1, 130.7, 129.9, 129.3, 128.3, 126.2, 92.8, 21.9, 16.3. HRMS (ESI-TOF) $m/z$: $[M + NH_4]^+$ calcd for $C_{16}H_{18}Cl_2NO_3S_2^+$ 406.0100, found 406.0096.




4-(2-Chloro-2-(methylthio)-2-tosylacetyl)benzonitrile (**2g**)

Colorless crystals; yield: 50 mg (88%); M.p. 121–122 °C; $R_f$ = 0.32 (PE/EA 10:1, $v/v$).

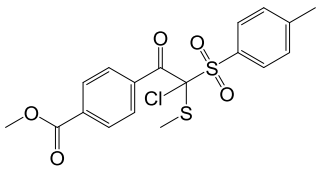
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.26 (d, $J$ = 8.4 Hz, 2H), 7.88 (d, $J$ = 8.1 Hz, 2H), 7.74 (d, $J$ = 8.5 Hz, 2H), 7.36 (d, $J$ = 8.3 Hz, 2H), 2.49 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.0, 146.6, 137.6, 132.0, 131.8, 130.8, 130.7, 129.4, 117.7, 116.7, 92.7, 21.9, 16.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for $C_{17}H_{14}ClNNaO_3S_2^+$ 401.9996, found 401.9990.



2-Chloro-2-(methylthio)-1-(4-nitrophenyl)-2-tosylethan-1-one (**2h**)

Colorless oil; yield: 45 mg (75%); $R_f$ = 0.43 (PE/EA 10:1, *v*/*v*)

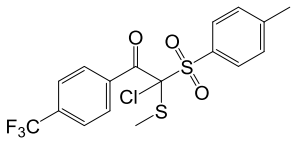
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.32 (d, $J$ = 9.0 Hz, 2H), 8.27 (d, $J$ = 9.0 Hz, 2H), 7.88 (d, $J$ = 8.4 Hz, 2H), 7.37 (d, $J$ = 8.0 Hz, 2H), 2.51 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.0, 150.2, 146.7, 139.3, 132.0, 131.4, 130.6, 129.4, 123.2, 92.7, 21.9, 16.3. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for $C_{16}H_{14}ClNNaO_5S_2^+$ 421.9894, found 421.9905.



Methyl 4-(2-chloro-2-(methylthio)-2-tosylacetyl)benzoate (**2i**)

Colorless oil; yield: 52 mg (84%); $R_f$ = 0.38 (PE/EA 10:1, v/v).

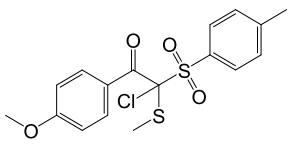
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21 (d, $J$ = 8.6 Hz, 2H), 8.08 (d, $J$ = 8.6 Hz, 2H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 3.95 (s, 3H), 2.50 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.5, 165.9, 146.3, 137.6, 134.2, 132.0, 131.0, 130.2, 129.3, 129.2, 92.5, 52.6, 21.8, 16.4. HRMS (ESI-TOF) $m/z$: [M + $NH_4$]$^+$ calcd for $C_{18}H_{21}ClNO_5S_2^+$ 430.0544, found 430.0549.



2-Chloro-2-(methylthio)-2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2j**)

Colorless crystals; yield: 54 mg (85%); M.p. 122–123 °C; $R_f$ = 0.48 (PE/EA 10:1, *v*/*v*).

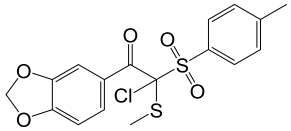
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.30 (d, $J$ = 8.0 Hz, 2H), 7.91 (d, $J$ = 8.4 Hz, 2H), 7.72 (d, $J$ = 8.4 Hz, 2H), 7.37 (d, $J$ = 8.0 Hz, 2H), 2.52 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.2, 146.5, 137.2, 134.8 (q, $J$ = 32.8 Hz), 132.1, 131.0, 130.8, 129.4, 125.2 (q, $J$ = 3.9 Hz), 123.5 (q, $J$ = 272.6 Hz), 92.7, 21.9, 16.4. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -63.3. HRMS (ESI-TOF) $m/z$: [M + $NH_4$]$^+$ calcd for $C_{17}H_{18}ClF_3NO_3S_2^+$ 440.0363, found 440.0353.



2-Chloro-1-(4-methoxyphenyl)-2-(methylthio)-2-tosylethan-1-one (**2k**)

Colorless oil; yield: 40 mg (69%); $R_f$ = 0.35 (PE/EA 10:1, *v*/*v*).

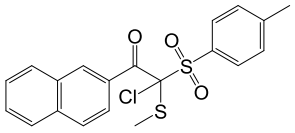
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.28 (d, $J$ = 9.1 Hz, 2H), 7.91 (d, $J$ = 8.4 Hz, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), 6.90 (d, $J$ = 9.1 Hz, 2H), 3.87 (s, 3H), 2.48 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 186.0, 164.2, 145.9, 133.5, 132.1, 131.6, 129.1, 125.9, 113.4, 92.9, 55.6, 21.8, 16.5. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{17}H_{21}ClNO_4S_2^+$ 402.0595, found 402.0592.



1-(Benzo[*d*][1,3]dioxol-5-yl)-2-chloro-2-(methylthio)-2-tosylethan-1-one (**2l**)

Yellow oil; yield: 54 mg (90%); $R_f$ = 0. 28 (PE/EA 10:1, *v*/*v*).

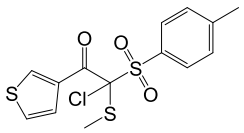
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.91 (d, $J$ = 8.4 Hz, 2H), 7.70 (d, $J$ = 1.8 Hz, 1H), 7.32 (d, $J$ = 8.0 Hz, 2H), 6.83 (d, $J$ = 8.4 Hz, 1H), 6.05 (s, 2H), 2.48 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 185.9, 152.7, 147.6, 146.0, 132.2, 131.6, 129.2, 128.0, 127.6, 110.7, 107.8, 102.2, 92.8, 21.9, 16.7. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{17}H_{19}ClNO_5S_2^+$ 416.0388, found 416.0383.



2-Chloro-2-(methylthio)-1-(naphthalen-2-yl)-2-tosylethan-1-one (**2m**)

Colorless oil; yield: 57 mg (94%); $R_f$ = 0. 38 (PE/EA 10:1, *v*/*v*).

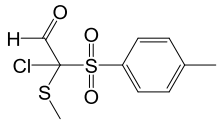
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.88 (d, $J$ = 1.8 Hz, 1H), 8.13 (dd, $J$ = 8.8, 1.8 Hz, 1H), 7.97 (d, $J$ = 8.0 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 2H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.84 (d, $J$ = 8.8 Hz, 1H), 7.61 (ddd, $J$ = 8.2, 6.8, 1.4 Hz, 1H), 7.54 (ddd, $J$ = 8.1, 6.8, 1.3 Hz, 1H), 7.32 (d, $J$ = 8.1 Hz, 2H), 2.52 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.2, 146.1, 135.7, 133.0, 132.2, 131.9, 131.5, 131.0, 130.2, 129.3, 129.2, 127.9, 127.8, 127.0, 125.7, 93.0, 21.9, 16.7. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{20}H_{21}ClNO_3S_2^+$ 422.0646, found 422.0652.



2-Chloro-2-(methylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one (**2n**)

Colorless oil; yield: 49 mg (91%); $R_f$ = 0. 37 (PE/EA 10:1, *v*/*v*).

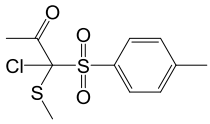
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.70 (dd, $J$ = 3.0, 1.3 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 2H), 7.71 (dd, $J$ = 5.2, 1.3 Hz, 1H), 7.31 (d, $J$ = 7.9 Hz, 2H), 7.27 (dd, $J$ = 5.2, 2.9 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 181.0, 146.2, 137.6, 136.2, 131.8, 131.3, 129.6, 129.3, 125.3, 94.4, 21.9, 16.3. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{14}H_{17}ClNO_3S_3^+$ 378.0054, found 378.0047.



2-Chloro-2-(methylthio)-2-tosylacetaldehyde (**2o**)

Colorless oil; yield: 12 mg (28%); $R_f$ = 0.28 (PE/EA 10:1, *v*/*v*).

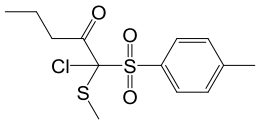
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.46 (s, 1H), 7.81 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 2.48 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 182.4, 147.2, 131.1, 130.2, 129.9, 93.8, 22.0, 13.7. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{10}H_{15}ClNO_3S_2^+$ 296.0176, found 296.0163.



1-Chloro-1-(methylthio)-1-tosylpropan-2-one (**2p**)

Colorless oil; yield: 35 mg (80%); $R_f$ = 0.38 (PE/EA 10:1, *v*/*v*).

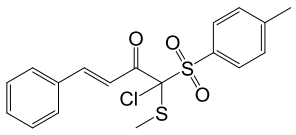
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.80 (d, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 8.0 Hz, 2H), 2.64 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 194.1, 146.7, 131.5, 130.6, 129.5, 95.7, 27.5, 22.0, 15.2. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{11}H_{17}ClNO_3S_2^+$ 310.0333, found 310.0332.



1-Chloro-1-(methylthio)-1-tosylpentan-2-one (**2q**)

Light yellow oil; yield: 43 mg (89%); $R_f$ = 0. 46 (PE/EA 10:1, *v*/*v*).

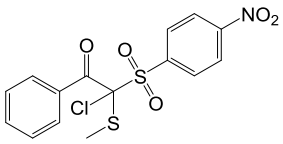
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.4 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 3.01 (t, $J$ = 7.2 Hz, 2H), 2.47 (s, 3H), 2.39 (s, 3H), 1.66 (dtq, $J$ = 14.0, 7.6, 7.2 Hz, 1H), 1.63 (dtq, $J$ = 14.0, 7.6, 7.2 Hz, 1H), 0.95 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 196.7, 146.5, 131.5, 130.7, 129.4, 95.5, 41.4, 21.9, 17.7, 15.2, 13.5. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{13}H_{21}ClNO_3S_2^+$ 338.0646, found 338.0640.



(*E*)-1-Chloro-1-(methylthio)-4-phenyl-1-tosylbut-3-en-2-one (**2r**)

Colorless oil; yield: 53 mg (93%); $R_f$ = 0. 21 (PE/EA 3:1, *v*/*v*).

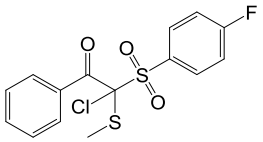
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (d, $J$ = 8.4 Hz, 2H), 7.78 (d, $J$ = 16.0 Hz, 1H), 7.65–7.61 (dd, $J$ = 7.6, 2.0 Hz, 2H), 7.59 (d, $J$ = 16.0 Hz, 1H), 7.51–7.39 (m, 3H), 7.32 (d, $J$ = 8.4 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 184.3, 147.4, 146.6, 134.0, 131.7, 131.4, 130.9, 129.5, 129.2, 129.1, 120.3, 96.3, 21.9, 15.1. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}ClNO_3S_2^+$ 398.0646, found 398.0642.



2-Chloro-2-(methylthio)-2-((4-nitrophenyl)sulfonyl)-1-phenylethan-1-one (**2s**)

Colorless oil; yield: 38 mg (66%); $R_f$ = 0.33 (PE/EA 10:1, *v*/*v*).

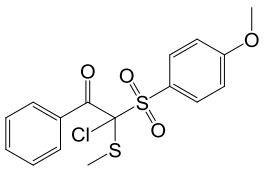
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.38 (d, $J$ = 8.8 Hz, 2H), 8.32 (d, $J$ = 8.8 Hz, 2H), 8.24–8.15 (m, 2H), 7.62 (tt, $J$ = 7.4, 1.2 Hz, 1H), 7.46 (t, $J$ = 8.0 Hz, 2H), 2.57 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.8, 151.3, 141.0, 134.6, 133.8, 133.0, 130.6, 128.5, 123.4, 91.9, 16.8. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{16}ClN_2O_5S_2^+$ 403.0184, found 403.0198.



2-Chloro-2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2t**)

Colorless oil; yield: 46 mg (86%); $R_f$ = 0.46 (PE/EA 10:1, *v*/*v*).

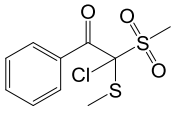
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.22–8.19 (m, 2H), 8.09 (dd, $J$ = 8.8, 5.1 Hz, 2H), 7.59 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.46–7.42 (m, 2H), 7.22 (t, $J$ = 8.4 Hz, 2H), 2.51 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.3, 166.6 (d, $J$ = 258.3 Hz), 135.2 (d, $J$ = 9.9 Hz), 134.2, 133.6, 130.6 (2C), 128.3, 115.9 (d, $J$ = 22.7 Hz), 92.0, 16.7. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -101.6. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{15}H_{16}ClFNO_3S_2^+$ 376.0239, found 376.0230.



2-Chloro-2-((4-methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2u**)

Colorless oil; yield: 45 mg (81%); $R_f$ = 0.24 (PE/EA 10:1, *v*/*v*).

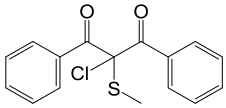
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.21–8.18 (m, 2H), 7.96 (d, $J$ = 8.8 Hz, 2H), 7.58 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.43 (t, $J$ = 8.0 Hz, 2H), 6.99 (d, $J$ = 8.8 Hz, 2H), 3.89 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.7, 164.8, 134.4, 134.1, 133.9, 130.6, 128.2, 125.5, 113.8, 92.7, 55.9, 16.6. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{16}H_{19}ClNO_4S_2^+$ 388.0439, found 388.0440.



2-Chloro-2-(methylsulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2v**)

Colorless oil; yield: 38 mg (91%); $R_f$ = 0.31 (PE/EA 10:1, *v*/*v*).

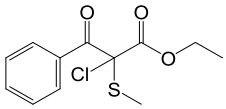
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23–8.21 (m, 2H), 7.62 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.47 (t, $J$ = 8.0 Hz, 2H), 3.38 (s, 3H), 2.55 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 189.7, 134.3, 133.4, 130.6, 128.4, 90.5, 38.0, 16.1. HRMS (ESI-TOF) *m*/*z*: $[M + NH_4]^+$ calcd for $C_{10}H_{15}ClNO_3S_2^+$ 296.0176, found 296.0165.



2-Chloro-2-(methylthio)-1,3-diphenylpropane-1,3-dione (**2w**)[9]

Colorless oil; yield: 38 mg (83%); $R_f$ = 0.58 (PE/EA 10:1, *v*/*v*).

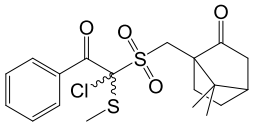
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (m, 4H), 7.43 (tt, $J$ = 8.6, 1.3 Hz, 2H), 7.33–7.27 (m, 4H), 2.15 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.2, 134.0, 133.3, 130.1, 128.7, 87.2, 12.6.



Ethyl 2-chloro-2-(methylthio)-3-oxo-3-phenylpropanoate (**2x**)

Colorless oil; yield: 32 mg (78%); $R_f$ = 0.58 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08–7.99 (m, 2H), 7.58 (tt, $J$ = 7.4, 2.0 Hz, 1H), 7.48–7.41 (m, 2H), 4.22 (q, $J$ = 7.2 Hz, 1H), 4.21 (q, $J$ = 7.2 Hz, 1H), 2.23 (s, 3H), 1.06 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 185.7, 165.7, 133.9, 132.8, 129.7, 128.6, 80.7, 63.8, 13.7, 13.0. HRMS (ESI-TOF) *m/z*: $[M + H - HCl]^+$ calcd for $C_{12}H_{13}O_3S^+$ 237.0580, found 237.0573.



1-(((1-Chloro-1-(methylthio)-2-oxo-2-phenylethyl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (**2y** + **2y'**)

Colorless oil; yield: 57 mg (92%); $R_f$ = 0.22 (PE/EA 10:1, *v*/*v*). Major isomer/minor isomer = 2/1. The isomers are inseparable and cannot be distinguished by NMR analysis.

**Major isomer:**

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.23–8.19 (m, 2H), 7.65–7.56 (m, 1H), 7.51–7.41 (m, 2H), 4.27 (d, $J$ = 14.4 Hz, 1H), 3.52 (d, $J$ = 14.4 Hz, 1H), 2.64 (s, 3H), 2.60–2.48 (m, 1H), 2.47–2.37 (m, 1H), 2.19–2.02 (m, 2H) 1.97 (d, $J$ = 18.4 Hz, 1H), 1.89 (ddd, $J$ = 14.0, 9.3, 4.4 Hz, 1H), 1.48 (ddd, $J$ = 13.6, 9.0, 3.8 Hz, 1H), 1.16 (s, 3H), 0.95 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 213.9, 190.3, 134.1, 133.7, 130.6, 128.2, 93.0, 59.2, 48.5, 46.5, 42.9, 42.6, 27.2, 25.0, 20.2, 20.0, 15.8.

**Minor isomer:**

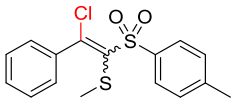
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.28–8.23 (m, 2H), 7.67–7.55 (m, 1H), 7.51–7.39 (m, 2H), 3.99 (d, $J$ = 14.4 Hz, 1H), 3.63 (d, $J$ = 14.4 Hz, 1H), 2.60–2.51 (m, 1H), 2.54 (s, 3H), 2.47–2.37 (m, 1H), 2.16–2.03 (m, 2H), 1.96 (d, $J$ = 18.4 Hz, 1H), 1.80 (ddd, $J$ = 14.0, 9.3, 4.7 Hz, 1H), 1.44 (dt, $J$ = 13.6, 9.0, 3.8 Hz, 1H), 1.19 (s, 3H), 0.97 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 214.0, 189.5, 134.2, 133.4, 130.7, 128.3, 91.7, 59.4, 48.2, 46.5, 43.1, 42.7, 27.0, 25.4, 20.3, 20.1, 16.4.

**Both isomers:**

$[\alpha]^{25}_D$ = 26.5 (c = 4.5, $CHCl_3$).

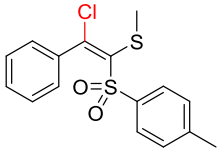
HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{19}H_{27}ClNO_4S_2^+$ 432.1065, found 432.1059.

### 1.4.2 Analytic date for products 3



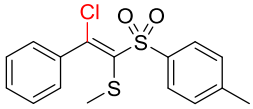
(2-Chloro-2-phenyl-1-tosylvinyl)(methyl)sulfane (**3**)

Major (*E*)/minor (*Z*) = 2/1. $R_f$ = 0.52 (PE/EA 3:1, *v*/*v*). (*E*)- and (*Z*)-isomers are inseparable on silica gel column and their $^{13}C$ NMR data cannot be distinguished.



((*E*)-2-Chloro-2-phenyl-1-tosylvinyl)(methyl)sulfane ((*E*)-**3**)

**Major isomer:** $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.00 (d, $J$ = 8.3 Hz, 2H), 7.48–7.31 (m, 7H), 2.48 (s, 3H), 2.32 (s, 3H).



((*Z*)-2-Chloro-2-phenyl-1-tosylvinyl)(methyl)sulfane ((*Z*)-**3**)

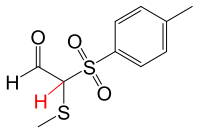
**Minor isomer:** $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (d, $J$ = 8.3 Hz, 2H), 7.48–7.31 (m, 5H), 7.25 (d, $J$ = 8.0 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H).

**Both isomers:**

$^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 154.2, 147.8, 144.8, 144.5, 139.3, 138.6, 138.4, 137.2, 137.2, 136.7, 130.1, 130.1, 129.6, 129.3, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 21.8, 21.7, 20.9, 19.1.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{16}ClO_2S_2^+$ 339.0275, found 339.0273.

### 1.4.3 Analytic date for product 4o



2-(Methylthio)-2-tosylacetaldehyde (**4o**)[10]

$^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.46 (s, 1H), 7.86 (d, $J$ = 8.3 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 5.53 (s, 1H), 2.45 (s, 3H), 2.33 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 182.4, 146.2, 132.1, 130.2, 129.9, 77.8, 21.9, 13.5.

## 1.5 Gram-scale preparation of 2a

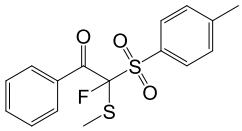
2-(Dimethyl-$\lambda^4$-sulfaneylidene)-1-phenyl-2-tosylethan-1-one (**1a**, 7.5 mmol) and sulfuryl chloride (728 μL, 9 mmol) were dissolved in MeCN (20.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 60 °C for 160 mins.

After cooling, the mixture was acidified with acetic acid and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (**Silica gel was acidified with 2% acetic acid**) with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/v) as eluent (**Acidified with 0.25% acetic acid**) to afford product **2a** (2.30 g, 87%).

## 1.6 General procedure for the synthesis of fluorinated products 5

Diacyl dimethylsulfonium methylide **1** (0.20 mmol) and selectfluor (0.6 mmol, 212.6 mg) were dissolved in DCE (3.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 80 °C for 6 h. After cooling, the mixture was acidified with acetic acid and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (**Silica gel was acidified with 2% acetic acid**) with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/*v*) as eluent (**Acidified with 0.25% acetic acid**) to afford product **5**.

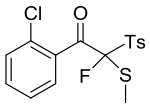
**Analytic date for products 5**




2-Fluoro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**5a**)

Colorless oil; yield: 62 mg (92%); $R_f$ = 0.41 (PE/EA 5:1, *v*/*v*).

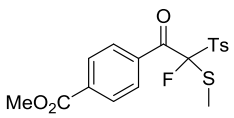
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11–7.92 (m, 2H), 7.77 (d, $J$ = 8.1 Hz, 2H), 7.65–7.55 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.42 (t, $J$ = 7.8 Hz, 2H), 7.37–7.25 (d, $J$ = 8.0 Hz, 2H), 2.43 (s, 3H), 2.42 (d, $J$ = 1.9 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.9 (d, $J$ = 22.1 Hz), 146.6, 134.3, 133.6 (d, $J$ = 1.6 Hz), 131.5, 130.9, 130.5 (d, $J$ = 5.0 Hz), 129.8, 128.4, 114.4 (d, $J$ = 275.4 Hz), 21.9, 13.0 (d, $J$ = 5.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -134.0. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{16}H_{19}FNO_3S_2^+$ 356.0785, found 356.0778.




1-(2-Chlorophenyl)-2-fluoro-2-(methylthio)-2-tosylethan-1-one (**5f**)

Colorless oil; yield: 60 mg (81%); $R_f$ = 0.50 (PE/EA 5:1, *v*/*v*).

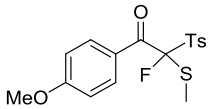
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 8.1 Hz, 2H), 7.65 (ddd, $J$ = 7.8, 2.4, 1.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.38 (d, $J$ = 7.9 Hz, 2H), 7.32 – 7.26 (m, 1H), 2.47 (s, 3H), 2.44 (d, $J$ = 1.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 191.0 (d, $J$ = 27.3 Hz), 146.9, 134.3, 132.7, 132.2, 131.25, 131.23, 130.6, 129.8 (d, $J$ = 5.3 Hz), 129.7, 126.2, 112.7 (d, $J$ = 275.5 Hz), 21.9, 13.0 (d, $J$ = 5.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -138.1. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{16}H_{18}ClFNO_3S_2^+$ 390.0395, found 390.0390.




Methyl 4-(2-fluoro-2-(methylthio)-2-tosylacetyl)benzoate (**5i**)

Colorless oil; yield: 60 mg (76%); $R_f$ = 0.39 (PE/EA 5:1, *v*/*v*).

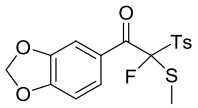
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.13 – 7.98 (m, 4H), 7.77 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 7.9 Hz, 2H), 3.95 (s, 3H), 2.44 (s, 3H), 2.42 (d, $J$ = 1.9 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.8 (d, $J$ = 22.7 Hz), 165.9, 146.8, 136.9 (d, $J$ = 1.7 Hz), 134.7, 131.3, 130.8, 130.3 (d, $J$ = 4.9 Hz), 129.8, 129.4, 114.3 (d, $J$ = 275.2 Hz), 52.7, 21.9, 13.0 (d, $J$ = 5.8 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -134.5. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}FNO_5S_2^+$ 414.0840, found 414.0850.




2-Fluoro-1-(4-methoxyphenyl)-2-(methylthio)-2-tosylethan-1-one (**5k**)

Colorless oil; yield: 55 mg (75%); $R_f$ = 0.42 (PE/EA 5:1, *v*/*v*).

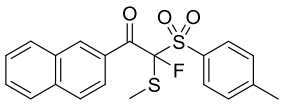
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10 (d, $J$ = 8.6 Hz, 2H), 7.75 (d, $J$ = 8.1 Hz, 2H), 7.30 (d, $J$ = 8.1 Hz, 2H), 6.90 (d, $J$ = 8.8 Hz, 2H), 3.87 (s, 3H), 2.43 (s, 3H), 2.44 – 2.38 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 186.4 (d, $J$ = 20.7 Hz), 164.6, 146.4, 133.4 (d, $J$ = 5.1 Hz), 131.6, 130.8, 129.7, 126.1 (d, $J$ = 1.5 Hz), 114.7 (d, $J$ = 275.1 Hz), 113.7, 55.7, 21.9, 13.1 (d, $J$ = 6.0 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -133.0. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{17}H_{21}FNO_4S_2^+$ 386.0891, found 386.0882.




1-(Benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-2-(methylthio)-2-tosylethan-1-one (**5l**)

Colorless oil; yield: 71 mg (93%); $R_f$ = 0.38 (PE/EA 5:1, *v*/*v*).

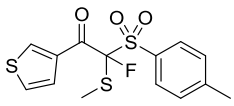
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 (ddt, $J$ = 8.4, 1.8, 0.9 Hz, 1H), 7.76 (d, $J$ = 8.1 Hz, 2H), 7.50 (dt, $J$ = 1.8, 0.9 Hz, 1H), 7.32 (d, $J$ = 8.1 Hz, 2H), 6.83 (d, $J$ = 8.4 Hz, 1H), 6.05 (s, 2H), 2.44 (s, 3H), 2.40 (d, $J$ = 1.8 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 186.1 (d, $J$ = 20.8 Hz), 153.1, 147.9, 146.5, 131.5, 130.8, 129.7, 128.1 (d, $J$ = 6.1 Hz), 127.7 (d, $J$ = 2.5 Hz), 114.6 (d, $J$ = 275.4 Hz), 110.2 (d, $J$ = 4.9 Hz), 108.0, 102.2, 21.9, 13.1 (d, $J$ = 5.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -132.8. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{17}H_{19}FNO_5S_2^+$ 400.0683, found 400.0689.




2-Fluoro-2-(methylthio)-1-(naphthalen-2-yl)-2-tosylethan-1-one (**5m**)

Sticky oil; yield: 66 mg (85%); $R_f$ = 0.35 (PE/EA 10:1, *v*/*v*).

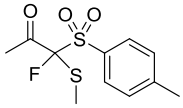
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.67 (s, 1H), 8.00–7.89 (m, 2H), 7.83 (d, $J$ = 8.1 Hz, 1H), 7.82 (d, $J$ = 8.4 Hz, 1H), 7.78 (d, $J$ = 8.1 Hz, 2H), 7.61 (ddd, $J$ = 8.2, 6.9, 1.3 Hz, 1H), 7.54 (ddd, $J$ = 8.2, 6.9, 1.3 Hz, 1H), 7.27 (d, $J$ = 8.1 Hz, 2H), 2.47 (d, $J$ = 1.9 Hz, 3H), 2.37 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 188.4 (d, $J$ = 21.0 Hz), 146.6, 135.9, 133.4 (d, $J$ = 6.8 Hz), 132.0, 131.5, 130.8, 130.6 (d, $J$ = 1.8 Hz), 130.3, 129.8, 129.5, 128.2, 127.8, 127.1, 125.2 (d, $J$ = 3.2 Hz), 114.8 (d, $J$ = 275.1 Hz), 21.8, 13.2 (d, $J$ = 5.8 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -133.3. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{20}H_{21}FNO_3S_2^+$ 406.0941, found 406.0945.



2-Fluoro-2-(methylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one **(5n)**

Sticky oil; yield: 58 mg (84%); $R_f$ = 0.32 (PE/EA 10:1, *v*/*v*).

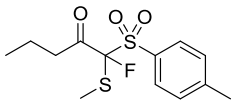
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (dt, *J* = 2.8, 1.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.58 (dt, *J* = 5.2, 0.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.26 (dd, *J* = 5.2, 2.8 Hz, 1H), 2.42 (s, 3H), 2.41 (d, *J* = 2.0 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 181.4 (d, *J* = 21.9 Hz), 146.6, 137.6 (d, *J* = 9.0 Hz), 136.5 (d, *J* = 2.0 Hz), 131.4, 130.7, 129.8, 128.8, 125.7, 114.6 (d, *J* = 274.8 Hz), 21.9, 12.9 (d, *J* = 5.5 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -134.9. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{14}H_{17}FNO_3S_3^+$ 362.0349, found 362.0356.



1-Fluoro-1-(methylthio)-1-tosylpropan-2-one (**5p**)

Colorless oil; yield: 47 mg (85%); $R_f$ = 0.43 (PE/EA 5:1, *v*/*v*).

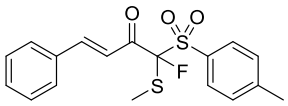
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.39 (d, *J* = 3.5 Hz, 3H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 195.3 (d, *J* = 23.3 Hz), 146.9, 131.2, 130.6, 130.0, 113.2 (d, *J* = 274.5 Hz), 26.7, 21.9, 12.2 (d, *J* = 5.3 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -140.6. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{11}H_{17}FNO_3S_2^+$ 294.0628, found 294.0635.



1-Fluoro-1-(methylthio)-1-tosylpentan-2-one **(5q)**

Colorless oil; yield: 40 mg (66%); $R_f$ = 0.50 (PE/EA 10:1, *v*/*v*).

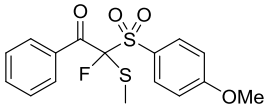
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 2.76 (dddd, *J* = 18.8, 7.7, 6.5, 2.2 Hz, 1H), 2.60 (dddd, *J* = 18.8, 7.6, 6.6, 2.0 Hz, 1H), 2.47 (s, 3H), 2.32 (d, *J* = 1.8 Hz, 3H), 1.58 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 197.9 (d, *J* = 22.2 Hz), 146.8, 131.4, 130.7, 129.9, 113.2 (d, *J* = 274.4 Hz), 40.7, 21.9, 16.6, 13.5, 12.2 (d, *J* = 5.5 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -142.1. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{13}H_{21}FNO_3S_2^+$ 322.0941, found 322.0945.



(*E*)-1-Fluoro-1-(methylthio)-4-phenyl-1-tosylbut-3-en-2-one (**5r**)

Sticky oil; yield: 60 mg (82%); $R_f$ = 0.48 (PE/EA 10:1, *v*/*v*).

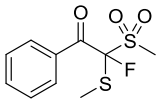
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 15.8 Hz, 1H), 7.63–7.56 (m, 2H), 7.48–7.39 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 15.8 Hz, 1H), 2.41 (s, 3H), 2.37 (d, *J* = 1.9 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 184.9 (d, *J* = 21.1 Hz), 147.4, 146.8, 133.9, 131.8, 131.5, 130.6, 129.9, 129.3, 129.2, 119.2, 113.8 (d, *J* = 273.8 Hz), 21.9, 12.2 (d, *J* = 4.5 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -141.7. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{21}FNO_3S_2^+$ 382.0941, found 382.0946.



2-Fluoro-2-((4-methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**5u**)

Colorless oil; yield: 60 mg (85%); $R_f$ = 0.31 (PE/EA 5:1, *v*/*v*).

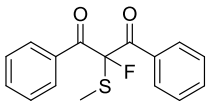
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.03 (d, $J$ = 7.2 Hz, 2H), 7.81 (d, $J$ = 8.9 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.36 (m, 2H), 6.97 (d, $J$ = 8.9 Hz, 2H), 3.86 (s, 2H), 2.41 – 2.40 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 189.1 (d, $J$ = 21.8 Hz), 165.1, 134.3, 133.6, 133.2, 130.5 (d, $J$ = 5.1 Hz), 128.4, 125.6, 114.43 (d, $J$ = 275.0 Hz), 114.37, 55.9, 13.0 (d, $J$ = 5.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -133.9. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{16}H_{19}FNO_4S_2^+$ 372.0734, found 372.0725.



2-Fluoro-2-(methylsulfonyl)-2-(methylthio)-1-phenylethan-1-one (**5v**)

Colorless oil; yield: 47 mg (90%); $R_f$ = 0.20 (PE/EA 10:1, *v*/*v*).

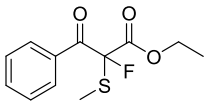
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (m, 2H), 7.68–7.60 (tt, $J$ = 8.0, 1.2 Hz, 1H), 7.49 (t, $J$ = 7.9 Hz, 2H), 3.25 (d, $J$ = 1.5 Hz, 3H), 2.48 (d, $J$ = 2.0 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 190.5 (d, $J$ = 21.6 Hz), 134.7, 133.3 (d, $J$ = 1.9 Hz), 130.5 (d, $J$ = 5.5 Hz), 128.6, 113.0 (d, $J$ = 274.6 Hz), 38.0, 12.6 (d, $J$ = 6.0 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -143.3. HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ calcd for $C_{10}H_{15}FNO_3S_2^+$ 280.0472, found 280.0472.



2-Fluoro-2-(methylthio)-1,3-diphenylpropane-1,3-dione (**5w**)[11]

Sticky oil; yield: 42 mg (73%); $R_f$ = 0.53 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.05 (m, 4H), 7.52 (tt, $J$ = 8.2, 1.2 Hz 2H), 7.38 (t, $J$ = 8.2 Hz, 4H), 2.14 (d, $J$ = 2.0 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 189.2 (d, $J$ = 24.8 Hz), 134.5, 133.2, 130.2 (d, $J$ = 2.9 Hz), 128.8, 108.7 (d, $J$ = 240.0 Hz), 11.1 (d, $J$ = 2.0 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -130.5.



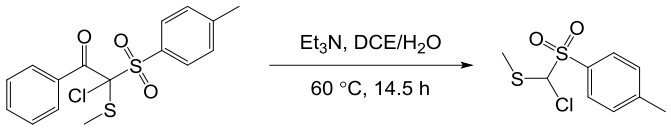
Ethyl 2-fluoro-2-(methylthio)-3-oxo-3-phenylpropanoate (**5x**)

Sticky oil; yield: 41 mg (80%); $R_f$ = 0.42 (PE/EA 10:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04 (m, 2H), 7.71–7.51 (tt, 7.8, 1.2 Hz, 1H), 7.47 (t, $J$ = 7.8 Hz, 2H), 4.28 (q, $J$ = 7.1 Hz, 2H), 2.22 (d, $J$ = 2.0 Hz, 3H), 1.17 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 187.4 (d, $J$ = 24.2 Hz), 164.9 (d, $J$ = 30.9 Hz), 134.4, 132.7 (d, $J$ = 1.7 Hz), 129.7 (d, $J$ = 4.0 Hz), 128.8, 103.8 (d, $J$ = 239.7 Hz), 63.4, 13.9, 11.1 (d, $J$ = 2.0 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -136.4. HRMS (ESI-TOF) *m/z*: $[M + H - HF]^+$ calcd for $C_{12}H_{13}O_3S^+$ 237.0580, found 237.0588.

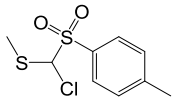
# 1.7 Applications and transformations

### 1.7.1 Synthesis of product 6




**2a** **6**, 91%

2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**, 71.0 mg, 0.20 mmol) and $Et_3N$ (55.6 μL, 0.40 mmol) were dissolved in DCE/$H_2O$ (2.0 mL/1.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 60 °C for 14.5 h. After cooling, the mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/v) as eluent to afford product **6** (43 mg, 91%).

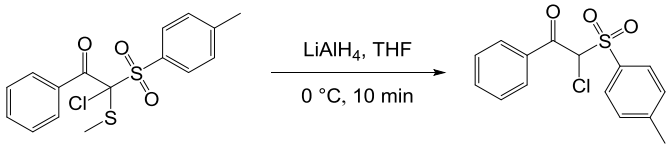


(Chloro(tosyl)methyl)(methyl)sulfane (**6**)[12]

Colorless crystals; yield: 43 mg (91%); M.p. 99–101 °C $R_f$ = 0.48 (PE/EA 5:1, *v*/*v*).

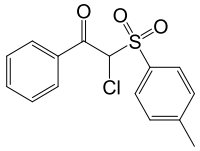
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 8.3 Hz, 2H), 7.39 (d, $J$ = 7.9 Hz, 2H), 5.54 (s, 1H), 2.47 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.1, 132.1, 130.2, 129.9, 77.8, 21.9, 13.5.

### 1.7.2 Synthesis of product 7




**2a** **7**, 41%

2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**, 71.0 mg, 0.20 mmol) and $LiAlH_4$ (7.6 mg, 0.20 mmol) were dissolved in dry THF (3.0 mL) in a 10 mL reaction tube at 0 °C without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 0 °C for 10 min. The mixture was quenched by HCl (0.5 mol/L, 3.0 mL) and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/v) as eluent to afford product **7** (25 mg, 41%).



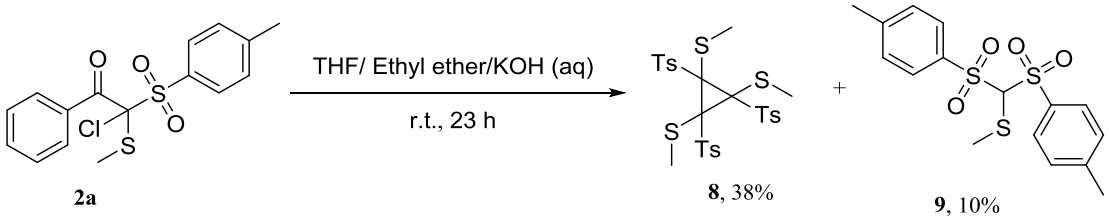
2-C0hloro-1-phenyl-2-tosylethan-1-one (**7**)[13]

Colorless crystals; yield: 25 mg (41%); M.p. 133–135 °C $R_f$ = 0.52 (PE/EA 5:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10–7.96 (m, 2H), 7.78 (d, $J$ = 8.4 Hz, 2H), 7.68 (t, $J$ = 7.6 Hz, 1H), 7.54

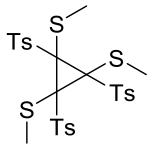
(t, $J$ = 7.8 Hz, 2H), 7.38 (d, $J$ = 8.1 Hz, 2H), 6.19 (s, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 186.5, 146.7, 134.9, 134.7, 131.3, 130.9, 129.83, 129.80, 129.1, 72.1, 22.0.

### 1.7.3 Synthesis of products 8 and 9




**2a** **8**, 38% **9**, 10%

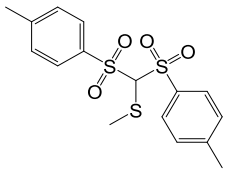
2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**, 71.0 mg, 0.20 mmol) was dissolved in a mixed solvents of THF/diethyl ether/KOH (aq, 50 wt%) (2.0 mL/ 1.0 mL/0.5 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at room temperature for 23 h. The mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (15:1, *v*/*v*) as eluent to afford products **8** (14 mg, 38%) and **9** (3 mg, 10%).




1,2,3-Tris(methylthio)-1,2,3-tritosylcyclopropane (**8**)

Colorless crystals; yield: 14 mg (33%); M.p. 59–60 °C $R_f$ = 0.60 (PE/EA 5:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 (d, $J$ = 8.4 Hz, 6H), 7.39 (d, $J$ = 8.2 Hz, 6H), 2.64 (s, 9H), 2.49 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.9, 132.5, 129.6, 128.6, 102.7, 22.0, 19.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{31}O_6S_6^+$ 643.0439, found 643.0429.

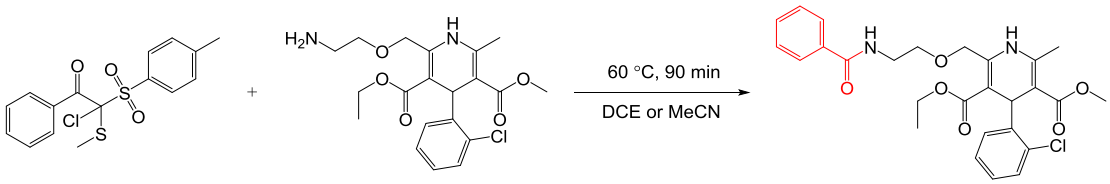


(Ditosylmethyl)(methyl)sulfane (**9**)[14]

Yellowish crystals; yield: 3 mg (10%); M.p. 137–138 °C $R_f$ = 0.22 (PE/EA 3:1, *v*/*v*).

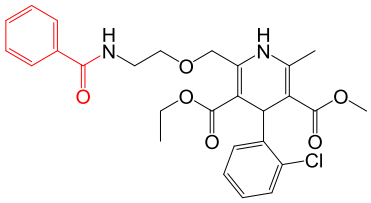
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.91 (d, $J$ = 8.3 Hz, 4H), 7.37 (d, $J$ = 7.8 Hz, 4H), 4.89 (s, 1H), 2.47 (s, 6H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.2, 134.7, 130.2, 129.7, 87.4, 22.0, 17.6.

### 1.7.4 Synthesis of product 10a




**2a** **amlodipine** **11a**, DCE: 94%; MeCN: 92%

2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**, 85.2 mg, 0.24 mmol) and amlodipine (81.8 mg, 0.2 mmol) were dissolved in DCE or MeCN (3.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 60 °C for 90 min. After cooling, the mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with DCM and MeOH (30:1, *v*/v) as eluent to afford product **10a**.

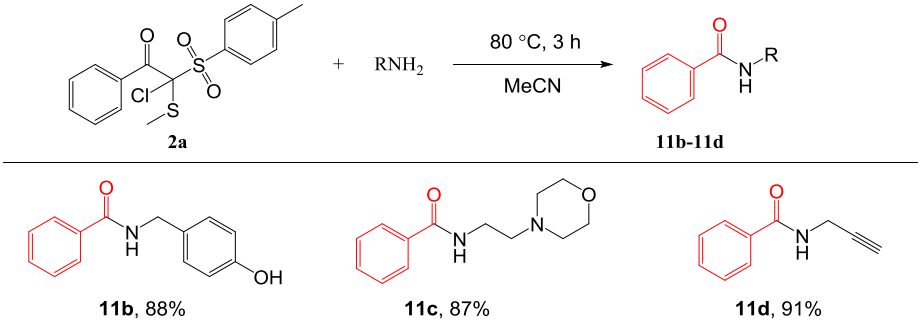


3-Ethyl 5-methyl 2-((2-benzamidoethoxy)methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (**10a**)

Sticky oil; yield: 96 mg (94%, DCE), 94 mg (92%, MeCN); $R_f$ = 0.45 (DCM/MeOH 20:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83–7.73 (m, 2H), 7.56–7.47 (m, 1H), 7.43 (dd, $J$ = 8.2, 6.8 Hz, 2H), 7.36 (dd, $J$ = 7.7, 1.7 Hz, 1H), 7.28 (bs, 1H), 7.22 (ddd, $J$ = 7.9, 1.4 Hz, 1H), 7.11 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.03 (td, $J$ = 7.7, 1.8 Hz, 1H), 6.63 (bs, 1H), 5.39 (s, 1H), 4.74 (q, $J$ = 7.1 Hz, 2H), 4.05 (ddd, $J$ = 14.0, 10.8, 7.0 Hz, 1H), 4.02 (ddd, $J$ = 14.0, 10.8, 7.0 Hz, 1H), 3.82–3.66 (m, 4H), 3.60 (s, 3H), 2.31 (s, 3H), 1.17 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.2, 168.1, 167.2, 145.8, 145.1, 144.5, 134.2, 132.2, 131.7, 131.4, 129.2, 128.6, 127.4, 127.0, 126.9, 103.7, 101.6, 70.6, 68.0, 59.8, 50.8, 39.7, 37.1, 19.2, 14.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{30}ClN_2O_3^+$ 513.1787, found 513.1779.

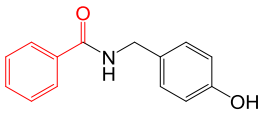
### 1.7.5 General procedure for the synthesis of products 10b–10c




**2a** **11b-11d**

**11b**, 88% **11c**, 87% **11d**, 91%

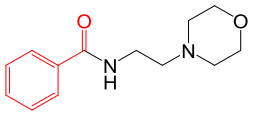
2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**, 85.2 mg, 0.24 mmol) and amines (0.2 mmol) were dissolved in MeCN (3.0 mL) in a 10 mL reaction tube without inert atmosphere (Sealed after addition). The reaction mixture was further stirred in an oil bath at 80 °C for 3 h. After cooling, the mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with DCM and MeOH (30:1, *v*/*v*) as eluent to afford products **10b**–**10c**.



*N*-(4-Hydroxybenzyl)benzamide (**10b**)[15]

Colorless crystals; yield: 40 mg (88%); M.p. 149–150 °C $R_f$ = 0.39 (PE/EA 3:1, *v*/*v*).

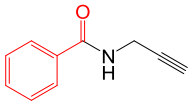
$^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 7.87–7.74 (m, 2H), 7.53–7.46 (m, 1H), 7.45–7.37 (m, 2H), 7.18 (d, $J$ = 8.4 Hz, 2H), 6.76 (d, $J$ = 8.5 Hz, 2H), 4.46 (s, 2H). $^{13}$C NMR (101 MHz, $CD_3OD$) $\delta$ 170.0, 157.6, 135.7, 132.6, 130.9, 129.9, 129.5, 128.3, 116.2, 44.1.



*N*-(2-Morpholinoethyl)benzamide (**10c**)[16]

Colorless crystals; yield: 41 mg (87%); M.p. 125–127 °C $R_f$ = 0.45 (DCM/MeOH 30:1, *v*/*v*).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.06–7.66 (m, 2H), 7.55–7.45 (m, 1H), 7.48–7.39 (m, 2H), 6.86 (bs, 1H), 3.72 (dd, $J$ = 4.8, 4.0 Hz, 4H), 3.55 (td, $J$ = 6.1, 5.0 Hz, 2H), 2.59 (t, $J$ = 6.1 Hz, 2H), 2.50 (dd, $J$ = 5.6, 3.7 Hz, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.4, 134.7, 131.4, 128.6, 127.0, 67.1, 57.0, 53.4, 36.2.



