## Supporting Information

# Catalytic and Direct Methyl Sulfonylation of Alkenes and Alkynes Using Methyl Sulfonyl Radical Generated from DMSO, Dioxygen and Copper System

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## Table of Contents

General methods ------------------------------------------------------------------------ 2

Optional reaction conditions and mechanism study -------------------------------- 3

General procedure for *β*-keto methyl sulfones and their spectral data ------------ 7

General procedure for (*E*)-vinyl methyl sulfones their spectral data -------------- 15

General procedure for applications and their spectral data ------------------------- 20

$^{1}$H and $^{13}$C NMR spectra of *β*-keto methyl sulfones -------------------------------- 22

$^{1}$H and $^{13}$C NMR spectra of (*E*)-vinyl methyl sulfones ----------------------------- 45

1H and 13C NMR spectra of applications of *β*-keto methyl sulfones ------------- 57

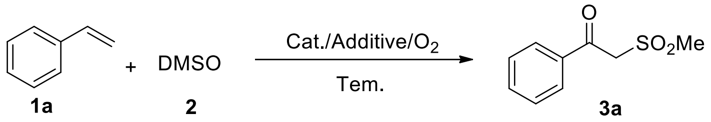
## General methods:

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 400 MHz Bruker spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for $^1$H NMR spectra and 77.0 ppm for $^{13}$C NMR spectra in $CDCl_3$). Chemical shift ($\delta$) is reported in ppm, coupling constants ($J$) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer.

**Materials:** All solvents were distilled under nitrogen atmosphere from the following drying agents immediately before use: THF was distilled from Na powder, $CH_3CN$ was distilled from $P_2O_5$.

# Detail Screening Reaction Conditions:

## Table-1 Optimization of reaction conditions for *β*-keto methyl sulfones[a]

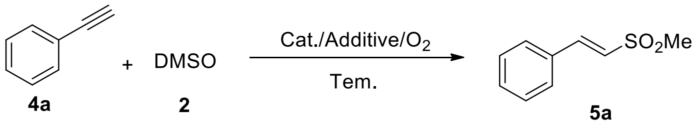


| Entry | Solvent | Catalyst | Additive[f] | Temp. | Yield[b] |
|---|---|---|---|---|---|
| **1** | **2** | $FeCl_2$ (10%)/$H_2O_2$ (10. Eq.) | D-1 (20%) | 90 | 15[e] |
| **2** | **2** | CuBr (10%)/$H_2O_2$ (10. Eq.) | D-1 (20%) | 90 | 27[e] |
| **3** | **2** | CuBr (10%) | D-1 (20%) | 90 | 24[e] |
| **4** | DCE[c] | CuBr (10%) | D-2 (2.0 eq.) | 90 | 5 |
| **5** | DMF[c] | CuBr (10%) | D-2 (2.0 eq.) | 90 | 4 |
| **6** | Tol[c] | CuBr (10%) | D-2 (2.0 eq.) | 90 | - |
| **7** | ACN[c] | CuBr (10%) | D-2 (2.0 eq.) | 90 | - |
| **8** | **2** | CuBr (10%) | D-2 (2.0 eq.) | 90 | 52 |
| **9** | **2** | CuBr (5%) | D-2 (2.0 eq.) | 90 | 47 |
| **10** | **2** | - | D-2 (2.0 eq.) | 90 | - |
| **11**[d] | **2** | - | Pyridine (2.0 eq.) | 90 | - |
| **12** | **2** | CuBr (20%) | D-2 (2.0 eq.) | 90 | 42 |
| **13** | **2** | CuBr (10%) | D-2 (2.0 eq.) | 55 | 10 |
| **14** | **2** | CuBr (10%) | D-2 (2.0 eq.) | 70 | 48 |
| **15** | **2** | CuBr (10%) | D-2 (2.0 eq.) | 110 | 45 |
| **16** | **2** | CuBr (10%) | D-2 (3.0 eq.) | 90 | 86(82[e]) |
| **17** | **2** | CuBr (10%) | D-2 (2.2 eq.) | 90 | 71 |
| **18** | **2** | CuBr (10%) | D-2 (1.5 eq.) | 90 | 50 |
| **19** | **2** | CuBr (10%) | D-2 (0.5 eq.) | 90 | 15 |
| **20** | **2** | CuBr (10%) | - | 90 | - |
| **21** | **2** | CuBr (10%) | D-3 (3.0 eq.) | 90 | 75 |
| **22** | **2** | CuBr (10%) | D-4 (3.0 eq.) | 90 | 80 |
| **23** | **2** | CuBr (10%) | D-5 (3.0 eq.) | 90 | 64 |
| **24** | **2** | CuBr (10%) | D-6 (3.0 eq.) | 90 | - |
| **25** | **2** | CuCl (10%) | D-2 (3.0 eq.) | 90 | 25 |
| **26** | **2** | CuI (10%) | D-2 (3.0eq.) | 90 | 55 |
| **27** | **2** | Cu(OTf).Benzene(10%) | D-2 (3.0eq.) | 90 | 77 |
| **28** | **2** | Cu(OAc) (10%) | D-2 (3.0eq.) | 90 | 54 |
| **29** | **2** | CuCN (10%) | D-2 (3.0eq.) | 90 | 47 |
| **30** | **2** | CuTC (10%) | D-2 (3.0eq.) | 90 | 73 |
| **31** | **2** | $Cu(OTf)_2$ (10%) | D-2 (3.0eq.) | 90 | 36 |
| **32** | **2** | $Cu(hfacac)_2$ (10%) | D-2 (3.0eq.) | 90 | 52 |
| **33** | **2** | $Cu_2O$ (10%) | D-2 (3.0eq.) | 90 | 69 |
| **34** | **2** | $Cu(OAc)_2$ (10%) | D-2 (3.0eq.) | 90 | 64 |

| | | | | | |
|---|---|---|---|---|---|
| **35** | **2** | $CuBr_2$ (10%) | D-2 (3.0eq.) | 90 | 28 |
| **36** | **2** | $FeBr_2$ (10%) | D-2 (3.0eq.) | 90 | - |
| **37** | **2** | $NiCl_2$ (10%) | D-2 (3.0eq.) | 90 | - |
| **38** | **2** | $CoBr_2$ (10%) | D-2 (3.0eq.) | 90 | - |
| **39**[g] | **2** | CuBr (10%) | D-2 (3.0eq.) | 90 | 73 |
| 40[h] | 2 | $CuBr_2$ (2.5 %)/$FeBr_3$(5 %) | - | 55 | - |

[a]Conditions: **1** **(**0.25 mmol, 28.6 $\mu$L), catalyst and additive were stirred in 1 mL DMSO under 1 atm. $O_2$ balloon for about 12h. [b]GC yields. [c]5 mmol DMSO in 1 mL referred solvent. [d]Lei's condition. [e]Isolated yield. [f] D-1:1,10-phenanthroline D-2:HPO(OEt)$_2$; D-3:HPO(OMe)$_2$; D-4:HP(O$^n$Bu)$_2$; D-5: HP(O$^i$Bu)$_2$; D-6:HPO(OPh)$_2$. [g]1 atm. air balloon. [h]Ji's condition

## Table-2 Optimization reaction conditions for (*E*)-vinyl methyl sulfones[a]

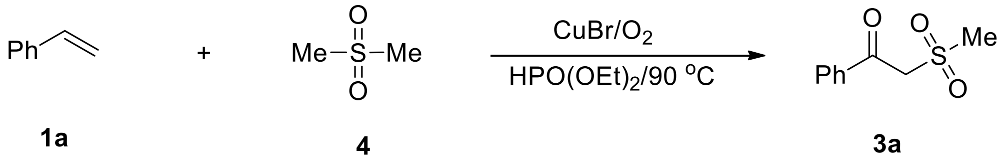


| Entry | Catalyst | Additives[f] | Temp. | GC Yield(%)[b] |
|---|---|---|---|---|
| 1 | CuBr(10%) | D-2 (3.0 eq.) | 90 | 64 |
| 2 | CuBr(10%) | - | 90 | - |
| 3 | - | D-2 (3.0 eq.) | 90 | - |
| 4 | CuBr (10%) | D-2 (4.0 eq.) | 90 | 53 |
| 5 | Cu(OTf)(10%).Benzene | D-2 (3.0 eq.) | 90 | 38 |
| 6 | Cu(OAc)(10%) | D-2 (3.0 eq.) | 90 | 32 |
| 7 | CuCN(10%) | D-2 (3.0 eq.) | 90 | 54 |
| 8 | CuTC(10%) | D-2 (3.0 eq.) | 90 | 27 |
| 9 | CuCl | D-2 (3.0 eq.) | 90 | 28 |
| 10 | CuI(10%) | D-2 (3.0 eq.) | 90 | 43 |
| 11 | Cu(OTf)$_2$(10%) | D-2 (3.0 eq.) | 90 | 39 |
| 12 | Cu(OAc)$_2$(10%) | D-2 (3.0 eq.) | 90 | 51 |
| 13 | CuBr(10%) | D-4 (3.0 eq.) | 90 | 60 |
| 14 | CuBr(10%) | D-6 (3.0 eq.) | 90 | - |
| 15 | CuBr(10%) | D-2 (3.0 eq.) | 120 | 75 |
| 16 | CuBr(10%) | D-2 (3.0eq.)+TEA[c] | 120 | - |
| 17 | CuBr(10%) | D-2 (3.0eq.)+HOAc[c] | 120 | 45 |
| 18 | CuBr(10%) | D-2 (3.0eq.)+Ag(OTf)[d] | 120 | 54 |
| 19 | CuBr(10%) | D-2 (3.0eq.)+$NiCl_2$[d] | 120 | - |
| 20 | CuBr(10%) | D-2 (3.0eq.)+$ZnBr_2$[d] | 120 | - |
| 21 | CuBr(10%) | D-2 (3.0eq.)+$FeBr_2$[d] | 120 | - |
| 22 | CuBr(10%) | D-2 (3.0eq.)+$H_2O$ (10 eq.) | 120 | 88 (85[e]) |
| 23 | CuBr(10%) | D-2 (3.0eq.)+$H_2O$ (20 eq.) | 120 | 83 |