*N*-(Prop-2-yn-1-yl)benzamide (**10d**)[17]

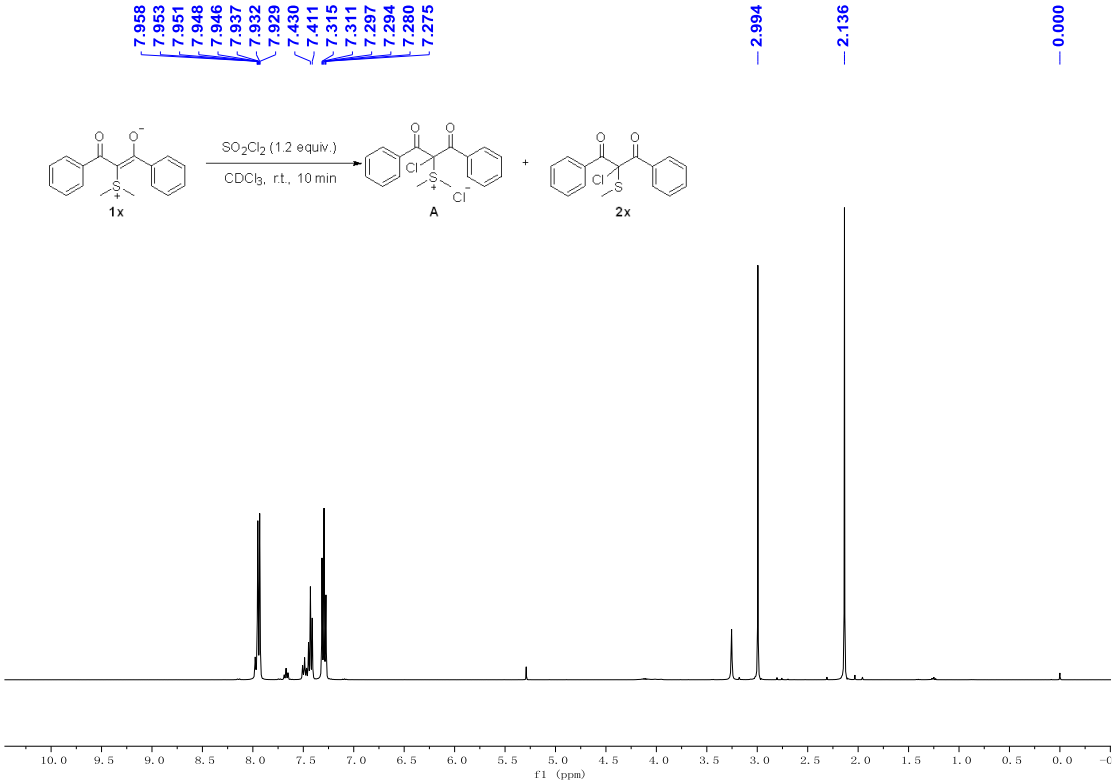
Sticky oil; yield: 29 mg (91%); $R_f$ = 0.39 (PE/EA 3:1, *v*/*v*).

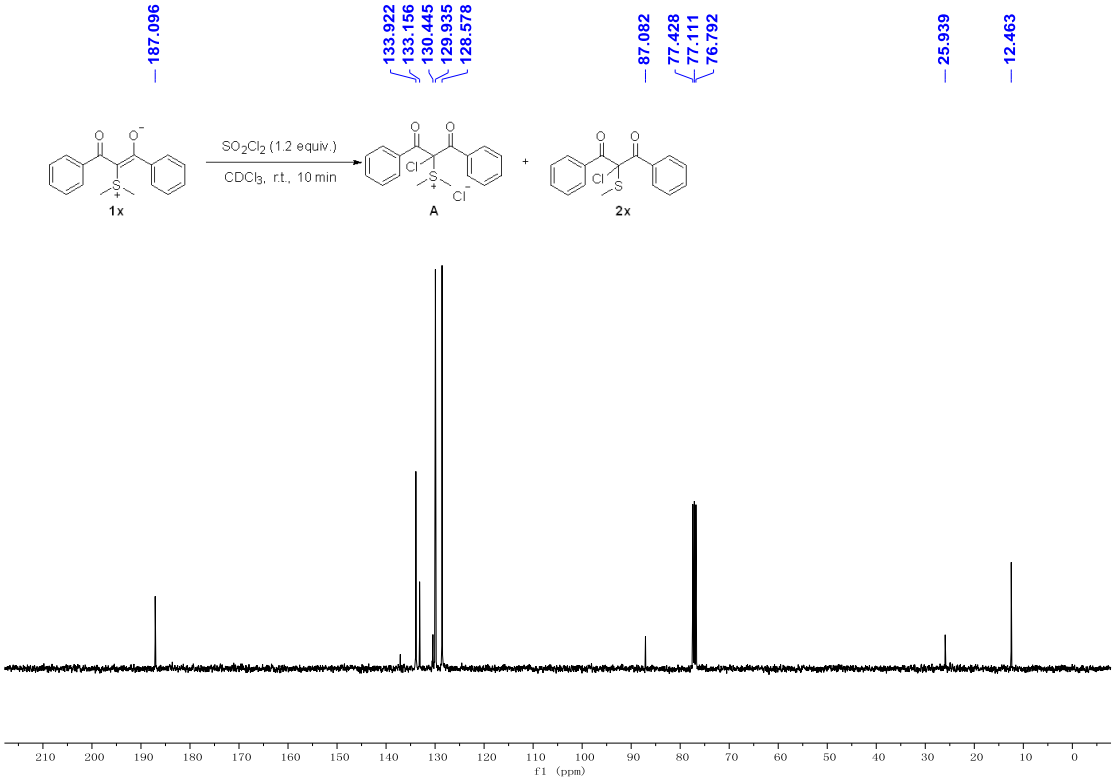
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96–7.64 (m, 2H), 7.55–7.47 (tt, $J$ = 7.5, 1.2 Hz, 1H), 7.42 (t, $J$ = 7.5 Hz, 2H), 6.55 (bs, 1H), 4.25 (dd, $J$ = 5.3, 2.6 Hz, 2H), 2.27 (t, $J$ = 2.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 167.3, 133.8, 131.9, 128.7, 127.2, 79.6, 71.9, 29.9.

# 1.8 Control experiments

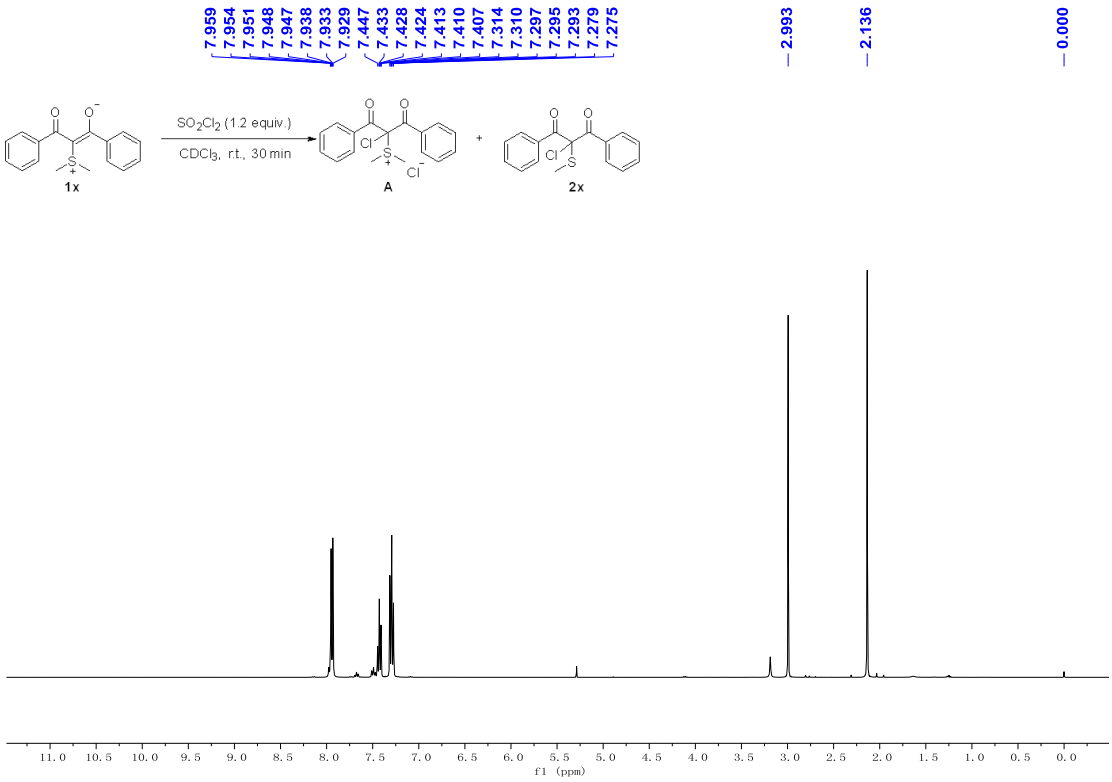
## 1.8.1 Control experiments for chlorination

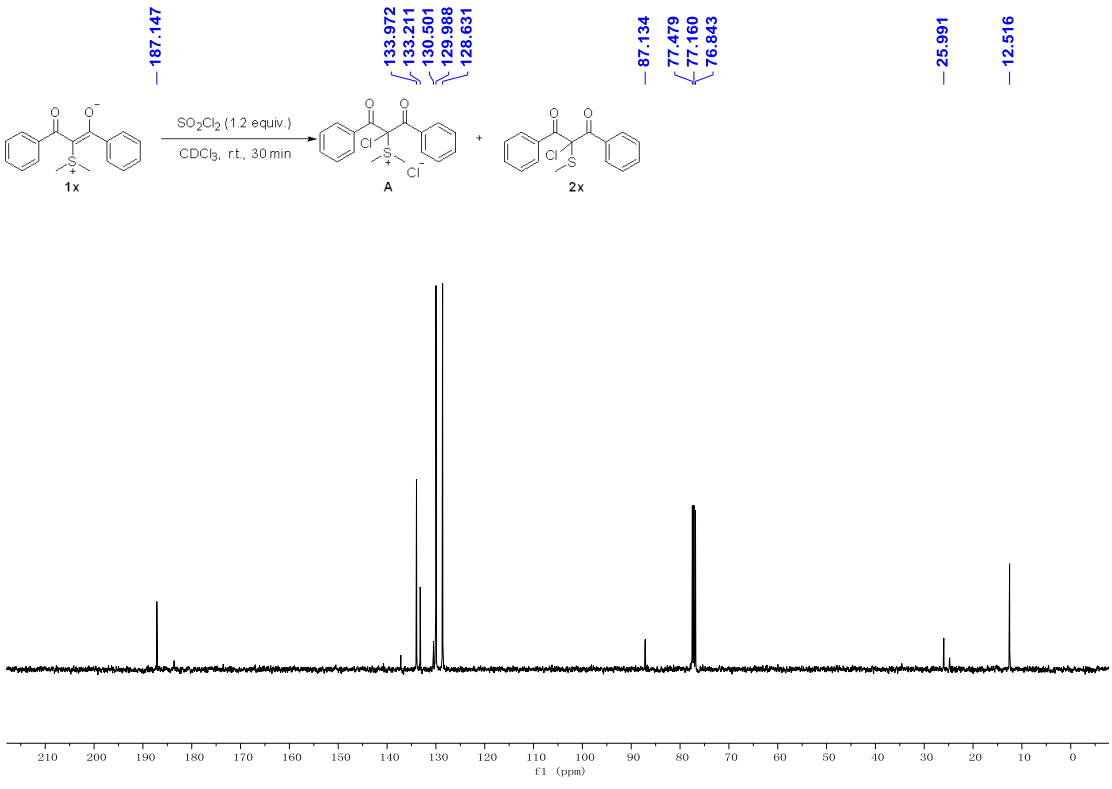
**1x** + $SO_2Cl_2$ in $CDCl_3$ at room temperature (10 min).



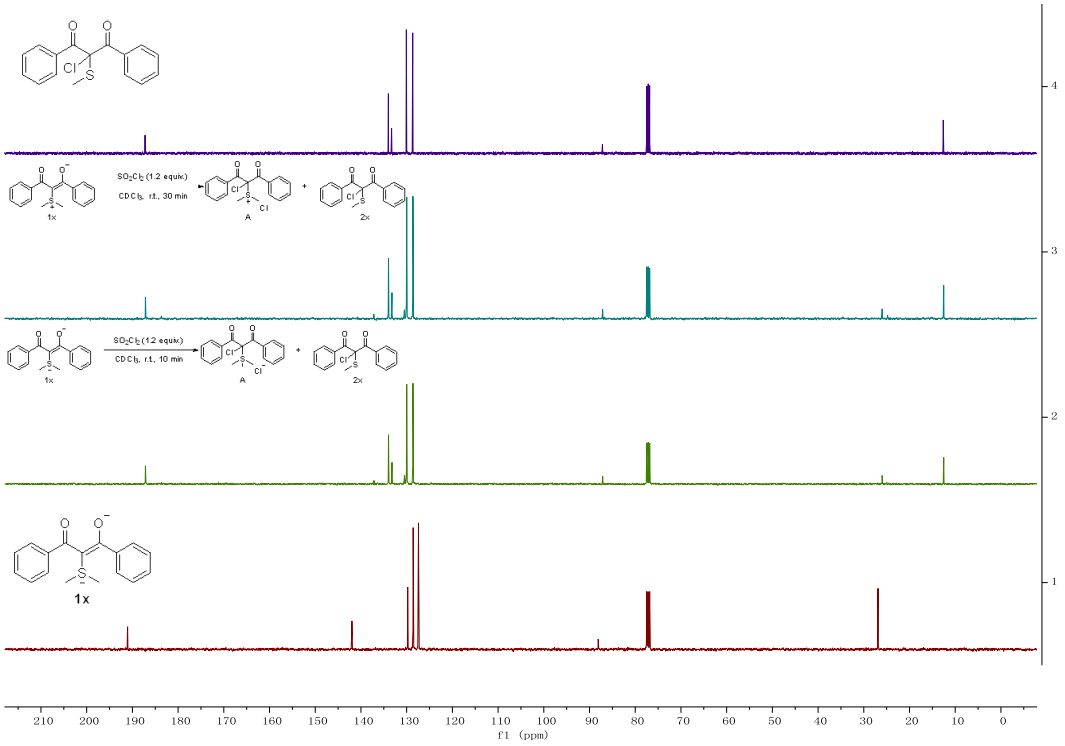



**1x** + $SO_2Cl_2$ in $CDCl_3$ at room temperature (30 min).

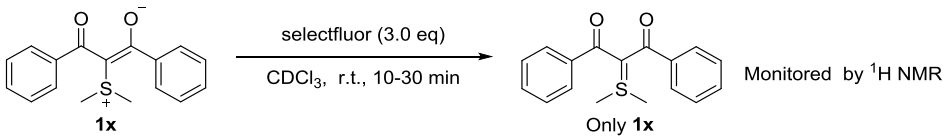


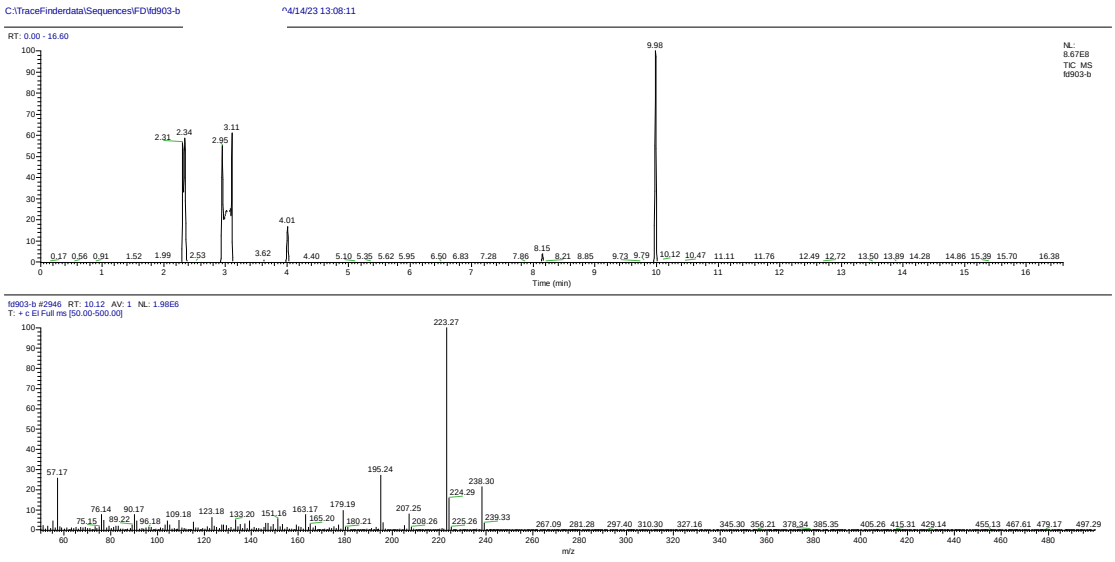
## Stack spectrogram




## 1.8.2 Control experiment for fluorination




GC-MS for the fluorination with NFSI in the presence of BHT



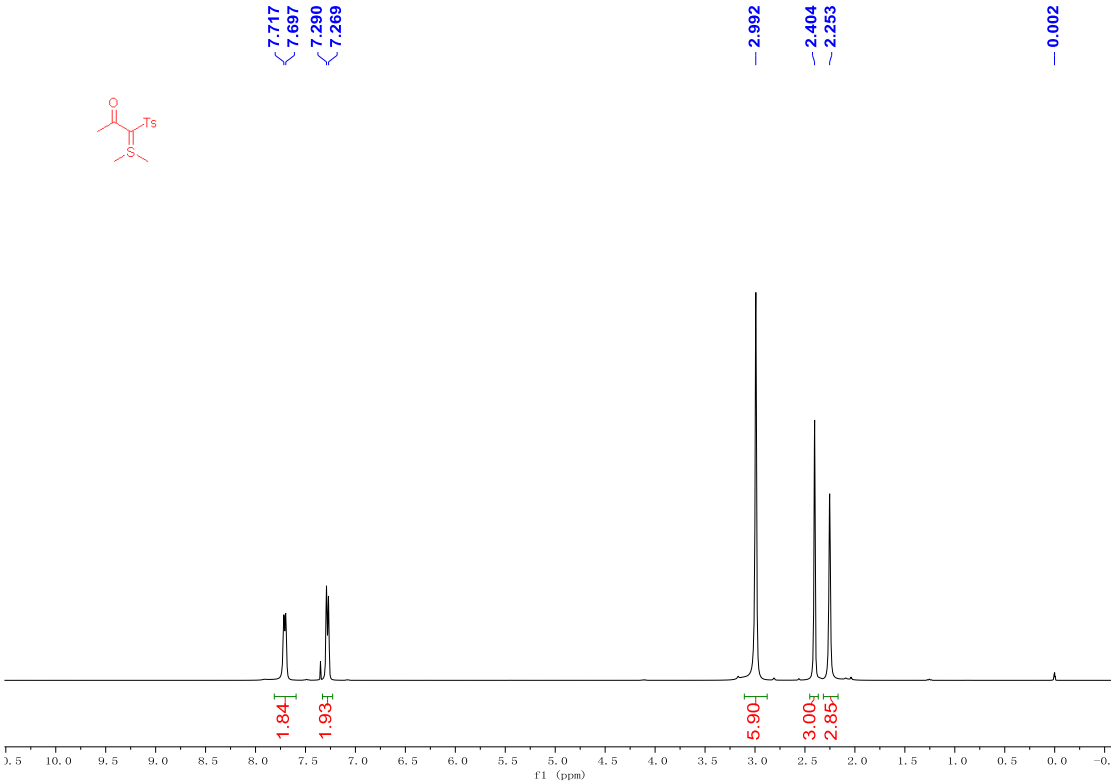
## 1.9 References

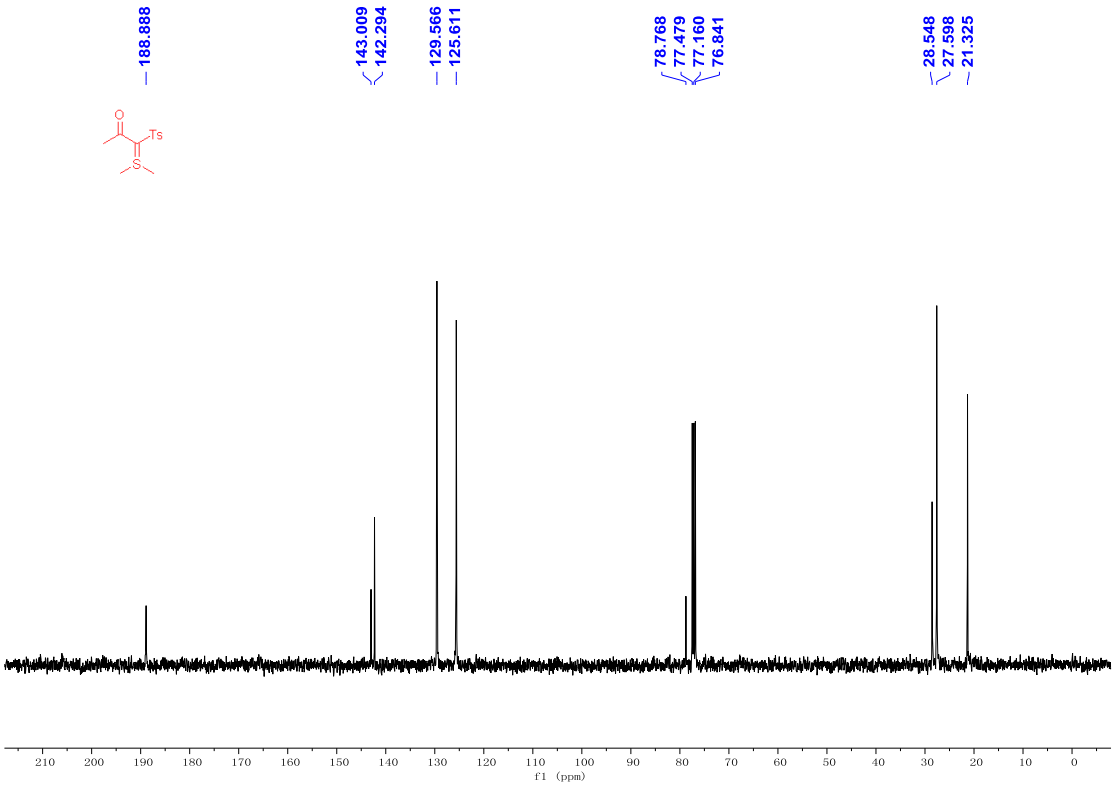

1. D. Fu, J. Y. Wang and J. X. Xu, *Synthesis*, 2021, **53**, 4086–4096.
2. D. Fu and J. X. Xu, *Org. Biomol. Chem.*, 2023, **21**, 1008–1013.
3. J. Dong, H. G. Du and J. X. Xu, *RSC Adv.*, 2019, **9**, 25034–25038.
4. J. Dong., H. G. Du. and J. X. Xu., *J. Org. Chem.*, 2019, **84**, 10724–10739.
5. V. N. Kalinin, G. B. Soifer and A. D. Gordeev, *Zh. Org. Khim.*, 1981, **17**, 1235–1241.
6. L. Waykole and L. A. Paquette, *Org. Synth.*, 1989, **67**, 149.
7. N. Suryakiran, T. S. Reddy, K. Ashalatha, M. Lakshman and Y. Venkateswarlu, *Tetrahedron Lett.*, 2006, **47**, 3853–3856.
8. S. Katayama, T. Watanabe and M. Yamauchi, *Chem. Lett.*, 1989, **18**, 973–976.
9. D. W. Sun, M. Jiang and J. T. Liu, *Chem. - Eur. J.*, 2019, **25**, 10797–10802.
10. G. Ferdinand and K. Schank, *Synthesis*, 1976, **1976**, 408–409.
11. F. Liu, *Org. Biomol. Chem.*, 2023, **21**, 1153–1157.
12. K. Ogura, S. Kiuchi, K. Takahashi and H. Iida, *Synthesis*, 1985, **1985**, 524–525.
13. M.-Y. Chang, R.-T. Hsu, C.-K. Chan and H.-S. Wang, *Synthesis*, 2017, **49**, 2045–2056.
14. K. Schank, A.-M. A. Abdel Wahab, S. Bügler, P. Eigen, J. Jager and K. Jost, *Tetrahedron*, 1994, **50**, 3721–3742.
15. M. U. Tariq and W. J. Moran, *Eur. J. Org. Chem*, 2020, **2020**, 5153–5160.
16. A. Alalla, M. Merabet-Khelassi, L. Aribi-Zouioueche and O. Riant, *Synth. Commun.*, 2014, **44**, 2364–2376.
17. R. Ramkumar and S. Chandrasekaran, *Synthesis*, 2019, **51**, 921–932.

# 2. Copies of NMR spectra

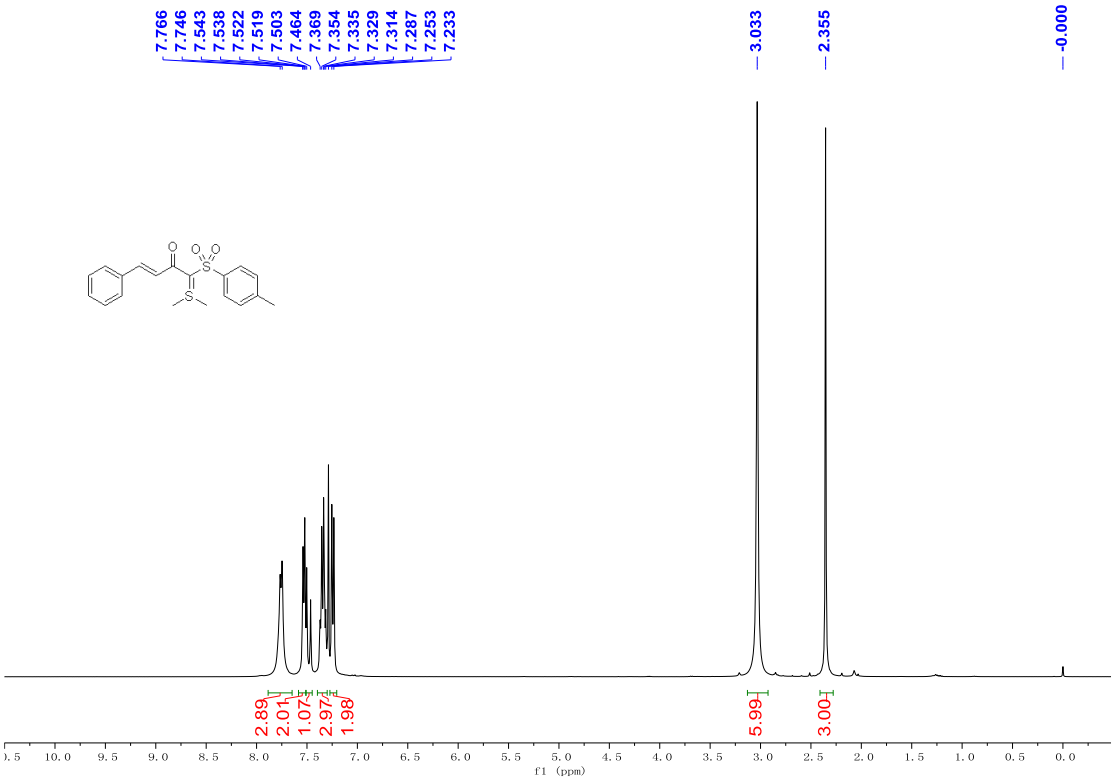
## 2.1 Copies of NMR spectra for 1p, 1r and 1w

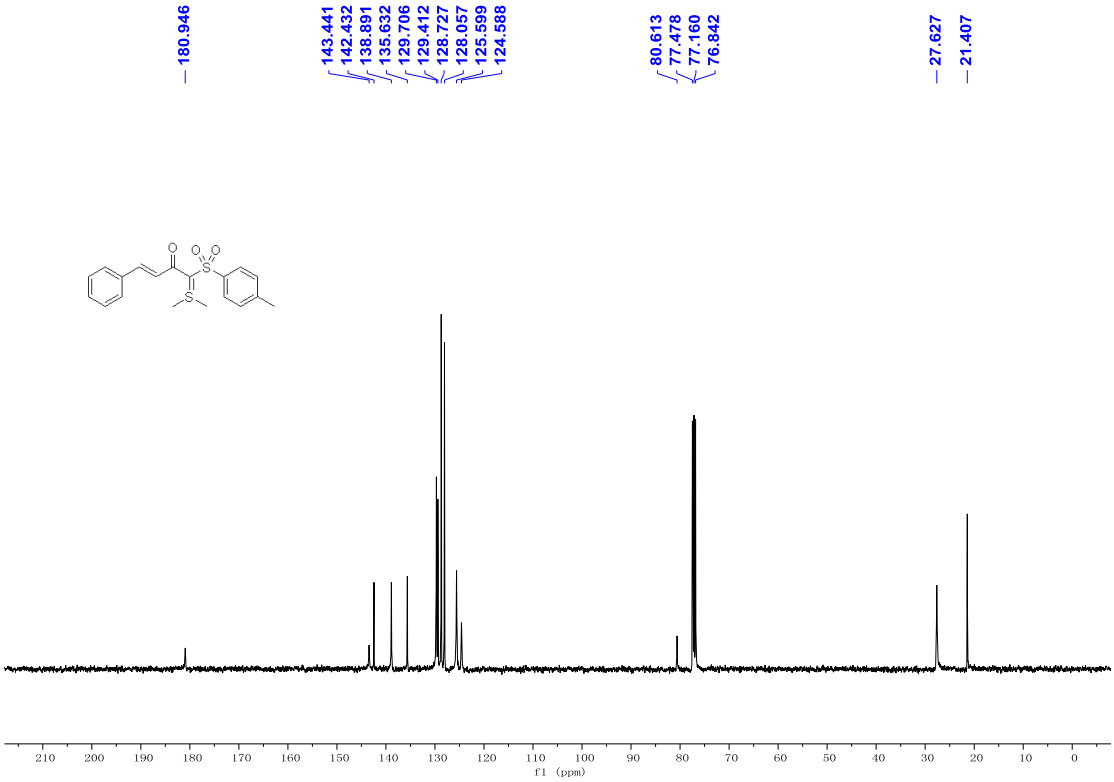
1-(Dimethyl-λ$^4$-sulfaneylidene)-1-tosylpropan-2-one (**1p**)



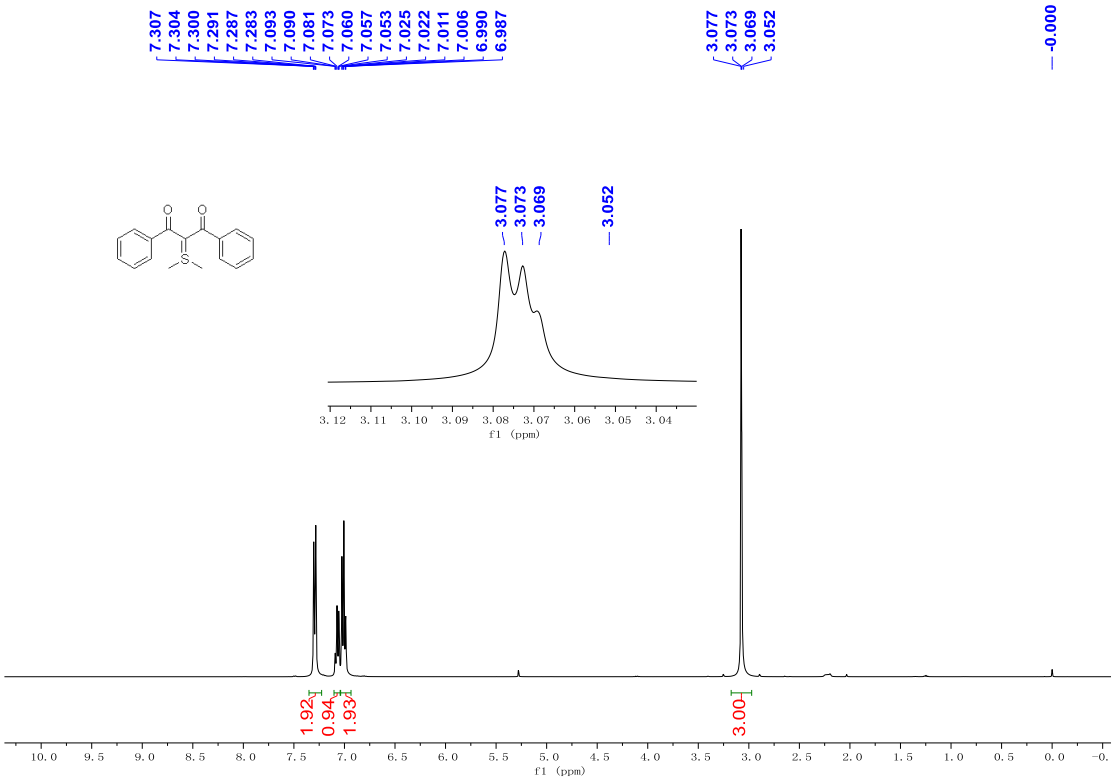



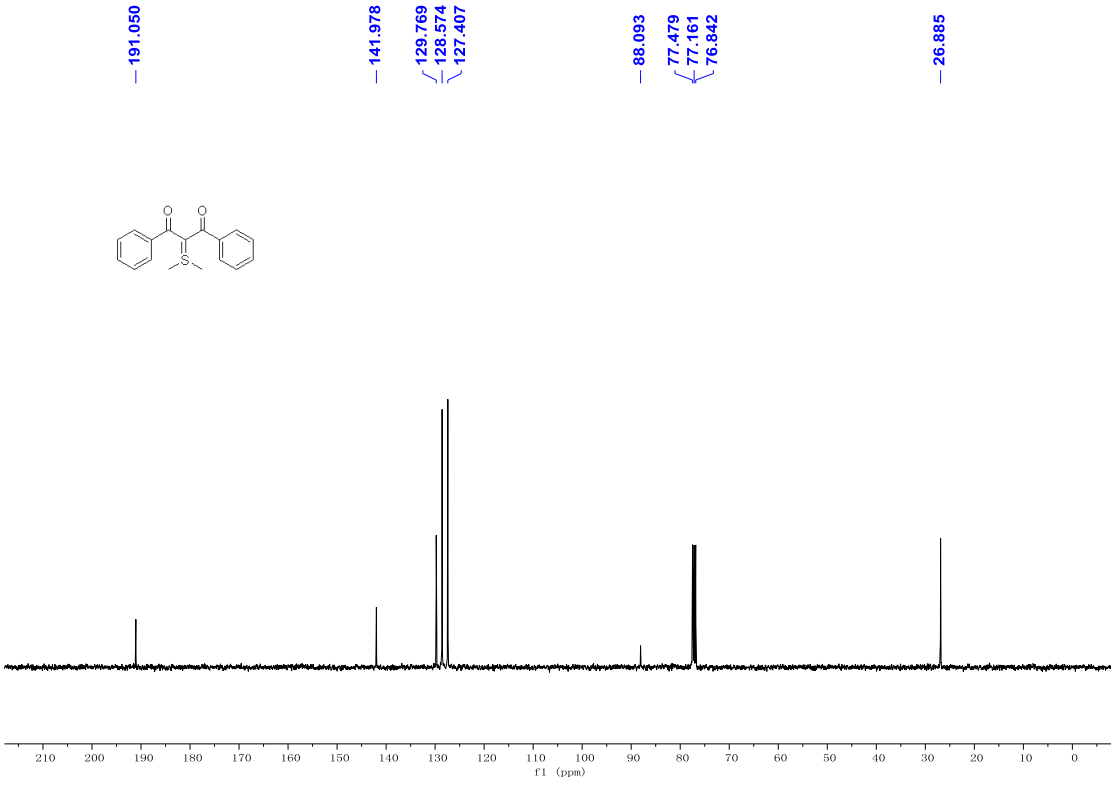
(*E*)-1-(Dimethyl-λ$^4$-sulfaneylidene)-4-phenyl-1-tosylbut-3-en-2-one (**1r**)



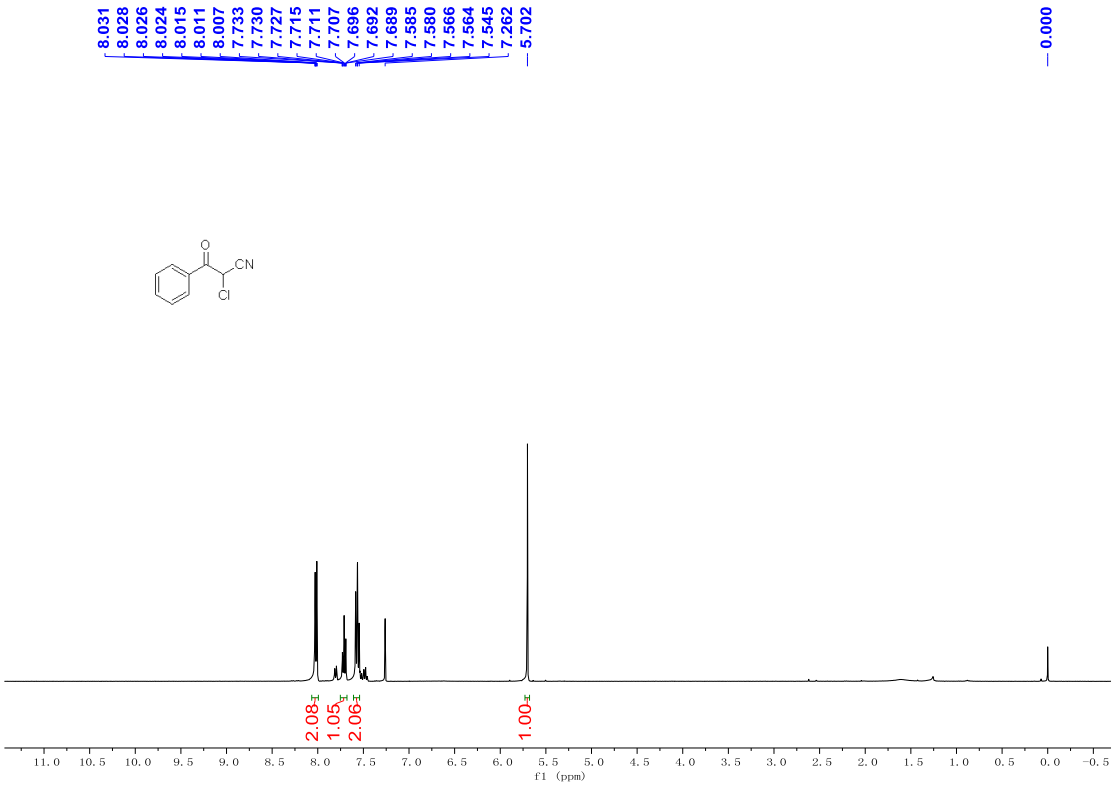



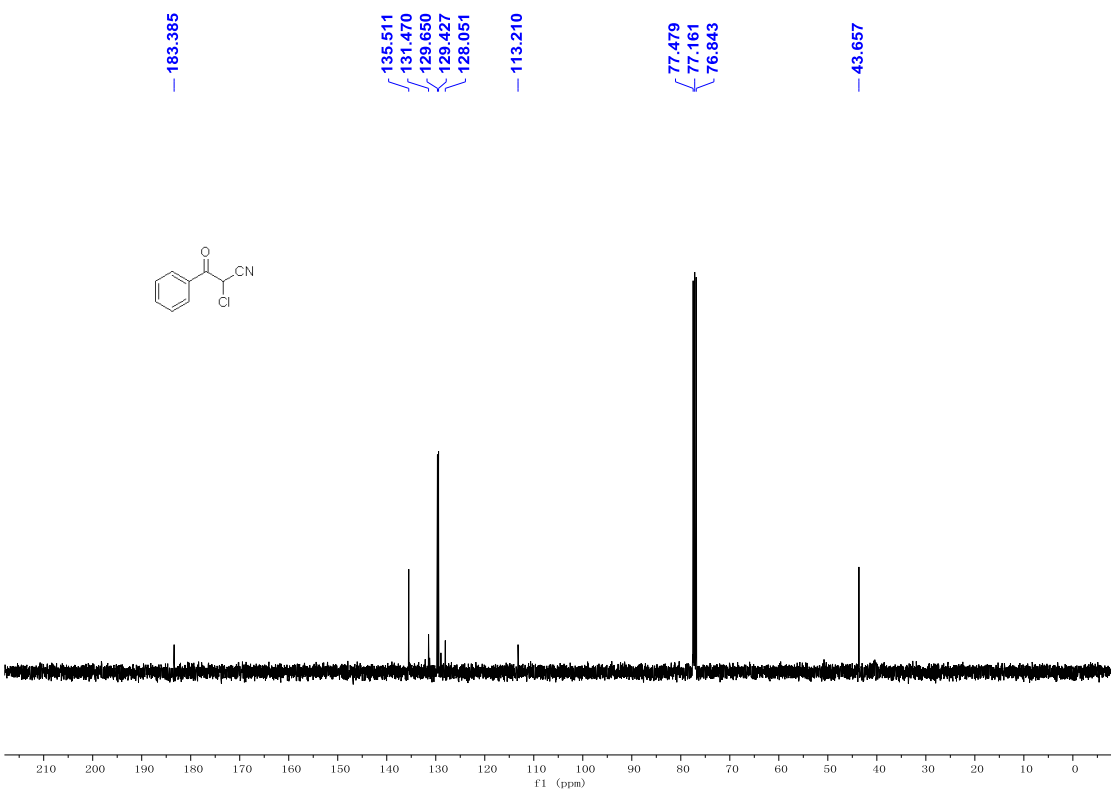
2-(Dimethyl-λ$^4$-sulfaneylidene)-1,3-diphenylpropane-1,3-dione (**1w**)



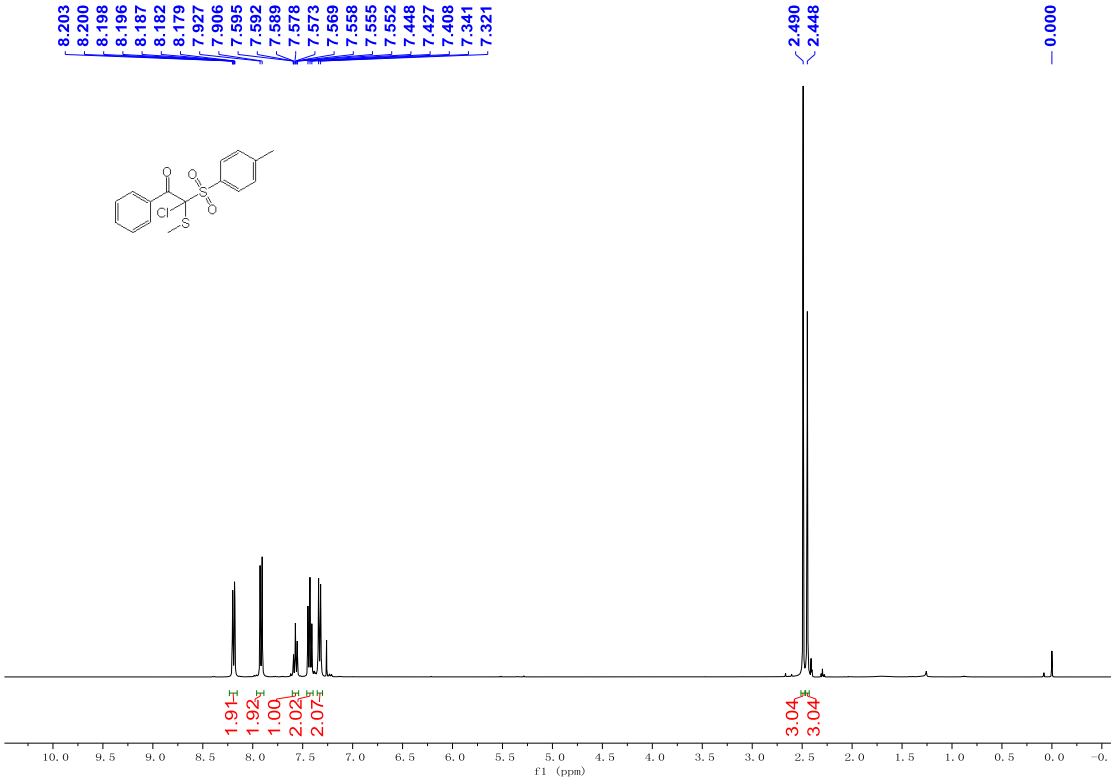
## 2.2 Copies of NMR spectra for 2aD

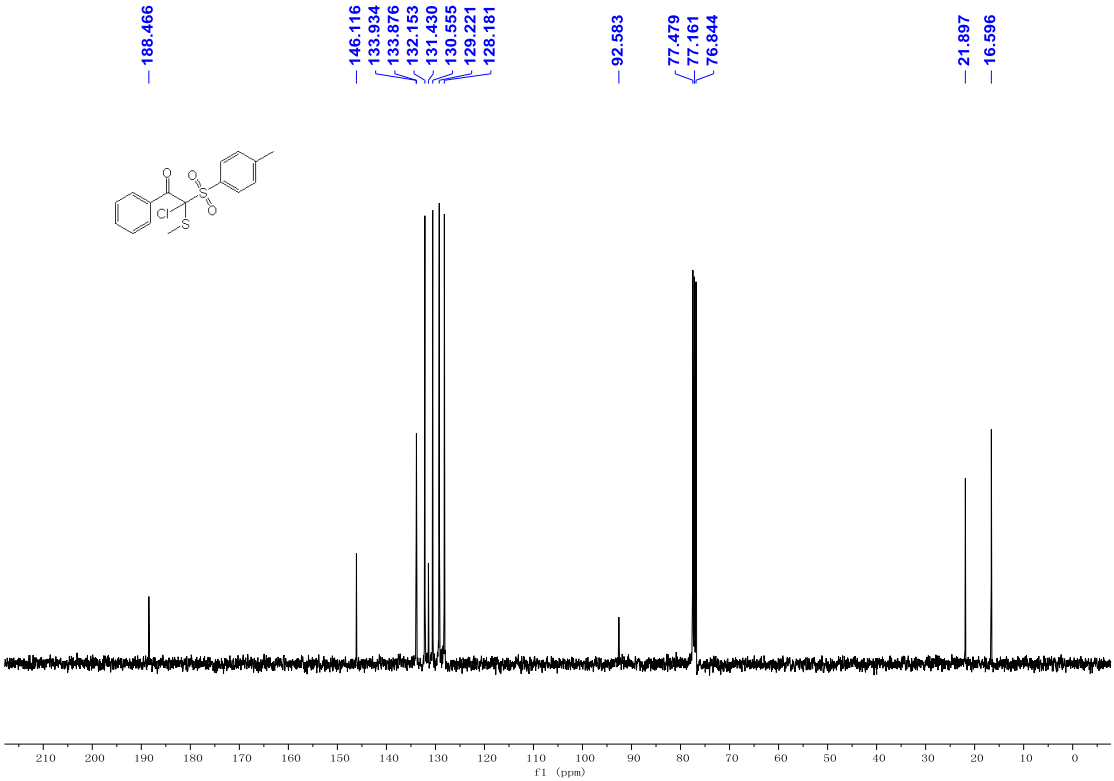


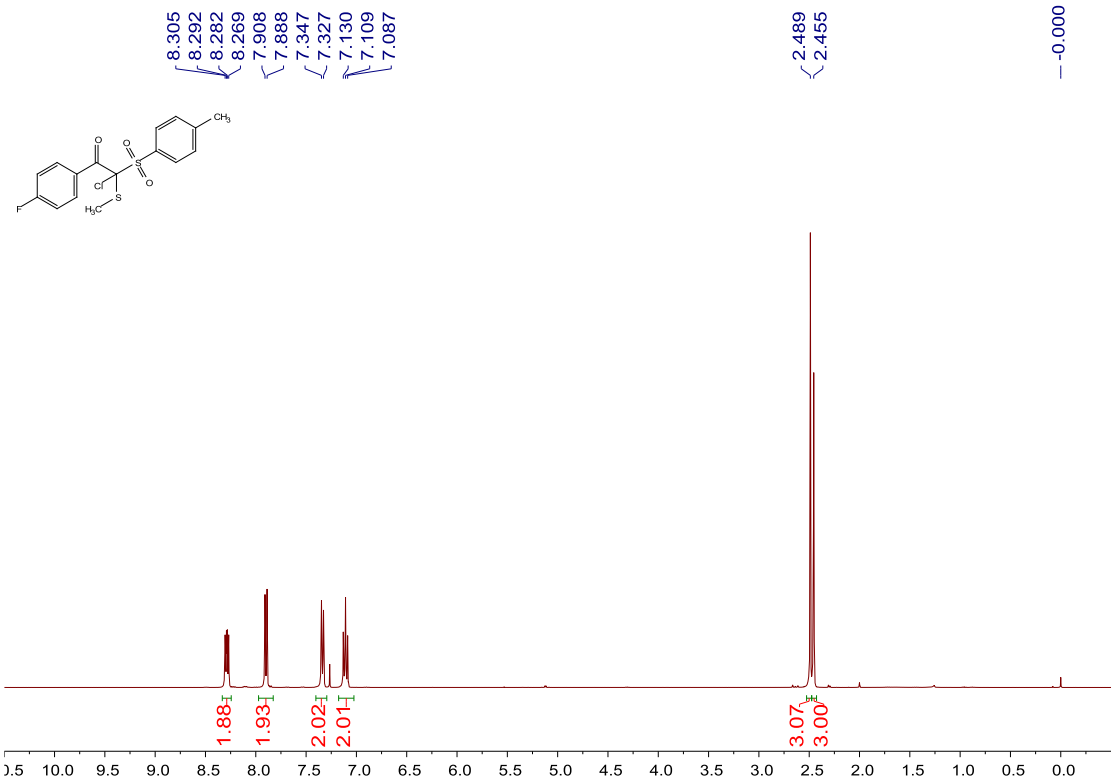
## 2.3 Copies of NMR spectra for products 2