[a]Conditions: **1** **(**0.25 mmol, 27.5 $\mu$L), catalyst and additive were stirred in 1 mL DMSO under 1 atm. $O_2$ balloon for about 24h. [b]GC yields. [c]3.0 eq. [d]20 mol%. [e]Isolated yield. [f]D-2:HPO(OEt)$_2$; D-3:HPO(OMe)$_2$; D-4:HP(O$^n$Bu)$_2$; D-5:HP(O$^i$Bu)$_2$; D-6: HPO(OPh)$_2$.

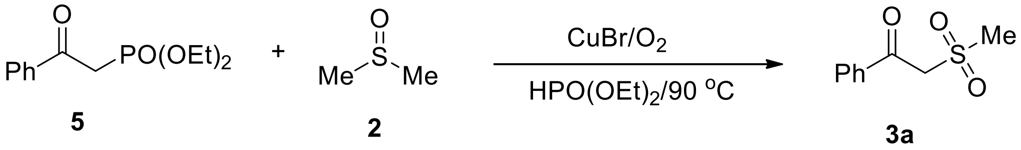
## Mechanism study:

### 1. Styrene reacted with dimethyl sulfone:



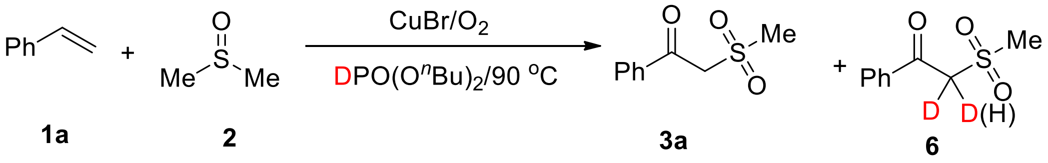
A mixture of alkene **1a** (0.25 mmol, 28.6 $\mu$L), dimethyl sulfone **4** (5 mmol, 470.5 mg), $HPO(OEt)_2$ (0.75 mmol, 96.6 $\mu$L) and CuBr (0.025 mmol, 3.6 mg) in 0.1 mL DCE in an oven-dried tube, which was stirred at 90 °C under 1 atm. $O_2$ atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material, there is no product was detected by GC analysis.

### 2. Keto phosphonate reacted with DMSO:



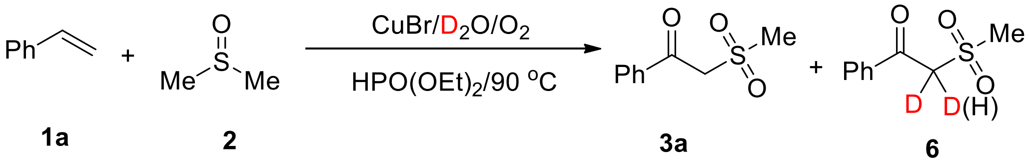
A mixture of phosphonate **5** (0.25 mmol, 64 mg), $HPO(OEt)_2$ (0.75 mmol, 96.6 $\mu$L) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 °C under 1 atm. $O_2$ atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material, there is no product was detected by GC analysis.

### 3. Styrene reacted with DMSO with D-labeling of dibutyl phosphite:



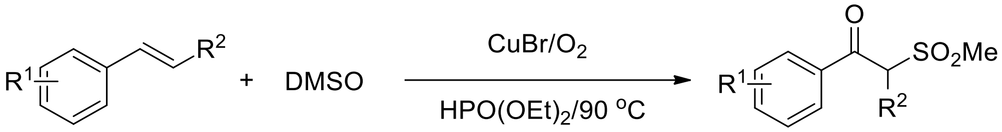
A mixture of alkene **1a** (0.25 mmol, 28.6 $\mu$L), $DPO(O^nBu)_2$ (0.75 mmol, 146.4 mg) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 °C under $O_2$ atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give **3a** in 80% isolated yield, there is no D-labeling product **6** was detected.

### 4. Styrene reacted with DMSO within $D_2O$



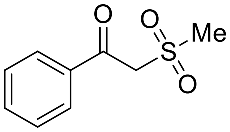
A mixture of alkene **1a** (0.25 mmol, 28.6 $\mu$L), $D_2O$ (5 mmol, 100 $\mu$L), $HPO(OEt)_2$ (0.75 mmol, 96.6 $\mu$L) and CuBr (0.025 mmol, 3.6 mg) in 1 mL DMSO in an oven-dried tube, which was stirred at 90 $^{o}$C under 1atm. $O_2$ atmosphere for 24h. After cooling down, the reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give **3a** in 83% isolated yield, there is no D-labeling product **6** was detected.

## General procedure for *β*-keto methyl sulfones:



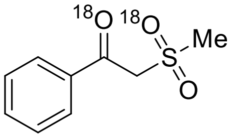
A mixture of alkene (0.25 mmol), DMSO **2** (1 mL), $HPO(OEt)_2$ (0.75 mmol, 96.6 *μ*L) and CuBr (0.025 mmol, 3.6 mg) in an oven-dried tube, which was stirred at 90 $^{o}$C under 1atm. $O_2$ atmosphere until the starting material was fully consumed (12 - 24 h). The reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give desired product.

**2-(Methylsulfonyl)-1-phenylethanone (3a):**



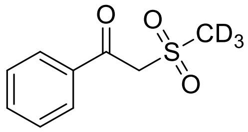
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp.104 - 105 ℃. Yield: 82%. $^{1}$H NMR (400 MHz, $CDCl_3$) *δ* 8.01 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 189.2, 135.6, 134.6, 129.2, 129.0, 61.2, 41.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{11}O_3S$: 199.0429. Found: 199.0424.

**2-(Methylsulfonyl)-1-phenylethanone (3a'):**



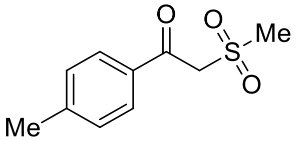
The title compound was prepared according to the general procedure with using 1atm. $^{18}O_2$ instead of $O_2$. The product was obtained as white solid, Mp.109 - 110 ℃. Yield: 64%. $^{1}$H NMR (400 MHz, $CDCl_3$) *δ* 8.01 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) *δ* 189.2, 189.2, 135.6, 134.7, 129.2, 129.0, 61.3, 41.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{11}O_3S$: 203.0514. Found: 203.0516.

**2-(Methylsulfonyl)-1-phenylethanone (3a''):**



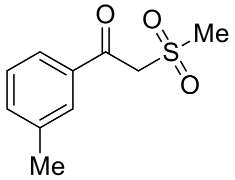
The title compound was prepared according to the general procedure with using *d*-DMSO instead. The product was obtained as white solid, Mp.114 - 115 ℃. Yield: 76%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.02 - 7.99 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.61 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_8D_3O_3S$: 202.0617. Found: 202.0617.

**2-(Methylsulfonyl)-1-(p-tolyl)ethanone (3b):**



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 116 - 117 ℃. Yield: 84%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.57 (s, 2H), 3.14 (s, 3H), 2.44 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 188.7, 146.0, 133.2, 129.7, 129.4, 61.2, 41.8, 21.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_3S$: 213.0585. Found: 213.0591.

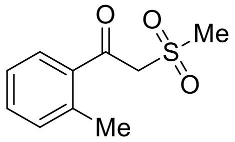
**Ethyl 2-isopropyl-6-phenylnicotinate (3c):**



The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp.65 - 66 ℃. Yield: 77%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.81 - 7.89 (m, 2H), 7.48 - 7.39 (m, 2H), 4.59 (m, 2H), 3.15 (s, 3H), 2.44 (s, 3H); $^{13}C$ NMR (100

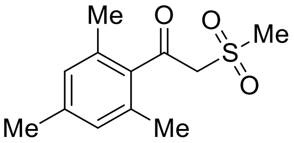
MHz, $CDCl_3$) $\delta$ 189.4, 139.0, 135.7, 135.5, 129.6, 128.9, 126.5, 61.3, 41.8, 21.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_3S$: 213.0585. Found: 213.0578.

**2-(Methylsulfonyl)-1-(o-tolyl)ethanone (3d):**



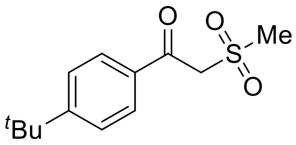
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 80%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.0 Hz, 1H), 7.49 - 7.45 (m, 1H), 7.36 - 7.29 (m, 2H), 4.56 (m, 2H), 3.17 (s, 3H), 2.56 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 191.6, 140.1, 135.7, 133.1, 132.5, 130.2, 126.1, 63.4, 42.0, 21.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_3S$: 213.0585. Found: 213.0591.

**1-Mesityl-2-(methylsulfonyl)ethanone (3e):**



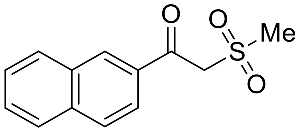
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 136 - 137 ℃. Yield: 43%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 6.88 (s, 2H), 4.34 (d, $J$ = 0.8 Hz, 2H), 3.23 (s, 3H), 2.29 (s, 3H), 2.28 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 197.9, 140.5, 137.1, 133.9, 129.2, 65.6, 42.6, 21.1, 19.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{17}O_3S$: 241.0898. Found: 241.0899.

**1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)ethanone (3f):**



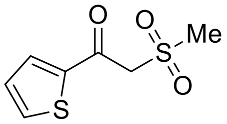
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 74%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (d, $J$ = 8.8 Hz, 2H), 7.53 (d, $J$ = 8.8 Hz, 2H), 4.58 (s, 2H), 3.14 (s, 3H), 1.35 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 188.7, 158.9, 133.1, 129.3, 126.0, 61.2, 41.7, 35.3, 30.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{19}O_3S$: 255.1055. Found: 255.1055.

**2-(Methylsulfonyl)-1-(naphthalen-2-yl)ethanone (3g):**



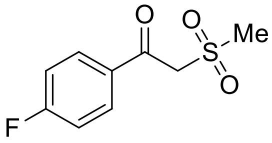
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 99 - 100 ℃. Yield: 78%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (s, 1H), 8.04 - 7.93 (m, 2H), 7.91 - 7.87 (m, 2H), 7.67 - 7.57 (m, 2H), 4.73 (s, 2H), 3.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 189.1, 136.1, 133.0, 132.3, 132.1, 130.0, 129.5, 129.0, 127.8, 127.3, 123.7, 61.3, 41.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{13}H_{13}O_3S$: 249.0585. Found: 249.0579.

**2-(methylsulfonyl)-1-(thiophen-2-yl)ethanone (3h):**



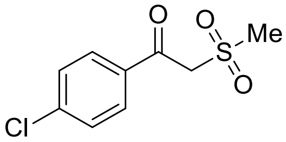
The title compound was prepared according to the general procedure. The product was obtained as brown solid, Mp. 121 - 122 ℃. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 - 7.84 (m, 1H), 7.82 - 7.81 (m, 1H), 7.23 - 7.20 (m, 1H), 4.51 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 181.2, 143.0, 137.0, 135.4, 128.9, 62.3, 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_7H_9O_3S_2$: 204.9993. Found: 204.9993.

**1-(4-fluorophenyl)-2-(methylsulfonyl)ethanone (3i):**



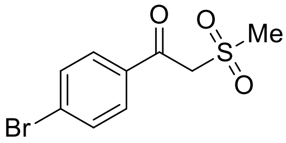
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp.89 - 90 ℃. Yield: 74%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 - 8.04 (m, 2H), 7.22 - 7.18 (m, 2H), 4.58 (s, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 187.6, 168.0, 165.4, 132.2 ($J$ = 9.8 Hz), 116.3 ($J_1$ = 22.2 Hz, $J_2$ = 1.3 Hz), 61.4 ($J$ = 2.8 Hz), 41.7; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_9H_{10}O_3SF$: 217.0335. Found: 217.0337.

**1-(4-Chlorophenyl)-2-(methylsulfonyl)ethanone (3j):**



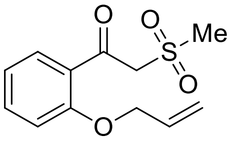
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 149 - 150 ℃. Yield: 65%. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 - 7.94 (m, 2H), 7.52 - 7.50 (m, 2H), 4.57 (s, 2H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 188.1, 141.5, 133.9, 130.7, 129.4, 61.3, 41.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}O_3SCl$: 233.0039. Found: 233.0033.

**1-(4-Bromophenyl)-2-(methylsulfonyl)ethanone (3k):**



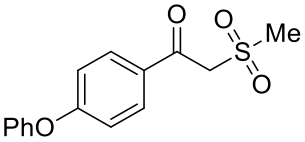
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 160 - 161 ℃. Yield: 77%. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.88 - 7.86 (m, 2H), 7.69 - 7.67 (m, 2H), 4.56 (s, 2H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 188.3, 134.3, 132.4, 130.7, 130.4, 61.3, 41.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}O_3SBr$: 276.9534. Found: 276.9535.

**1-(2-(allyloxy)phenyl)-2-(methylsulfonyl)ethanone (3l):**



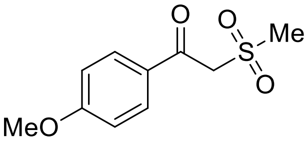
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 75%. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.83 - 7.81 (m, 1H), 7.55 - 7.51 (m, 1H), 7.07 - 7.03 (m, 1H), 6.99 (d, $J$ = 8.4 Hz, 1H), 6.16 - 6.06 (m, 1H), 5.47 - 5.37 (m, 2H), 4.78 (s, 2H), 4.71 - 4.69 (m, 2H), 3.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 190.2, 158.3, 135.5, 131.9, 131.3, 126.4, 121.3, 119.4, 113.1, 69.9, 65.4, 42.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{15}O_4S$: 255.0691. Found: 255.0702.

**2-(Methylsulfonyl)-1-(4-phenoxyphenyl)ethanone (3m):**



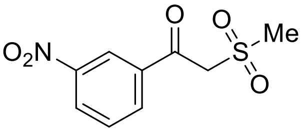
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp. 124 - 125 ℃. Yield: 75%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 - 7.97 (m, 2H), 7.44 - 7.40 (m, 2H), 7.26 - 7.22 (m, 1H), 7.10 - 7.07 (m, 2H), 7.04 - 7.02 (m, 2H), 4.55 (s, 2H), 3.14 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.5, 163.6, 154.8, 131.8, 130.2, 125.1, 120.5, 117.3, 61.2, 41.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{15}O_4S$: 291.0691. Found: 291.0686.

**1-(4-Methoxyphenyl)-2-(methylsulfonyl)ethanone (3n):**



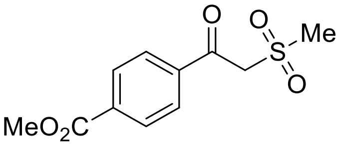
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp.139 - 140 ℃. Yield: 68%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.99 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2H), 6.98 (dd, $J_1$ = 7.2 Hz, $J_2$ = 2.4 Hz, 2H), 4.55 (s, 2H), 3.89 (s, 3H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.3, 164.8, 131.8, 128.7, 114.2, 61.2, 55.6, 41.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_4S$: 229.0535. Found: 229.0529.

**2-(Methylsulfonyl)-1-(3-nitrophenyl)ethanone (3o):**



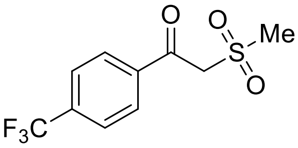
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 104 - 105 ℃. Yield: 66%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.85 - 8.84 (m, 1H), 8.53 - 8.50 (m, 1H), 8.37 - 8.34 (m, 1H), 7.79 - 7.75 (m, 1H), 4.67 (s, 2H), 3.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 187.5, 148.7, 136.9, 134.7, 130.4, 128.7, 124.1, 61.5, 41.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}NO_5S$: 244.0280. Found: 244.0285.

**Methyl 4-(2-(methylsulfonyl)acetyl)benzoate (3p):**



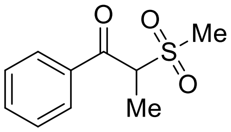
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 129 - 130 ℃. Yield: 52%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 - 8.17 (m, 2H), 8.08 - 8.06 (m, 2H), 4.63 (s, 2H), 3.97 (s, 3H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 188.9, 165.8, 138.6, 135.2, 130.1, 129.2, 61.6, 52.6, 41.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{13}O_5S$: 257.0484. Found: 257.0489.

**2-(Methylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethanone (3q):**



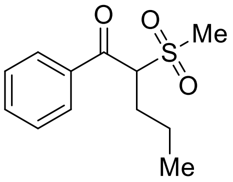
The title compound was prepared according to the general procedure. The product was obtained as white solid, Mp.100 - 101 ℃. Yield: 81%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.13 (d, $J$ = 8.4 Hz, 2H), 7.80 (d, $J$ = 8.0 Hz, 2H), 4.64 (s, 2H), 3.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 188.5, 138.2, 135.8 ($J$ = 32.8 Hz), 129.6, 126.1 ($J$ = 3.5 Hz), 123.3 ($J$ = 271.3 Hz), 61.5, 41.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{10}O_3SF_3$: 267.0303. Found: 267.0311.