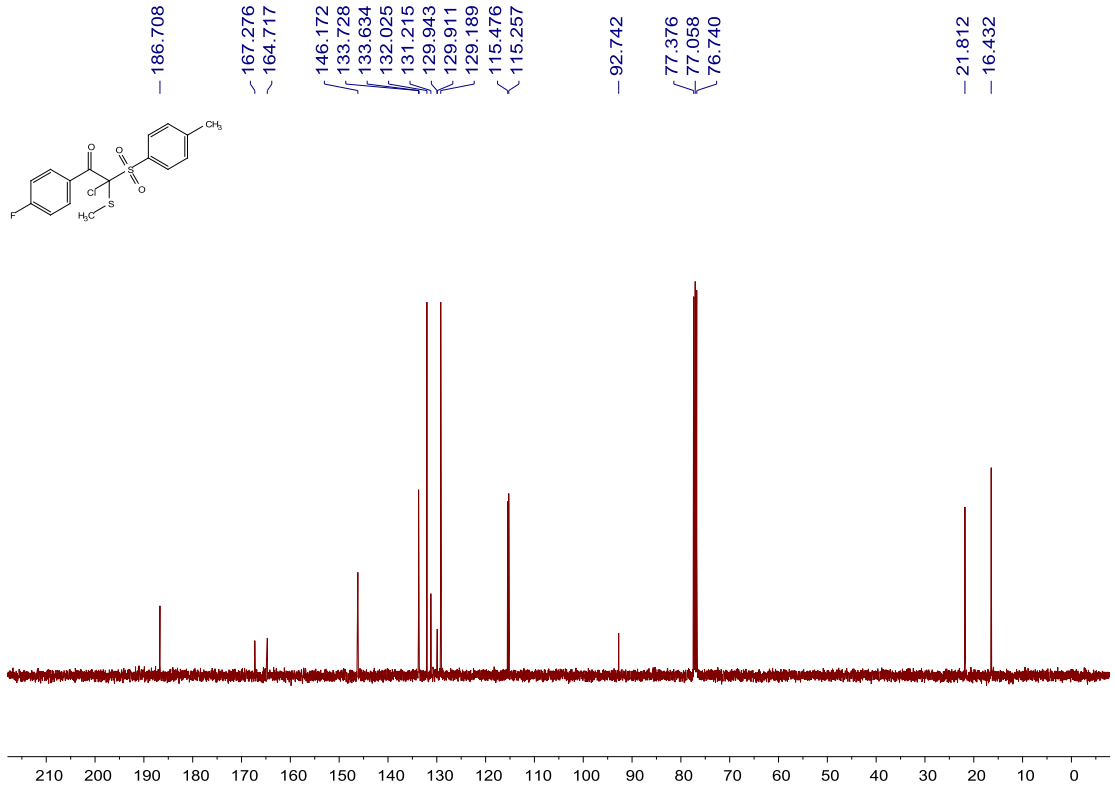
2-Chloro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**2a**)

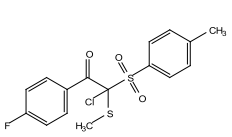


2-Chloro-1-(4-fluorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2b**)

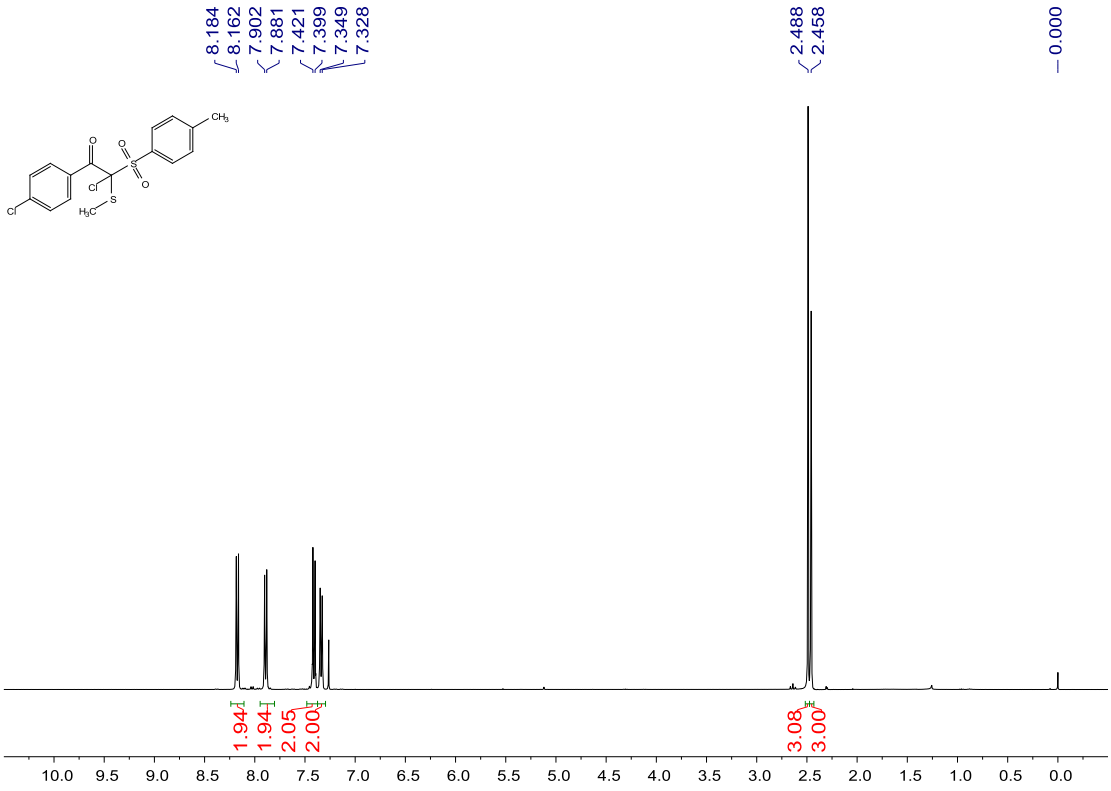


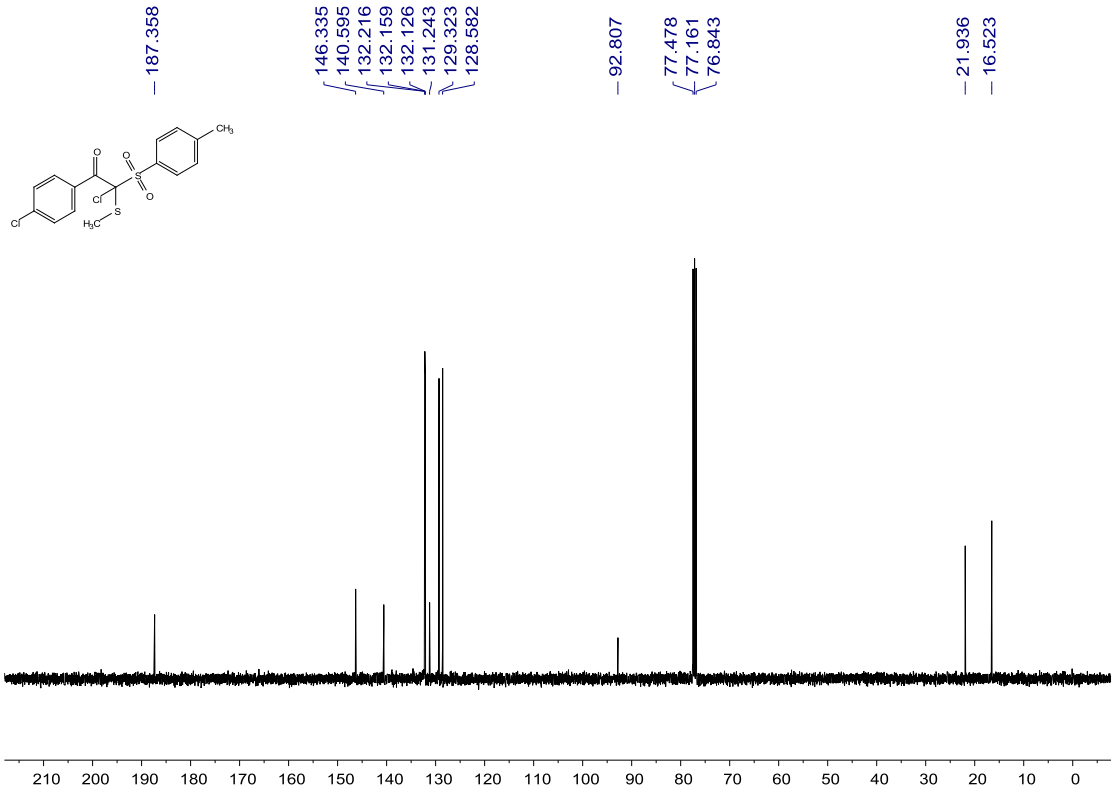




O
O
S
O
Cl
S
$H_3C$
F
$CH_3$

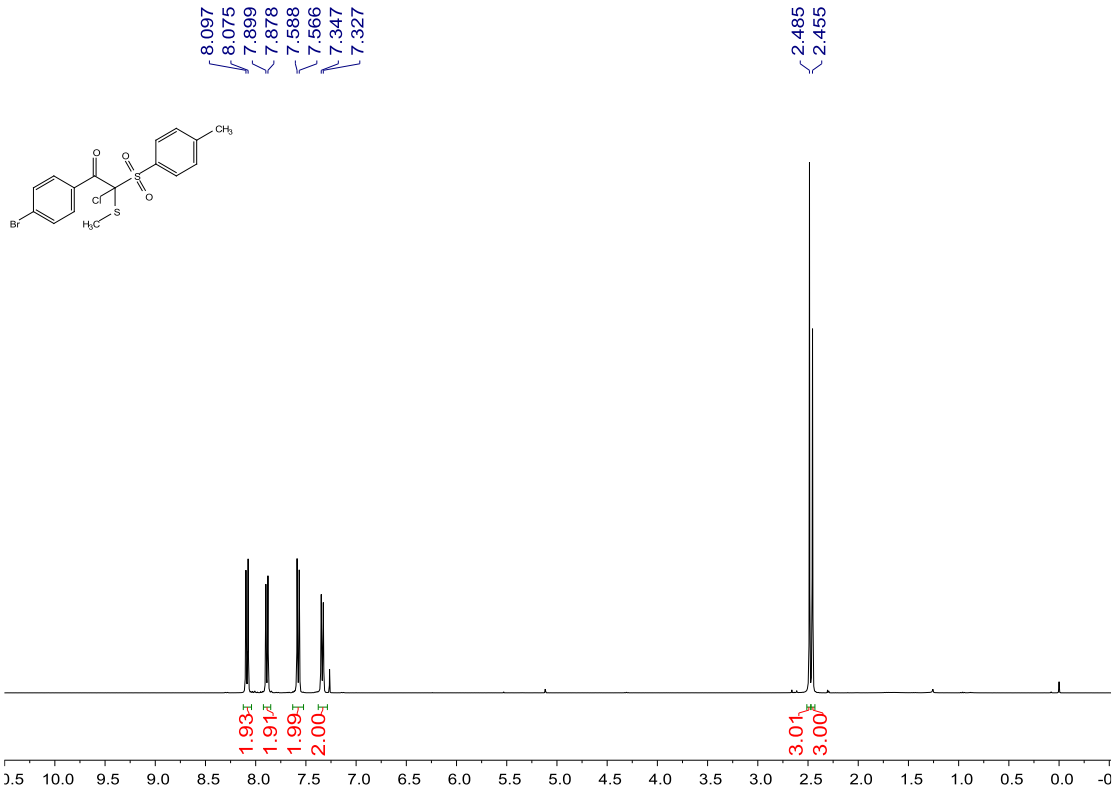

-102.744
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

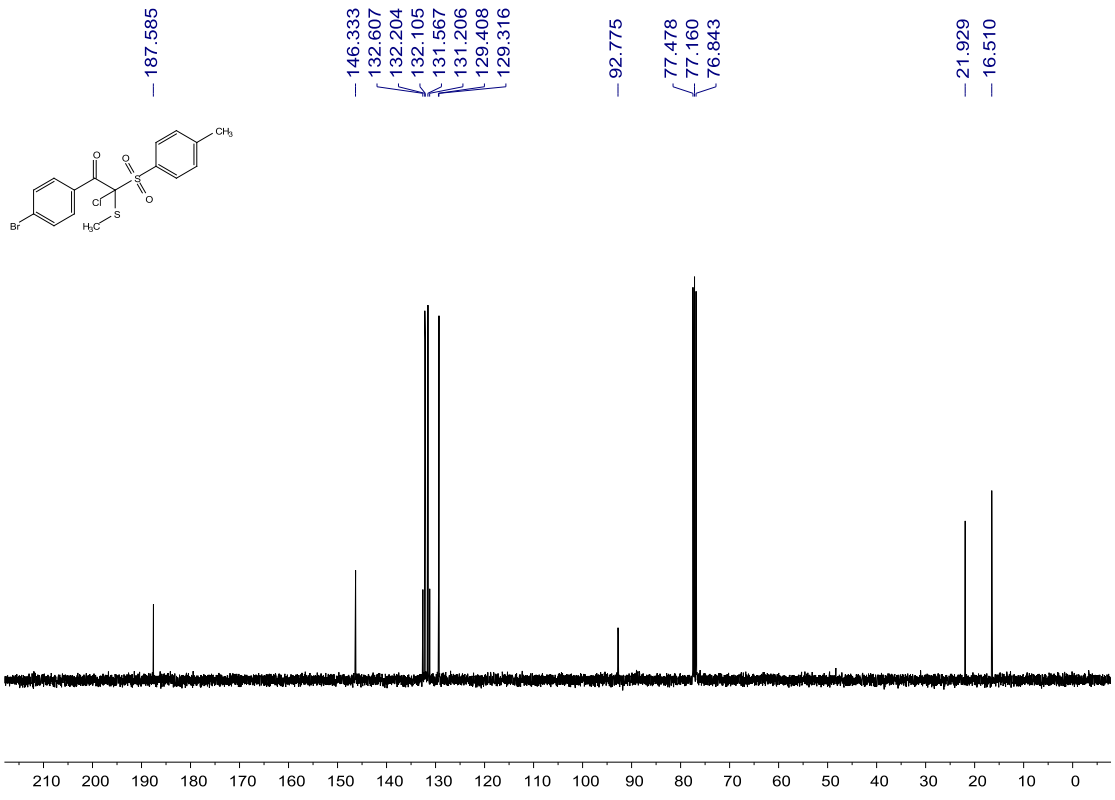
2-Chloro-1-(4-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2c**)



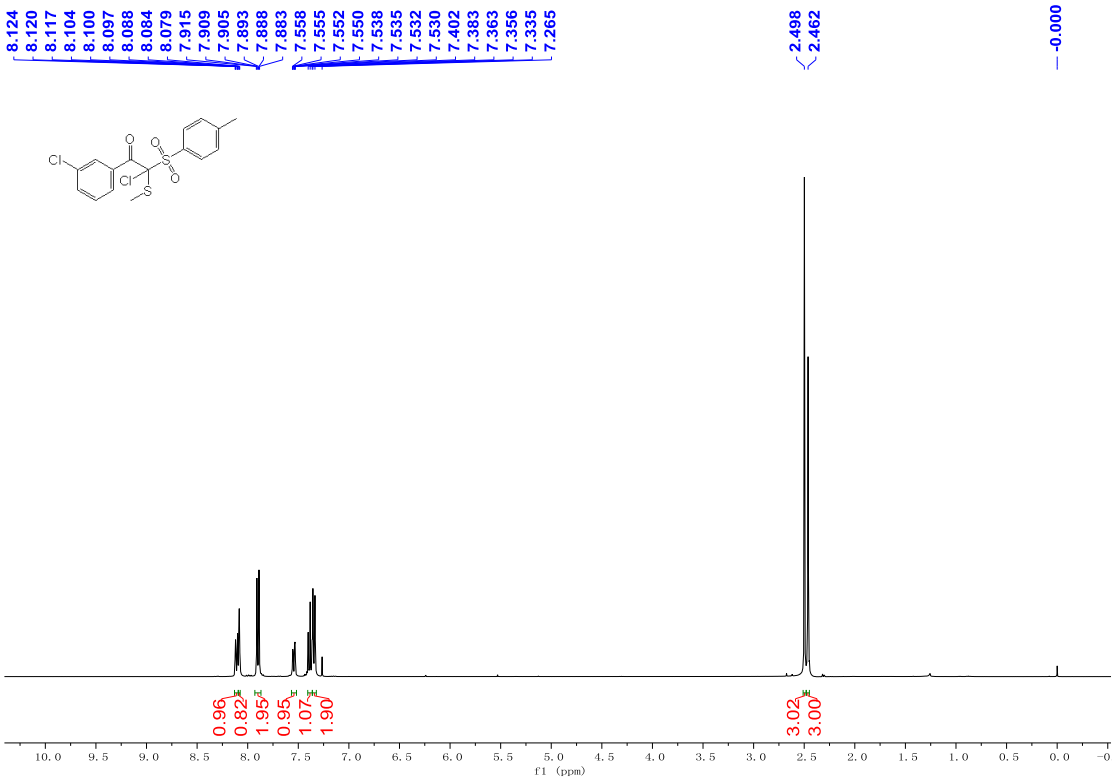



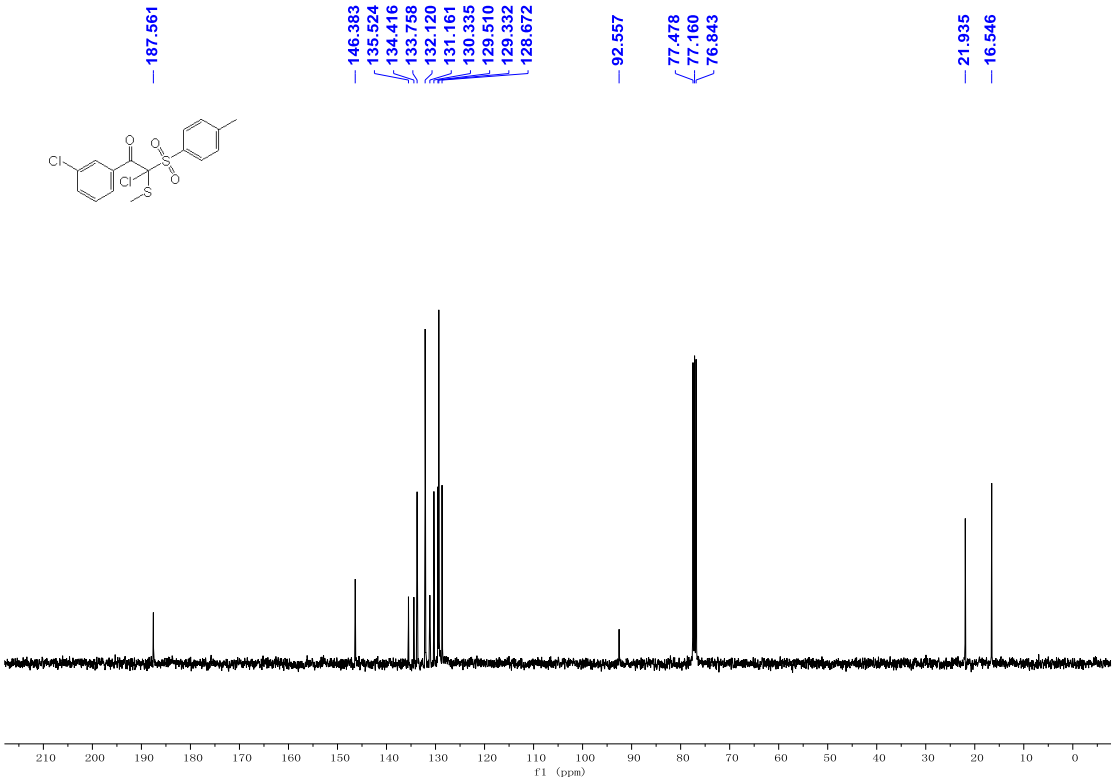
1-(4-Bromophenyl)-2-chloro-2-(methylthio)-2-tosylethan-1-one (**2d**)



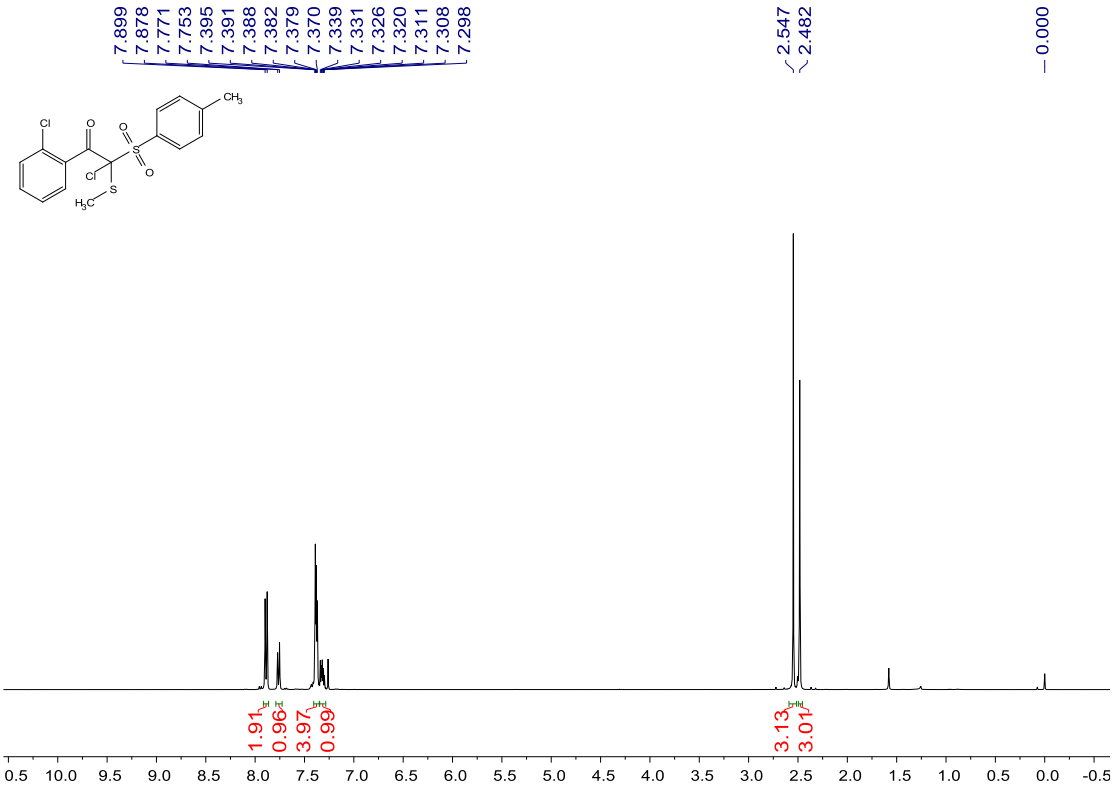



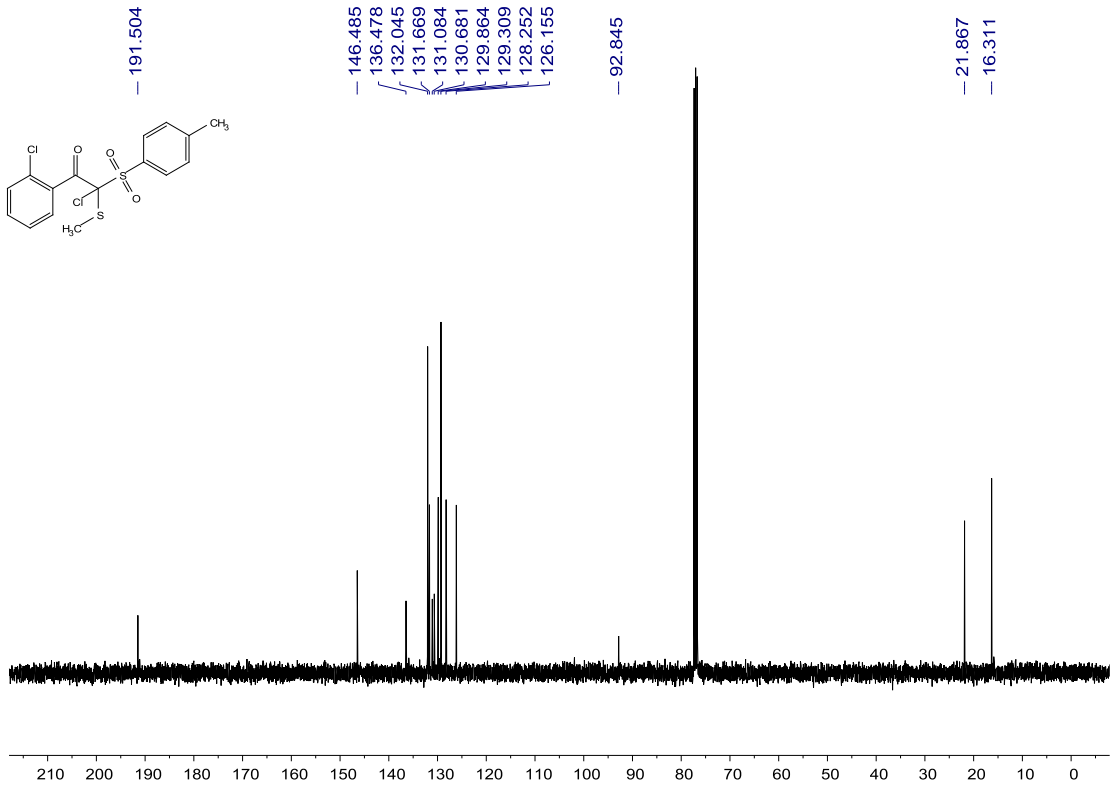
2-Chloro-1-(3-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2e**)



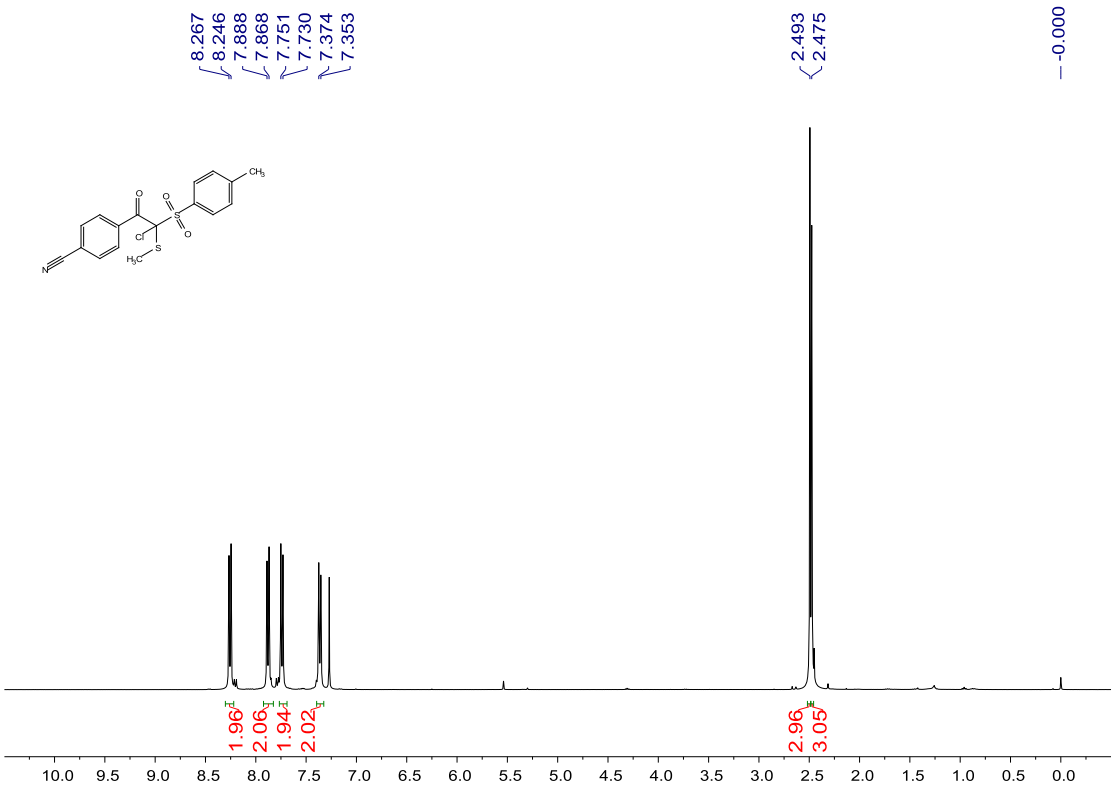



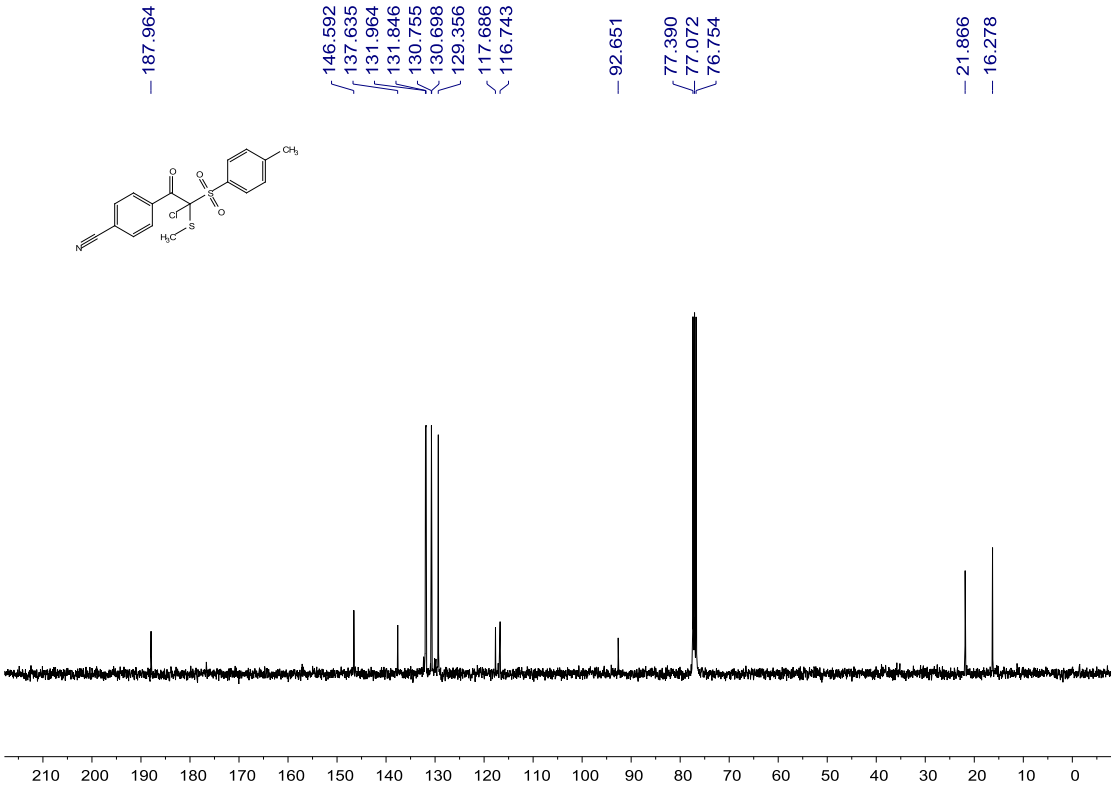
2-Chloro-1-(2-chlorophenyl)-2-(methylthio)-2-tosylethan-1-one (**2f**)



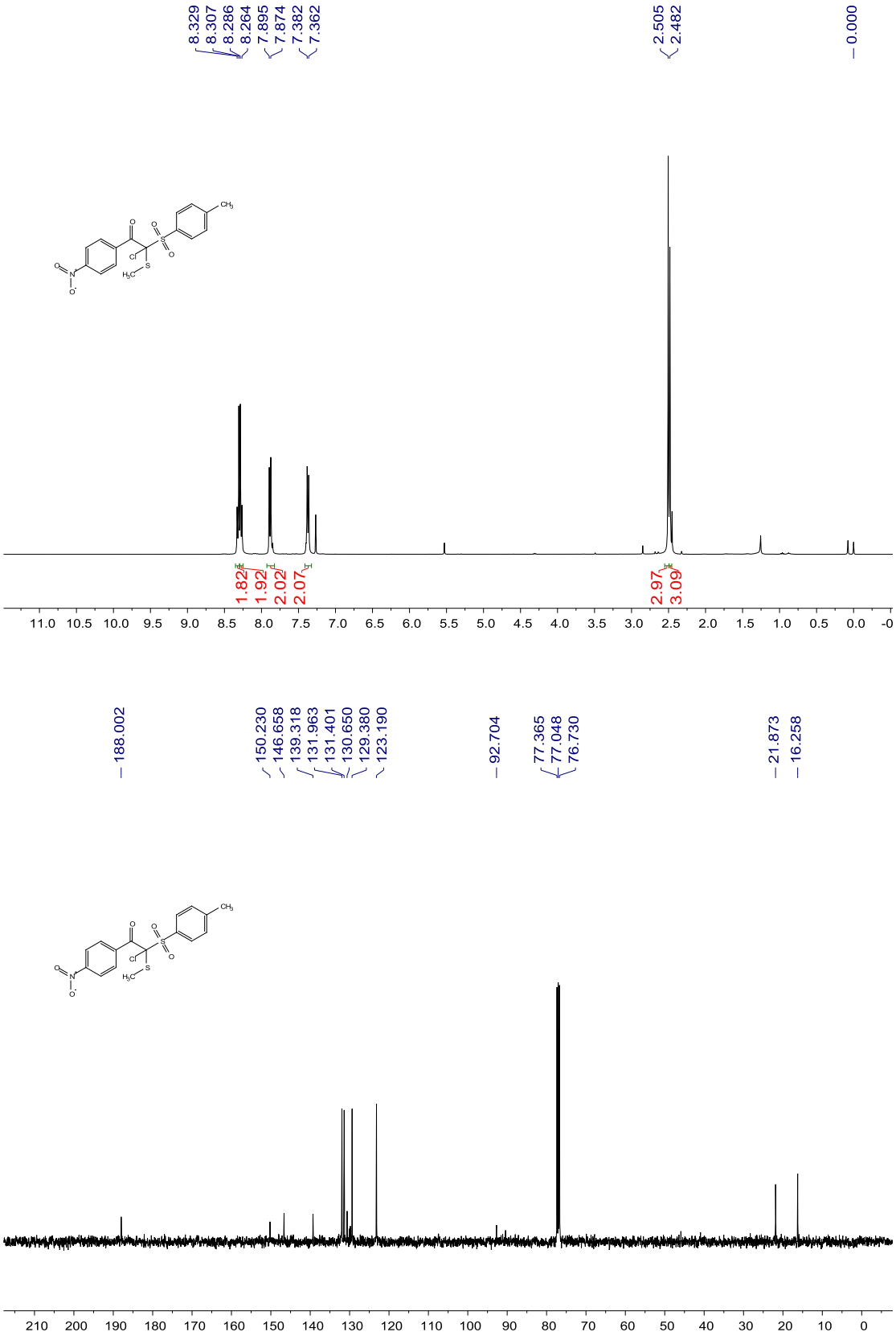



4-(2-Chloro-2-(methylthio)-2-tosylacetyl)benzonitrile (**2g**)

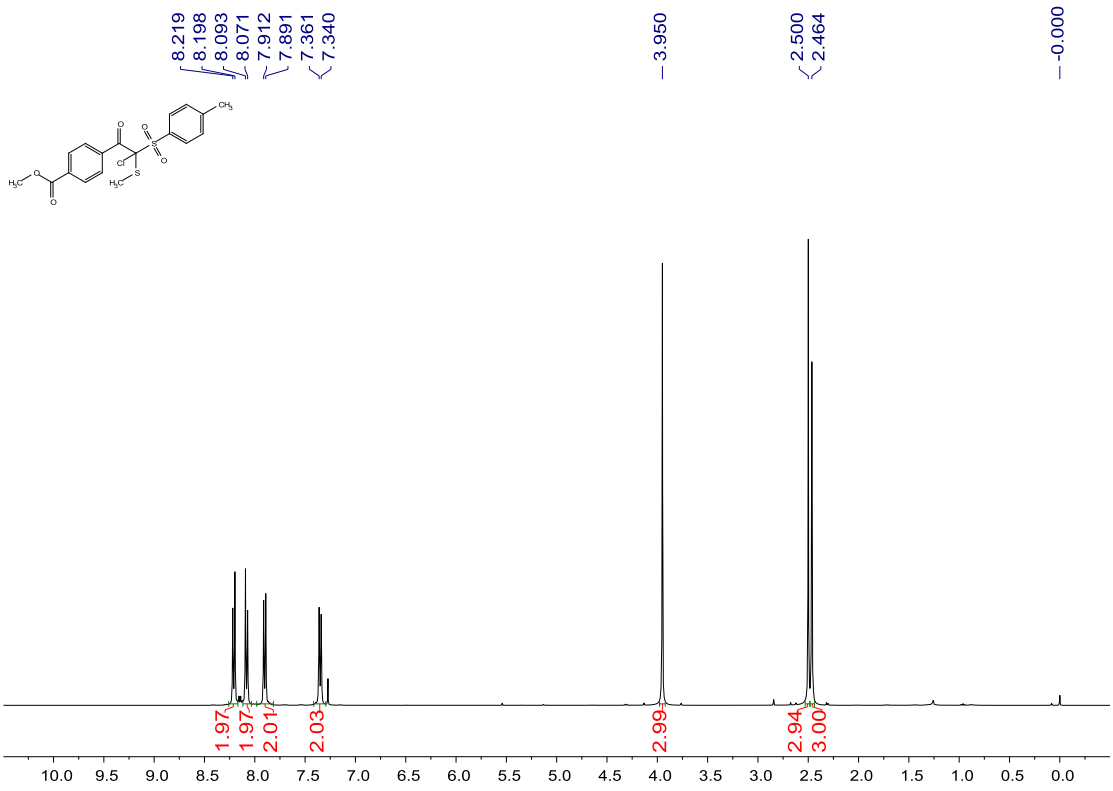


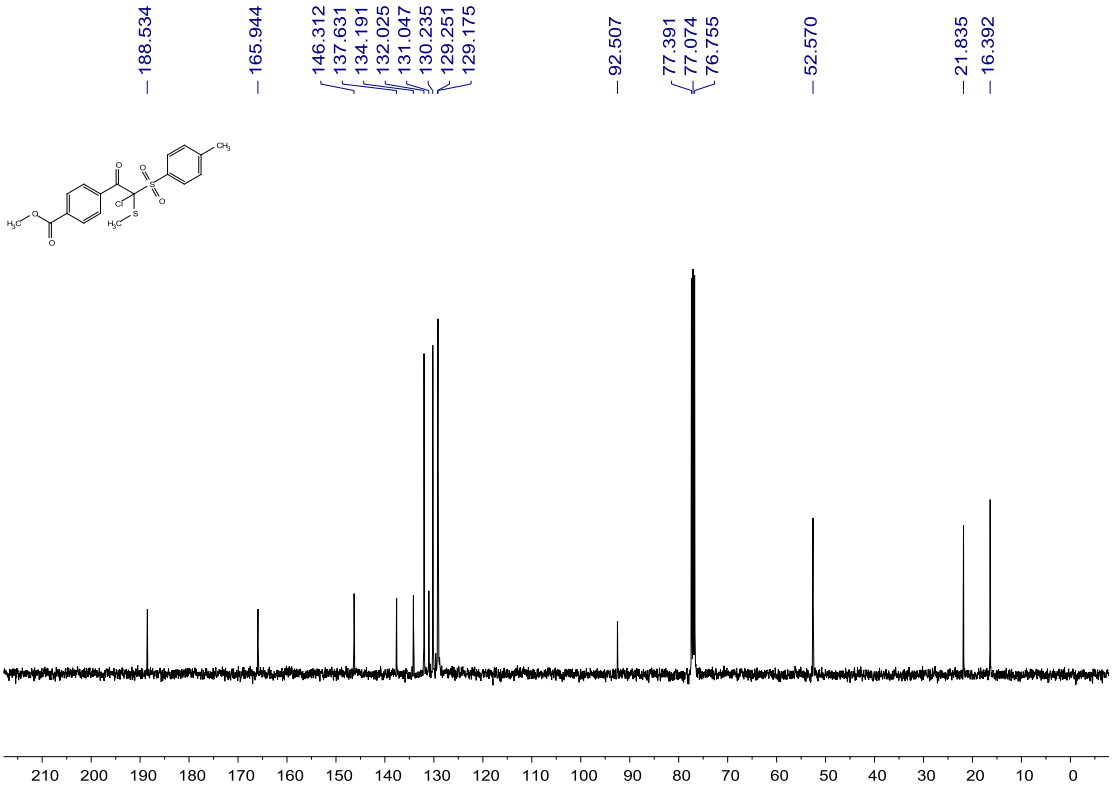



2-Chloro-2-(methylthio)-1-(4-nitrophenyl)-2-tosylethan-1-one (**2h**)

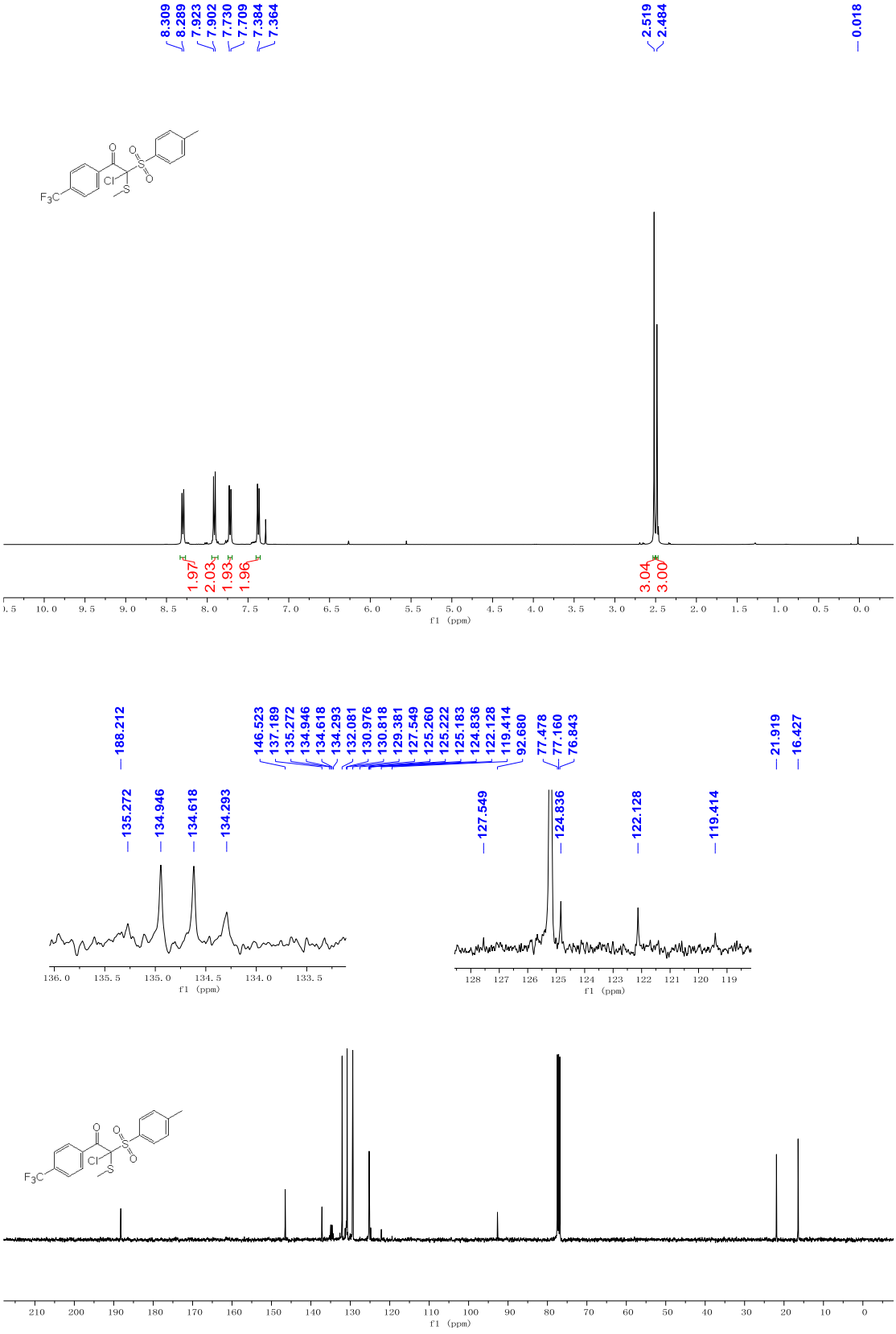


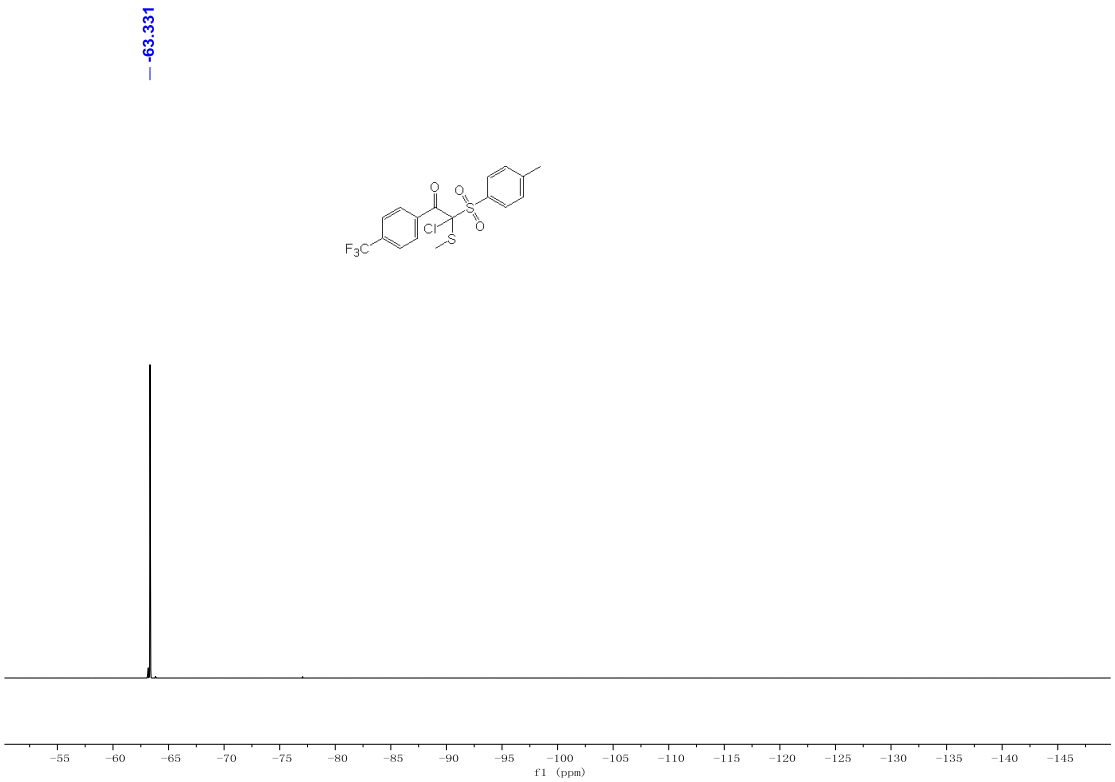
Methyl 4-(2-chloro-2-(methylthio)-2-tosylacetyl)benzoate (**2i**)