**2-(Methylsulfonyl)-1-phenylpropan-1-one (3r):**



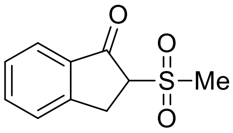
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 71%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04 - 8.02 (m, 2H), 7.68 - 7.64 (m, 1H), 7.55 - 7.51 (m, 2H), 4.96 (q, $J$ = 7.2 Hz, 1H), 2.98 (s, 3H), 1.75 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 194.0, 135.7, 134.5, 129.2, 129.0, 64.0, 36.9, 13.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_3S$: 213.0585. Found: 213.0591.

**2-(Methylsulfonyl)-1-phenylpentan-1-one (3r'):**



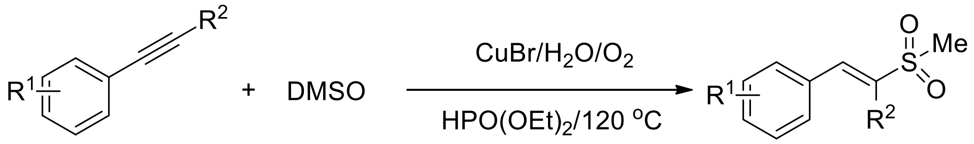
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 50%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 - 8.02 (m, 2H), 7.67 - 7.63 (m, 1H), 7.55 - 7.51 (m, 2H), 4.87 (dd, $J_1$ = 11.6 Hz, $J_1$ = 3.2 Hz, 1H), 2.96 (s, 3H), 2.32 - 2.15 (m, 2H), 1.38 - 1.32 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.2, 136.9, 134.4, 129.1, 129.0, 68.8, 37.2, 31.2, 20.7, 13.8; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{12}H_{17}O_3S$: 241.0898. Found: 241.0902.

**2-(methylsulfonyl)-2,3-dihydro-*1H*-inden-1-one (3s):**



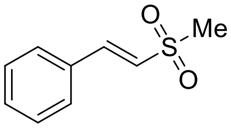
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. Mp: 157 - 158 ℃. Yield: 70%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 7.6 Hz, 1H), 7.70 - 7.66 (m, 1H), 7.56 - 7.54 (m, 1H), 7.46 - 7.42 (m, 1H), 4.15 (dd, $J_1$ = 8.4 Hz, $J_2$ = 3.6 Hz, 1H), 3.80 (dd, $J_1$ = 18.0 Hz, $J_2$ = 3.6 Hz, 1H), 3.51 (dd, $J_1$ = 18.0 Hz, $J_2$ = 8.4 Hz, 1H), 3.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 195.7, 152.5, 136.3, 135.4, 128.4, 126.6, 125.1, 67.0, 40.2, 26.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{10}H_{11}O_3S$: 211.0429. Found: 211.0428.

## General procedure for (*E*)-vinyl methyl sulfones:



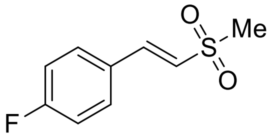
A mixute of alkyne compound (0.25 mmol), DMSO **2** (1 mL), $HPO(OEt)_2$ (0.75 mmol, 96.6 $\mu$L), $H_2O$ (2.5 mmol, 45 $\mu$L) and CuBr (0.025 mmol, 3.6 mg) in an oven-dried tube, which was stirred at 120 $^{o}$C under 1atm. $O_2$ atmosphere until the starting material was fully consumed. The reaction mixture was diluted with 10 mL ethyl acetate (EA) and washed with water (2 mL) for 3 times. The water solution was extracted with EA twice and combined top layer with previous organic mixtures. After dried with $Na_2SO_4$, the mixture was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (1:1) to give desired product.

### (*E*)-(2-(methylsulfonyl)vinyl)benzene (5a):



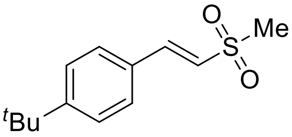
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 85%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64 (d, *J* = 15.2 Hz, 1H), 7.54 - 7.51 (m, 2H), 7.46 - 7.43 (m, 3H), 6.92 (d, *J* = 15.2 Hz, 1H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 144.0, 132.0, 131.3, 129.1, 128.5, 126.2, 43.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{11}O_2S$: 183.0480. Found: 183.0476.

### (E)-1-fluoro-4-(2-(methylsulfonyl)vinyl)benzene (5b):



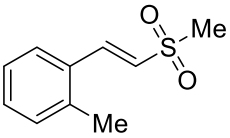
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 126 - 127 ℃. Yield: 82%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60 (d, *J* = 15.2 Hz, 1H), 7.54 - 7.51 (m, 2H), 7.15 - 7.10 (m, 2H), 6.86 (d, *J* = 15.6 Hz, 1H), 3.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5 (*J* = 251.9 Hz), 142.7, 130.6 (*J* = 34.5 Hz), 128.3, 125.9, 116.4 ($J$ = 22.1 Hz), 43.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}O_2SF$: 201.0386. Found: 201.0382.

**(*E*)-1-(*tert*-butyl)-4-(2-(methylsulfonyl)vinyl)benzene (5c):**



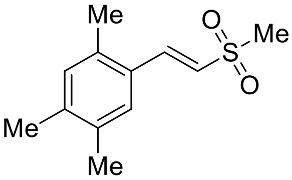
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 87 - 88 ℃. Yield: 79%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.61 (d, $J$ = 15.2 Hz, 1H), 7.48 - 7.43 (m, 4H), 6.88 (d, $J$ = 15.6 Hz, 1H), 3.03 (s, 3H), 1.33 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 155.2, 144.0, 129.3, 128.4, 126.1, 125.1, 43.4, 35.0, 31.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{19}O_2S$: 239.1106. Found: 239.1104.

**(*E*)-1-methyl-2-(2-(methylsulfonyl)vinyl)benzene (5d):**



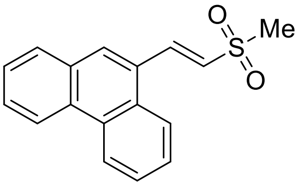
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 85 -86 ℃. Yield: 75%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 15.2 Hz, 1H), 7.52 - 7.50 (m, 1H), 7.36 - 7.32 (m, 1H), 7.26 - 7.23 (m, 2H), 6.84 (d, $J$ = 15.2 Hz, 1H), 3.04 (m, 3H), 2.46 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 141.7, 138.3, 131.1, 131.0, 127.1, 126.8, 126.6, 43.3, 19.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{13}O_2S$: 197.0636. Found: 197.0639.

**(*E*)-1,2,4-trimethyl-5-(2-(methylsulfonyl)vinyl)benzene (5e):**



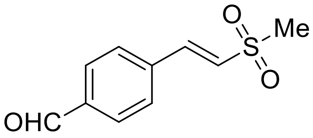
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 97 - 98 ℃. Yield: 54%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 (d, $J$ = 15.2 Hz, 1H), 7.29 (s, 1H), 7.01 (s, 1H), 6.80 (d, $J$ = 15.2 Hz, 1H), 3.03 (s, 3H), 2.38 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.6, 140.5, 135.8, 134.7, 132.4, 128.3, 127.9, 125.5, 43.4, 19.7, 19.2, 19.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{17}O_2S$: 225.0949. Found: 225.0953.

**(E)-9-(2-(methylsulfonyl)vinyl)phenanthrene (5f):**



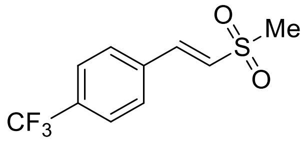
The title compound was prepared according to the general procedure. The product was obtained as dark solid, Mp: 122 - 123 ℃. Yield: 77%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.75 (d, $J$ = 8.0 Hz, 1H), 8.68 (d, $J$ = 8.4 Hz, 1H), 8.48 (d, $J$ = 15.2 Hz, 1H), 8.15 (d, $J$ = 8.4 Hz, 1H), 7.98 (s, 1H), 7.92 (d, $J$ = 8.0 Hz, 1H), 7.76 - 7.72 (m, 4H), 7.11 (d, $J$ = 15.2 Hz, 1H), 3.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.0, 131.5, 130.8, 130.5, 129.6, 129.4, 129.3, 128.6, 128.3, 127.6, 127.4, 127.3, 127.3, 124.1, 123.4, 122.7, 43.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{15}O_2S$: 283.0793. Found: 283.0799.

**(*E*)-4-(2-(methylsulfonyl)vinyl)benzaldehyde (5g):**



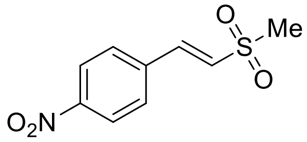
The title compound was prepared according to the general procedure. The product was obtained as colorless solid, Mp. 140 - 141 ℃. Yield: 71%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.06 (s, 1H), 7.95 (d, $J$ = 8.0 Hz, 2H), 7.69 (d, $J$ = 8.4 Hz, 2H), 7.68 (d, $J$ = 15.2 Hz, 1H), 7.05 (d, $J$ = 15.6 Hz, 1H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 191.2, 142.3, 137.9, 137.6, 130.3, 129.3, 129.1, 43.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{10}H_{11}O_3S$: 211.0429. Found: 211.0425.

**(*E*)-1-(2-(methylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (5h):**



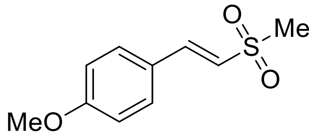
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.142 - 143 ℃. Yield: 83%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 - 7.63 (m, 5H), 7.02 (d, *J* = 15.6 Hz, 1H), 3.07 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.2, 135.5, 132.9 (*J* = 32.5 Hz), 128.9, 128.7, 126.2 (*J* = 3.7 Hz), 123.6 (*J* = 270.8 Hz), 43.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{10}H_{10}O_2SF_3$: 251.0354. Found: 251.0352.

**(*E*)-1-(2-(methylsulfonyl)vinyl)-4-nitrobenzene (5i):**



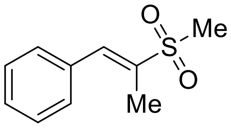
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp. 189 - 190 ℃. Yield: 63%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 - 8.28 (m, 2H), 7.71 - 7.67 (m, 3H), 7.08 (d, *J* = 15.6 Hz, 1H), 3.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.2, 141.1, 138.1, 130.5, 129.3, 124.4, 43.1; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_9H_{10}NO_4S$: 228.0331. Found: 228.0333.

**(*E*)-1-methoxy-4-(2-(methylsulfonyl)vinyl)benzene (5j):**



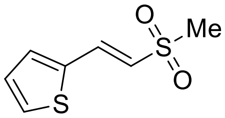
The title compound was prepared according to the general procedure. The product was obtained as yellow solid, Mp.119 - 120 ℃. Yield: 80%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, *J* = 15.6 Hz, 1H), 7.47 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2H), 6.94 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2H), 6.76 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 3H), 3.02 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 143.7, 130.4, 124.7, 123.4, 114.6, 55.5, 43.5; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{10}H_{13}O_3S$: 213.0585. Found: 213.0583.

**(*E*)-(2-(methylsulfonyl)prop-1-en-1-yl)benzene (5k):**



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 75%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (s, 1H), 7.46 - 7.39 (m, 5H), 2.98 (s, 3H), 2.34 (d, *J* = 1.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.1, 136.8, 133.6, 129.6, 129.5, 128.8, 40.4, 13.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_{10}H_{13}O_2S$: 197.0636. Found: 197.0639.

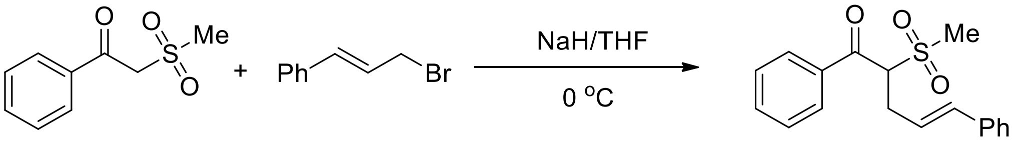
**(*E*)-2-(2-(methylsulfonyl)vinyl)thiophene (5l):**



The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield: 68%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, *J* = 15.2 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.11 - 7.09 (m, 1H), 6.70 (d, J = 15.2 Hz, 1H), 3.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.6, 136.5, 132.7, 130.1, 128.4, 124.2, 43.4; HRMS (ESI) m/z [M+H]$^+$: Calcd for $C_7H_9O_2S_2$: 189.0044. Found: 189.0047.

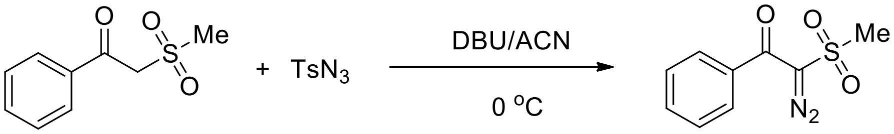
## Applications of *β*-keto methyl sulfones:

### (*E*)-2-(methylsulfonyl)-1,5-diphenylpent-4-en-1-one



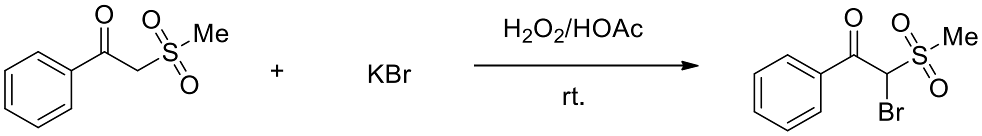
The title compound was prepared according to the following procedure: To a solution of NaH (0.24 mmol, 9.6 mg) in 5 mL THF, **3a** (0.20 mmol, 39.6 mg) in 1mL THF solution was added dropwise, the resulted mixture was stirred for 0.5h, then (*E*)-(3-bromoprop-1-en-1-yl)benzene (0.24 mmol, 47.3 mg) in 1mL THF solution was added at 0 °C. The reaction mixture was allowed at 50 °C for around 6h until the **3a** was consumed completely. It quenched with 5mL $NH_4Cl$, and extracted with ethyl acetate for 3 times. The combined organic lay was concentrated under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as yellow solid, Mp. 133-135 °C. Yield: 92%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 7.6 Hz, 2H), 7.62 (t, $J$ = 7.6 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 2H), 7.26 - 7.20 (m, 5H), 6.50 (d, $J$ = 15.6 Hz, 1H), 6.03 - 5.95 (m, 1H), 5.00 (dd, $J_1$ = 10.0 Hz, $J_2$ = 4.4 Hz, 1H), 3.22 - 3.13 (m, 2H), 3.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 193.6, 136.7, 136.3, 134.5, 134.5, 129.2, 129.0, 128.5, 127.8, 126.3, 122.6, 68.7, 37.7, 32.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{19}O_3S$: 315.1055. Found: 315.1059.

### 2-Diazo-2-(methylsulfonyl)-1-phenylethanone:



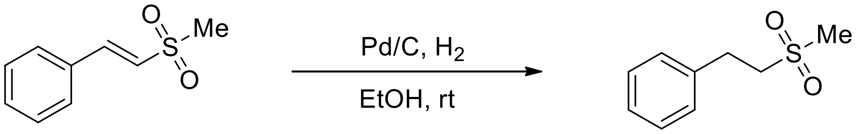
The title compound was prepared according to the following procedure: **3a** (0.20 mmol, 39.6 mg) and tosyl azide (0.24 mmol, 47.3 mg) was added to 5 mL dry $CH_3CN$, the resulting mixture was cooled at 0 °C. DBU (0.24 mmol, 36.5 mg) was then added dropwisely and the mixture was stirred for around 2h until the **3a** was consumed completely based on TLC. The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as yellow oil. Yield: 88%. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 - 7.66 (m, 2H), 7.64 - 7.60 (m, 1H), 7.53 - 7.49 (m, 2H), 3.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 183.3, 135.5, 133.4, 129.1, 127.4, 45.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}N_2O_3S$: 225.0334. Found: 225.0338.

**2-Bromo-2-(methylsulfonyl)-1-phenylethanone**



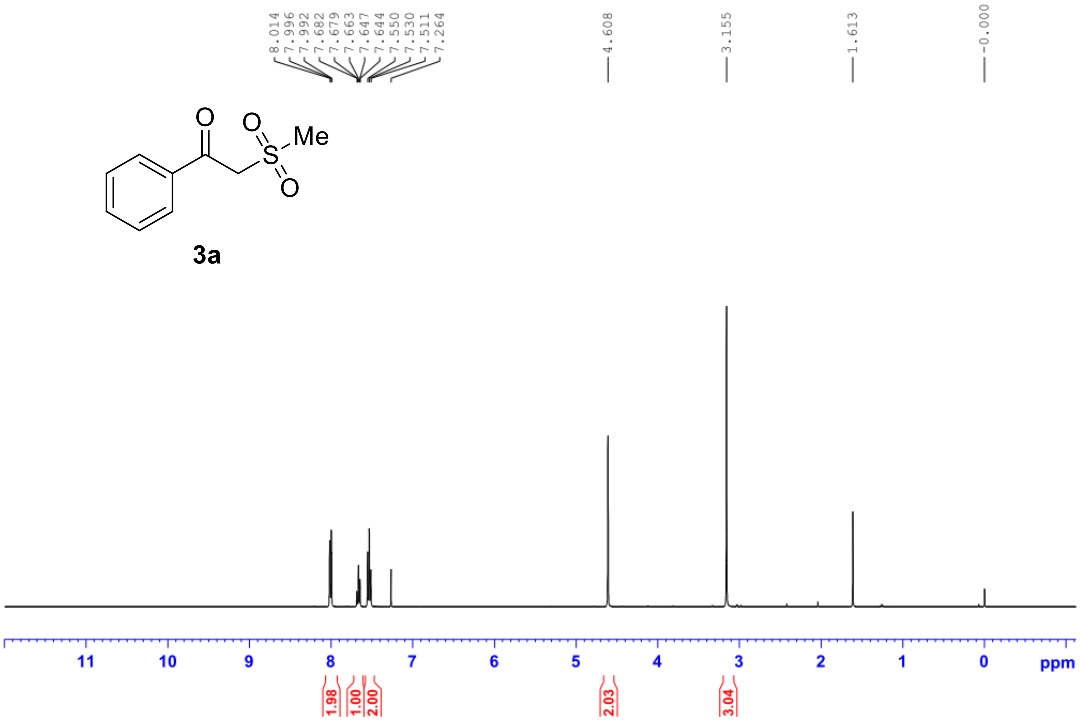
The title compound was prepared according to the reported procedure. **3a** (0.20 mmol, 39.6 mg) and KBr (0.24 mmol, 28.6 mg) was added to 2 mL acetic acid, the resulting mixture was cooled at 0 °C. $H_2O_2$ (1.6 mmol, 48.0 $\mu$L) was then added slowly and the mixture was stirred for overnight at room temperature until the **3a** was consumed completely based on TLC. The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (4:1) to give desired product as white solid, mp. 80-82 °C. Yield: 86%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.01- 7.98 (m, 2H), 7.72 - 7.68 (m, 1H), 7.57 - 7.53 (m, 2H), 6.00 (s, 1H), 3.35 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 187.8, 135.1, 133.8, 129.3, 129.2, 55.9, 37.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{10}BrO_3S$: 276.9534. Found: 276.9536.