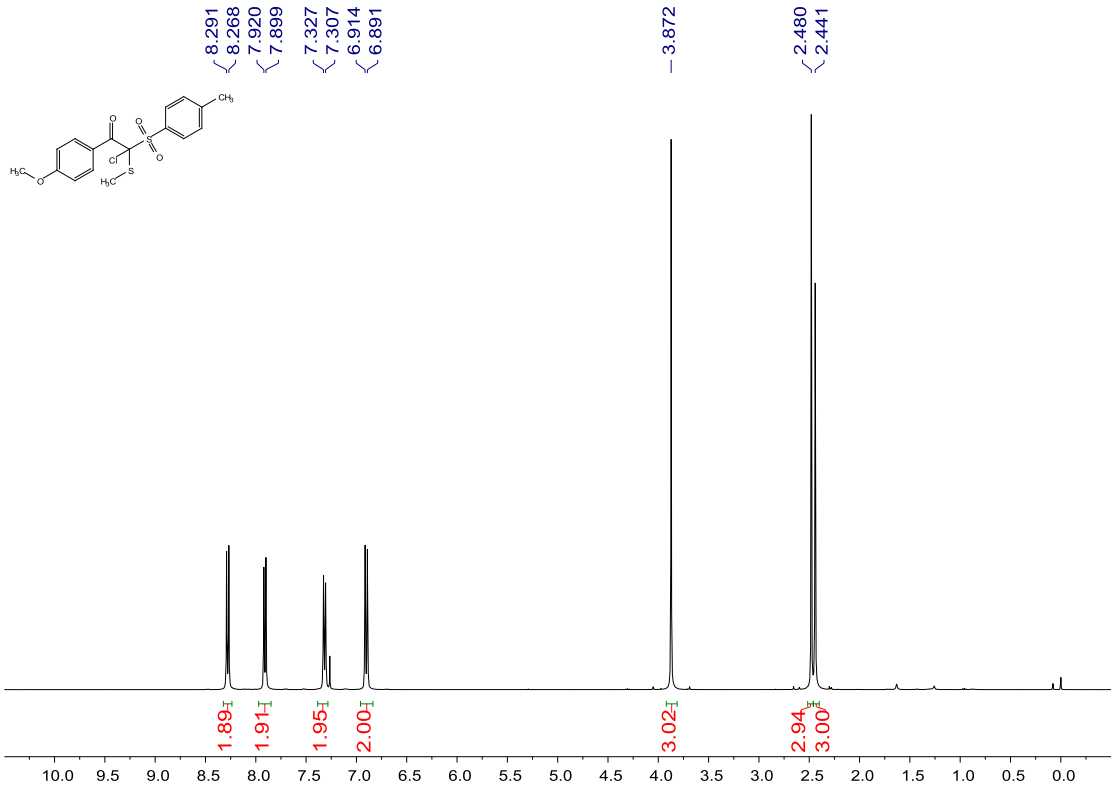



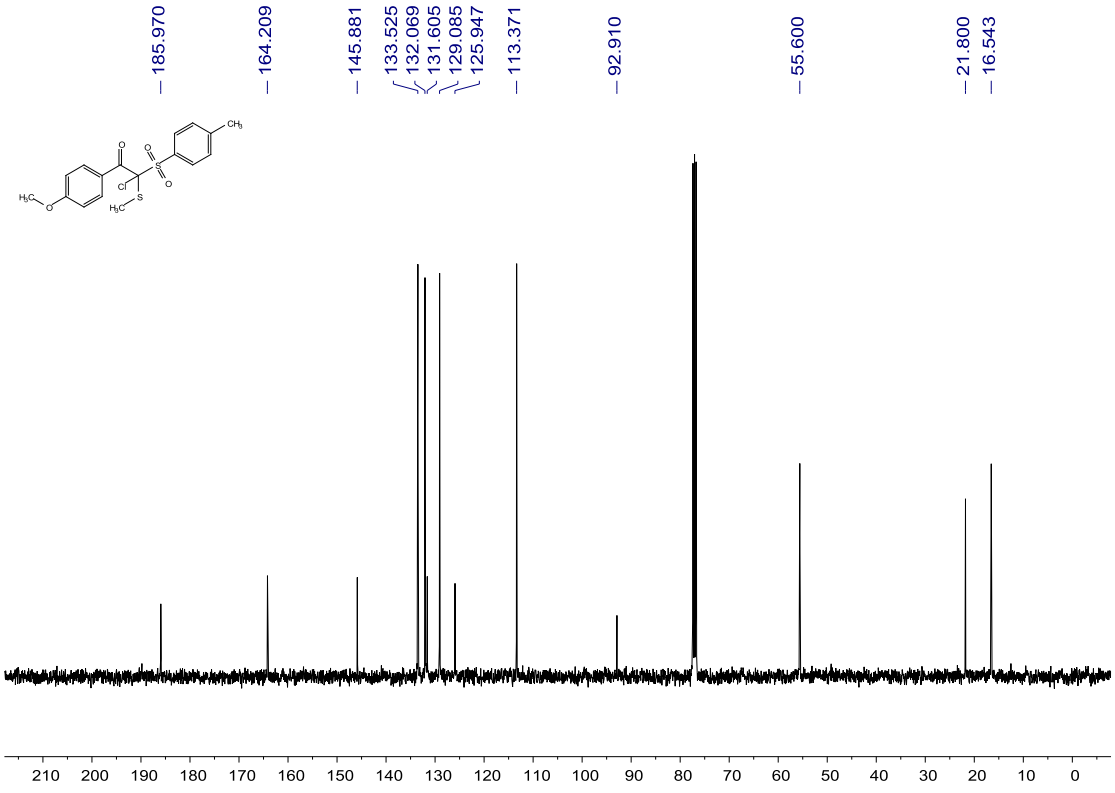
2-Chloro-2-(methylthio)-2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2j**)



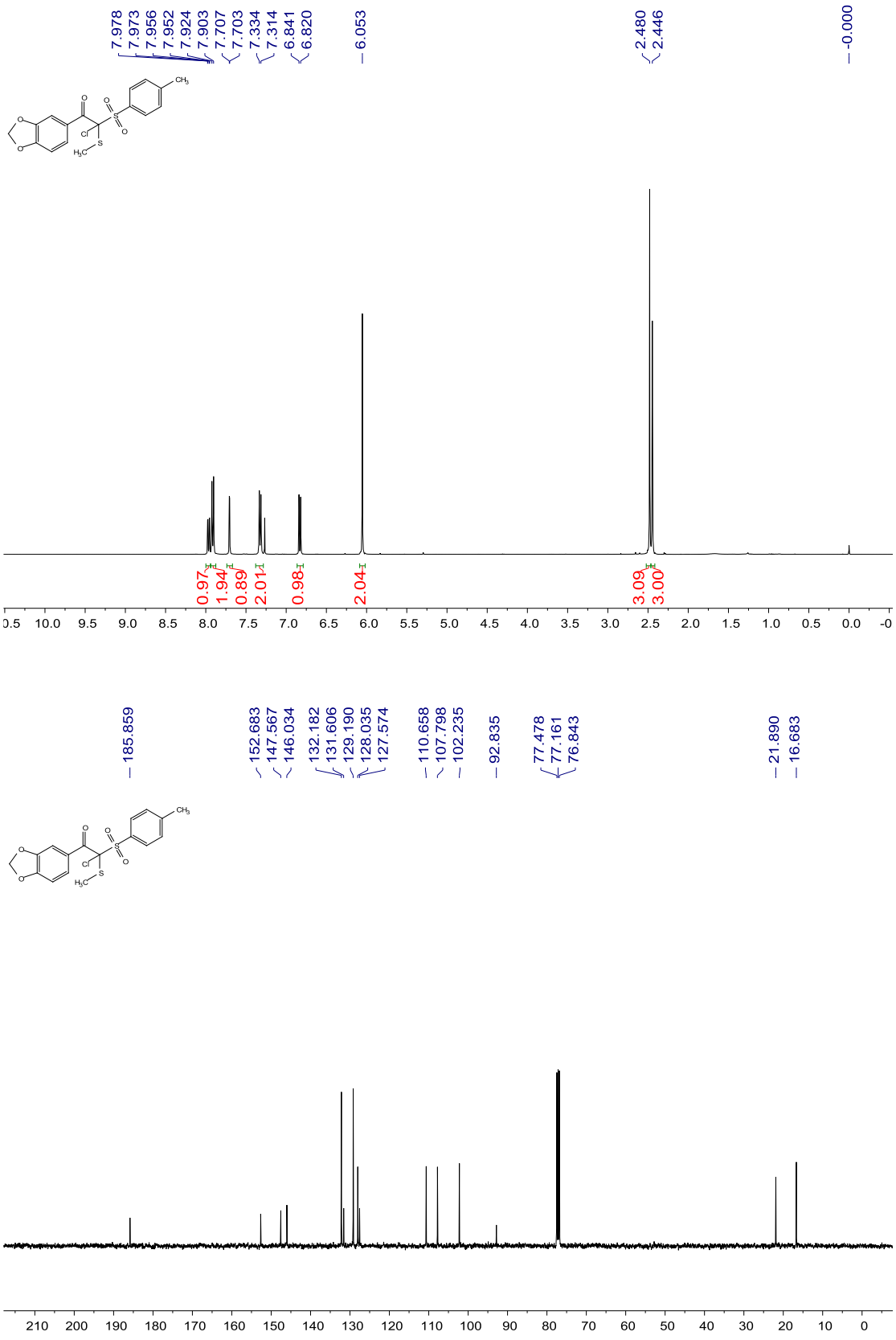

-63.331
O
O
S
O
Cl
S
F3C
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

2-Chloro-1-(4-methoxyphenyl)-2-(methylthio)-2-tosylethan-1-one (**2k**)

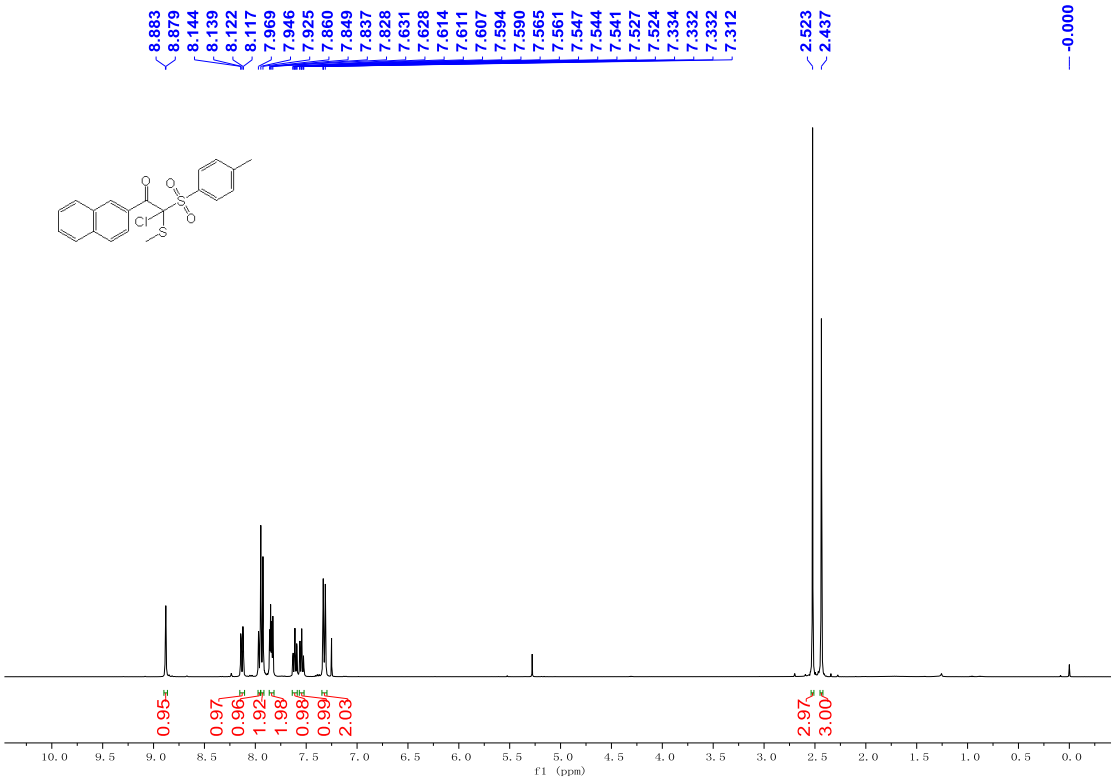


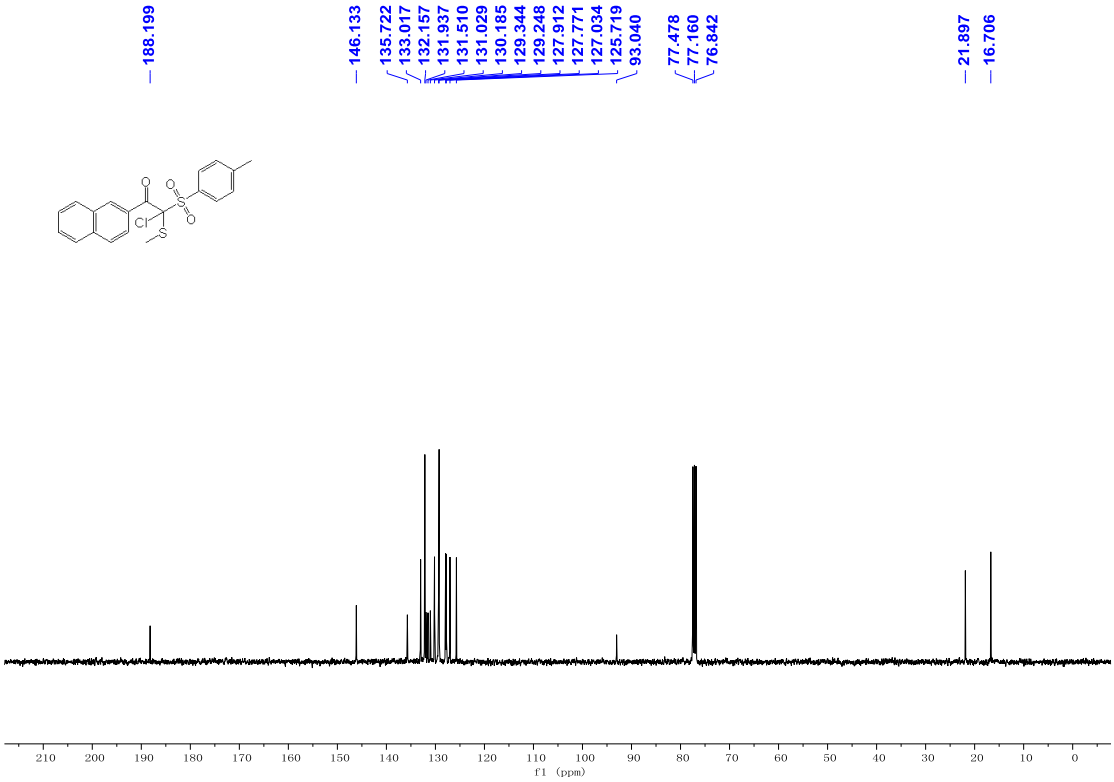



1-(Benzo[*d*][1,3]dioxol-5-yl)-2-chloro-2-(methylthio)-2-tosylethan-1-one (**2l**)

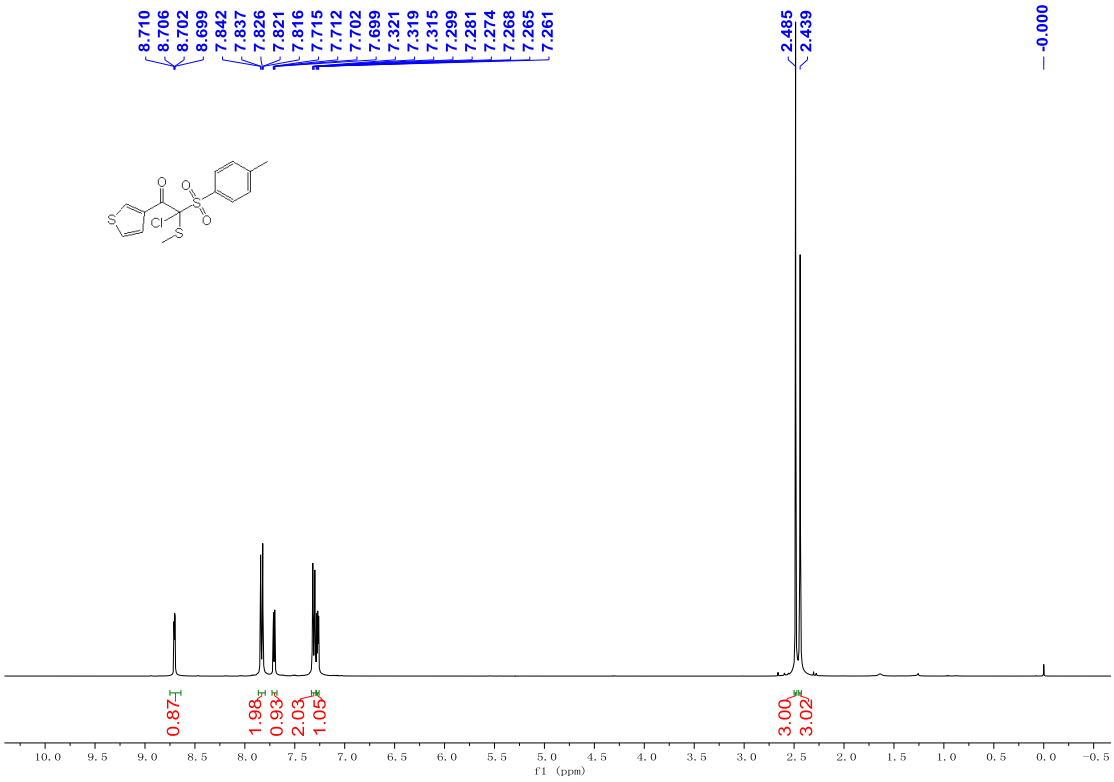


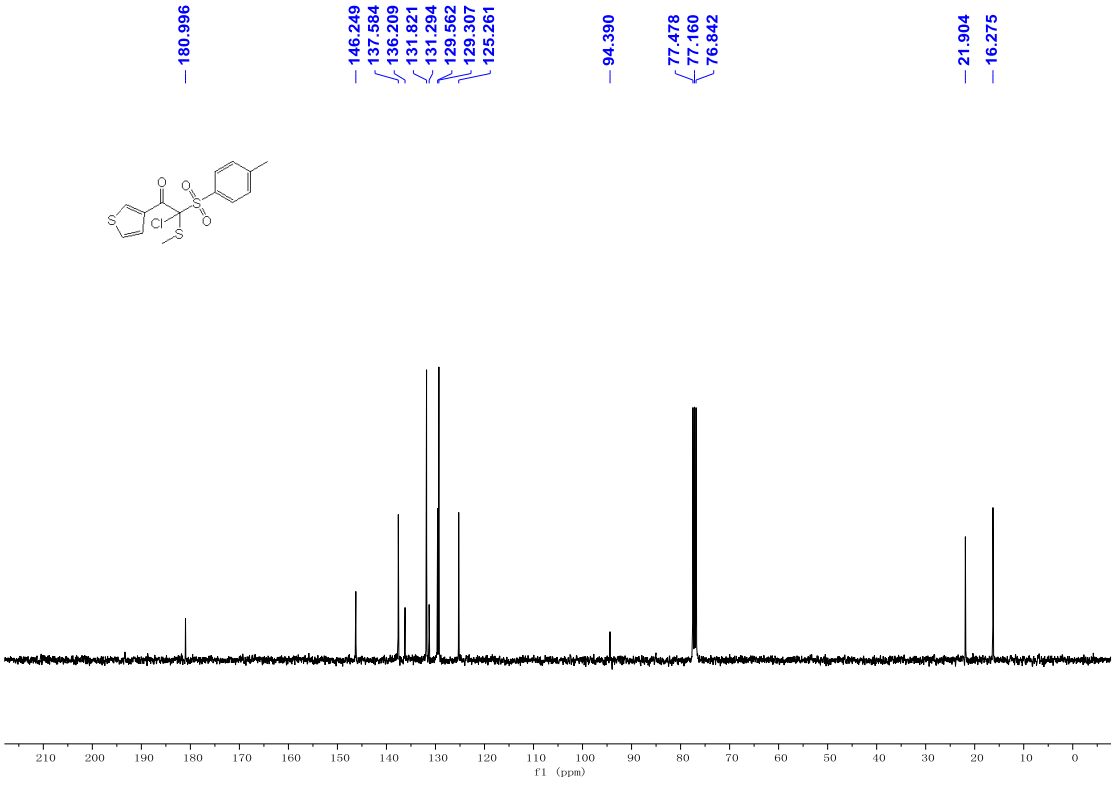
2-Chloro-2-(methylthio)-1-(naphthalen-2-yl)-2-tosylethan-1-one (**2m**)



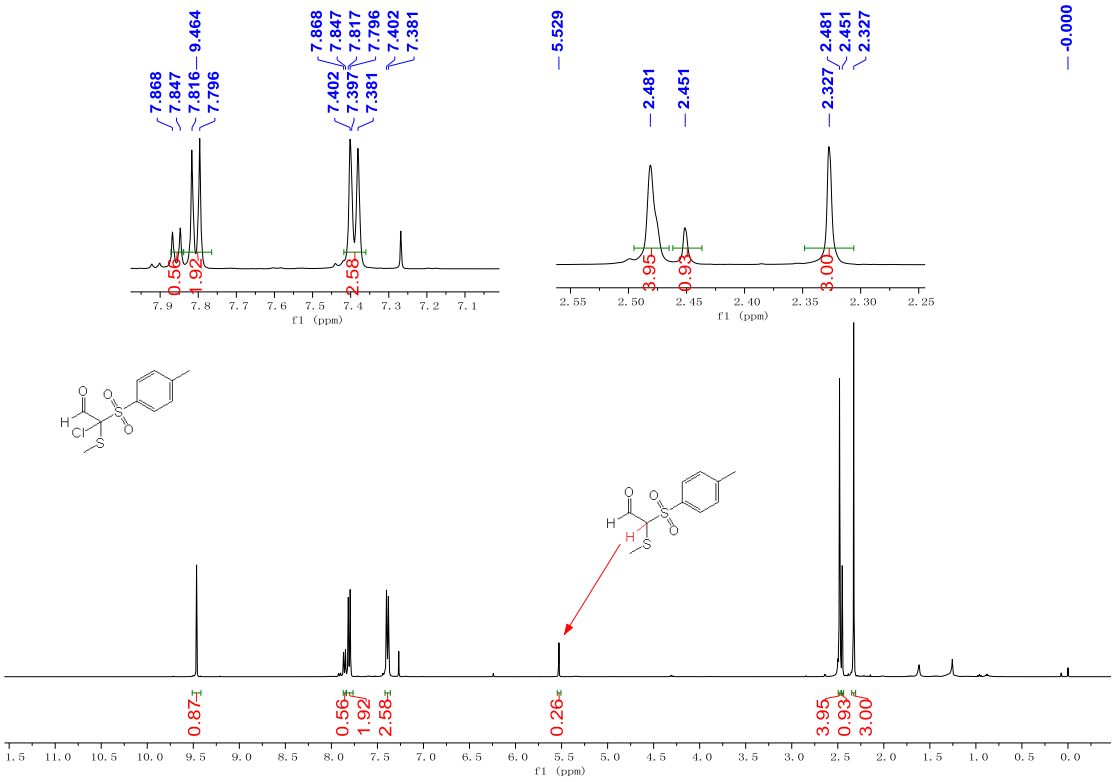



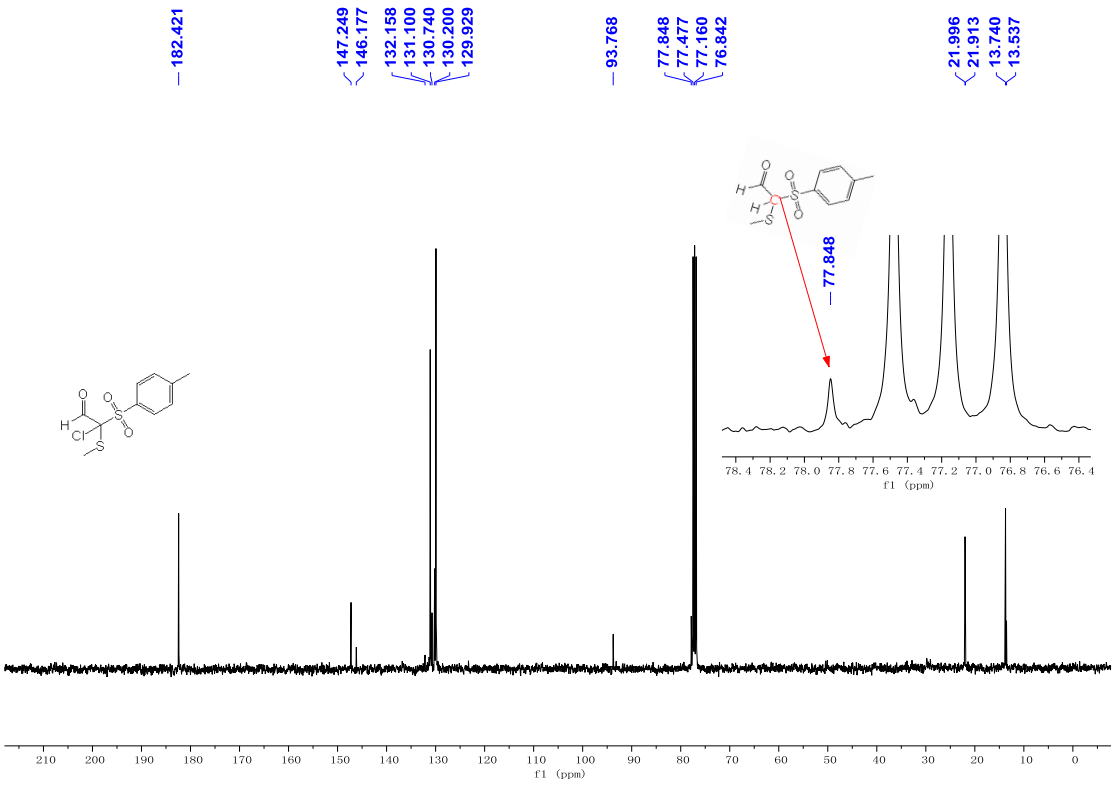
2-Chloro-2-(methylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one (**2n**)



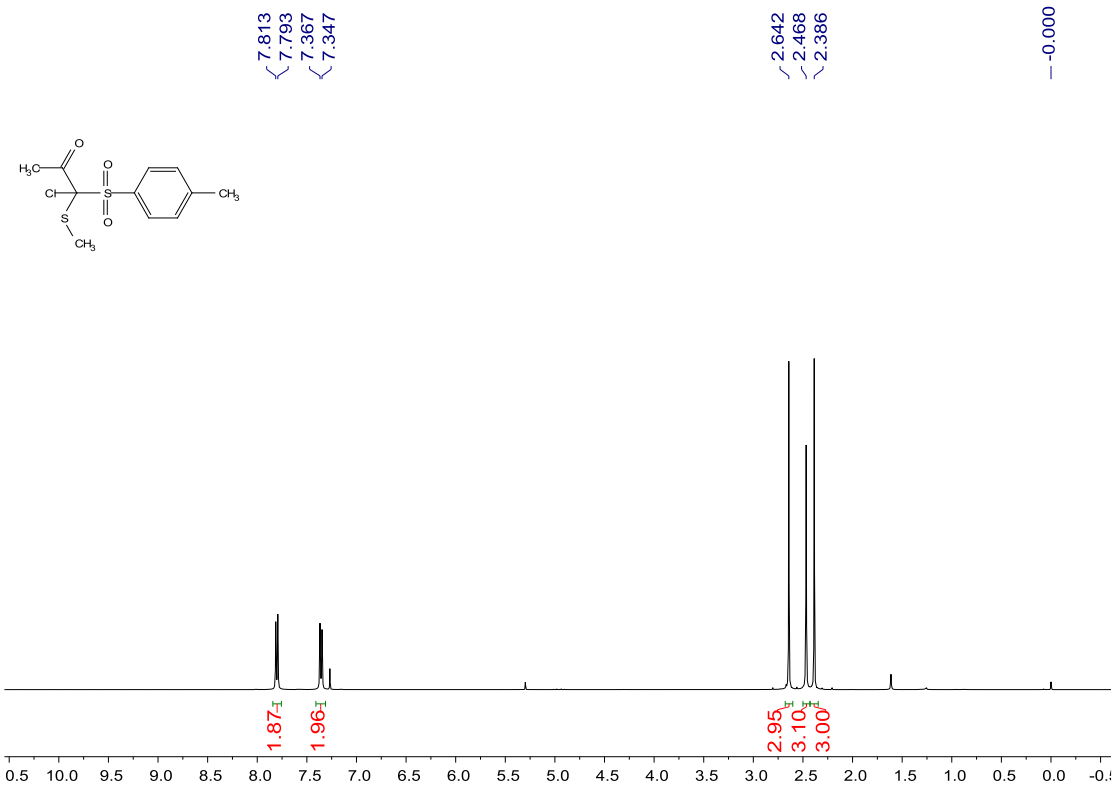



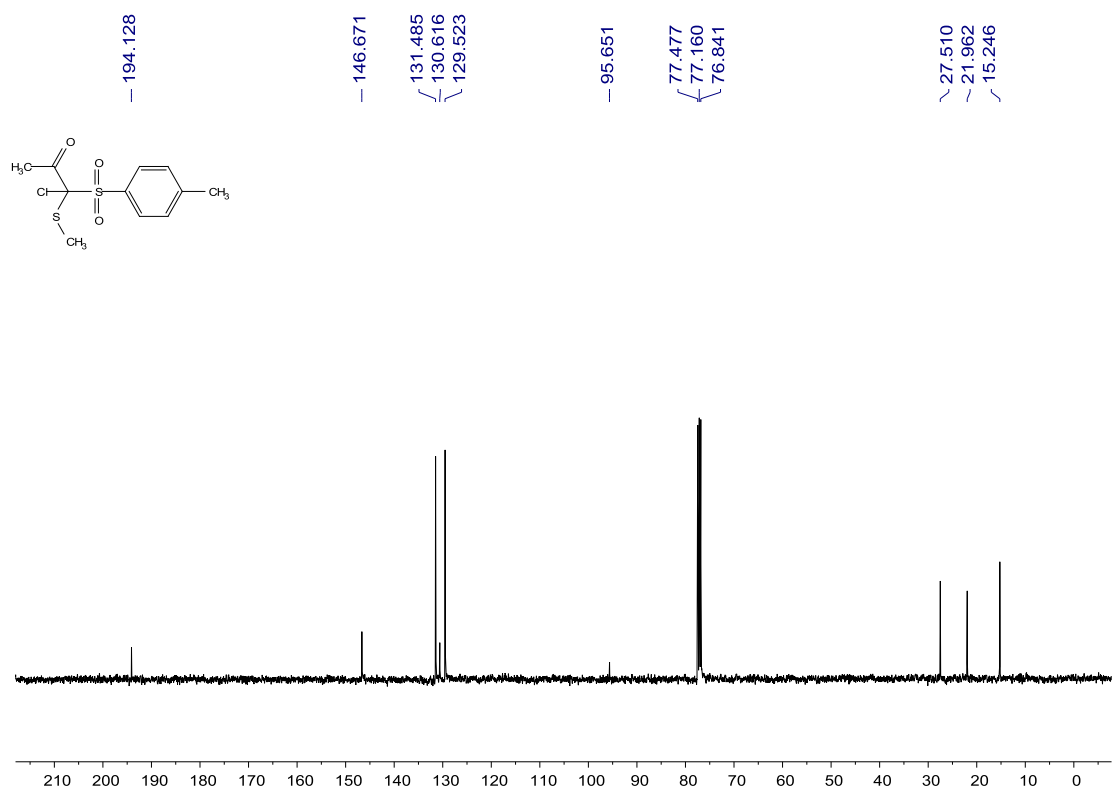
2-Chloro-2-(methylthio)-2-tosylacetaldehyde (**2o**)



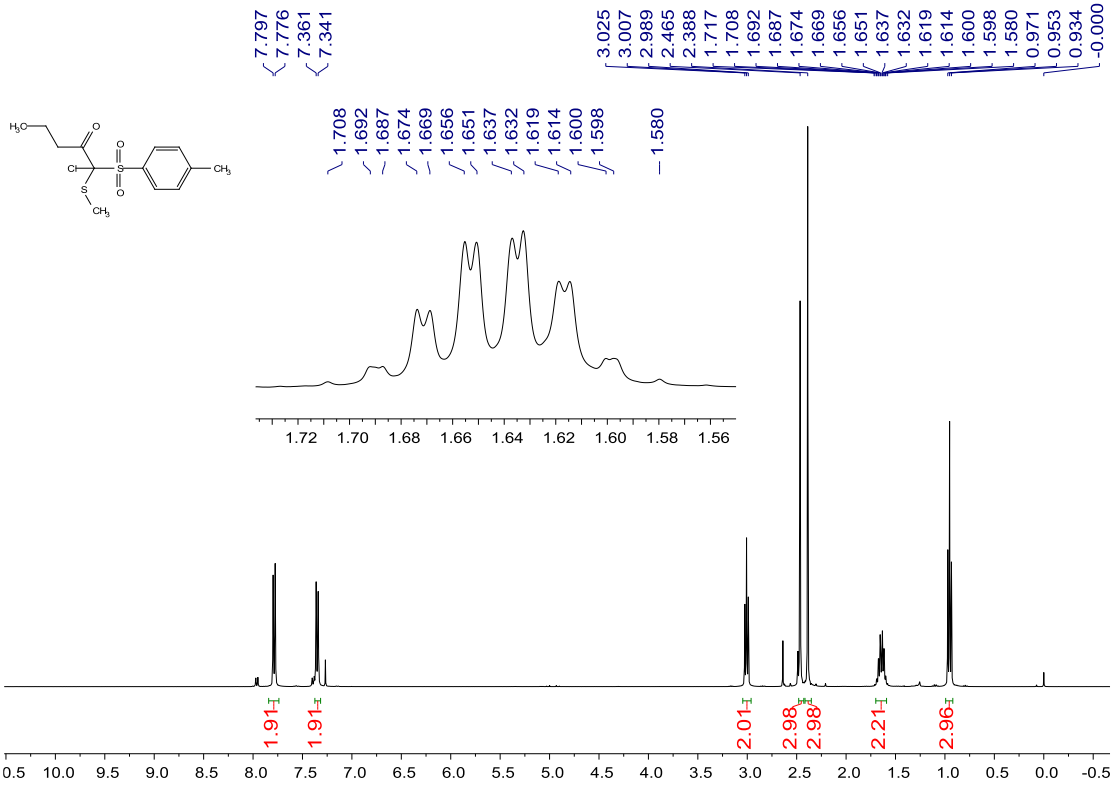



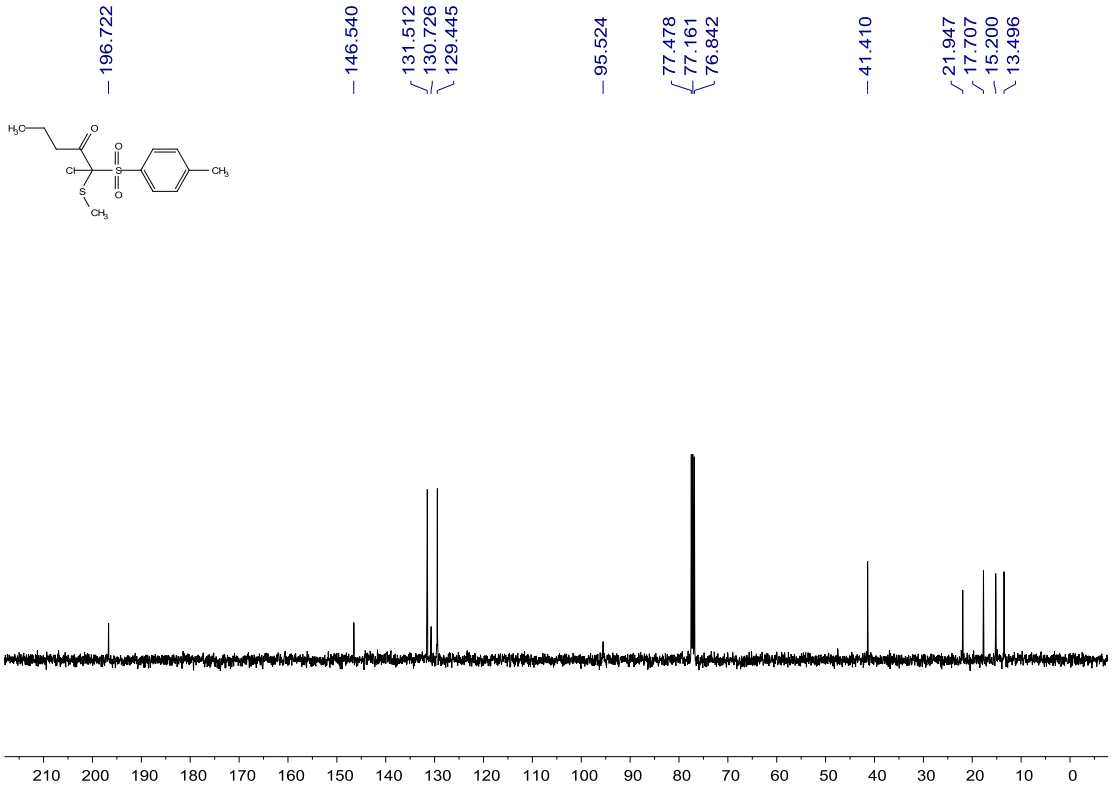
1-Chloro-1-(methylthio)-1-tosylpropan-2-one (**2p**)



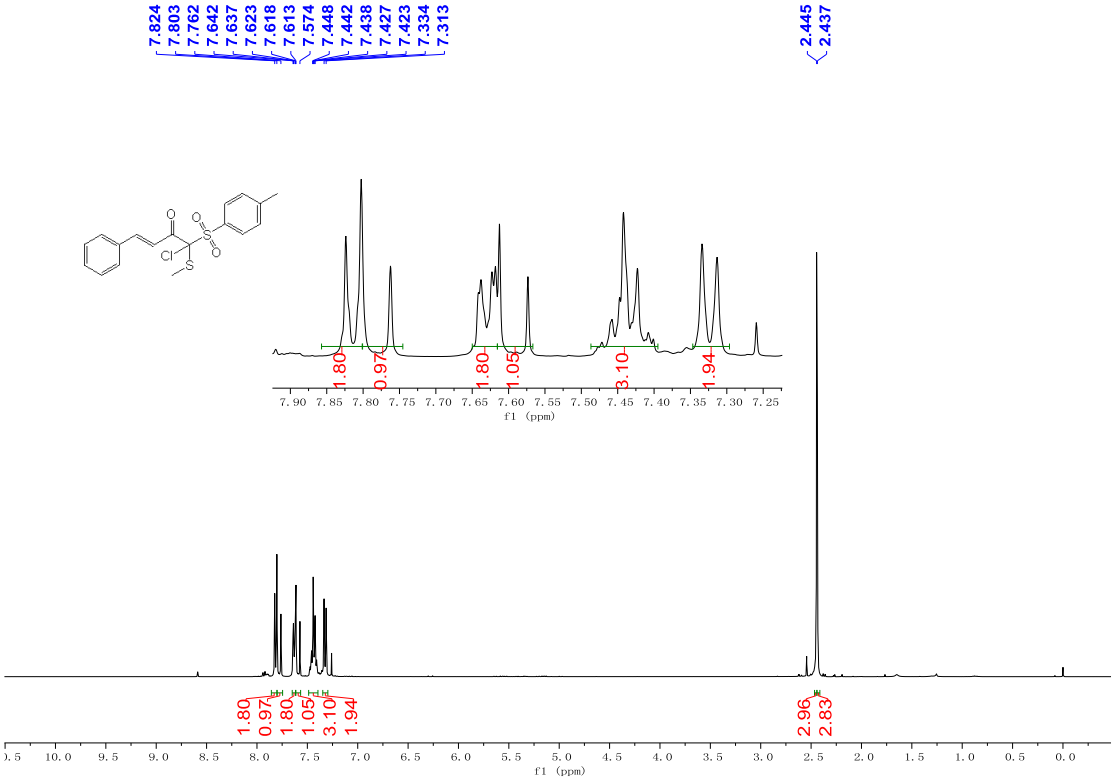



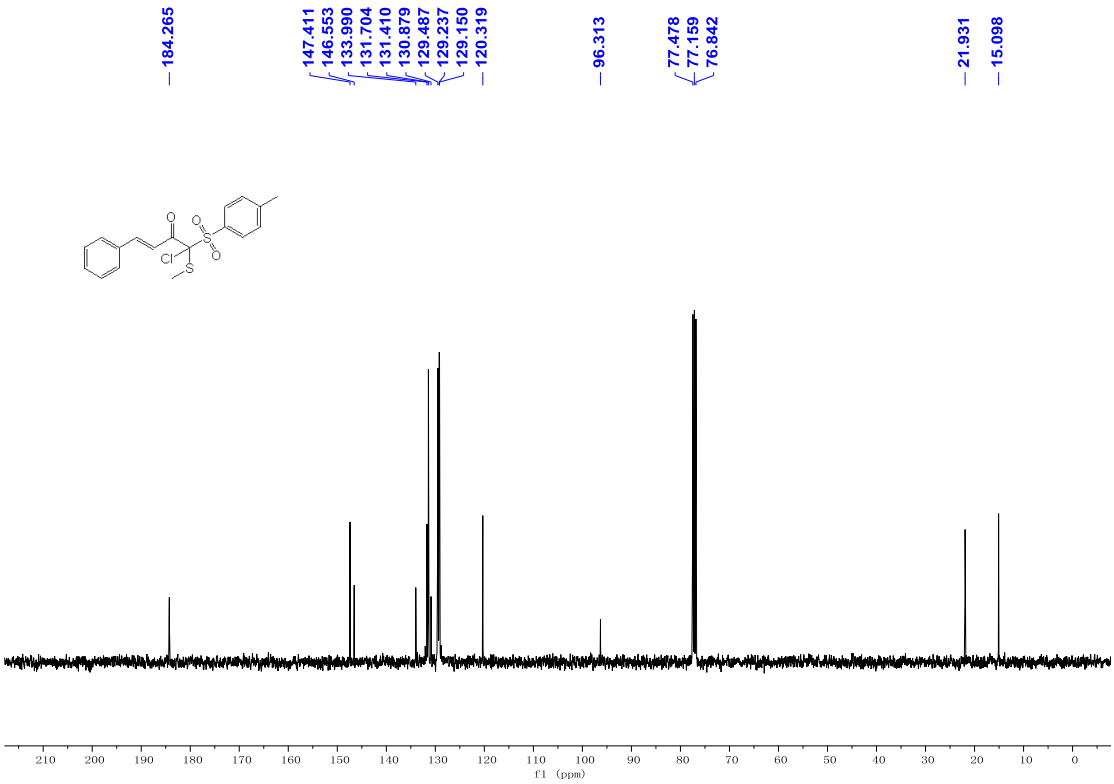
1-Chloro-1-(methylthio)-1-tosylpentan-2-one (**2q**)



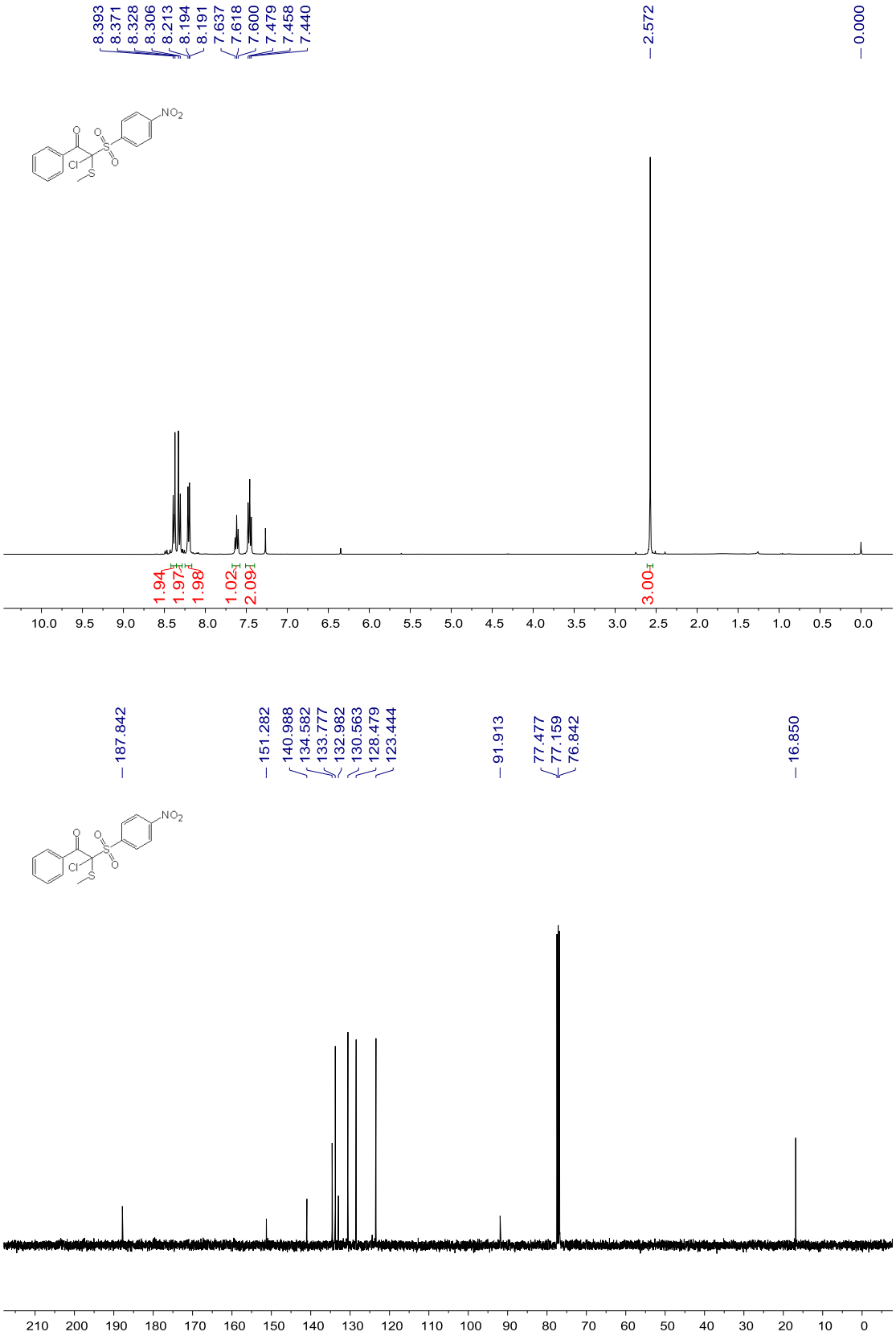



(*E*)-1-Chloro-1-(methylthio)-4-phenyl-1-tosylbut-3-en-2-one (**2r**)

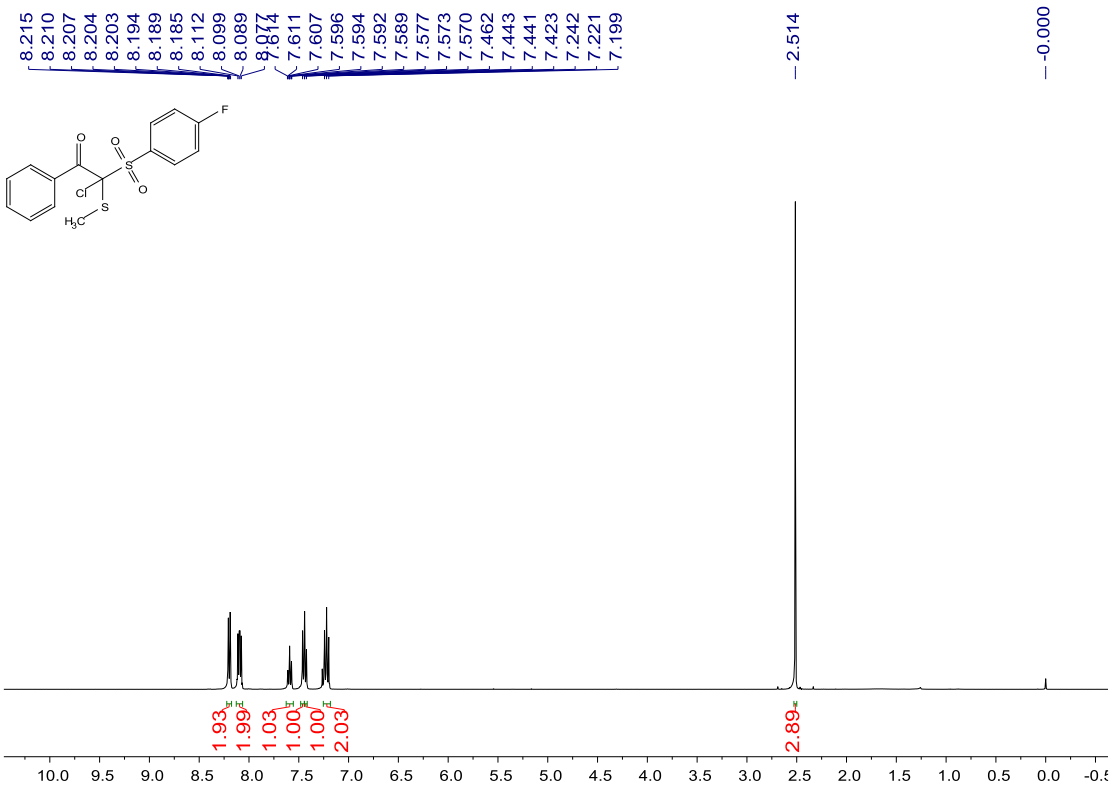


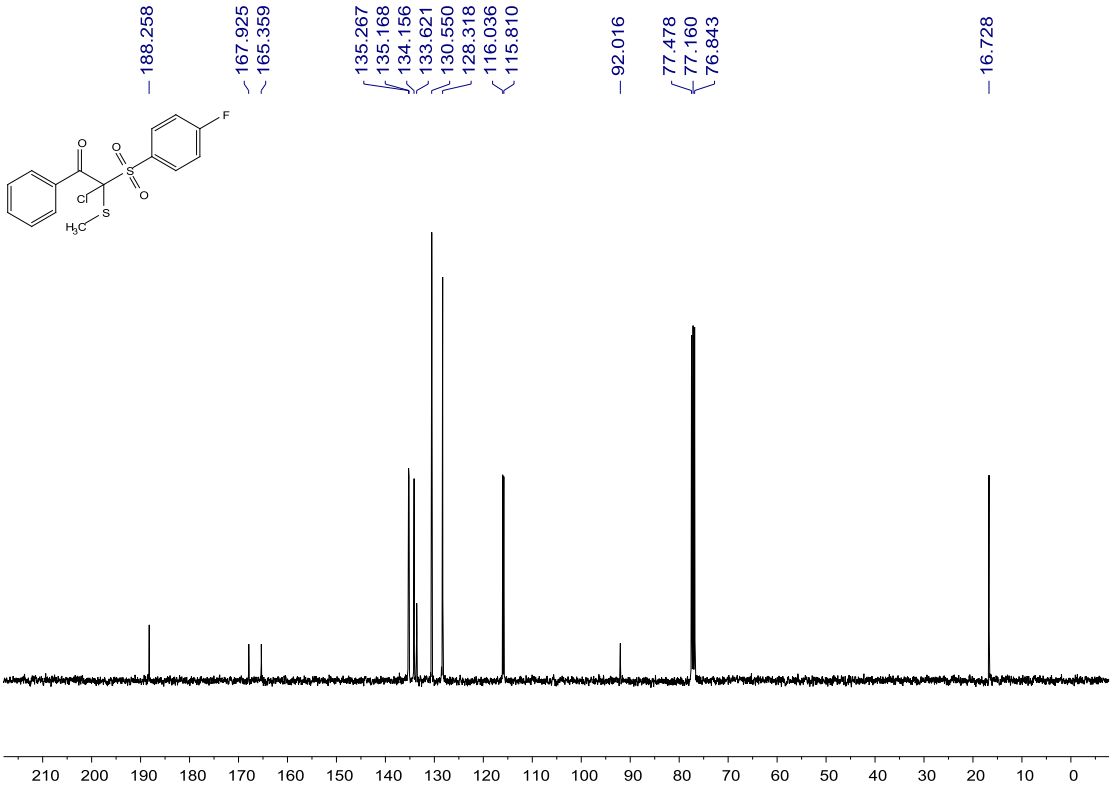



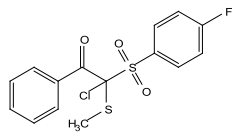
2-Chloro-2-(methylthio)-2-((4-nitrophenyl)sulfonyl)-1-phenylethan-1-one (**2s**)



2-Chloro-2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2t**)

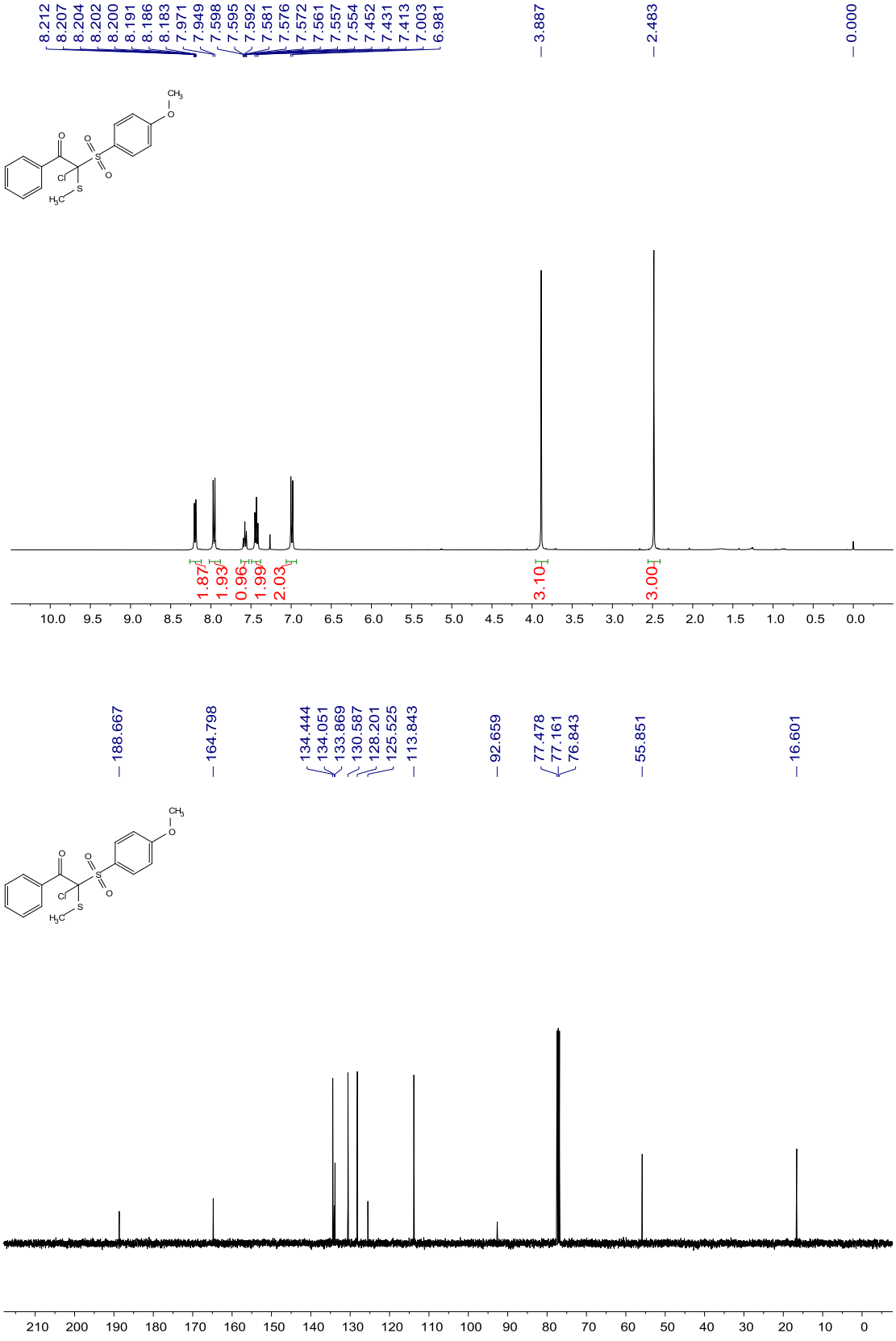


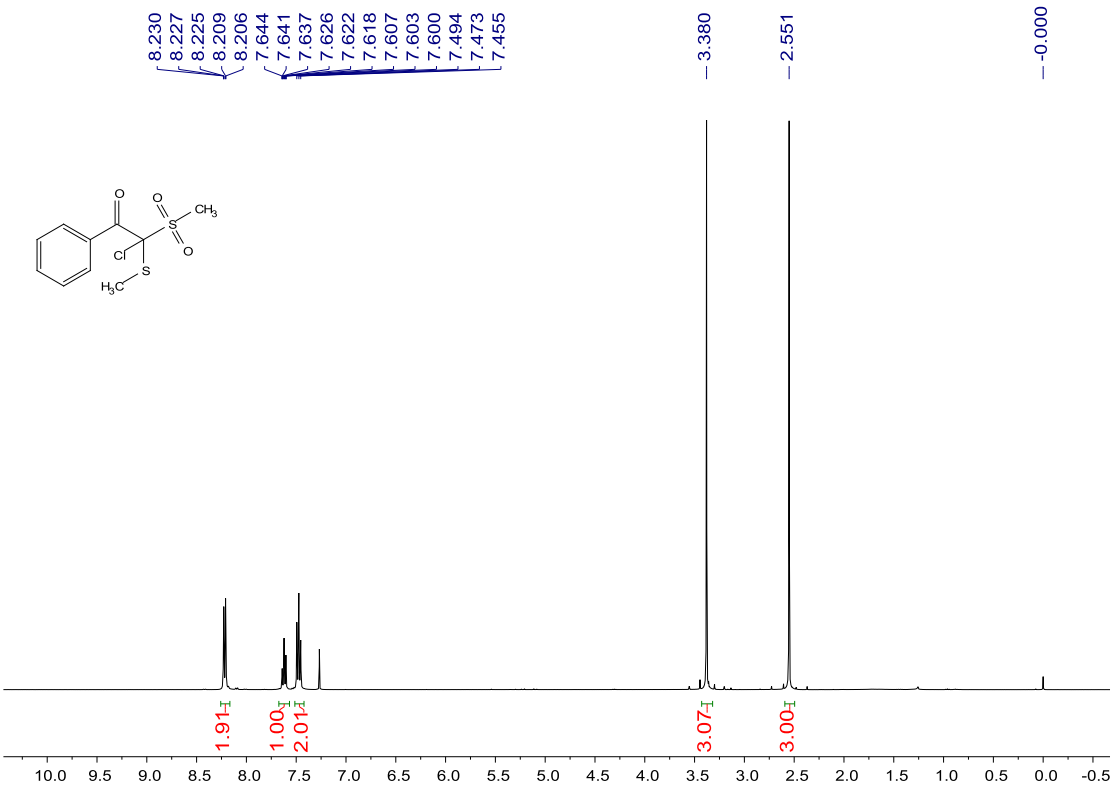

O
O
S
O
Cl
S
H3C
F

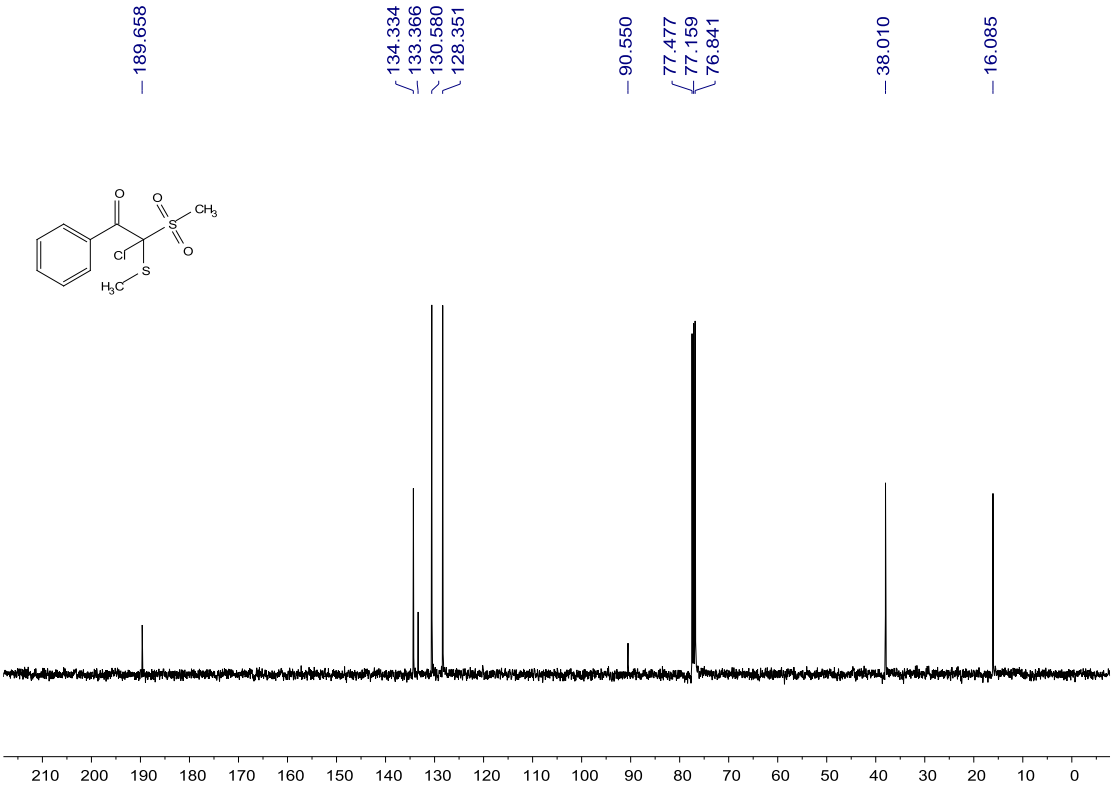

-101.582
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

2-Chloro-2-((4-methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2u**)

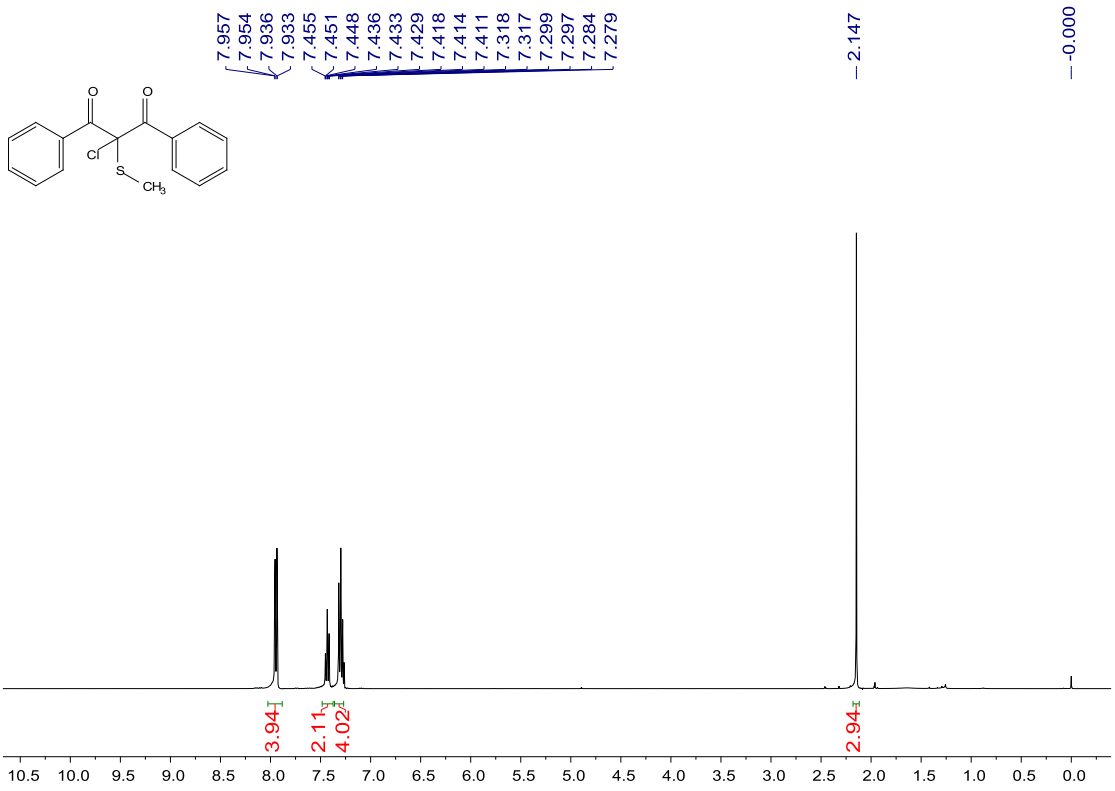


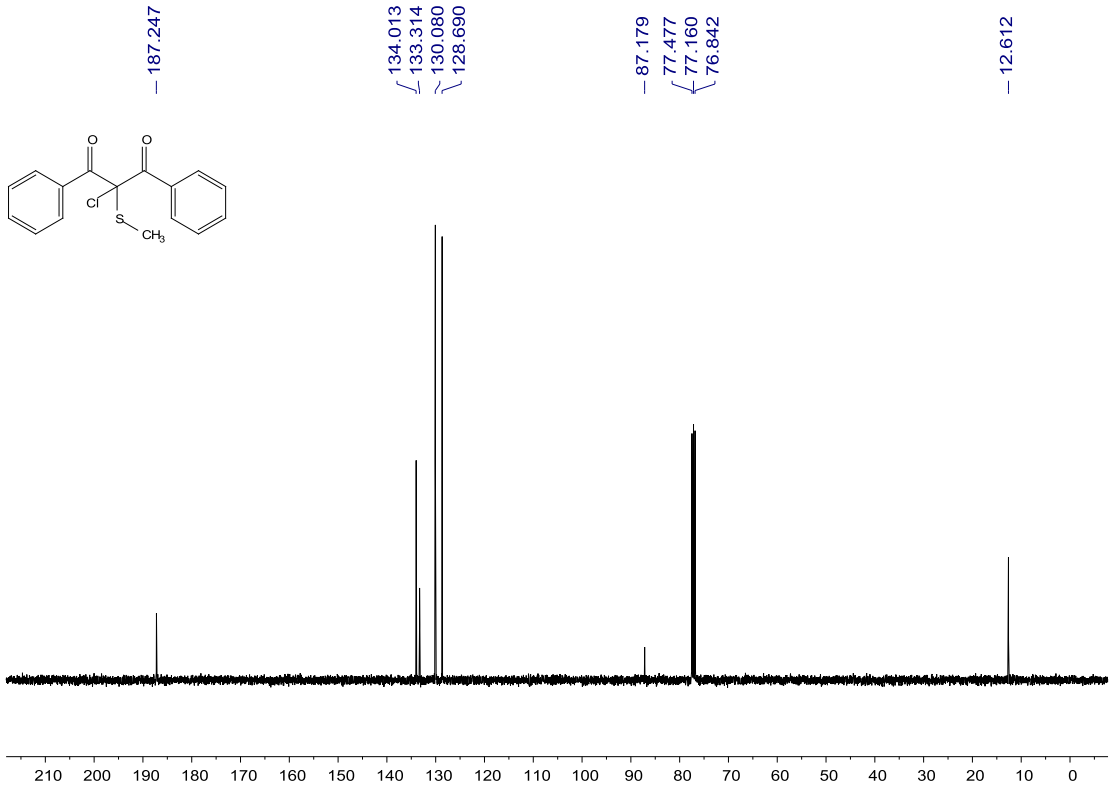
2-Chloro-2-(methylsulfonyl)-2-(methylthio)-1-phenylethan-1-one (**2v**)



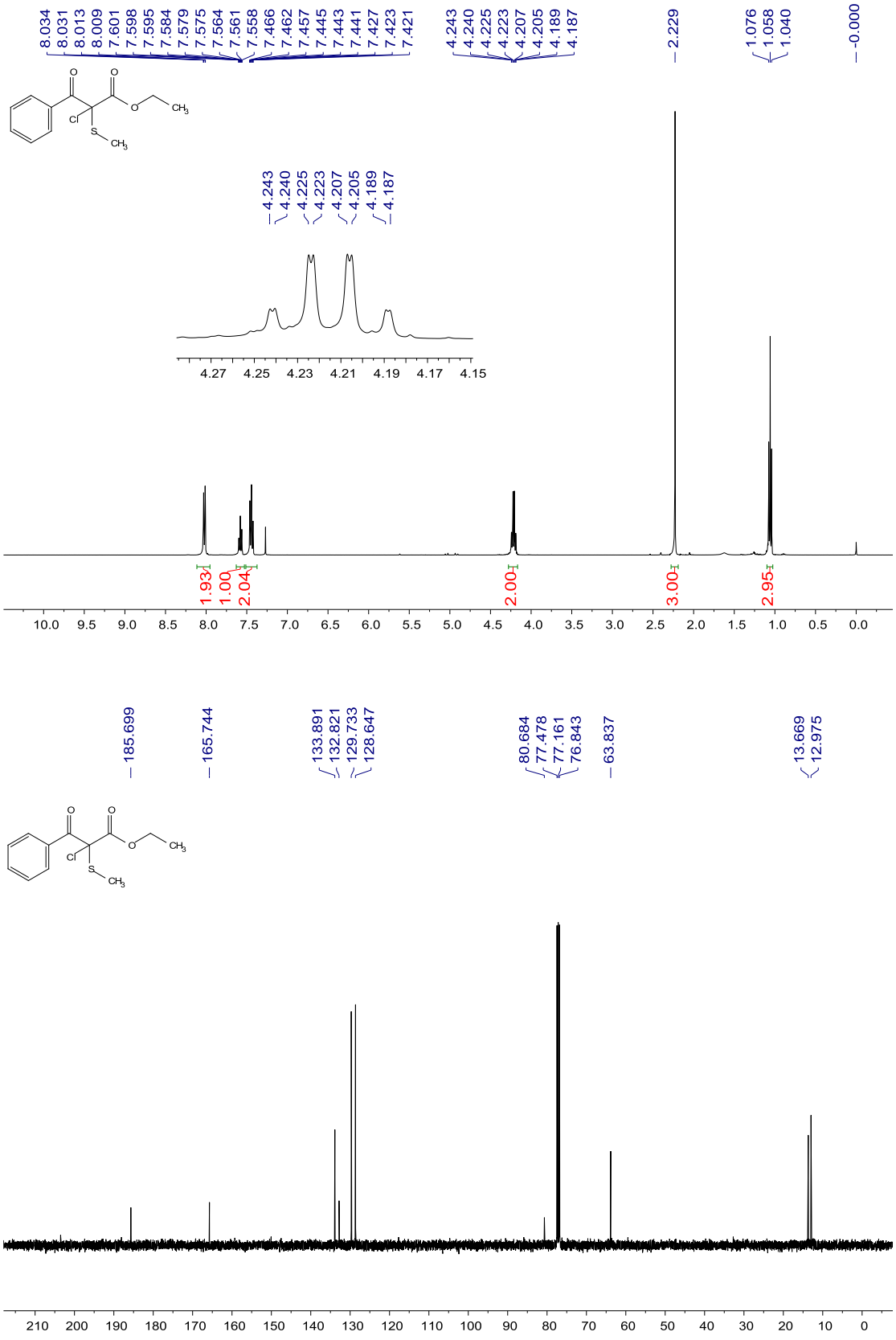



2-Chloro-2-(methylthio)-1,3-diphenylpropane-1,3-dione (**2w**)

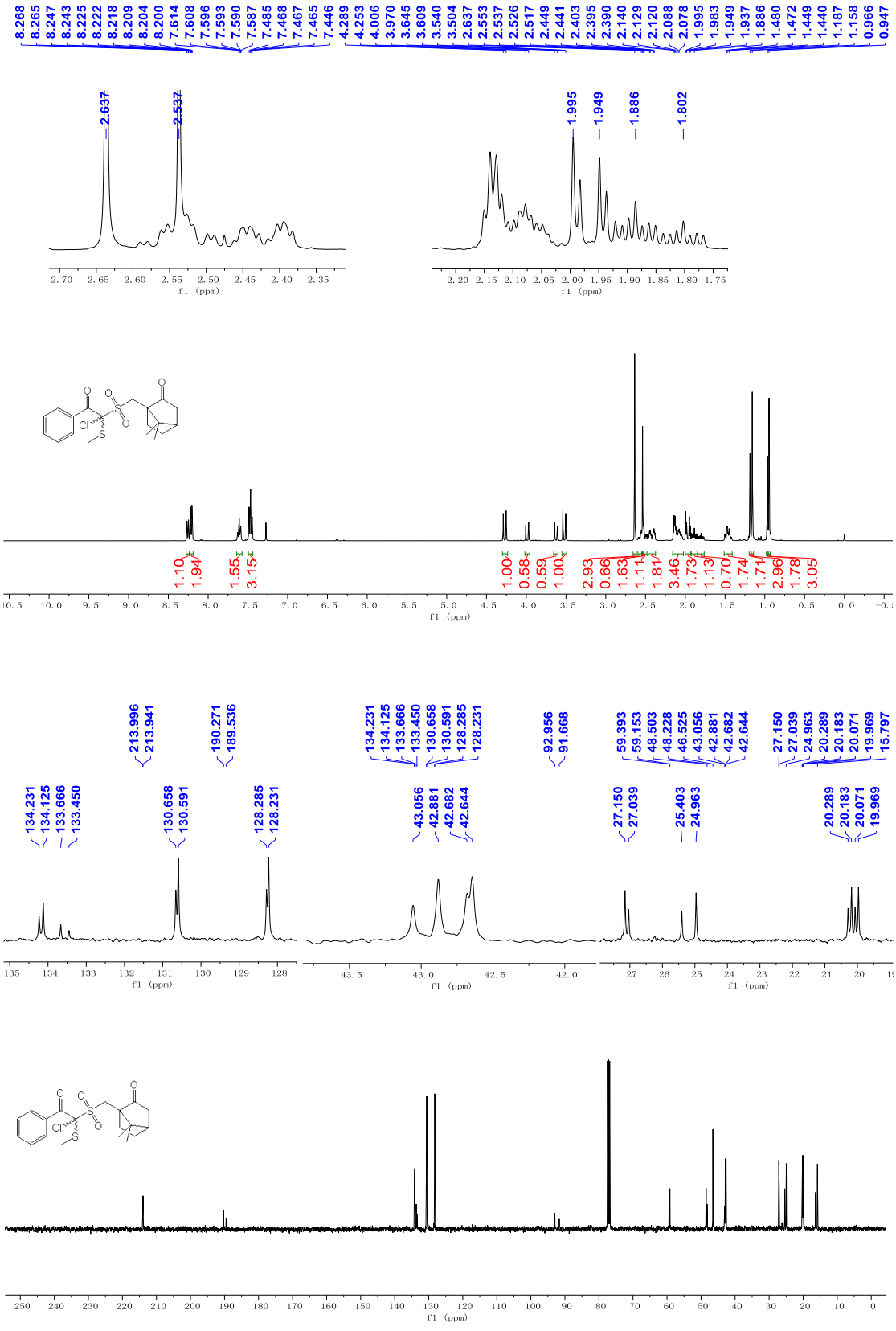


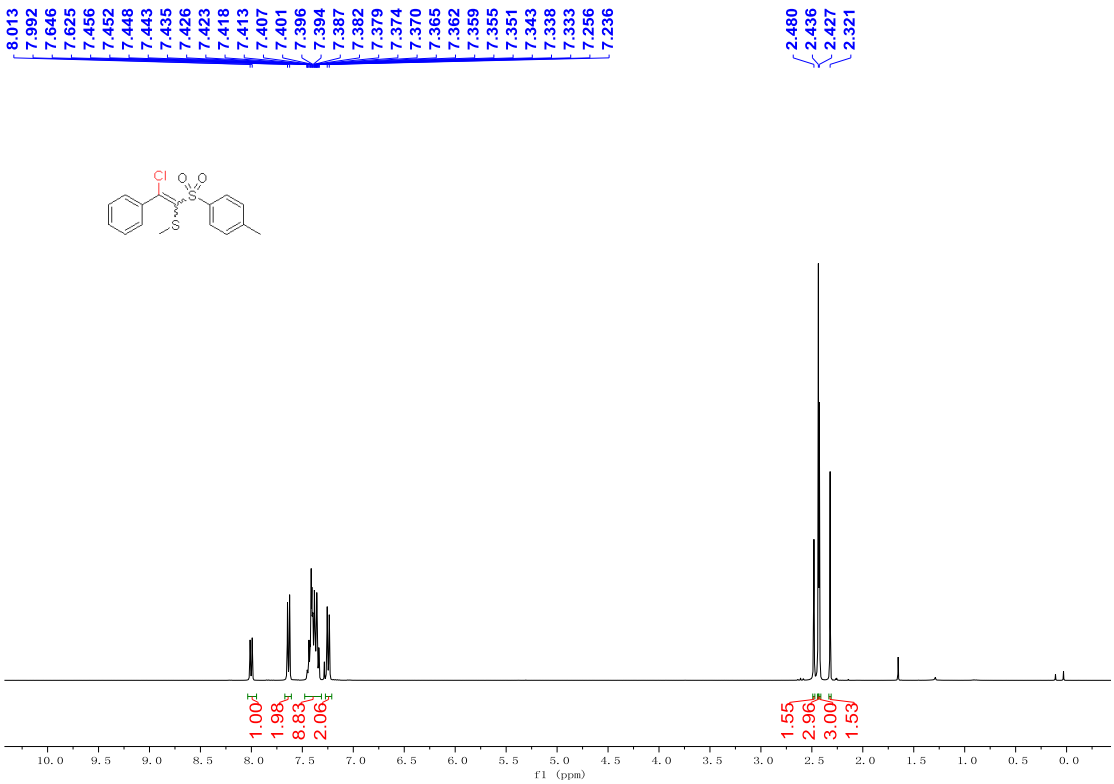
Ethyl 2-chloro-2-(methylthio)-3-oxo-3-phenylpropanoate (**2x**)

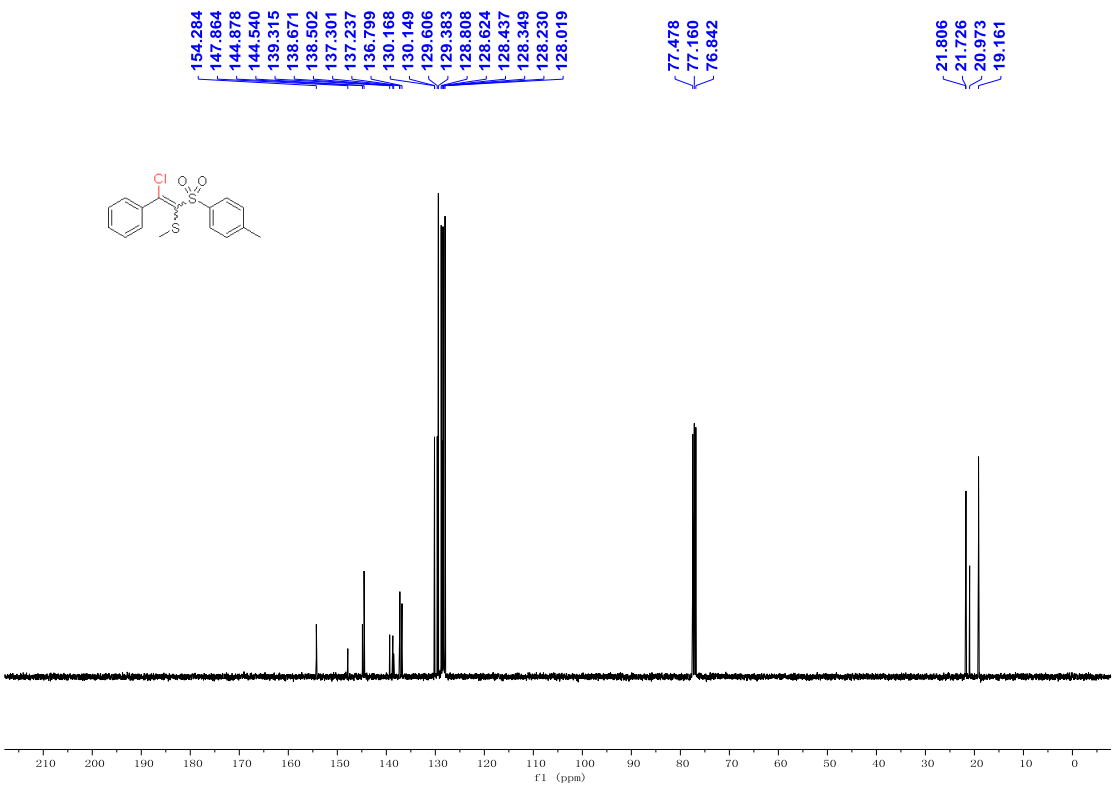


1-(((1-Chloro-1-(methylthio)-2-oxo-2-phenylethyl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (**2y**+**2y'**)



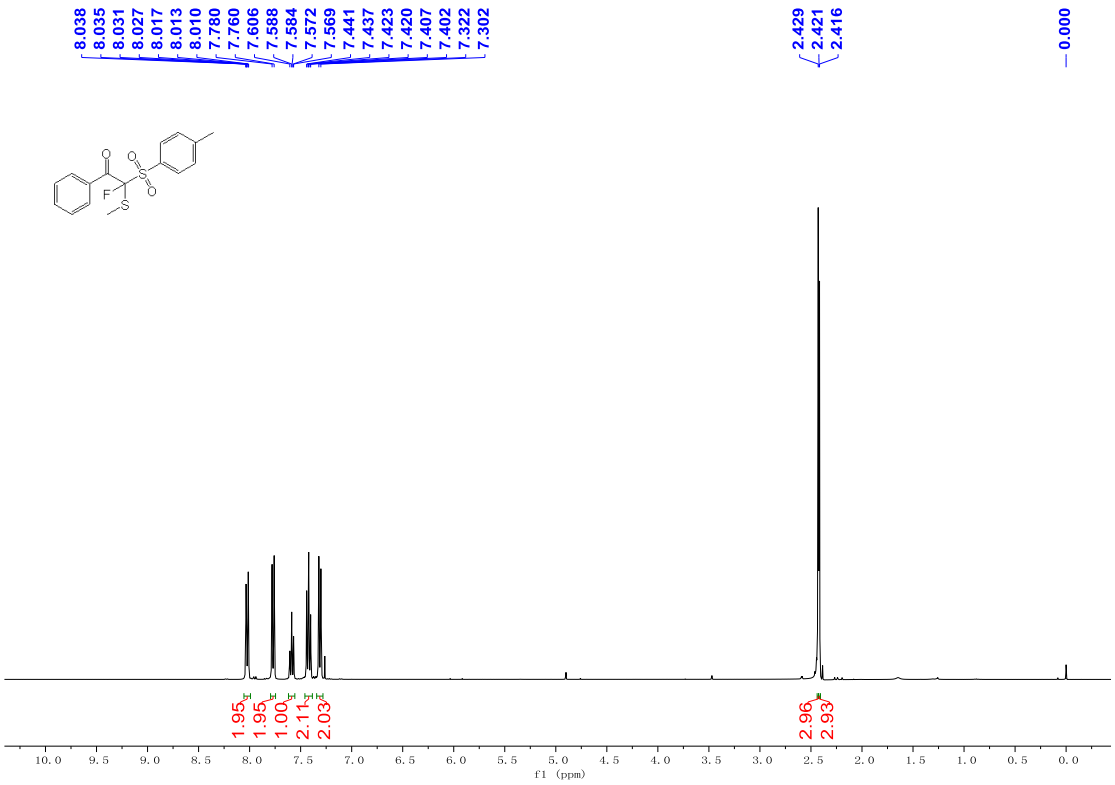
## 2.4 Copies of NMR spectra for product 3

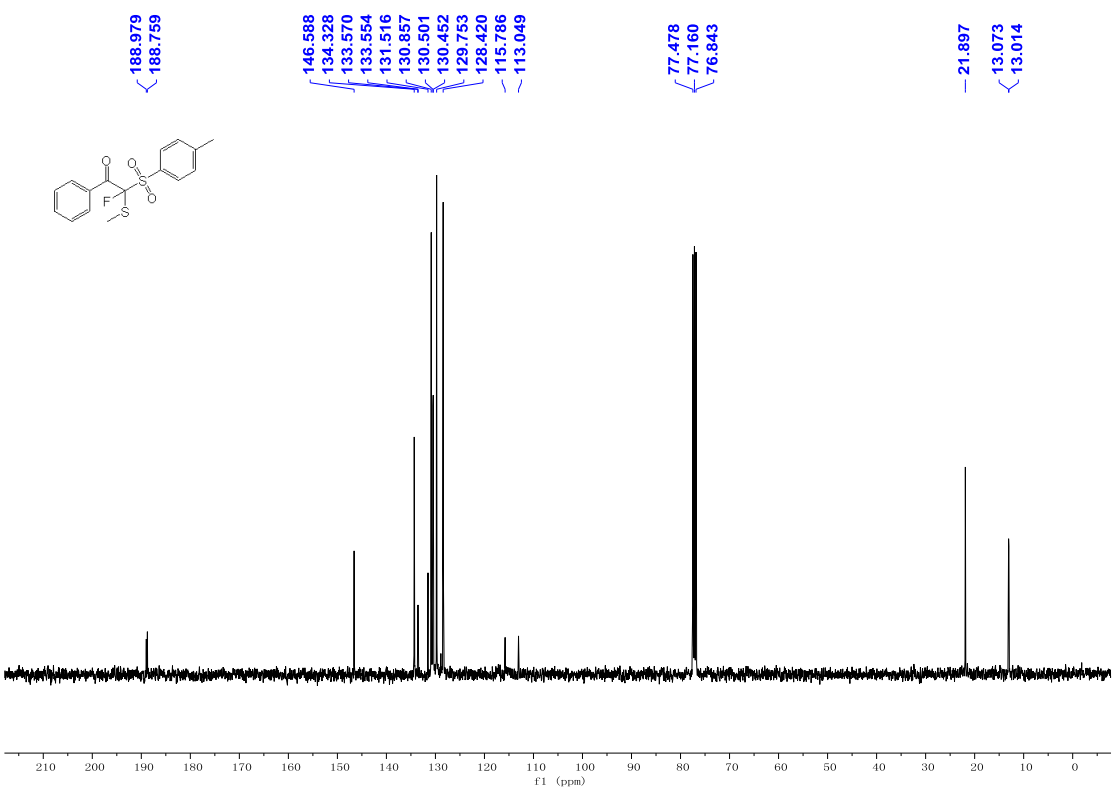


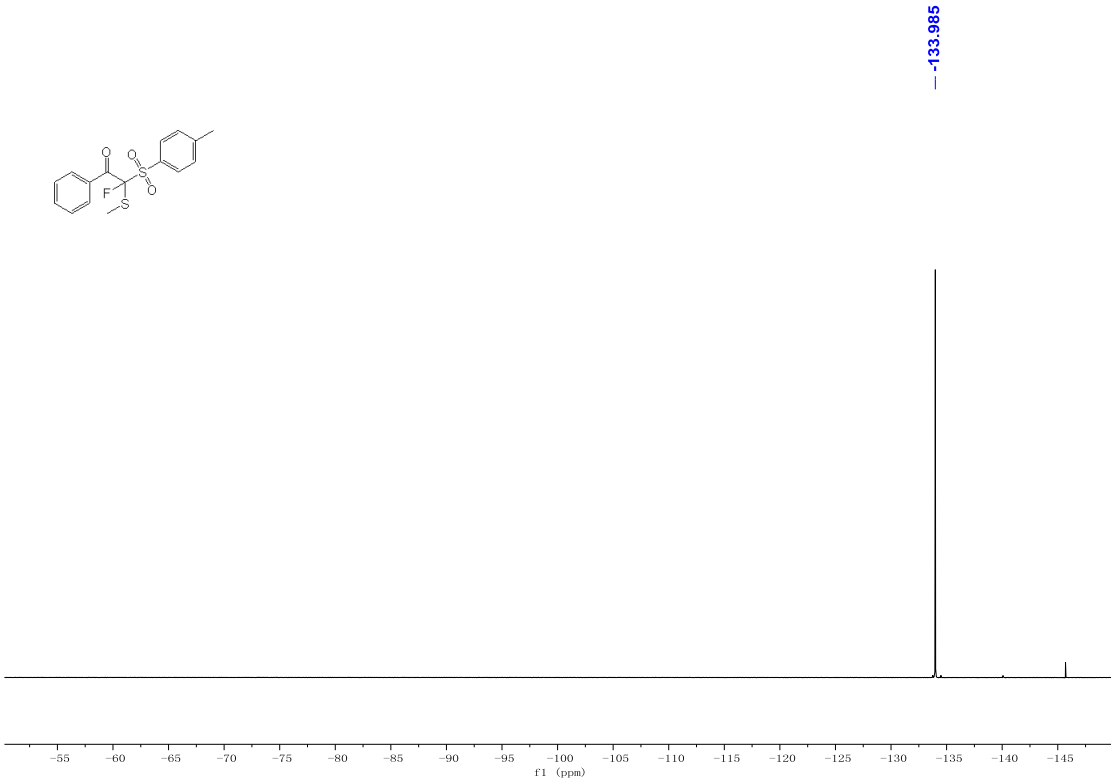



## 2.5 Copies of NMR spectra for products 5

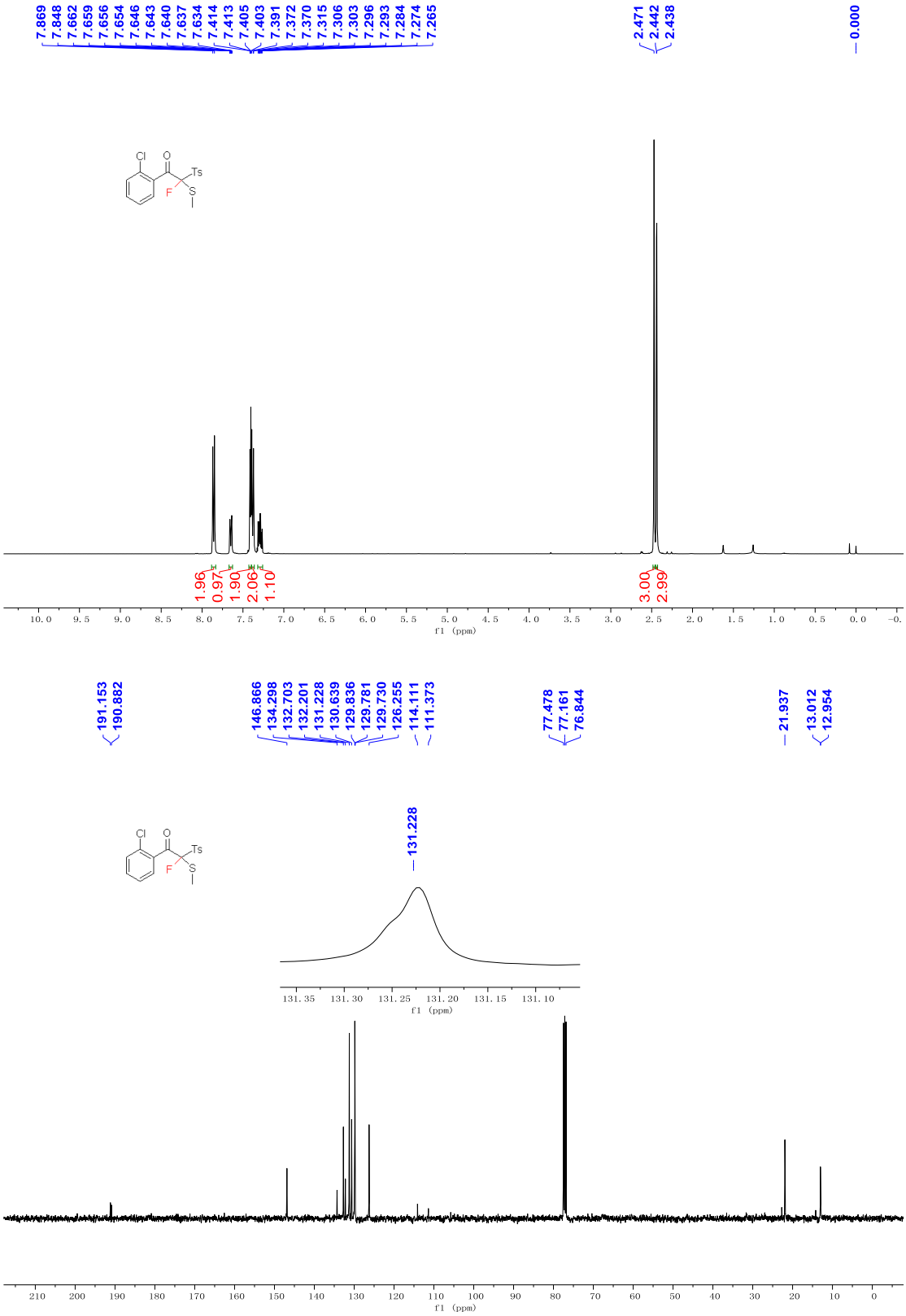
2-Fluoro-2-(methylthio)-1-phenyl-2-tosylethan-1-one (**5a**)