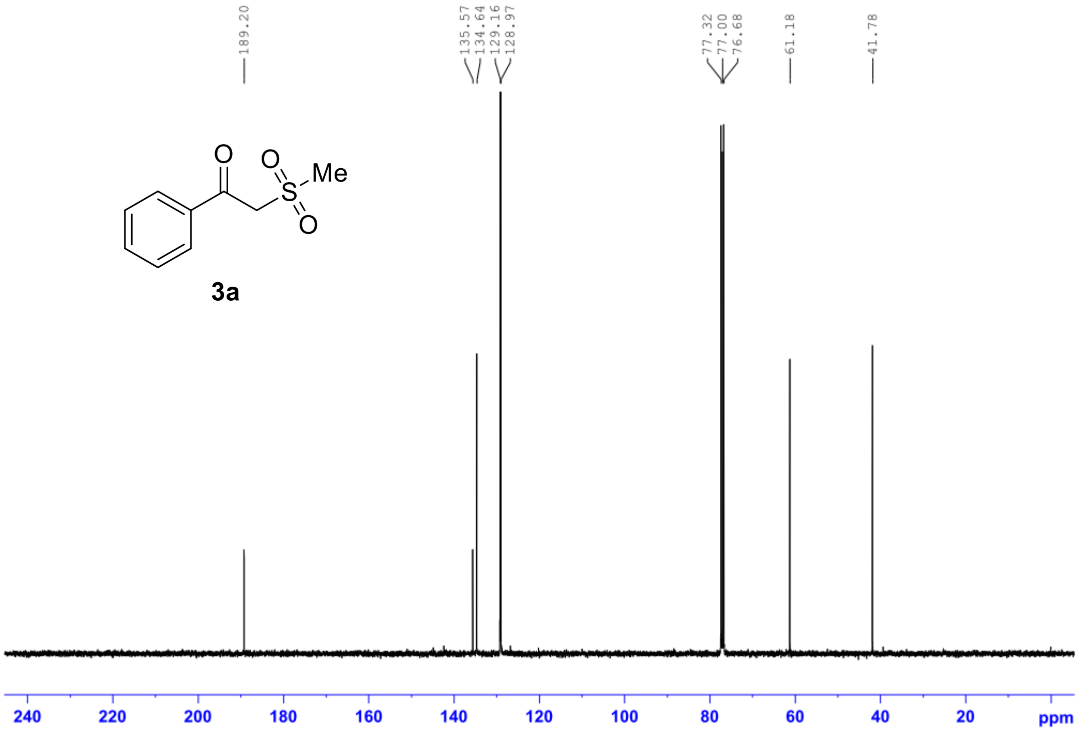
**(2-(Methylsulfonyl)ethyl)benzene**

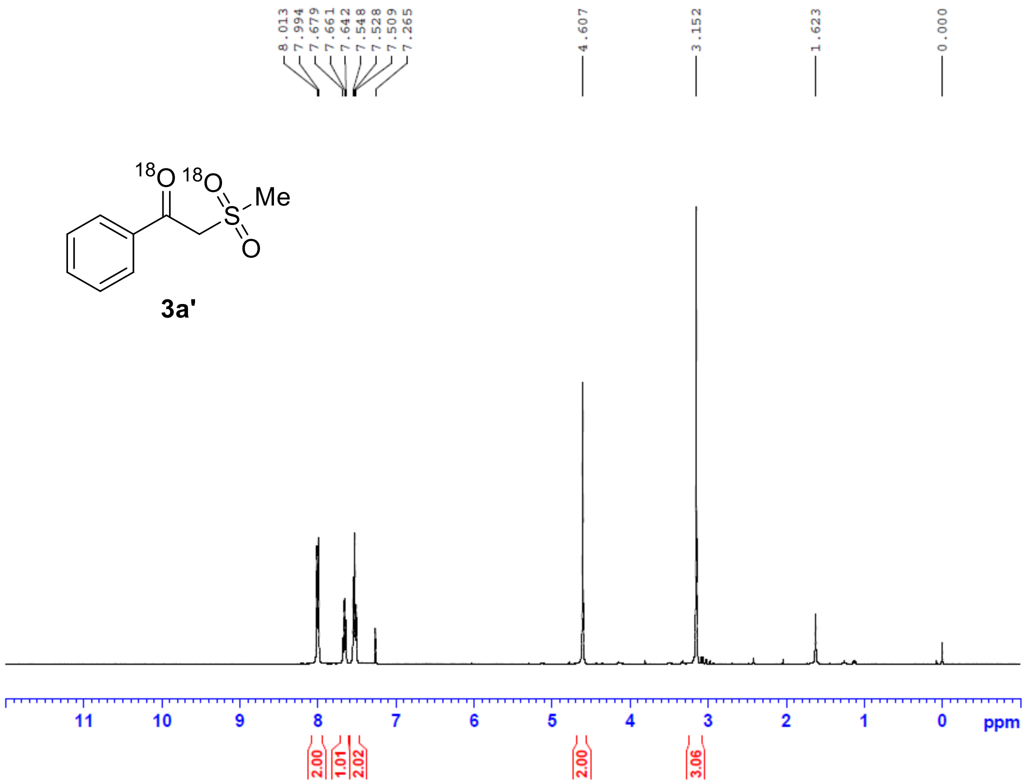


The title compound was prepared according to the following procedure. **3a** (0.20 mmol, 36.4 mg) and Pd/C (10%, 4 mg) was added to 2 mL anhydrous ethanol, the resulting mixture was stirred under 1 atm. $H_2$ balloon for overnight at room temperature until the **3a** was consumed completely based on TLC (the product is positive to $KMnO_4$ solution on TLC). The reaction mixture was concentrated directly under reduced pressure to give the crude material which was purified by flash chromatography using hexane - ethyl acetate (2:1) to give desired product as white solid, mp. 88-89 °C. Yield: 95%. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.36 - 7.28 (m, 2H), 7.26 - 7.23 (m, 3H), 3.32 - 3.28 (m, 2H), 3.19 - 3.15 (m, 2H), 2.82 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 137.4, 129.0, 128.4, 127.1, 56.2, 41.0, 28.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_9H_{13}O_2S$: 185.0636. Found: 185.0637.

## NMR Spetra for *β*-keto methyl sulfones



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Me
O
3a'
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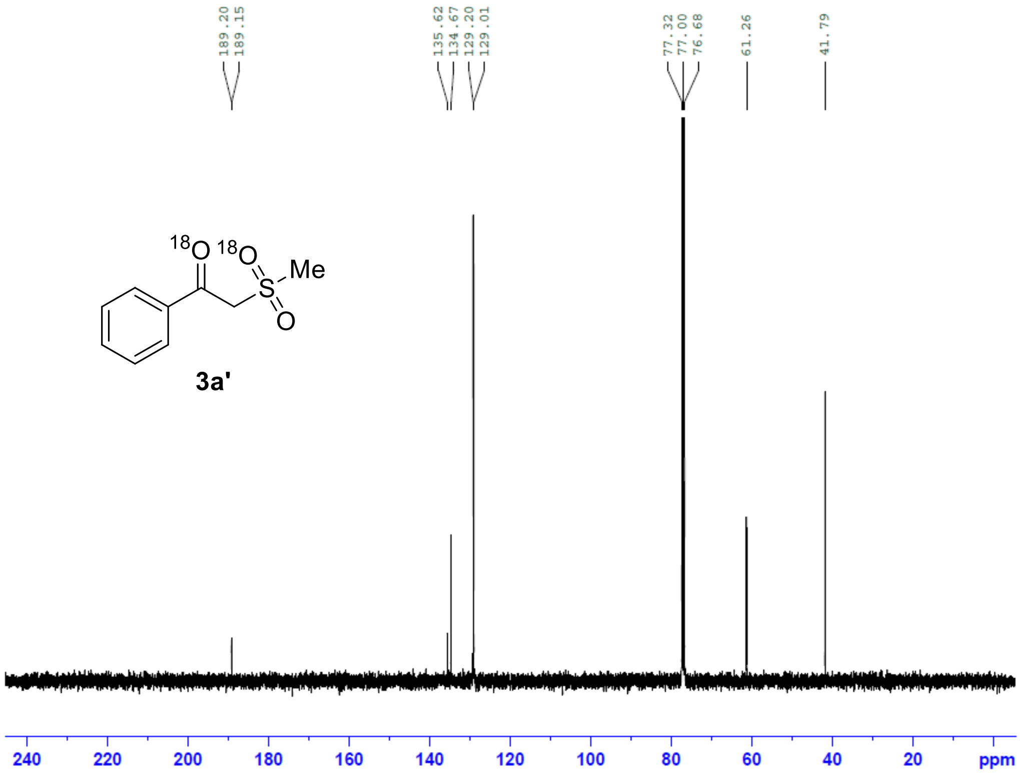
3.06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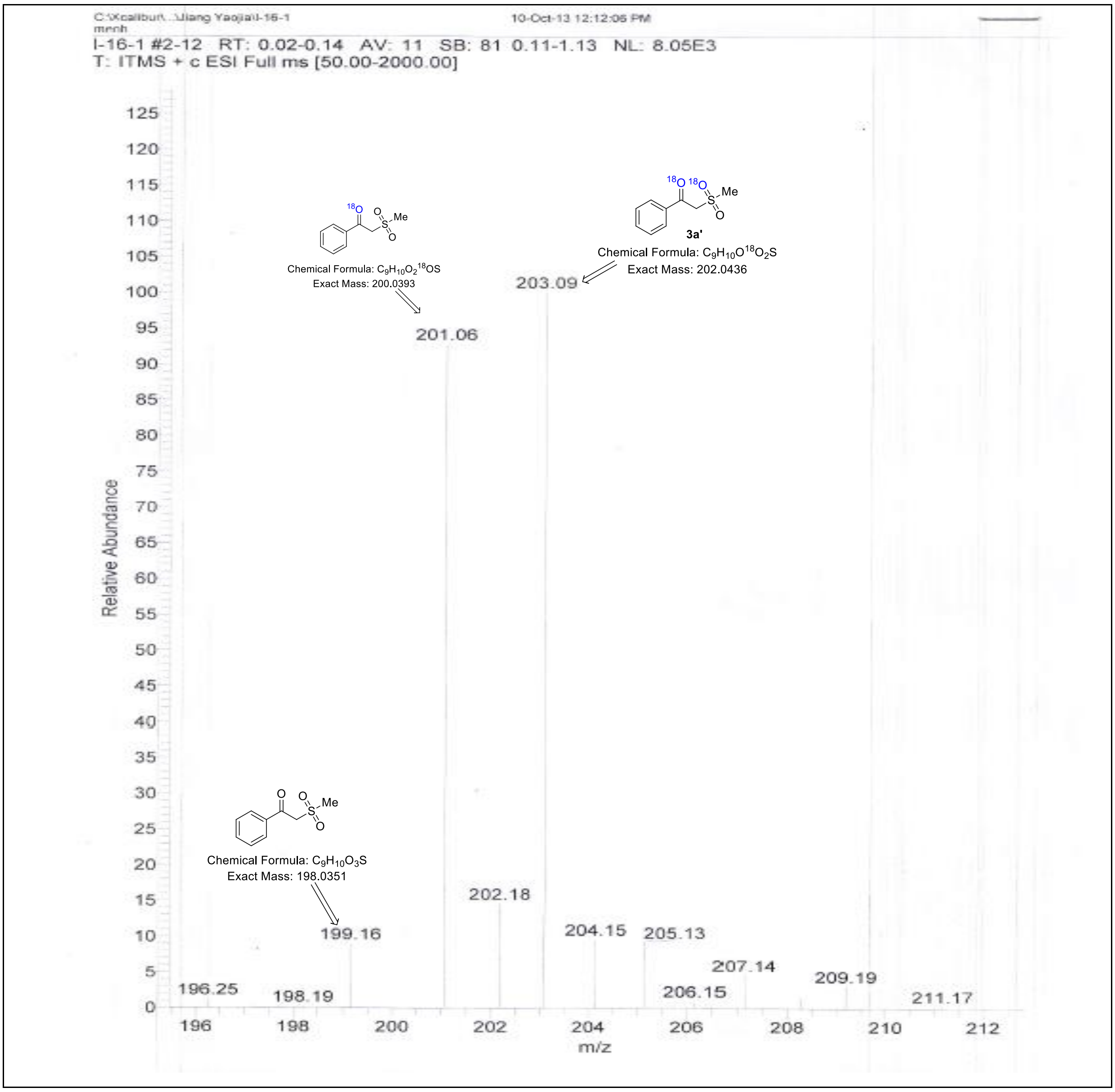
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meoh
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Relative Abundance