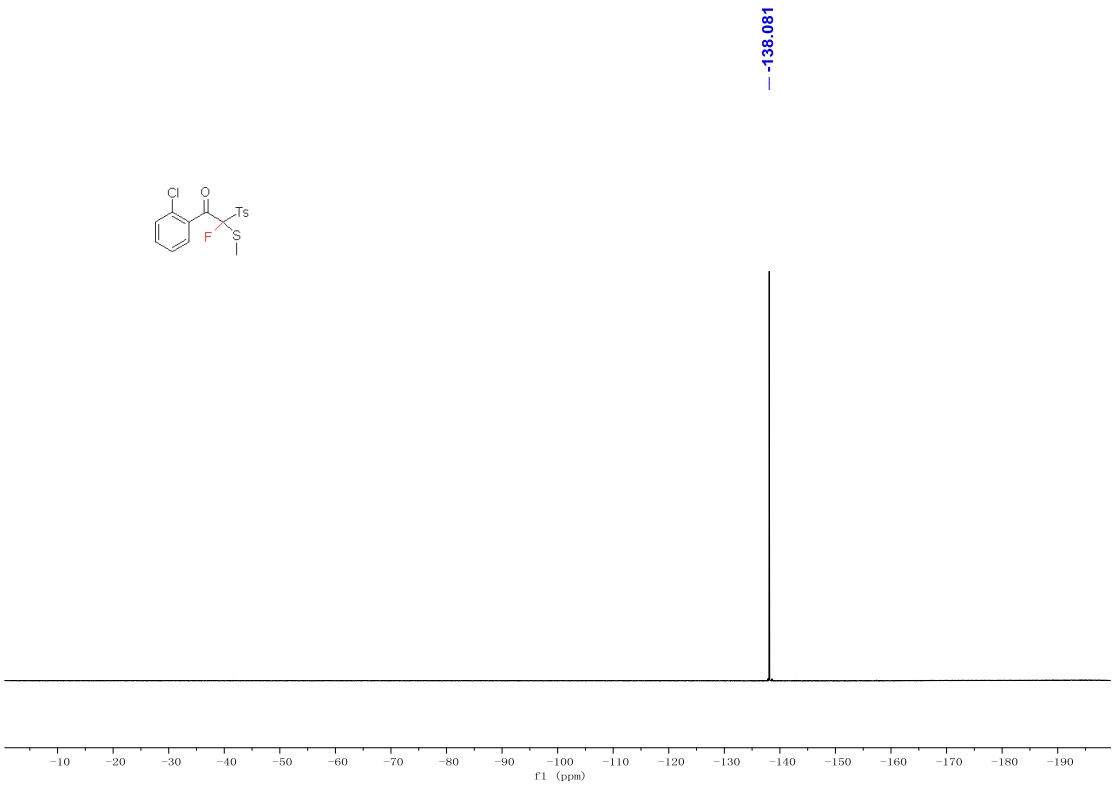


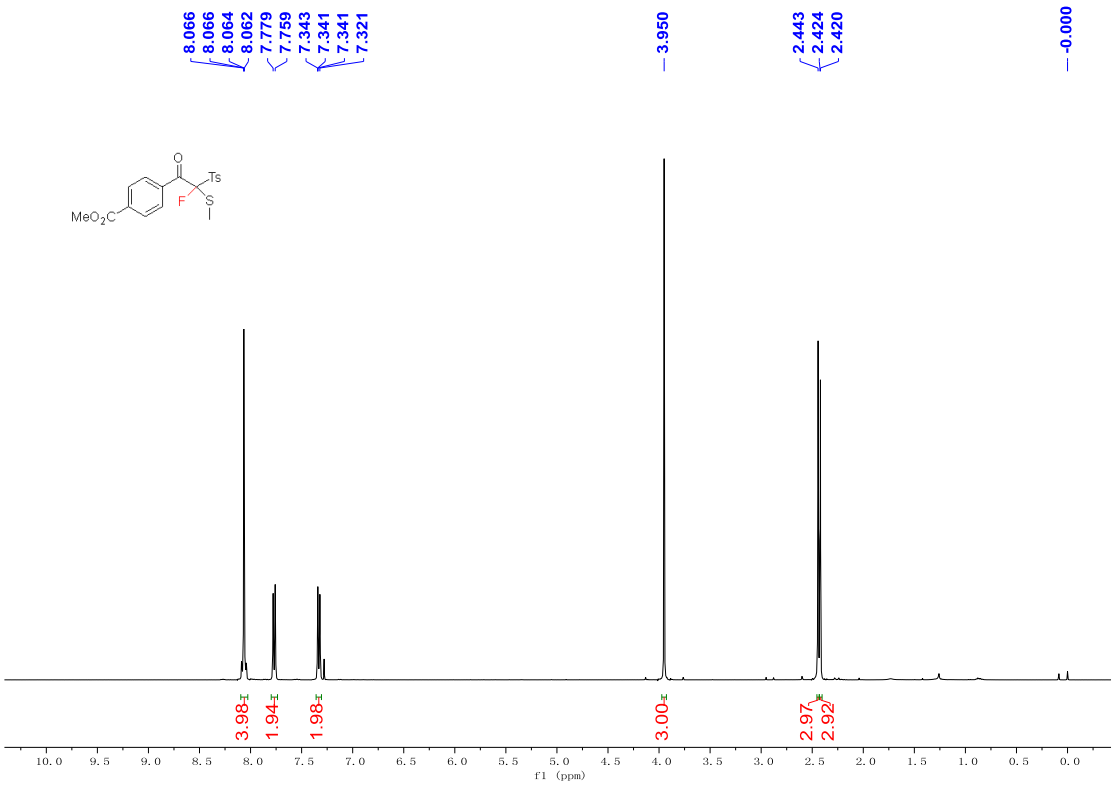

-133.985
O
O
S
O
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

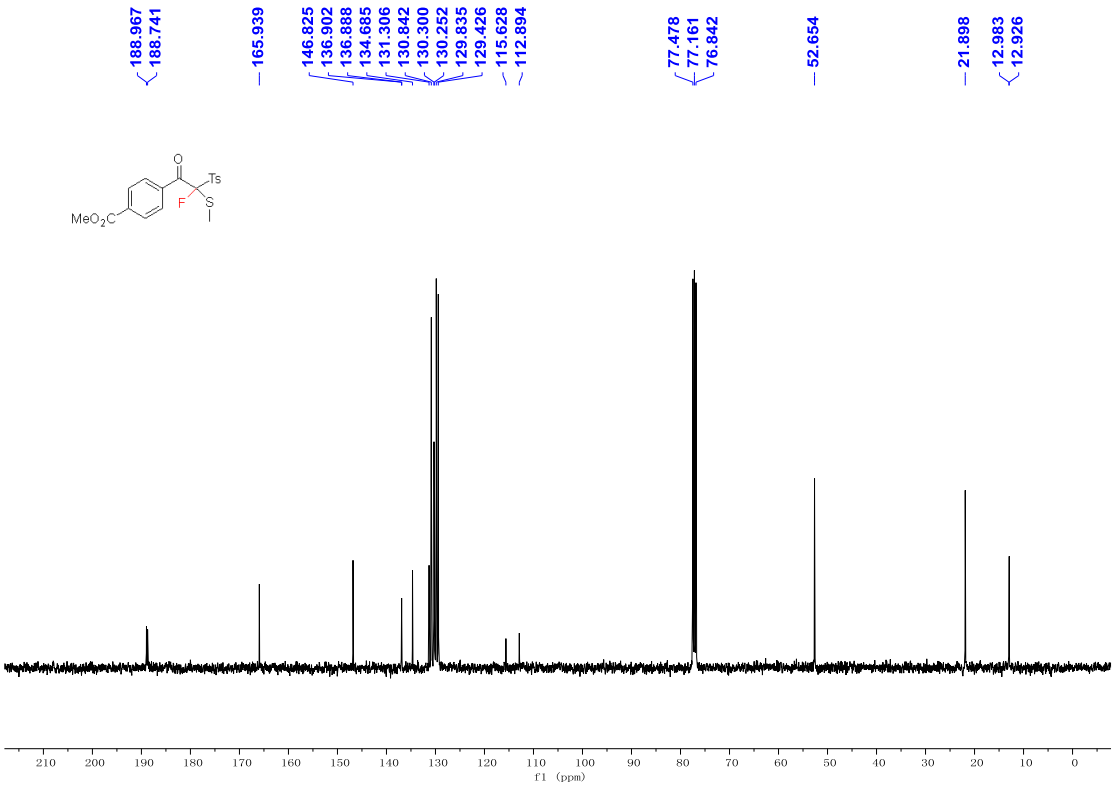
1-(2-Chlorophenyl)-2-fluoro-2-(methylthio)-2-tosylethan-1-one (**5f**)

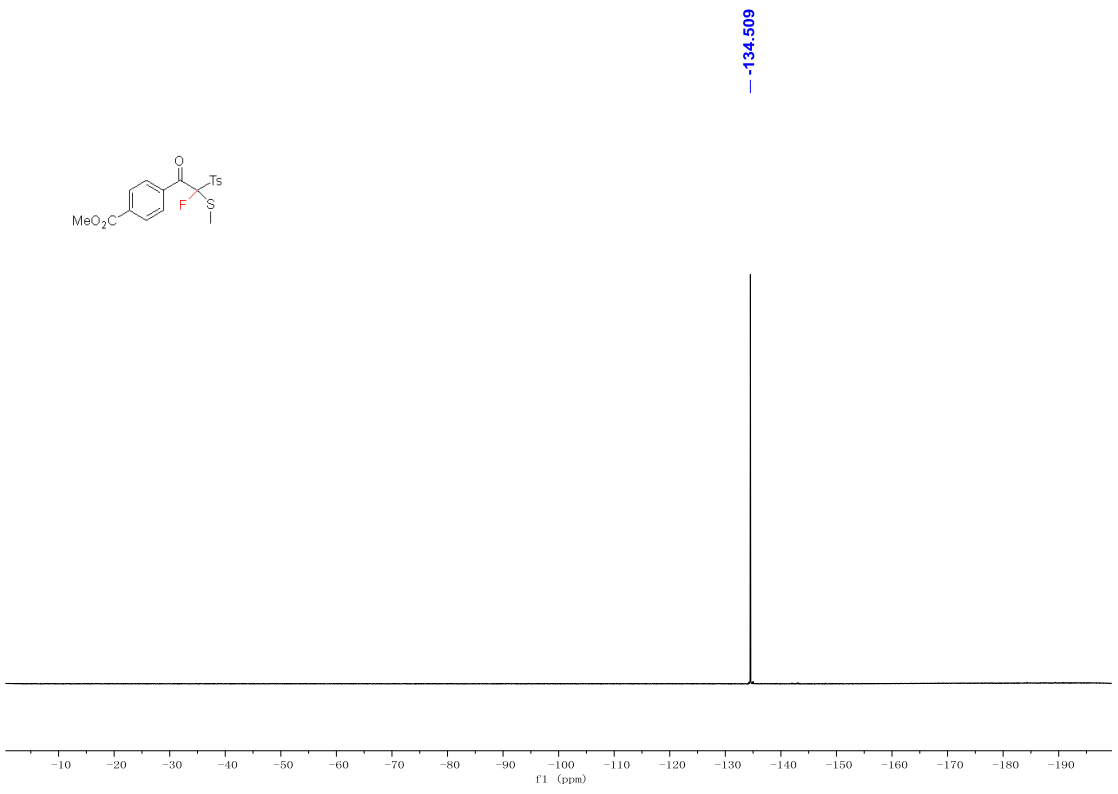



-138.081
Cl
O
Ts
F
S
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

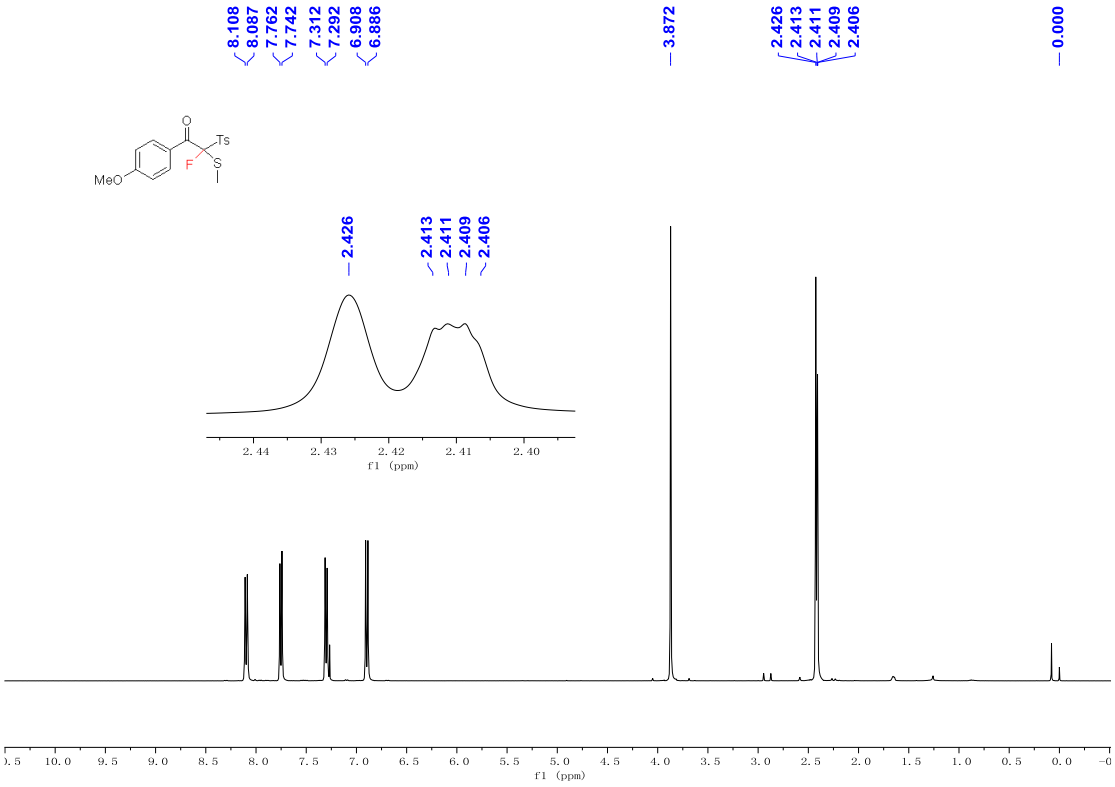
Methyl 4-(2-fluoro-2-(methylthio)-2-tosylacetyl)benzoate (**5i**)

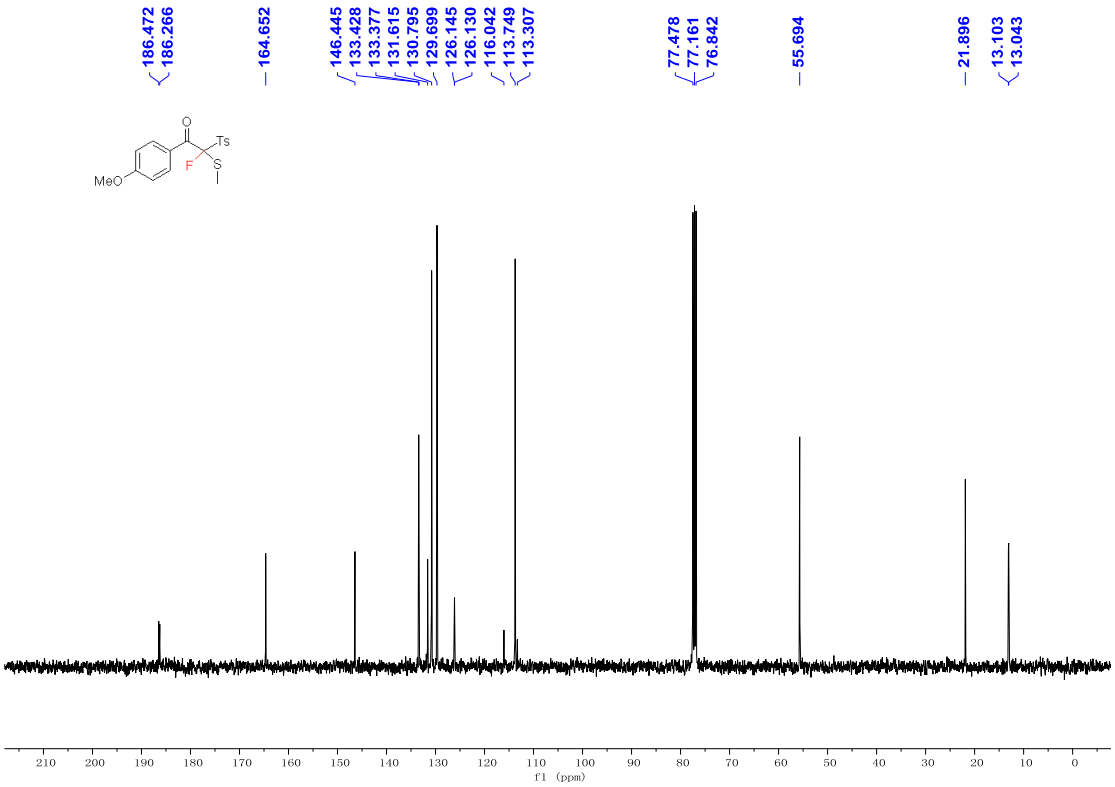


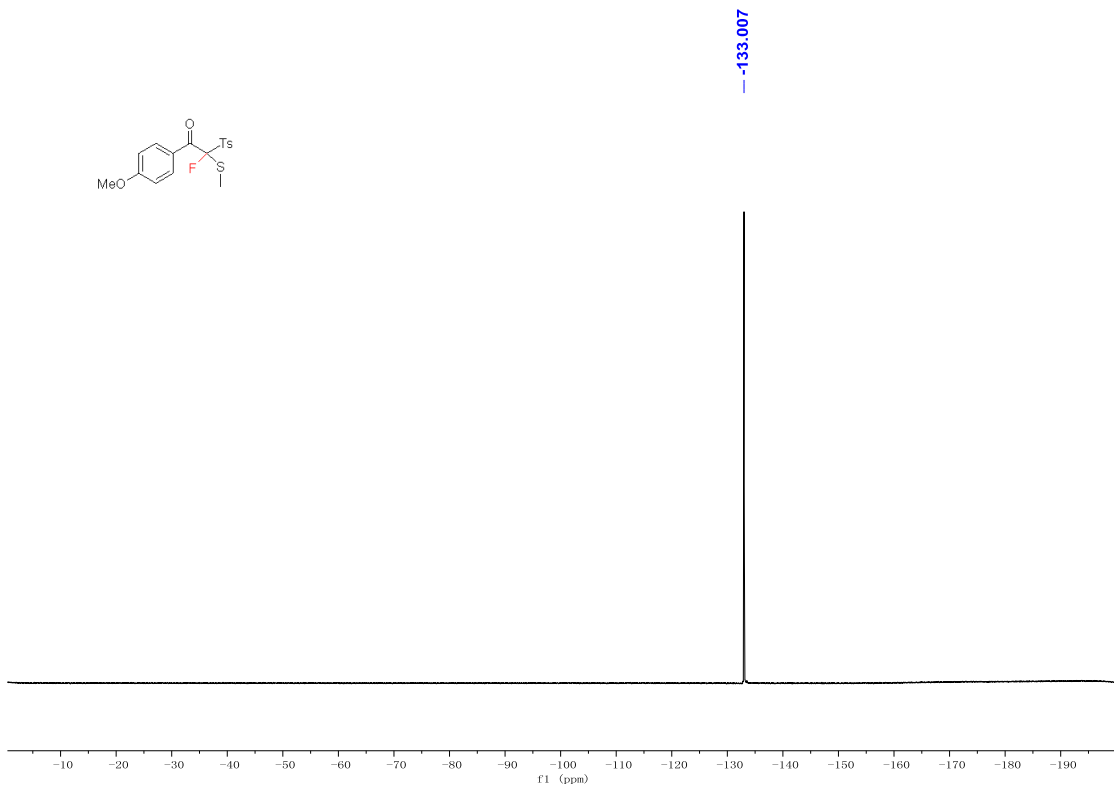




-134.509
O
Ts
F
S
MeO2C
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

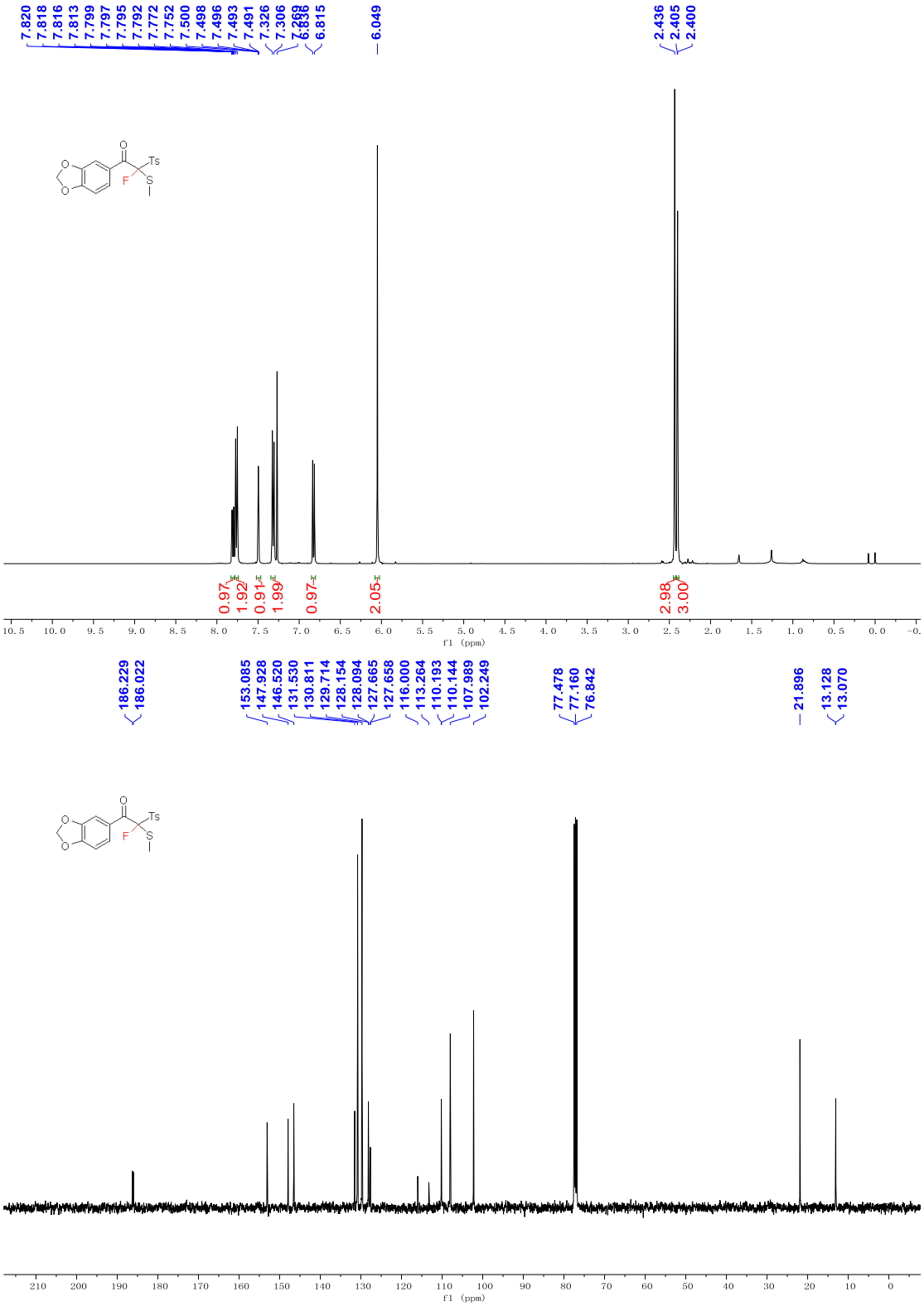
2-Fluoro-1-(4-methoxyphenyl)-2-(methylthio)-2-tosylethan-1-one (**5k**)

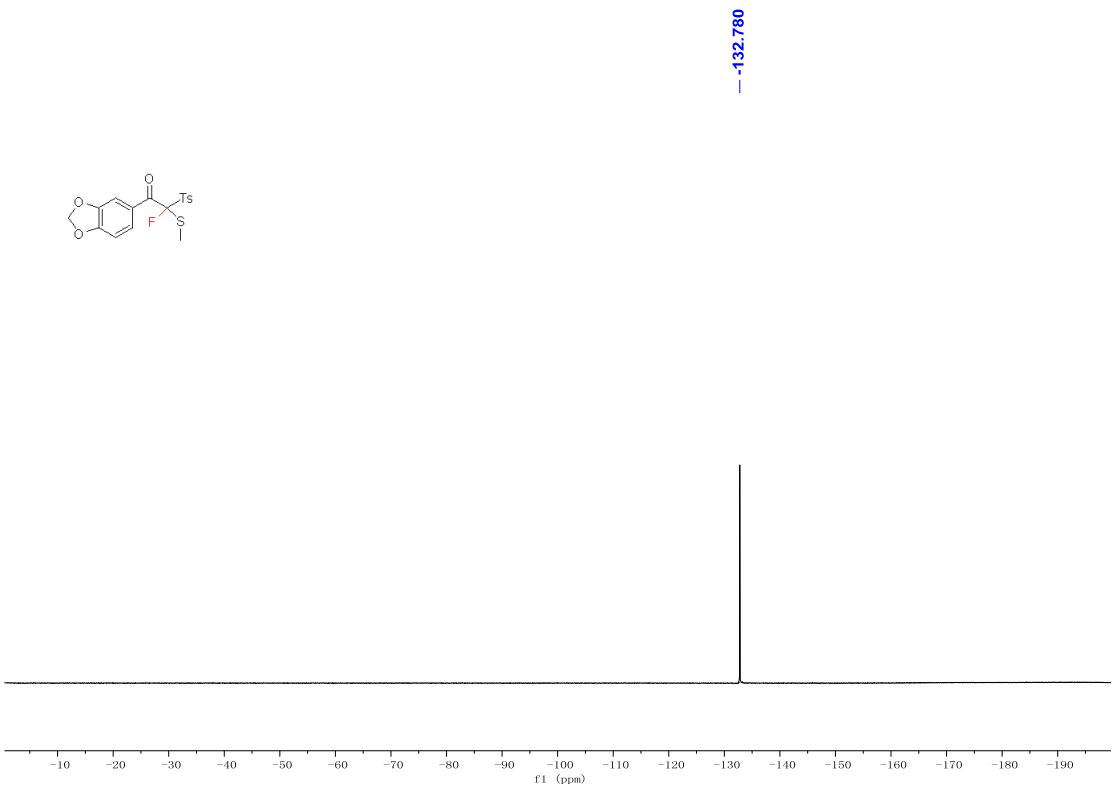


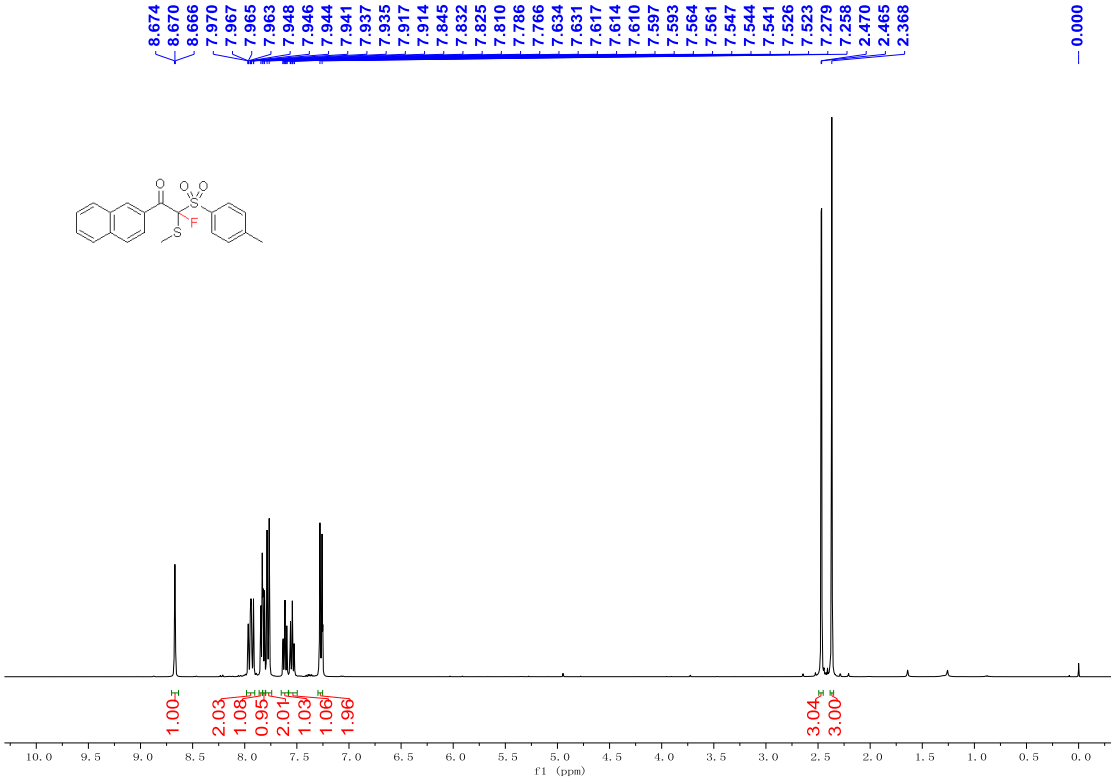

-133.007
O
Ts
F
S
MeO
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

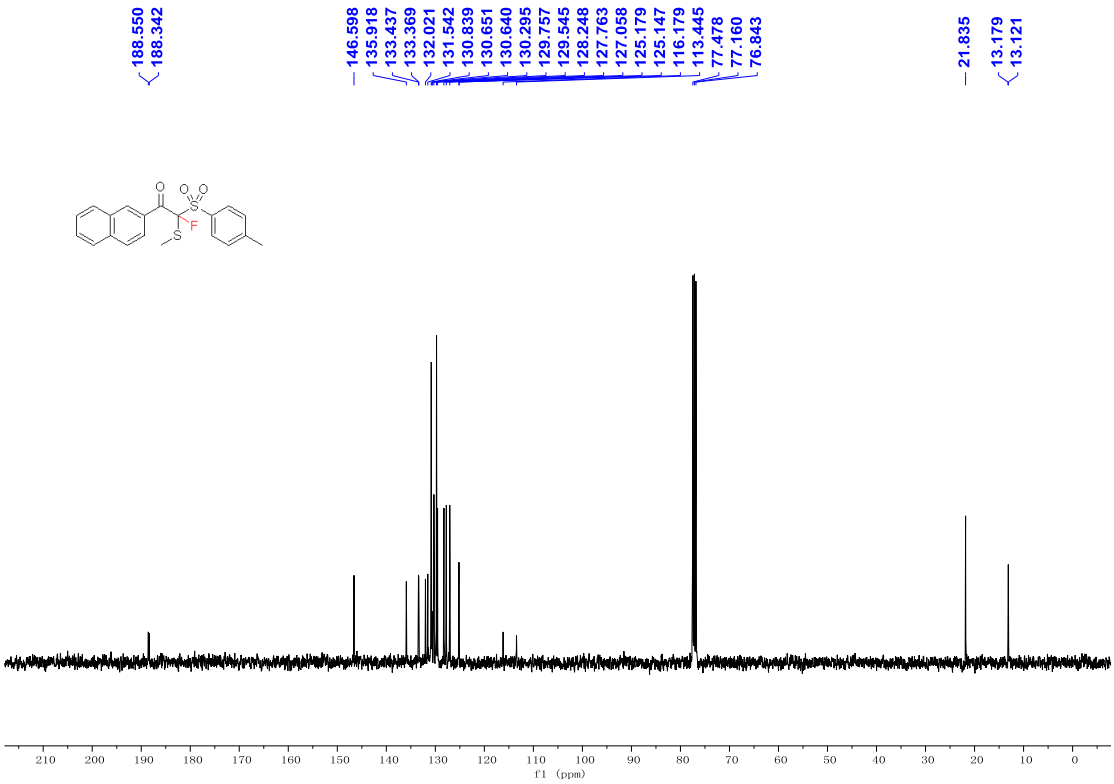
1-(Benzo[*d*][1,3]dioxol-5-yl)-2-fluoro-2-(methylthio)-2-tosylethan-1-one (**5l**)

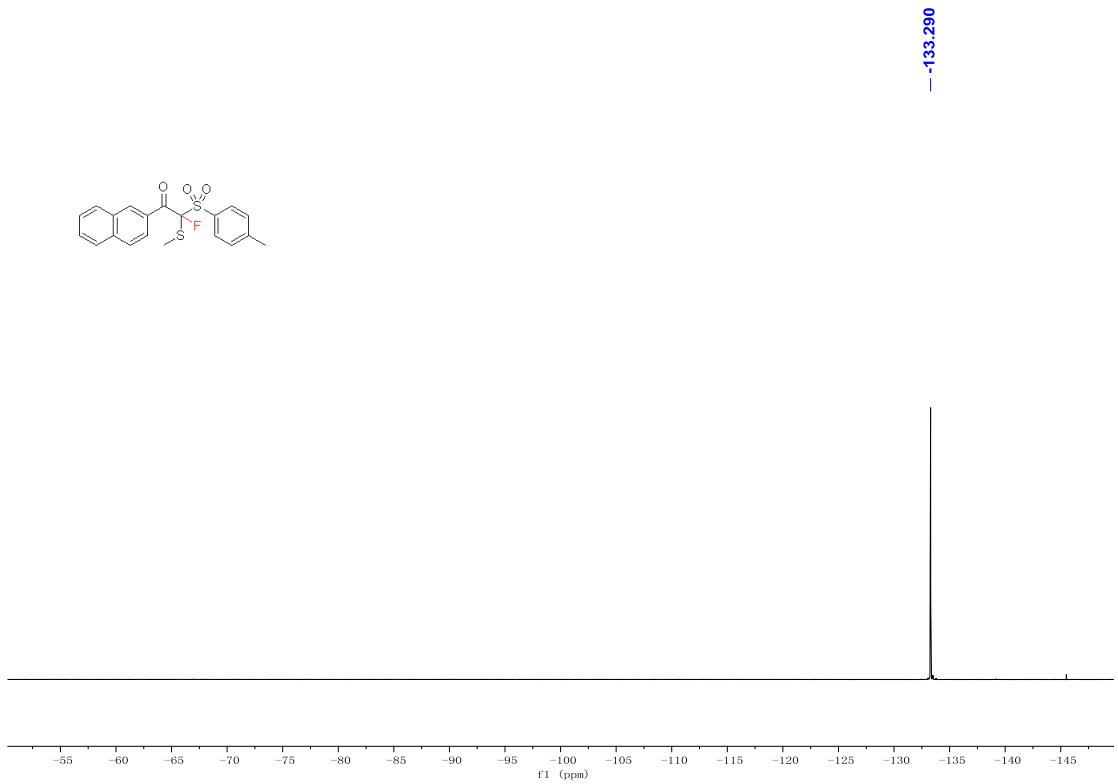



-132.780
O
Ts
F
S
O
O
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

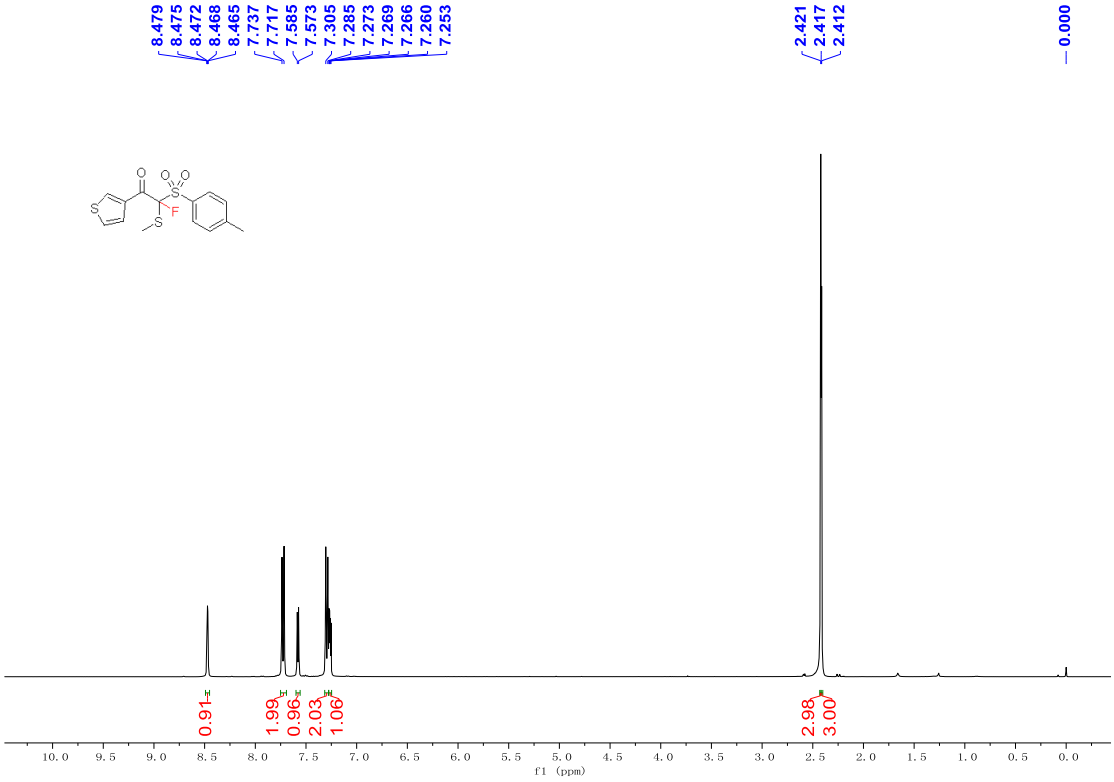
2-Fluoro-2-(methylthio)-1-(naphthalen-2-yl)-2-tosylethan-1-one (**5m**)

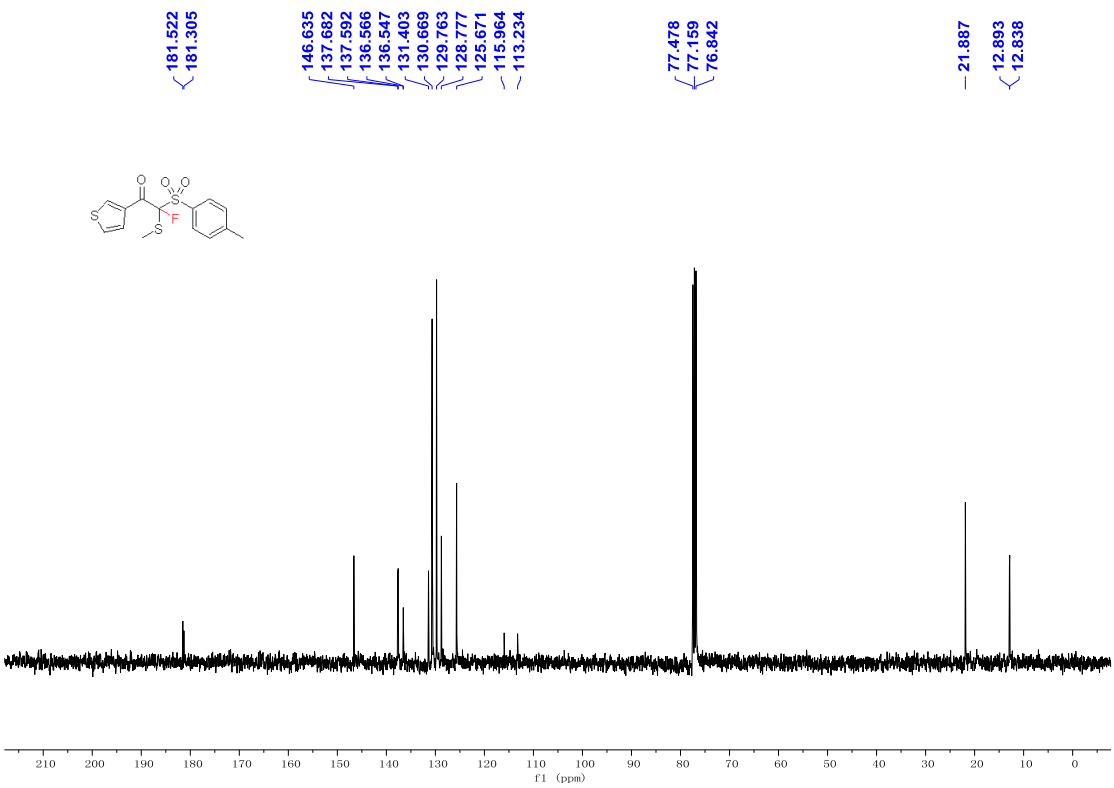


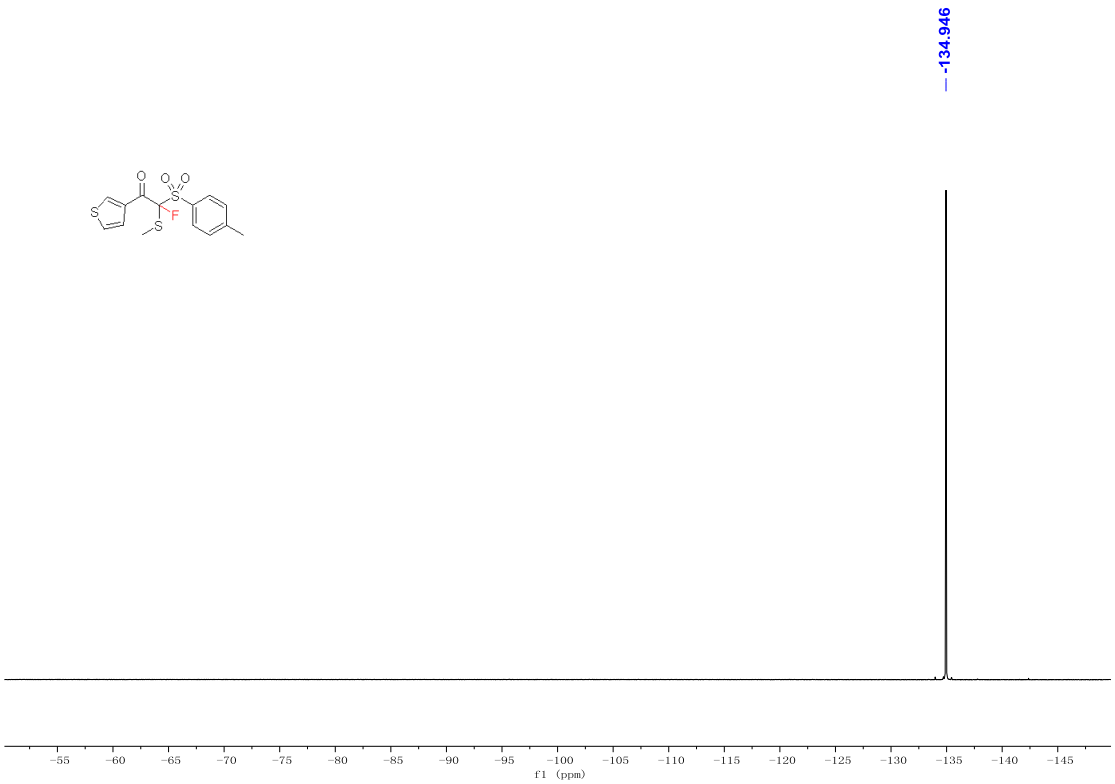




-133.290
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

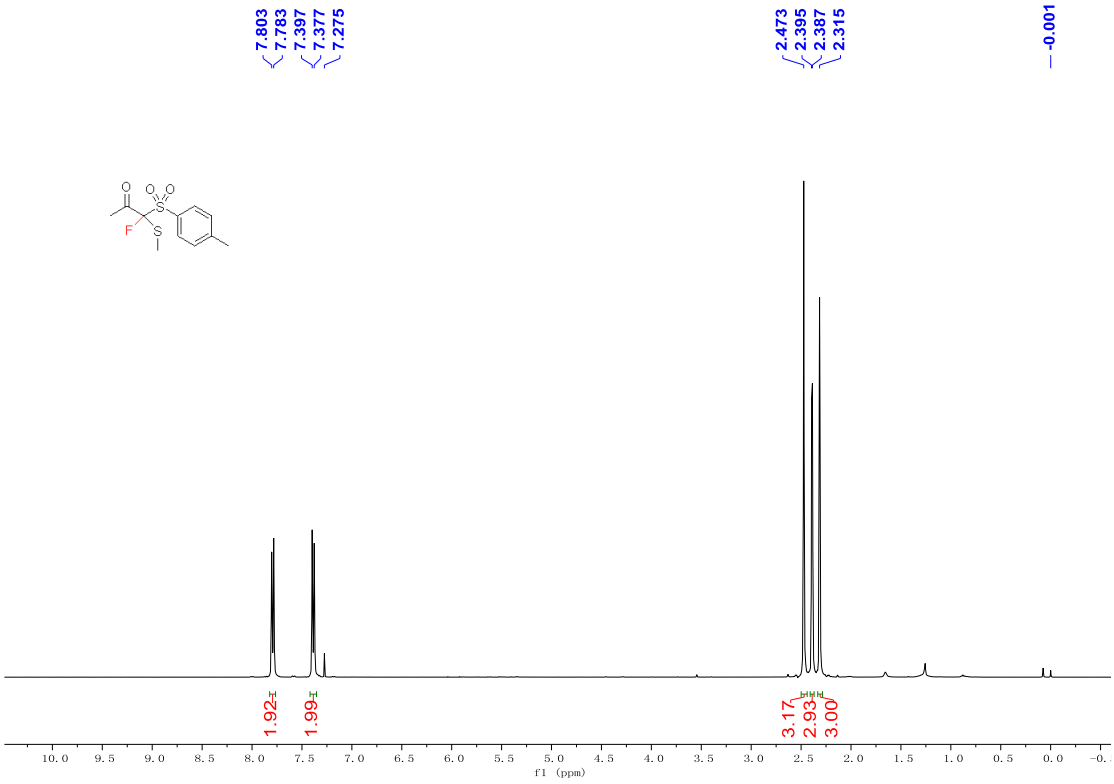
2-Fluoro-2-(methylthio)-1-(thiophen-3-yl)-2-tosylethan-1-one **(5n)**

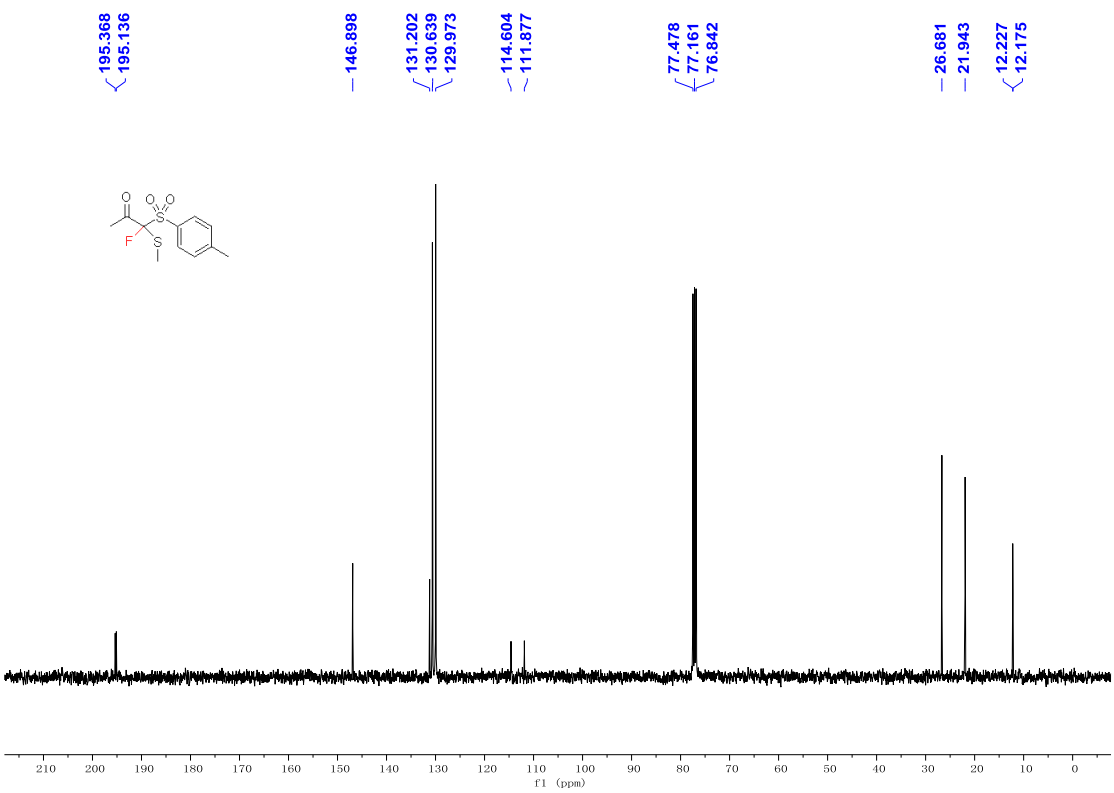


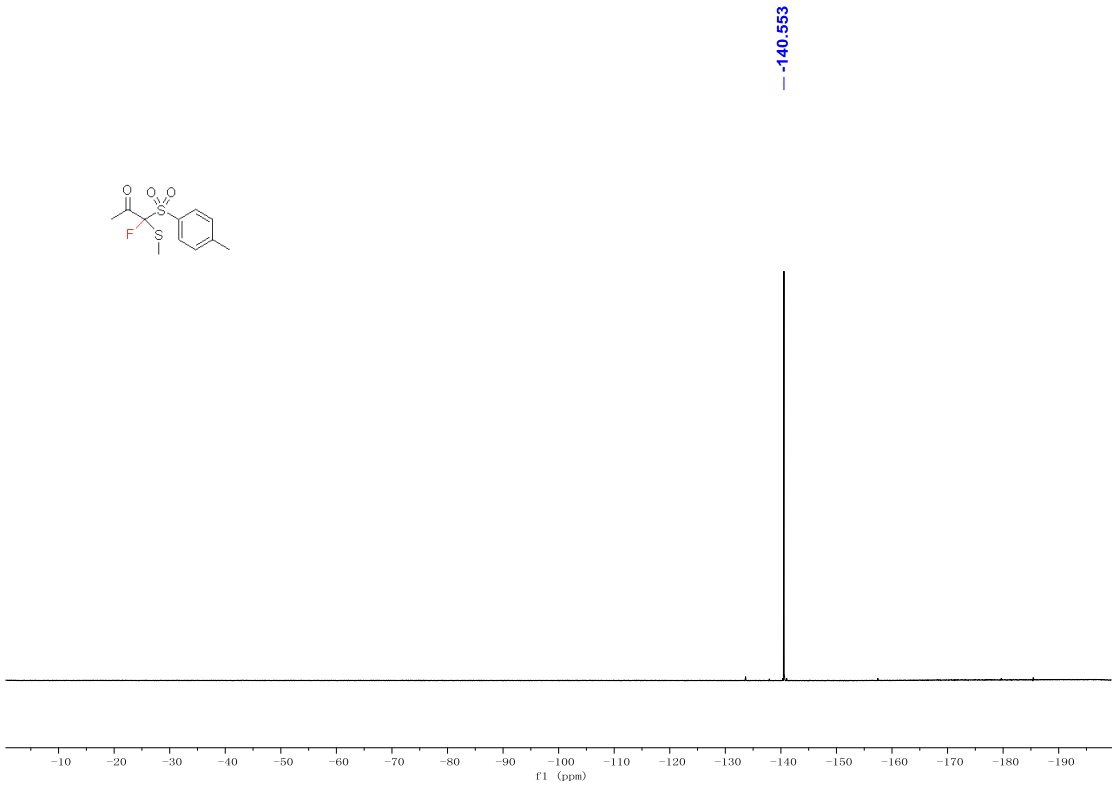




-134.946
O
O
O
S
S
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

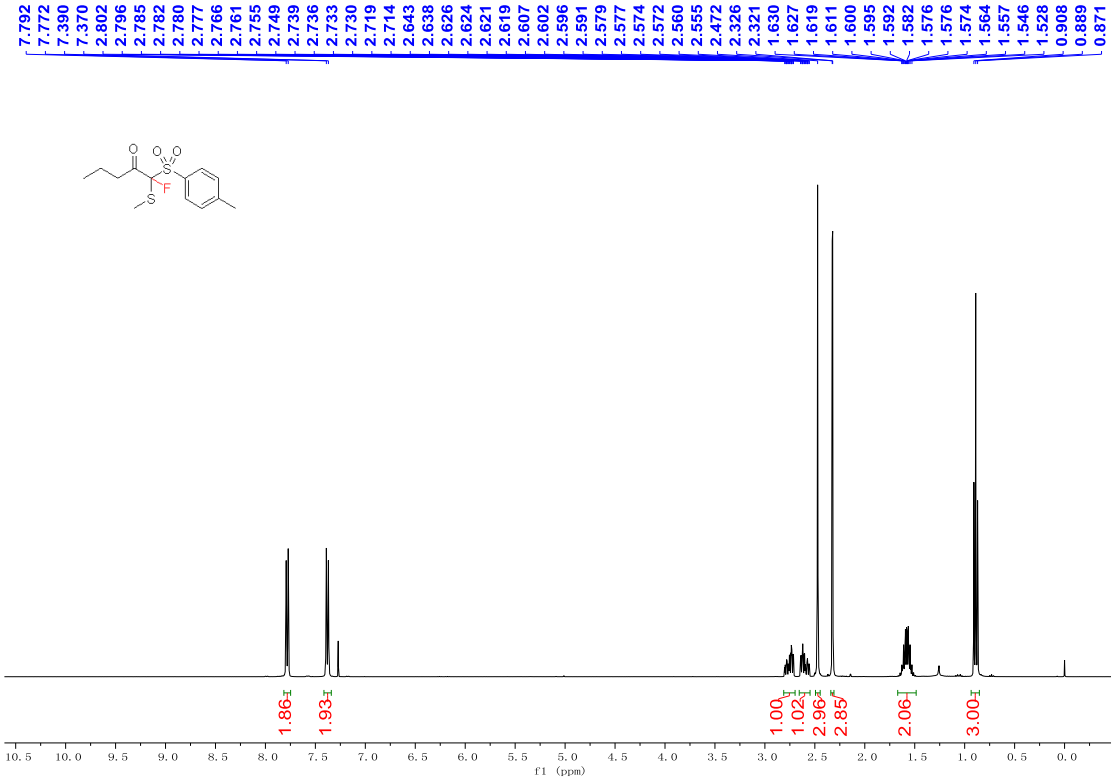
1-Fluoro-1-(methylthio)-1-tosylpropan-2-one (**5p**)

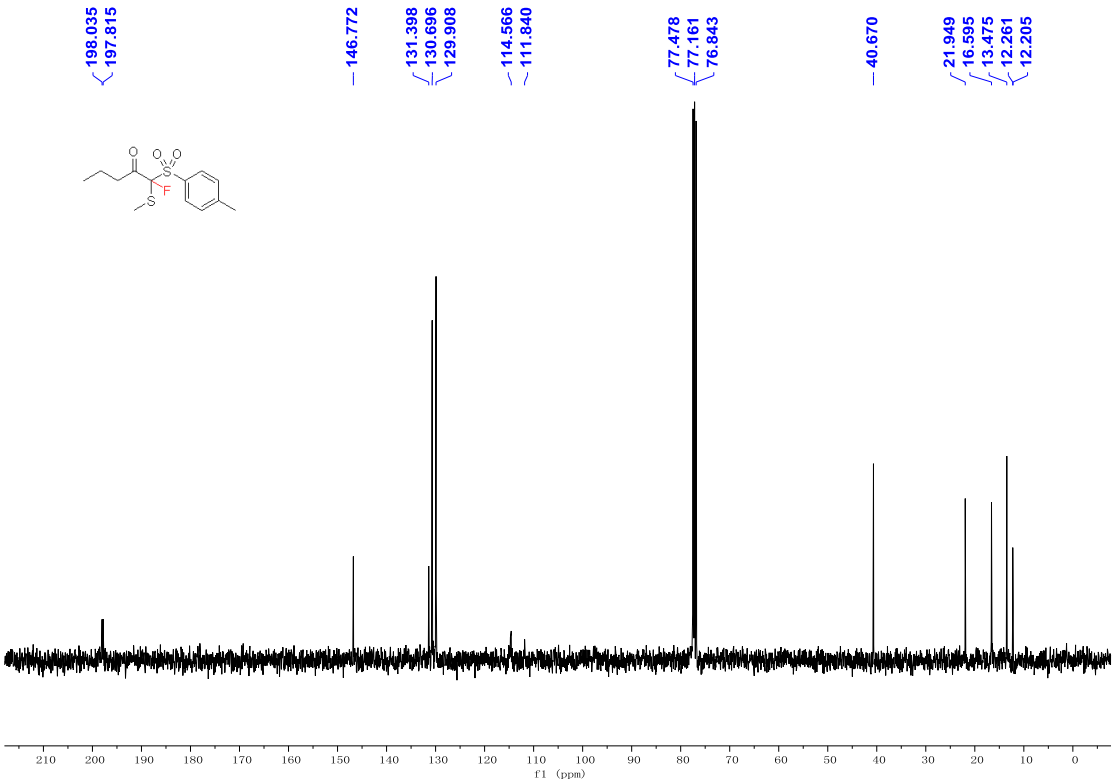


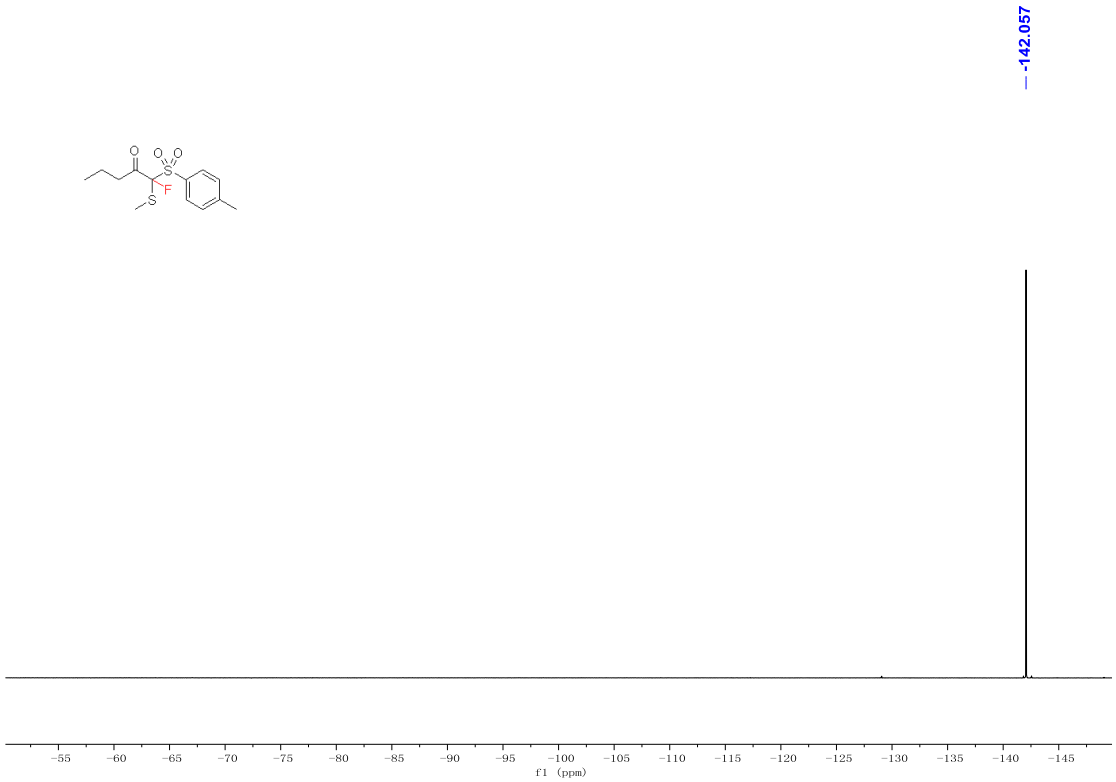




-140.553
O
O
O
S
F
S
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

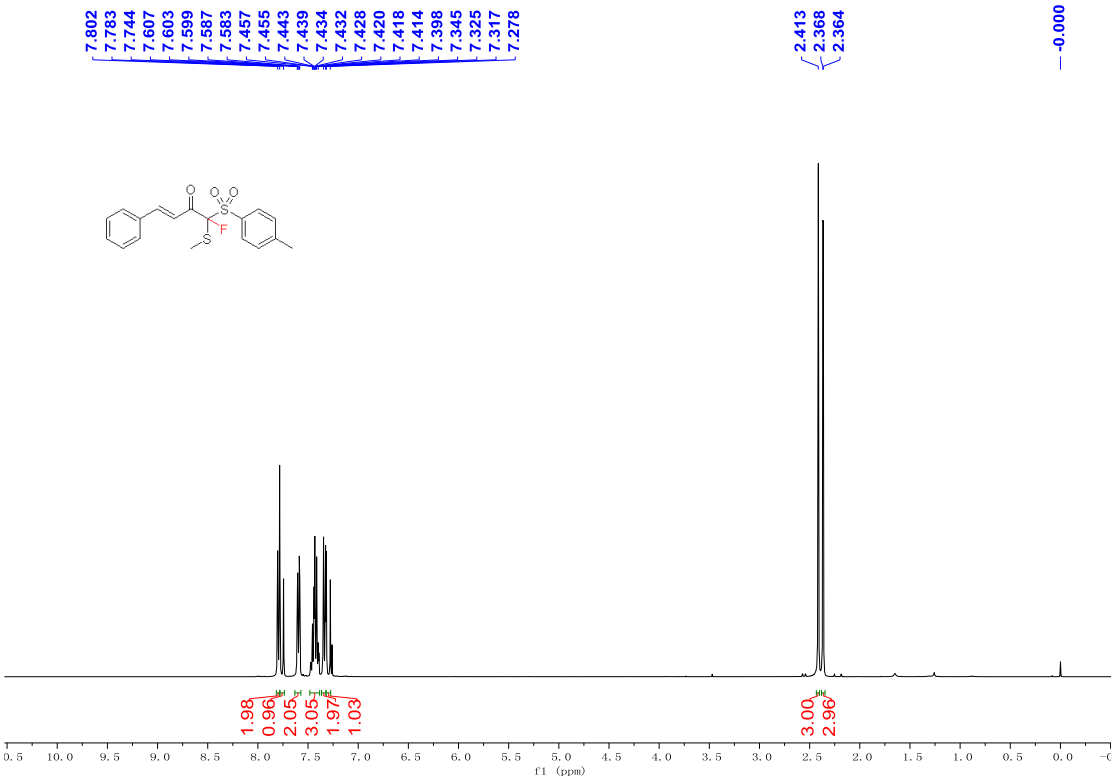
1-Fluoro-1-(methylthio)-1-tosylpentan-2-one **(5q)**

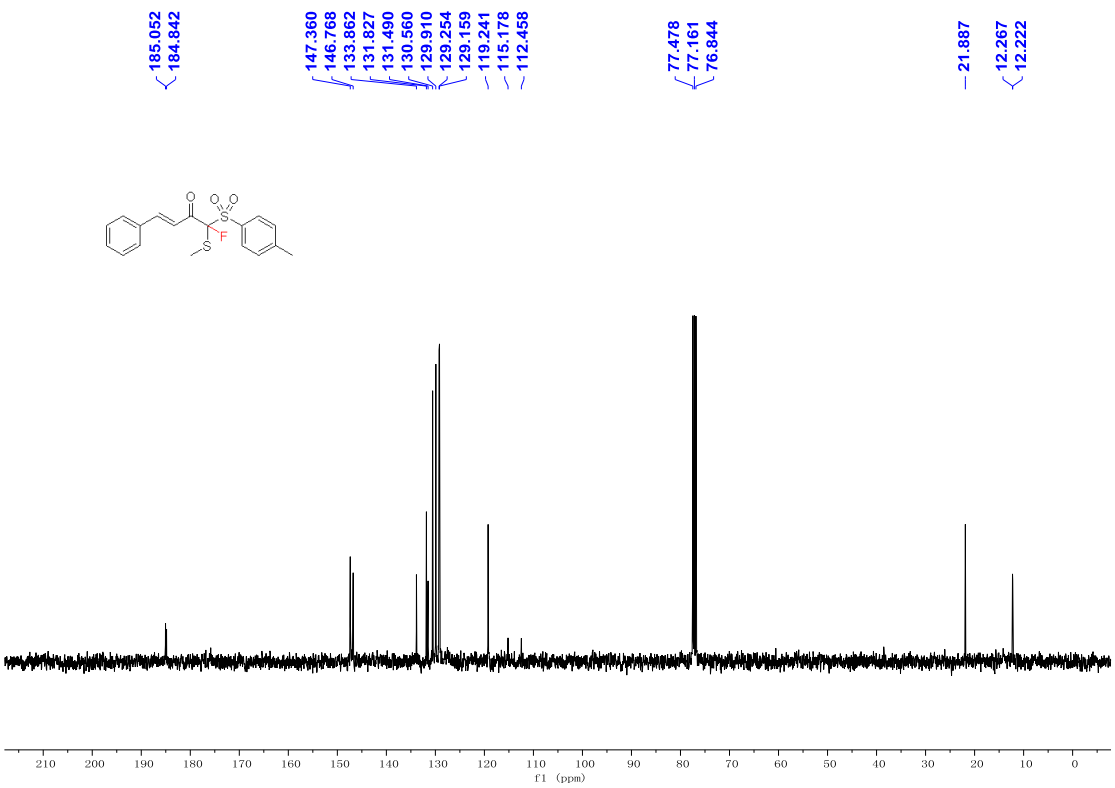


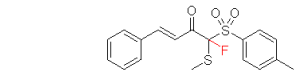




-142.057
O
O
O
S
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

(*E*)-1-Fluoro-1-(methylthio)-4-phenyl-1-tosylbut-3-en-2-one (**5r**)

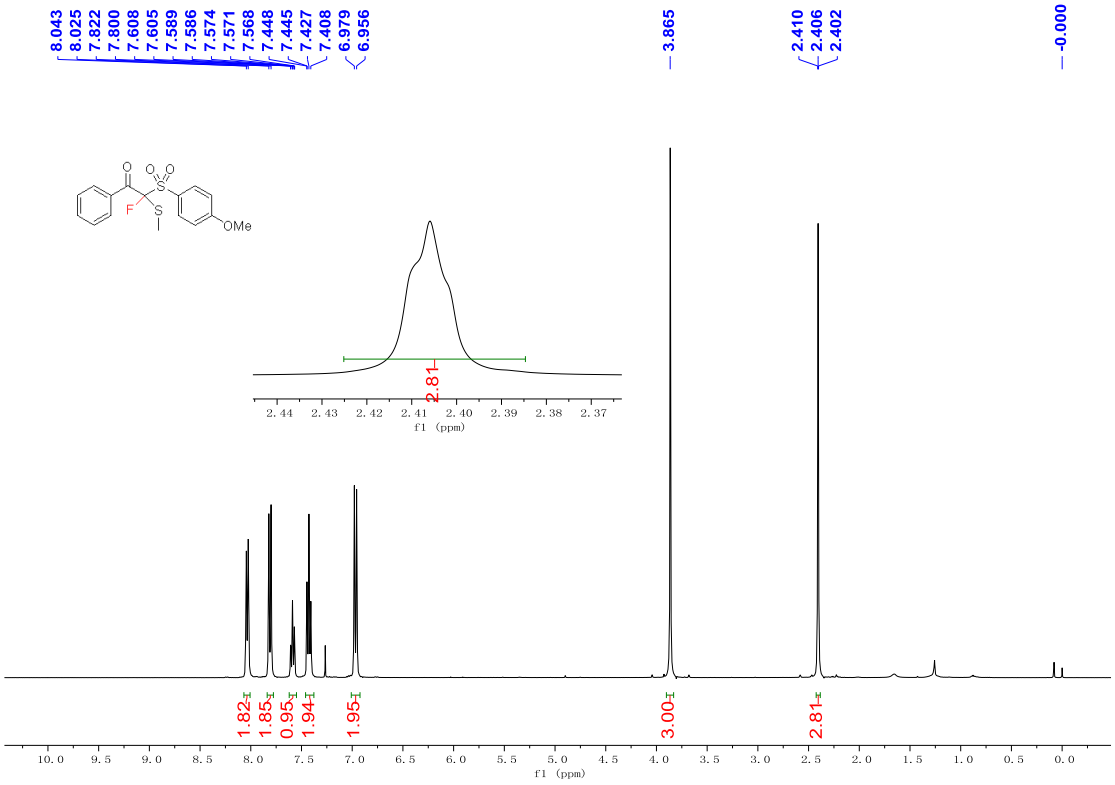


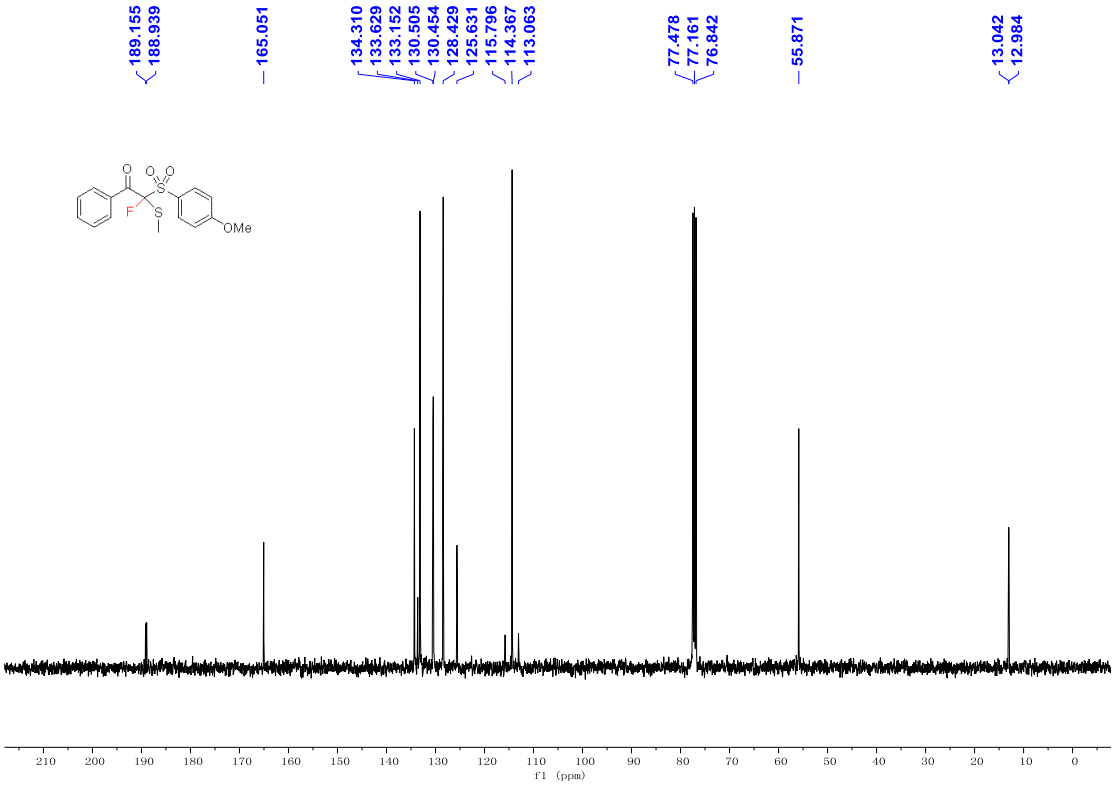



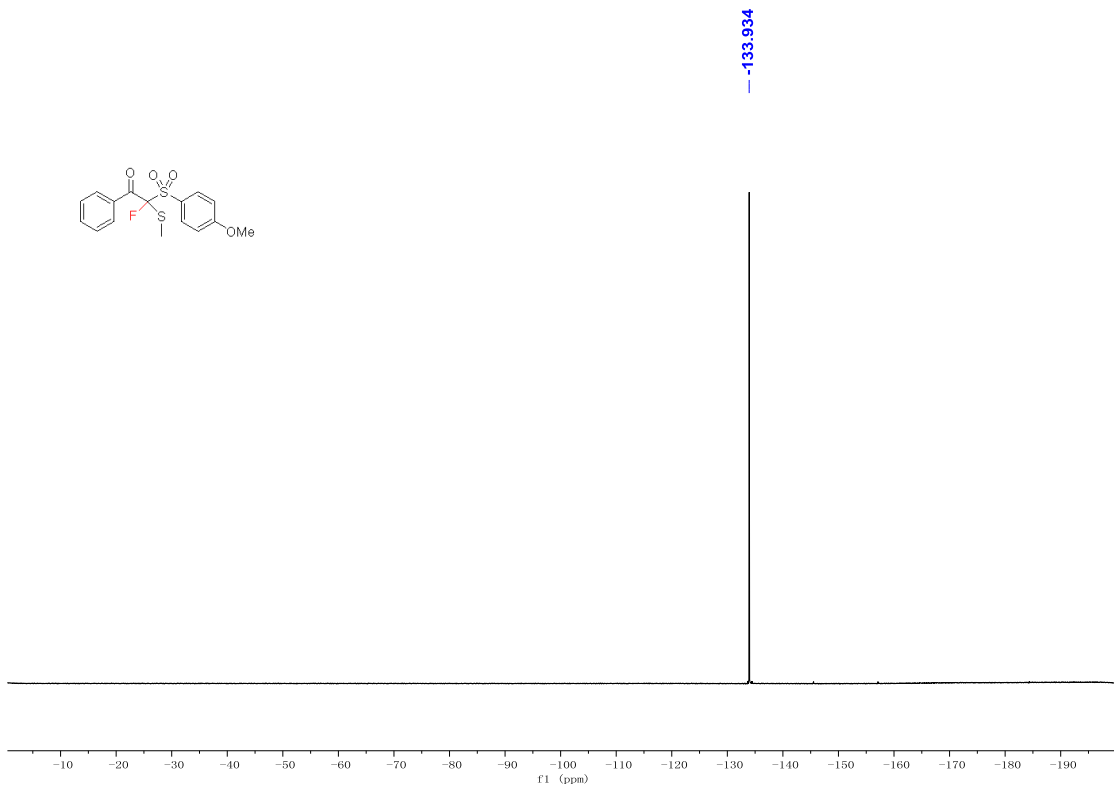



-141.696
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

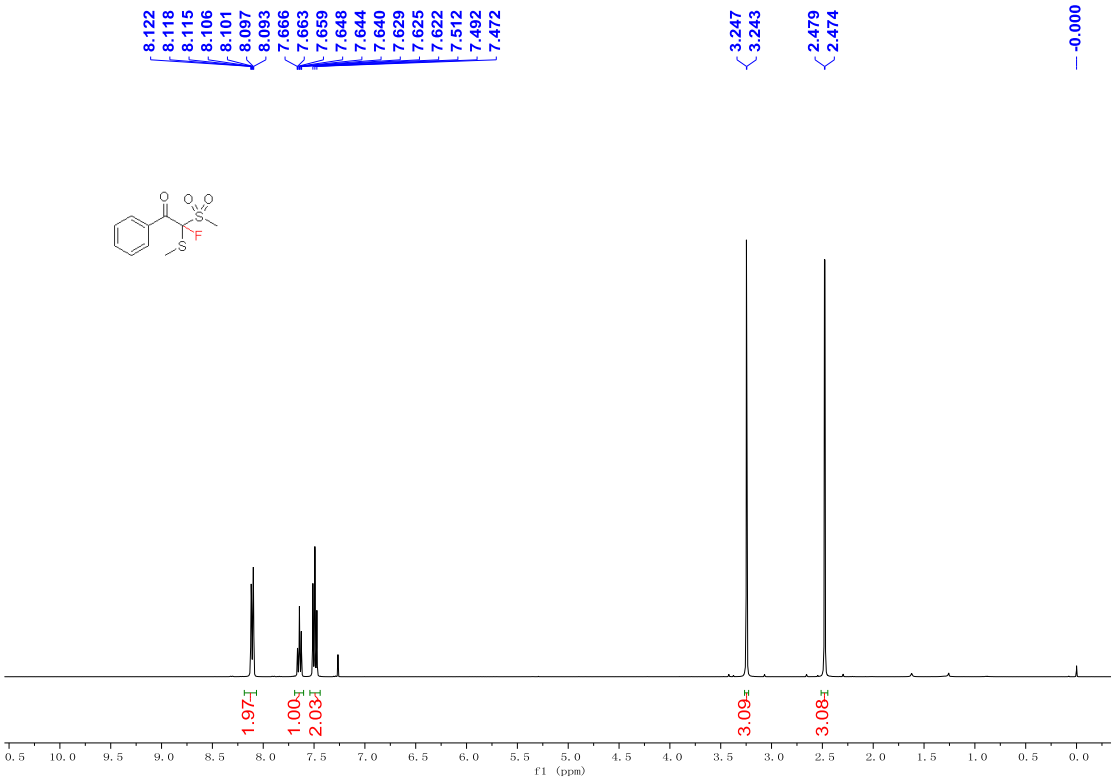
2-Fluoro-2-((4-methoxyphenyl)sulfonyl)-2-(methylthio)-1-phenylethan-1-one (**5u**)

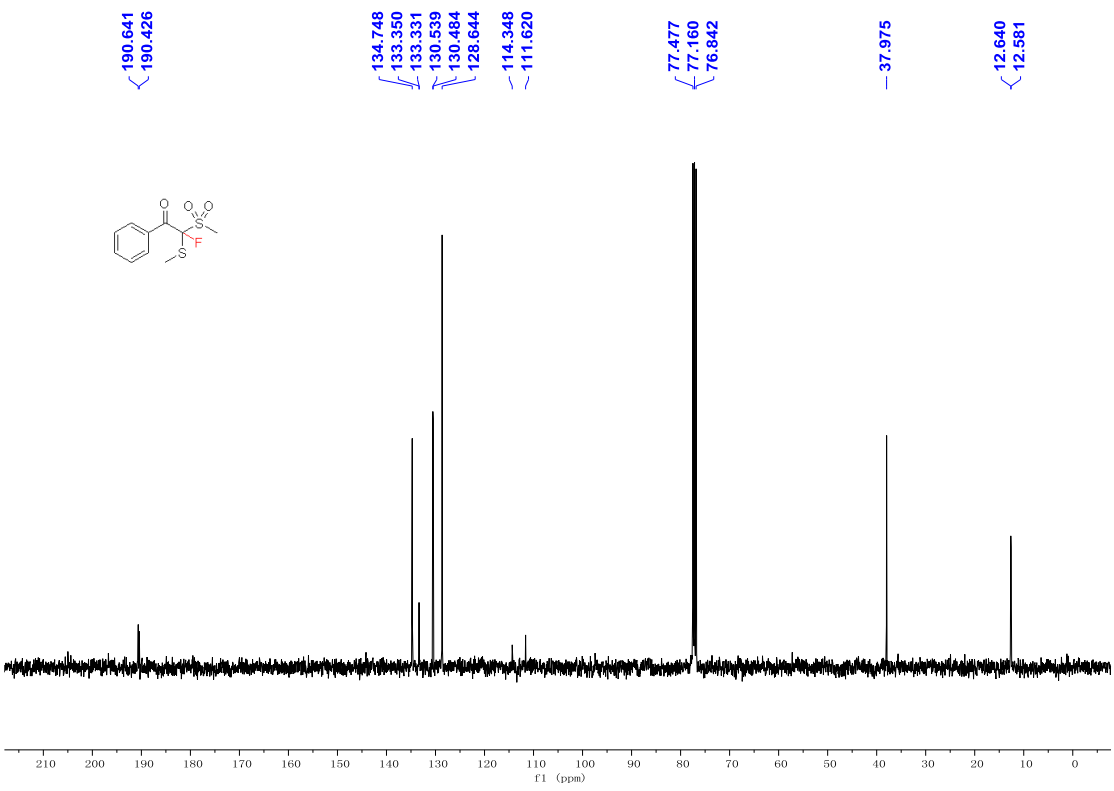


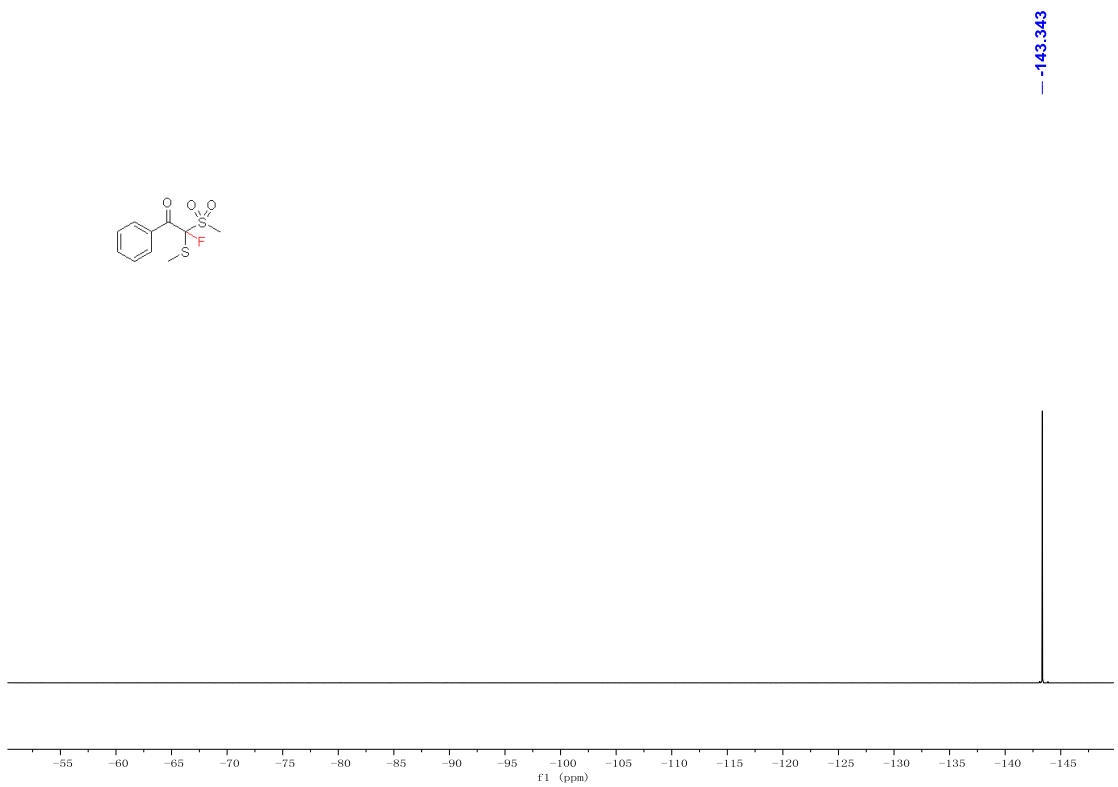




-133.934
O
O
O
S
F
S
OMe
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

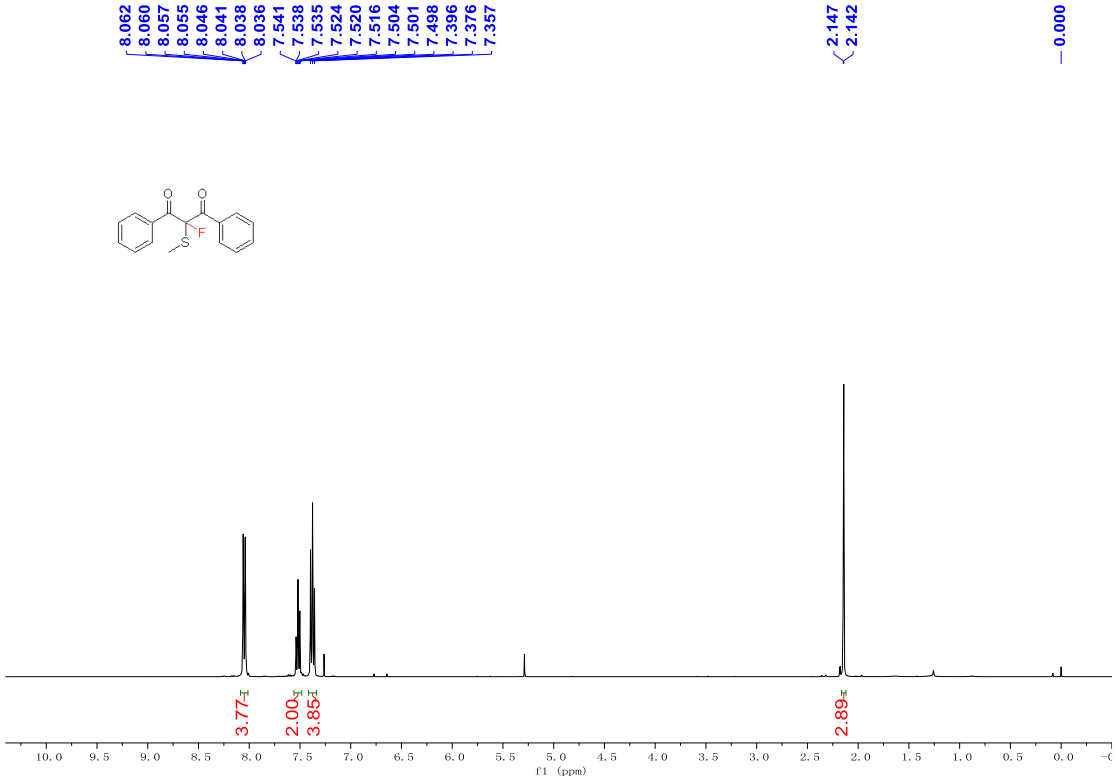
2-Fluoro-2-(methylsulfonyl)-2-(methylthio)-1-phenylethan-1-one (**5v**)

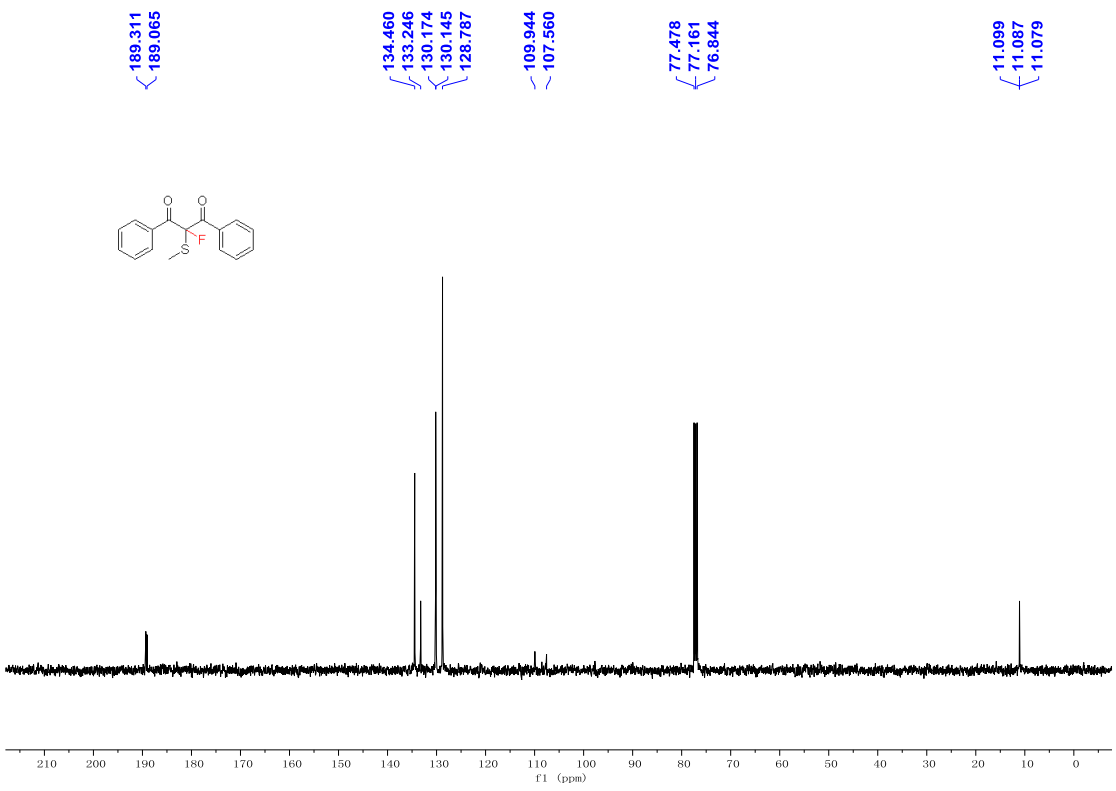


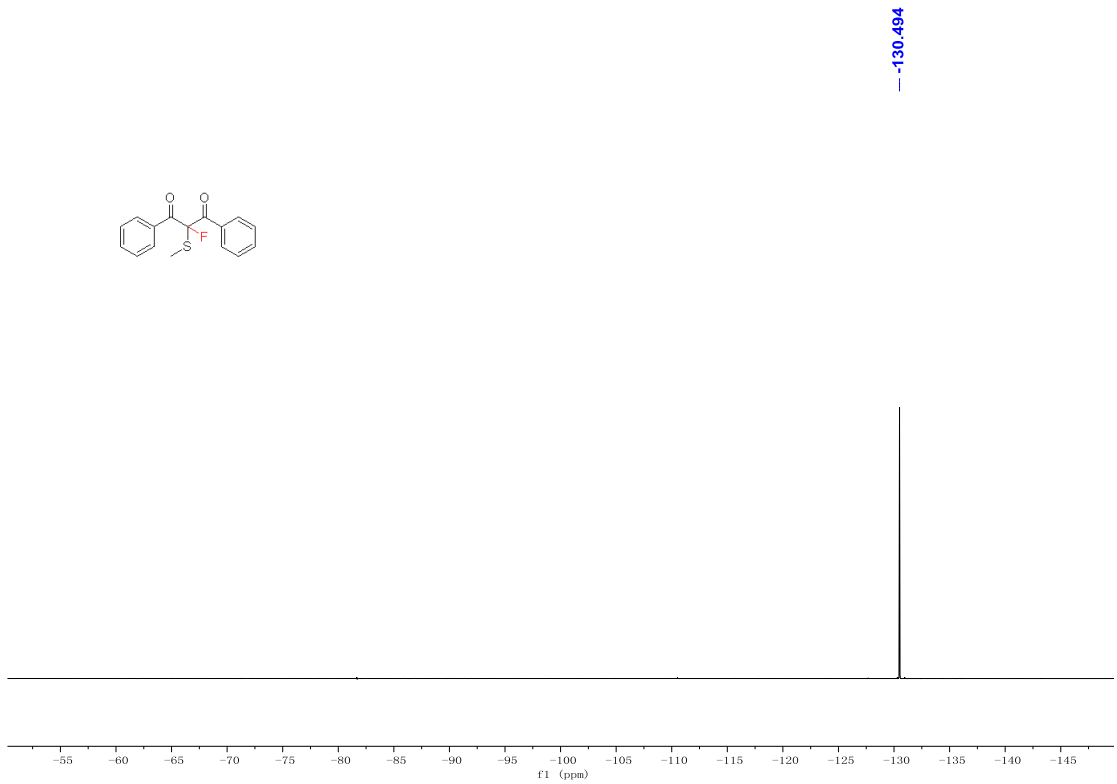




-143.343
O
O
O
S
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

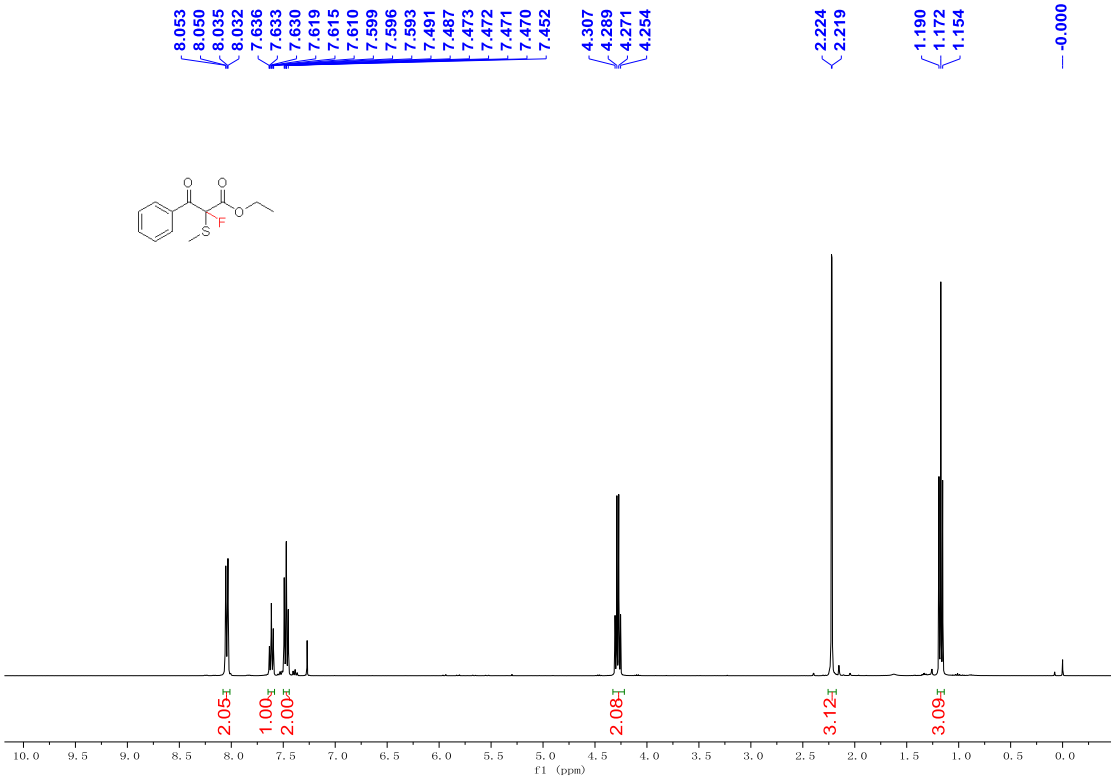
2-Fluoro-2-(methylthio)-1,3-diphenylpropane-1,3-dione (**5w**)

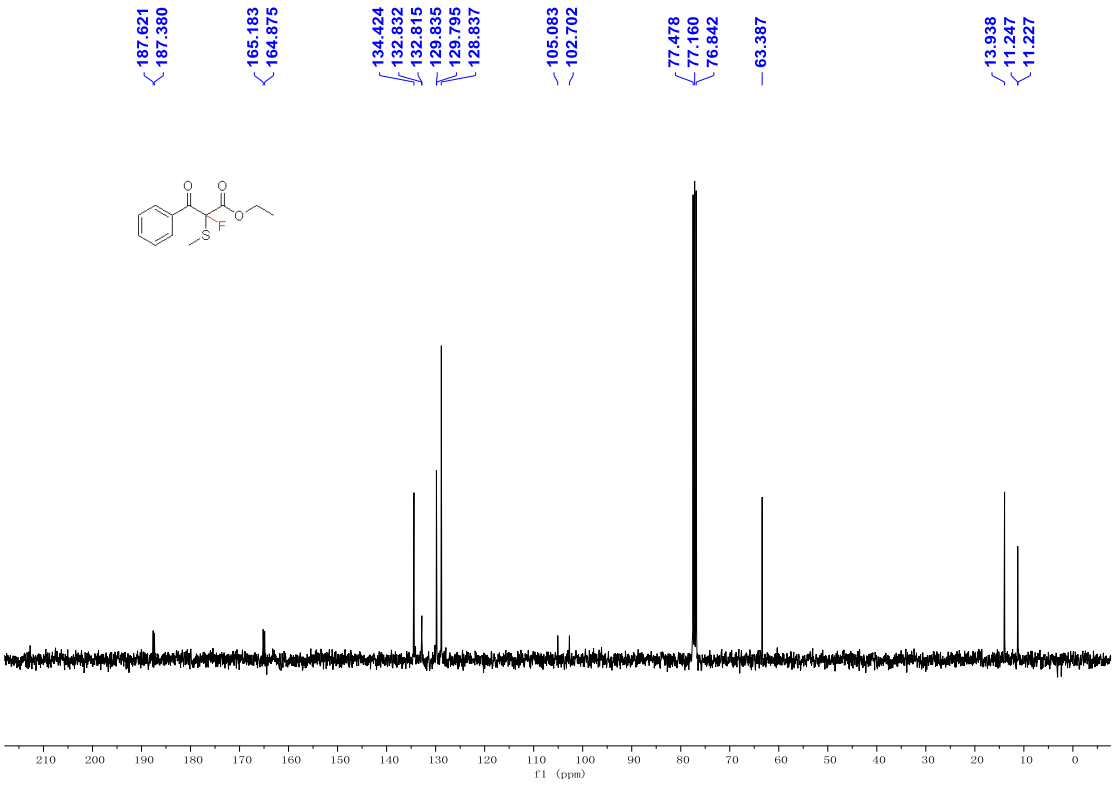


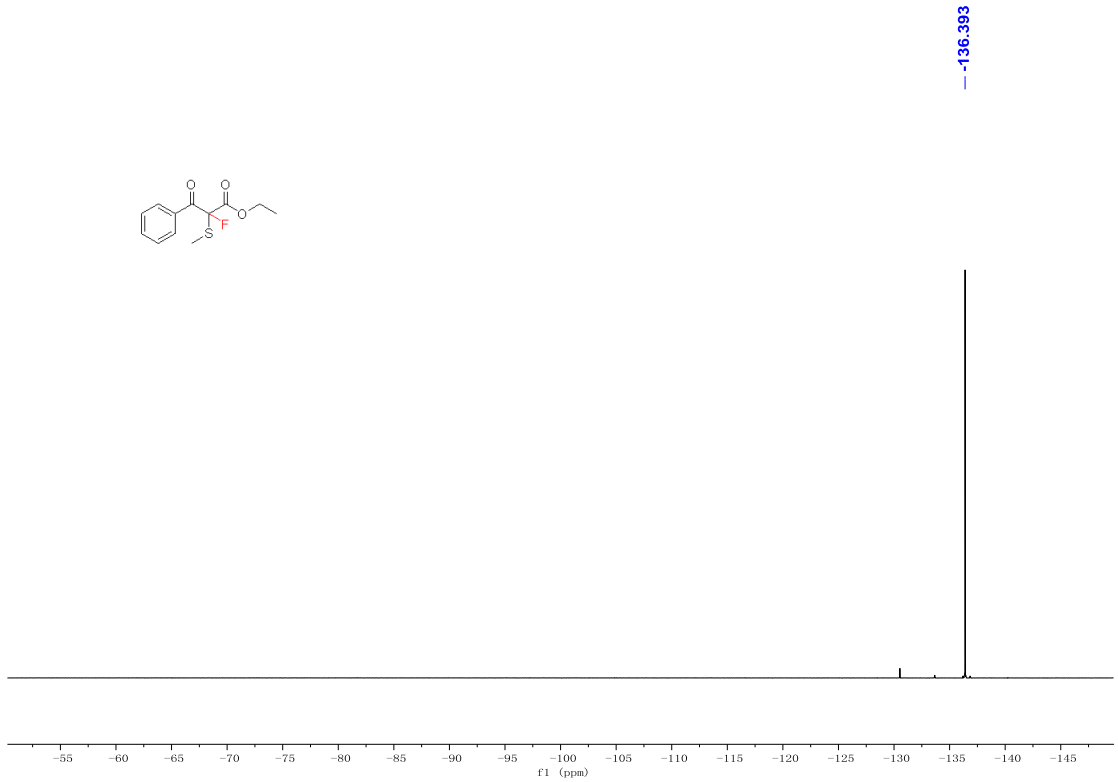




-130.494
O
O
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

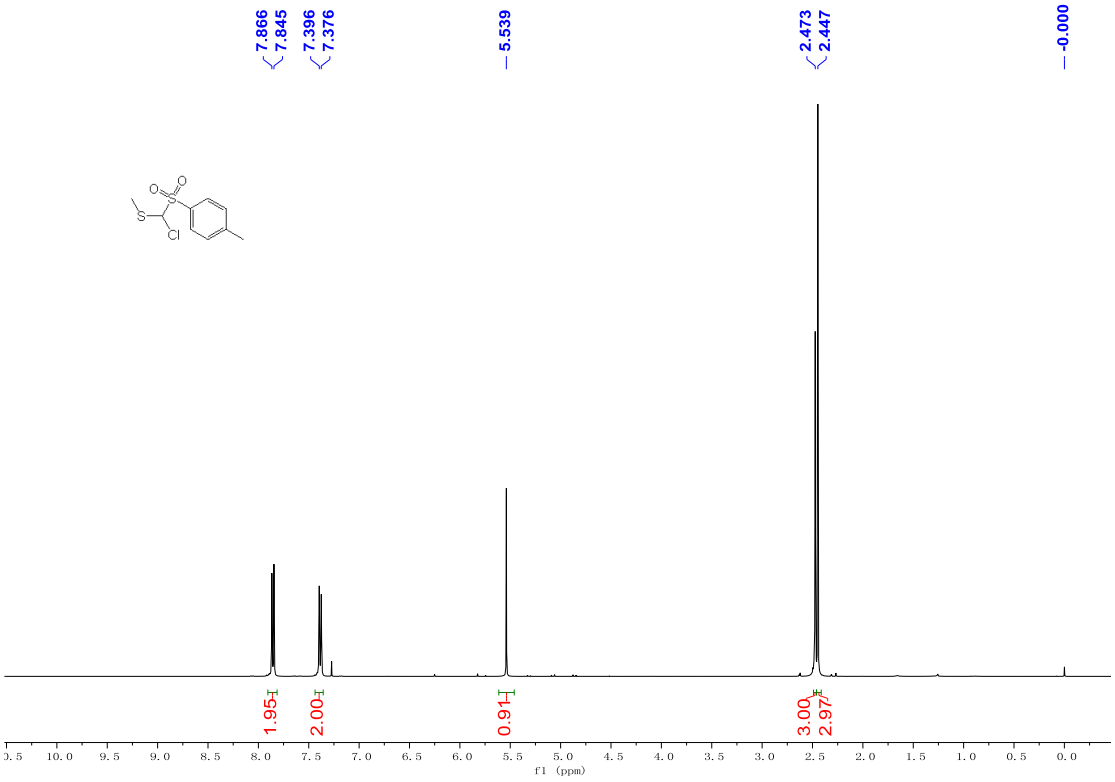
Ethyl 2-fluoro-2-(methylthio)-3-oxo-3-phenylpropanoate (**5x**)

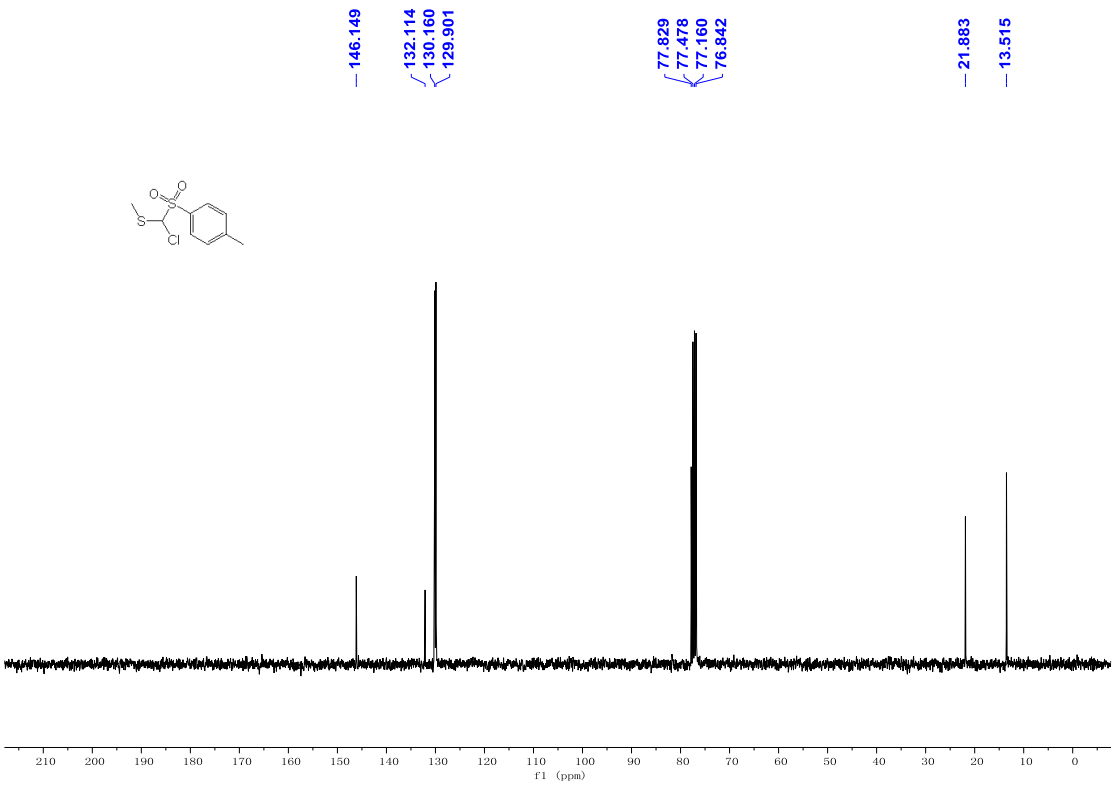


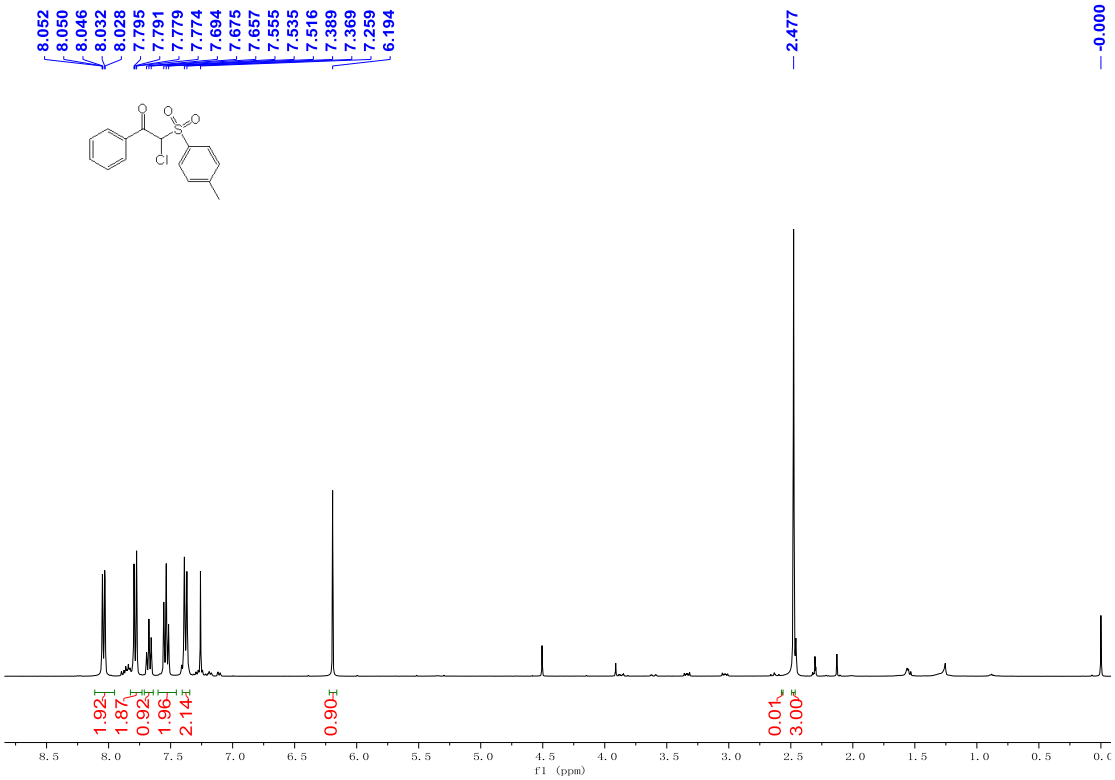

-136.393
O
O
O
F
S
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140
−145
f1 (ppm)

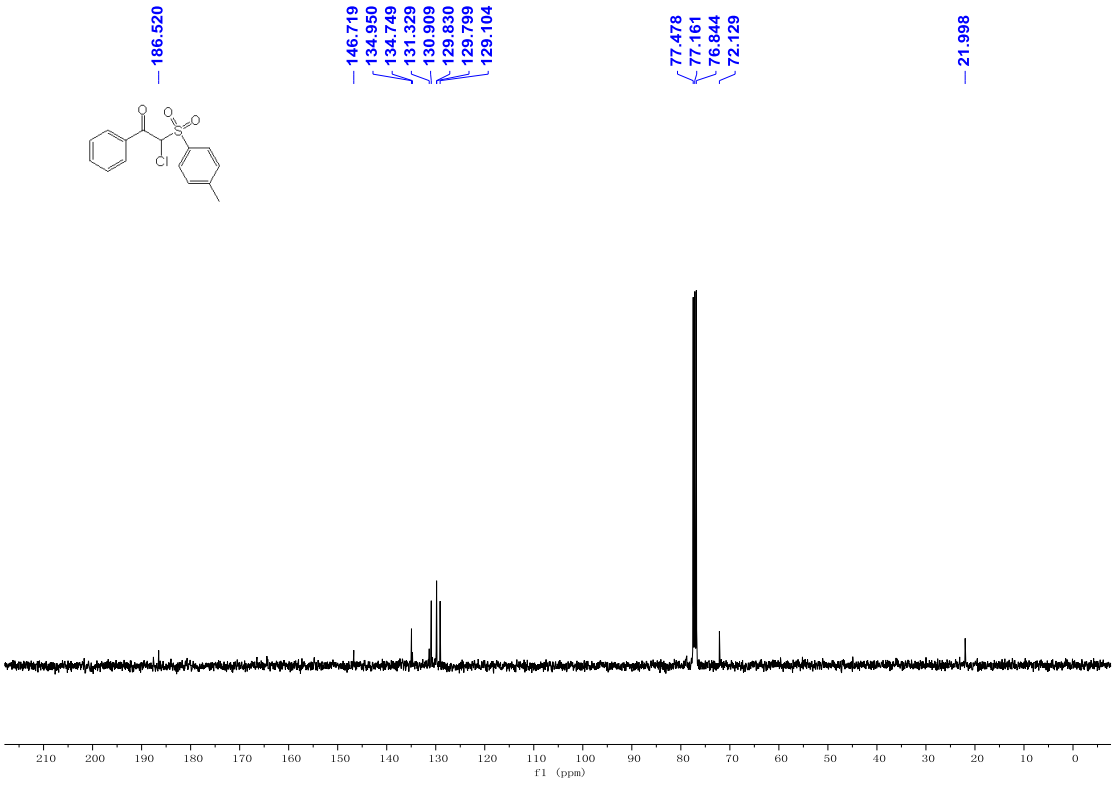
## 2.6 Copies of NMR ppectra for product 6



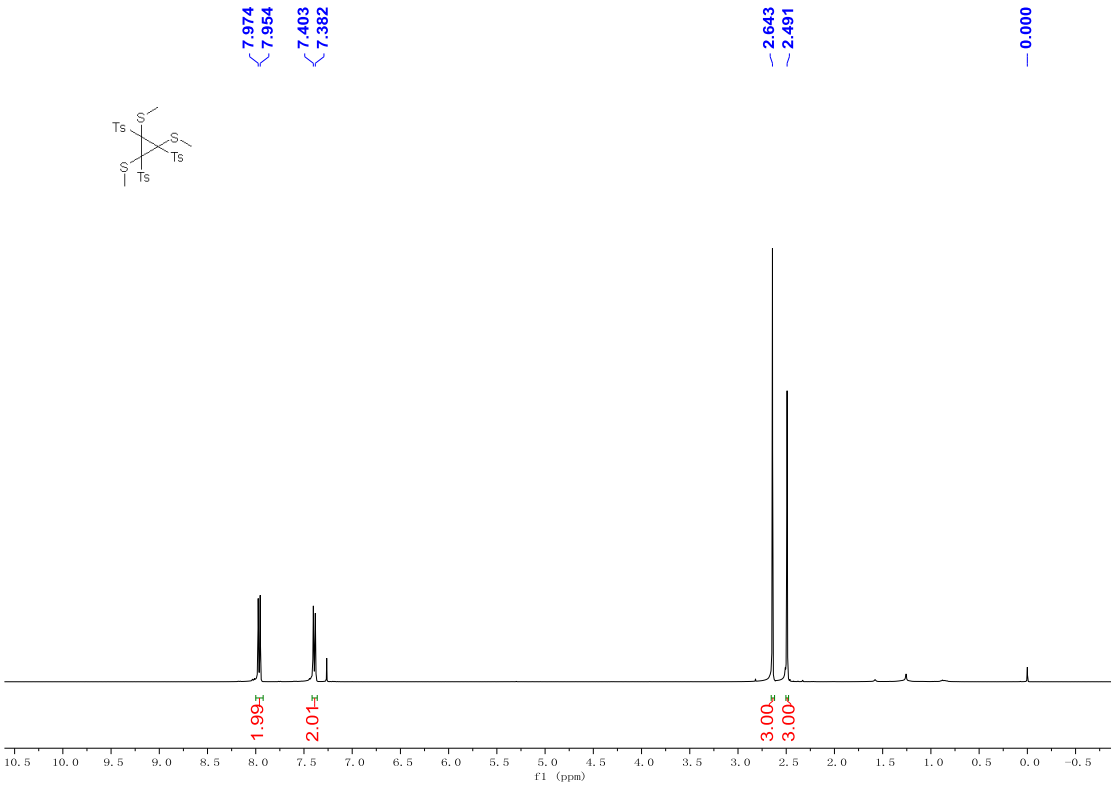
## 2.7 Copies of NMR spectra for product 7

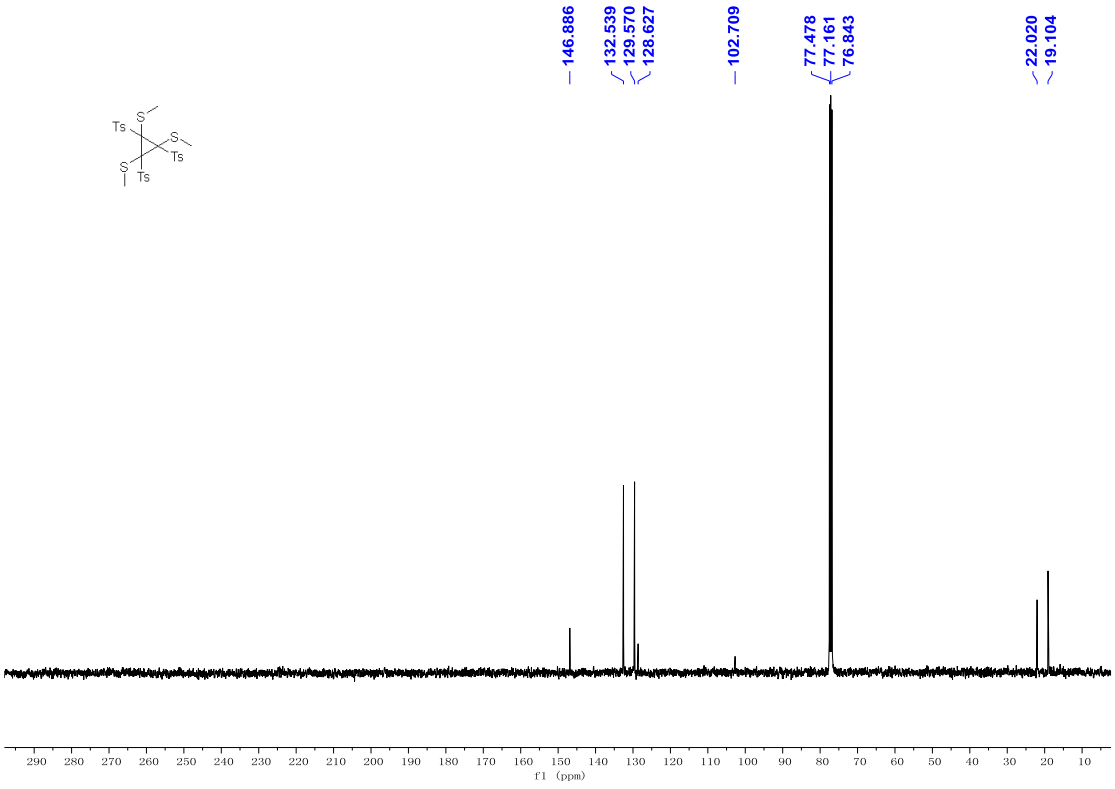


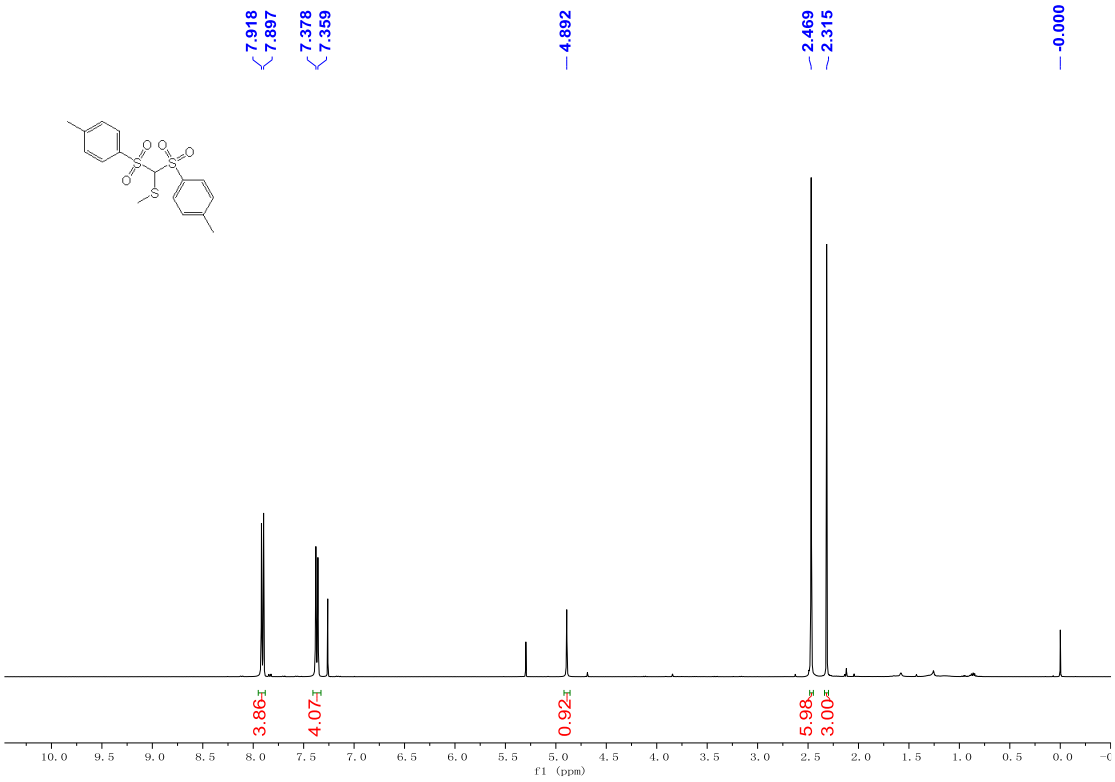
## 2.8 Copies of NMR spectra for products 8 and 9

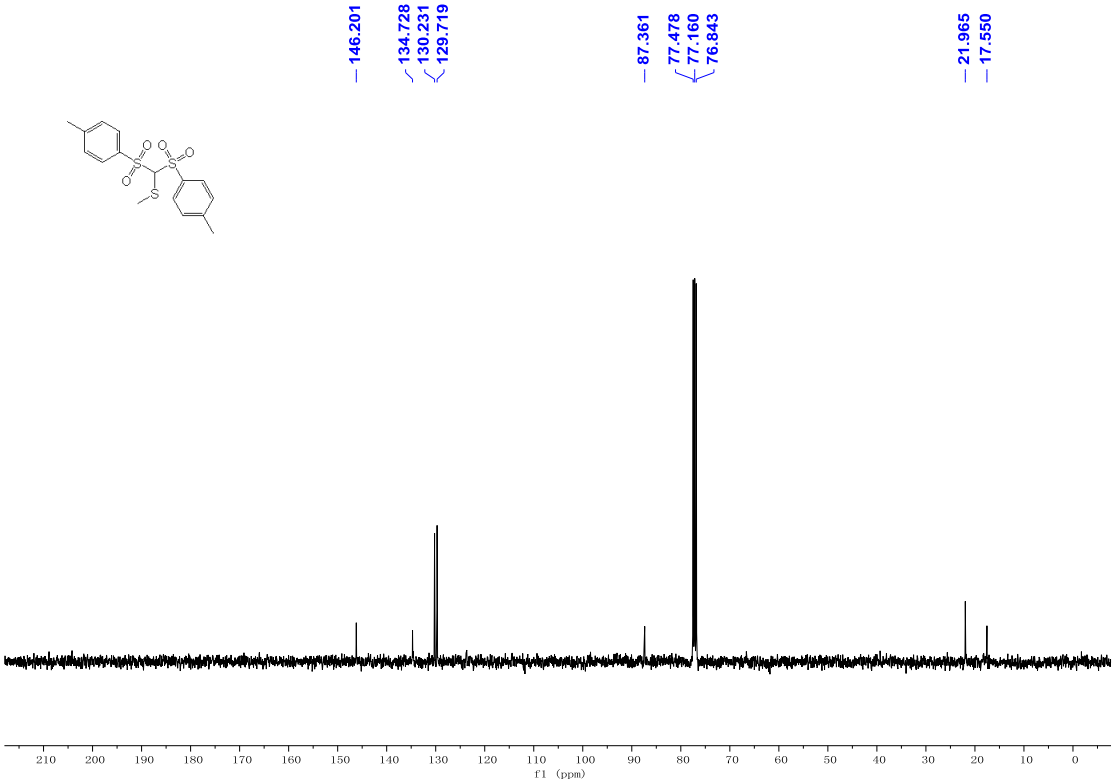
1,2,3-Tris(methylthio)-1,2,3-tritosylcyclopropane (**8**)



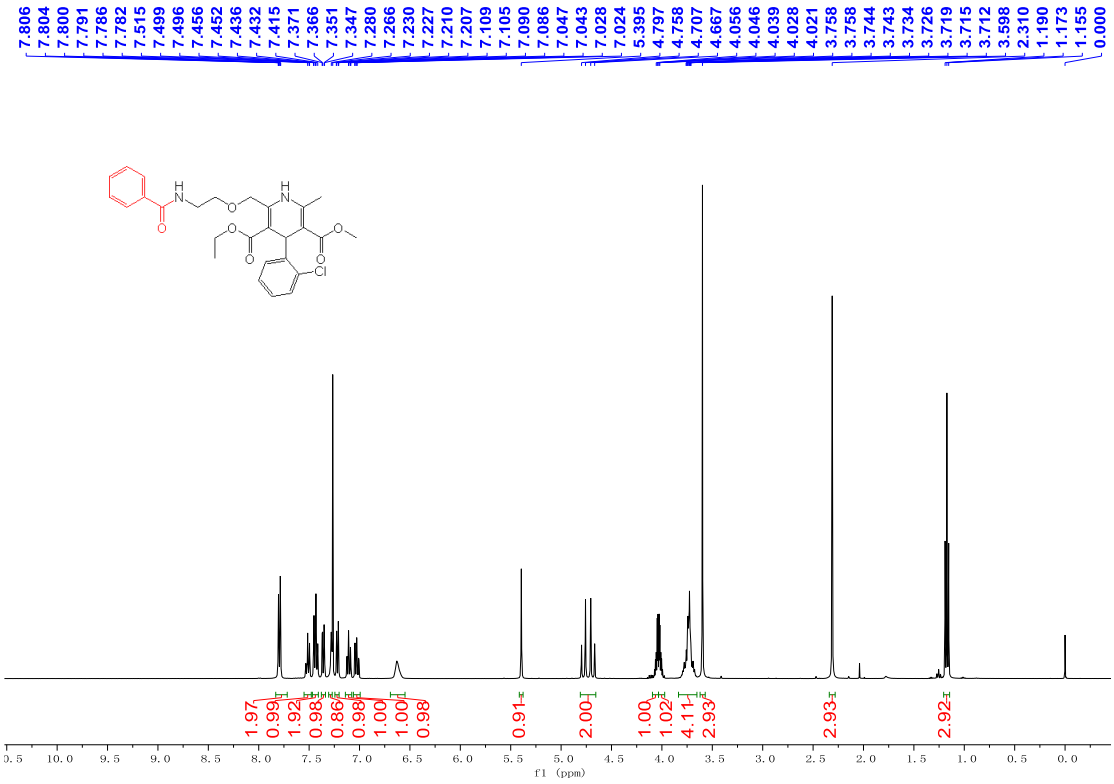
(Ditosylmethyl)(methyl)sulfane (**9**)

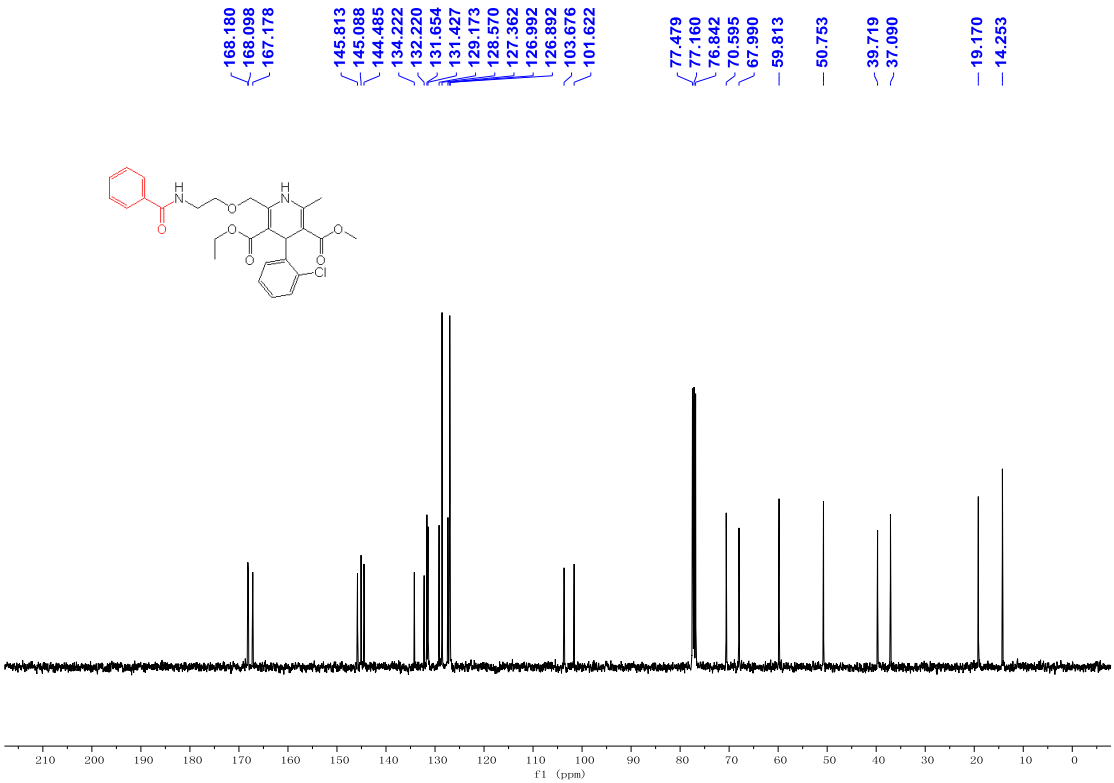


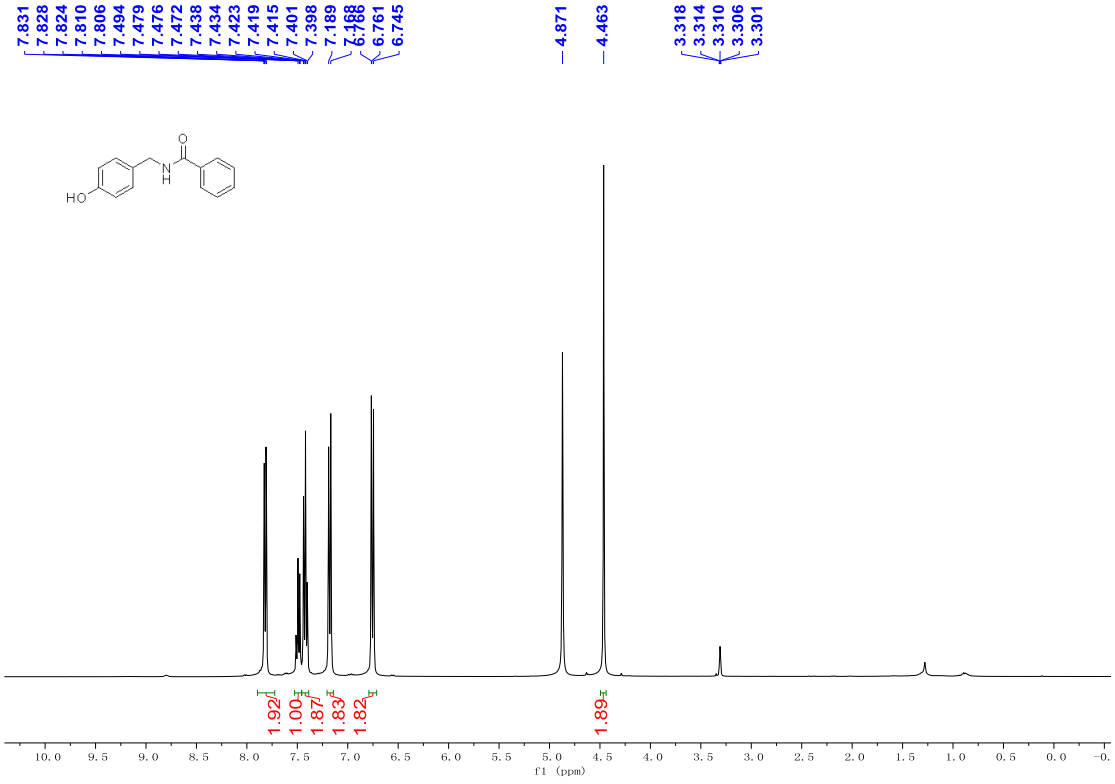
## 2.9 Copies of NMR spectra for products 10

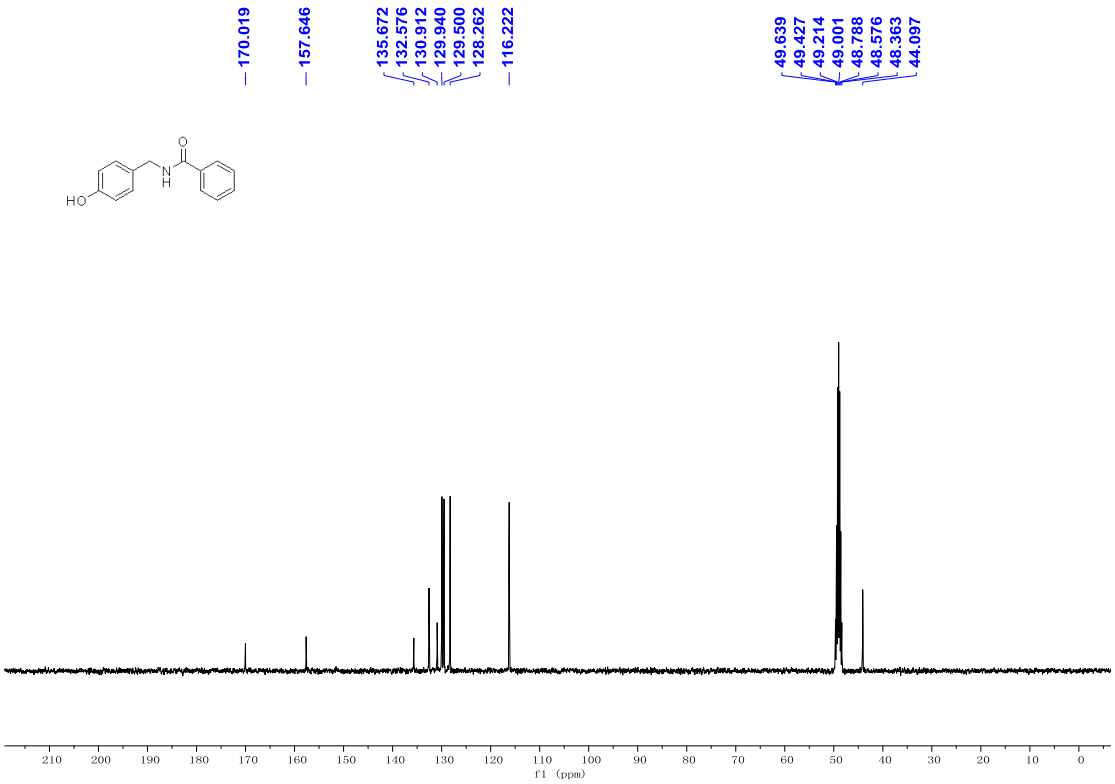
3-Ethyl 5-methyl 2-((2-benzamidoethoxy)methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (**10a**)



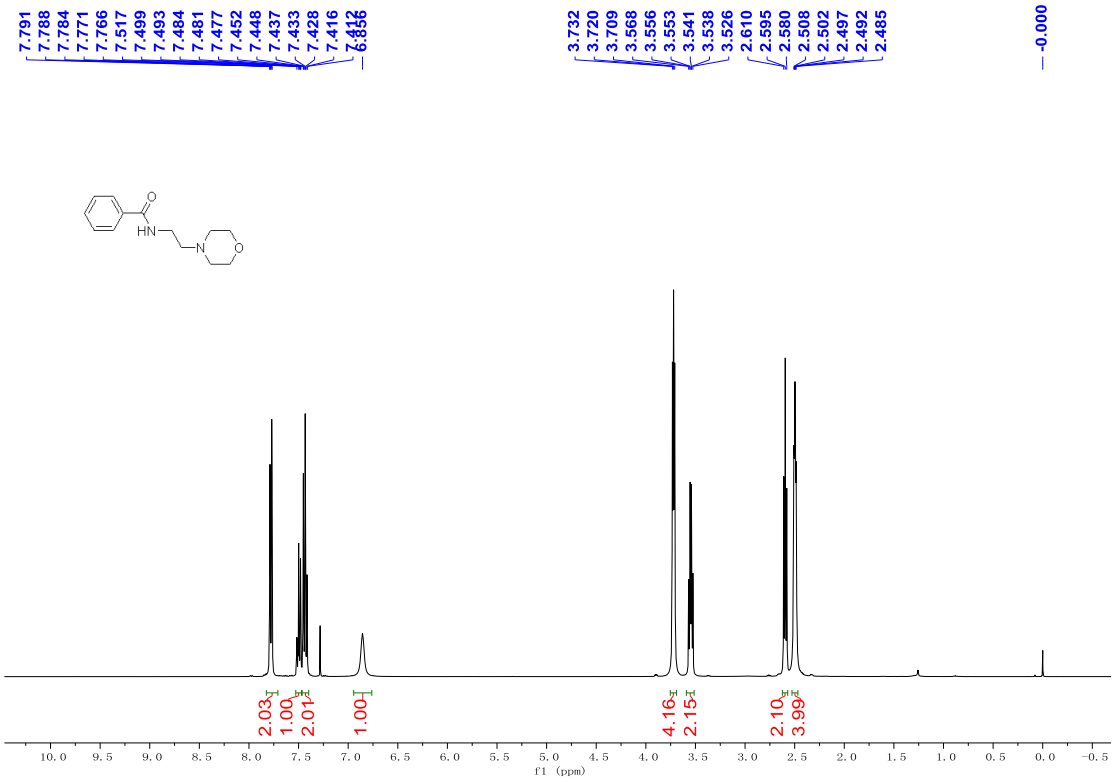



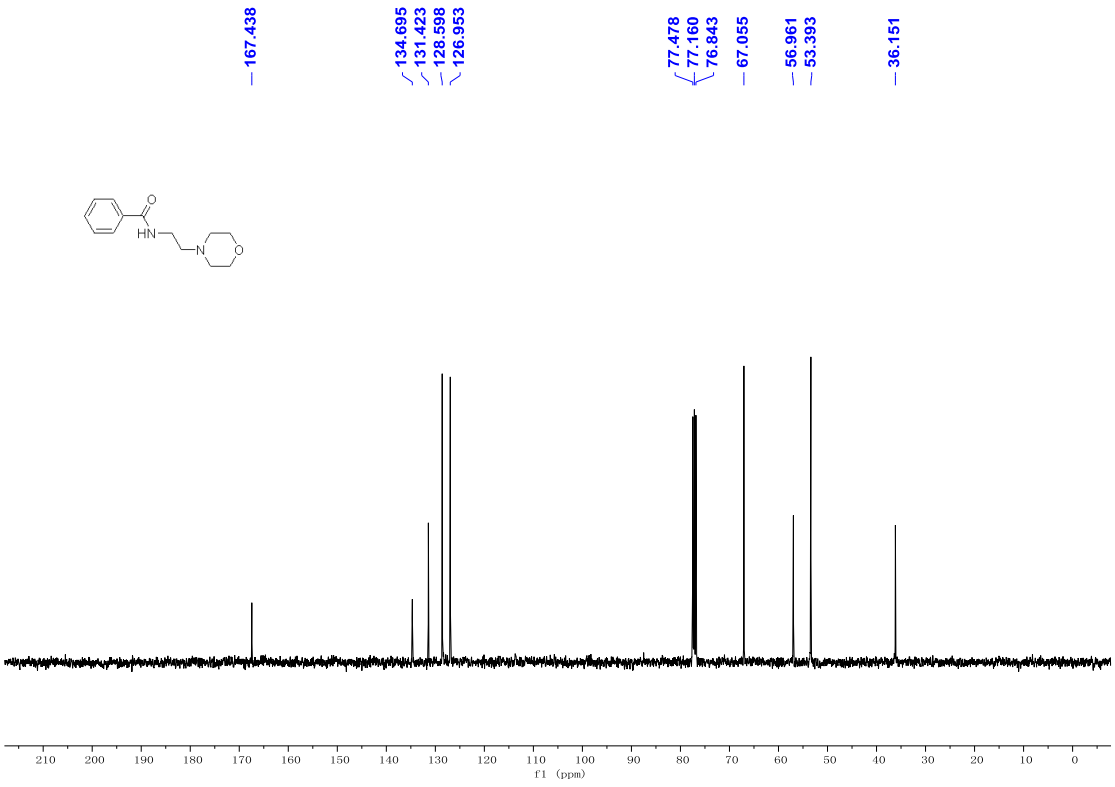
*N*-(4-Hydroxybenzyl)benzamide (**10b**)



*N*-(2-morpholinoethyl)benzamide (**10c**)



*N*-(prop-2-yn-1-yl)benzamide (**10d**)