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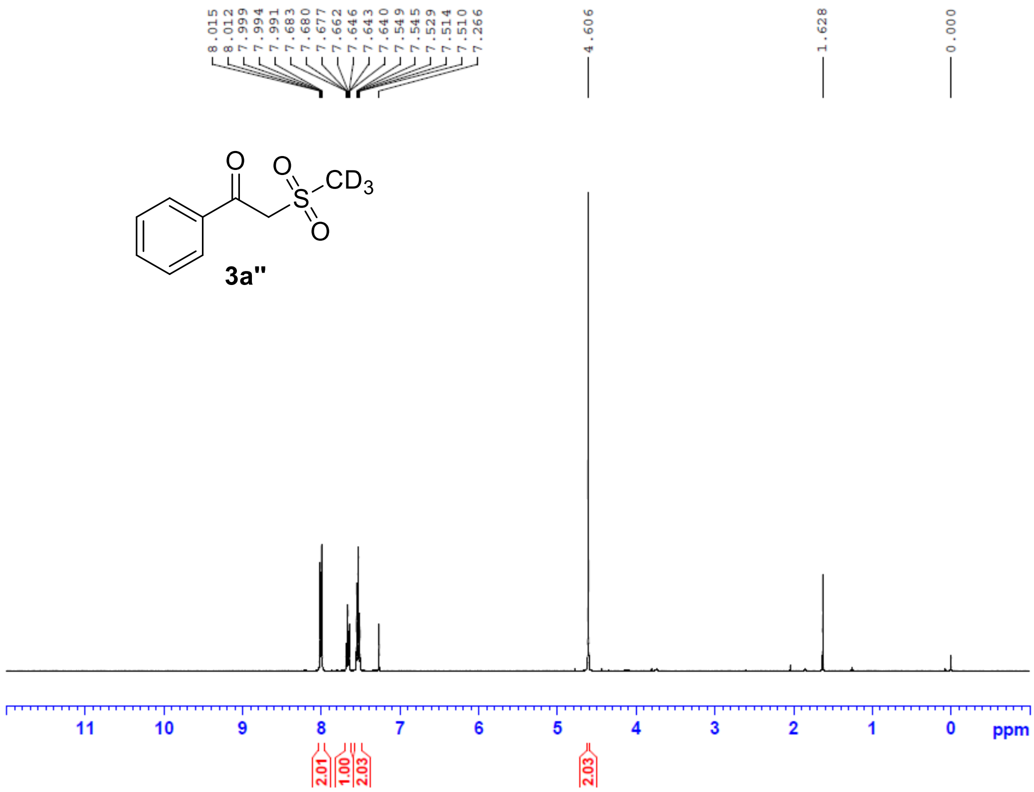
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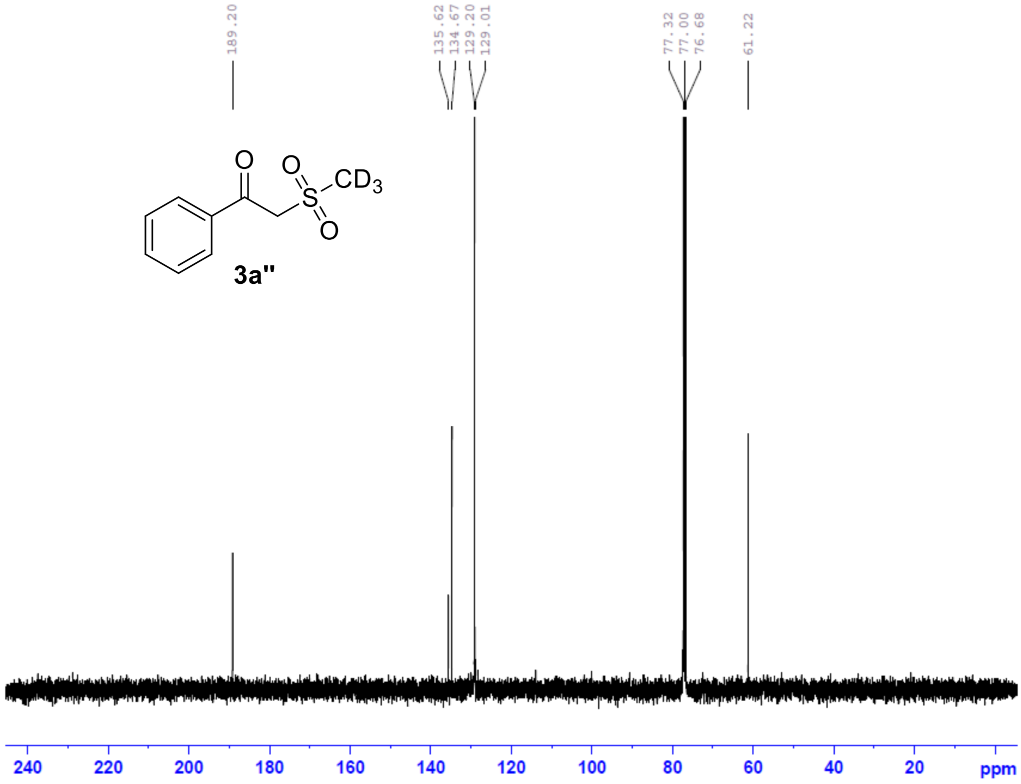
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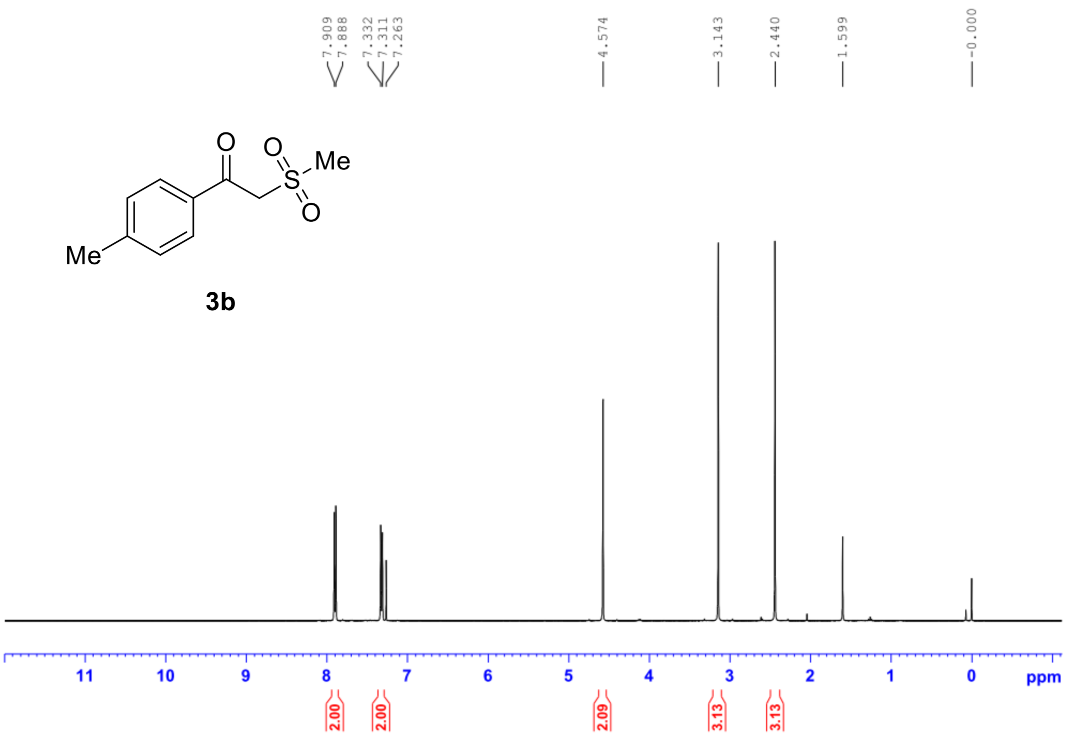
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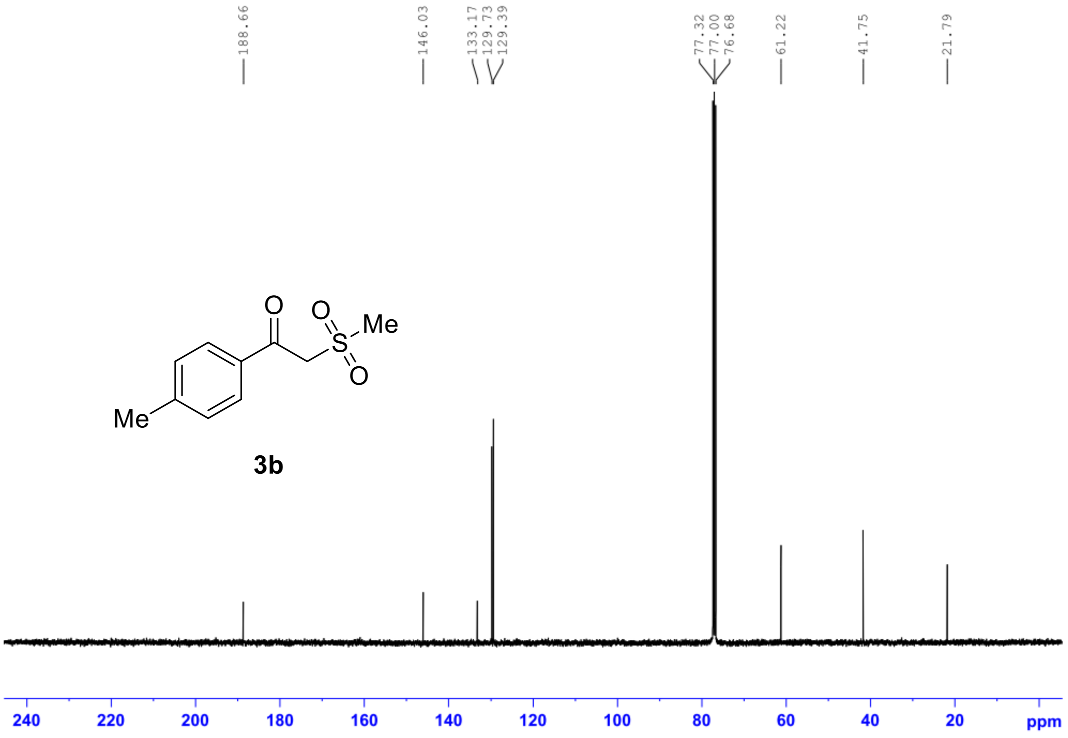
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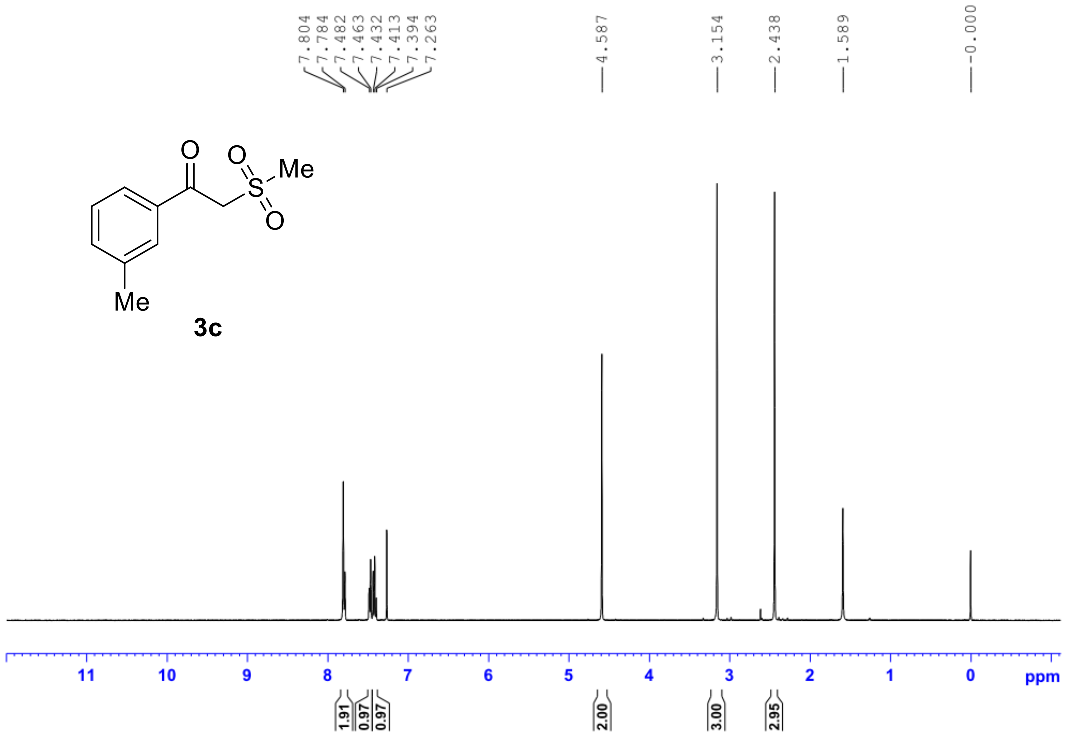
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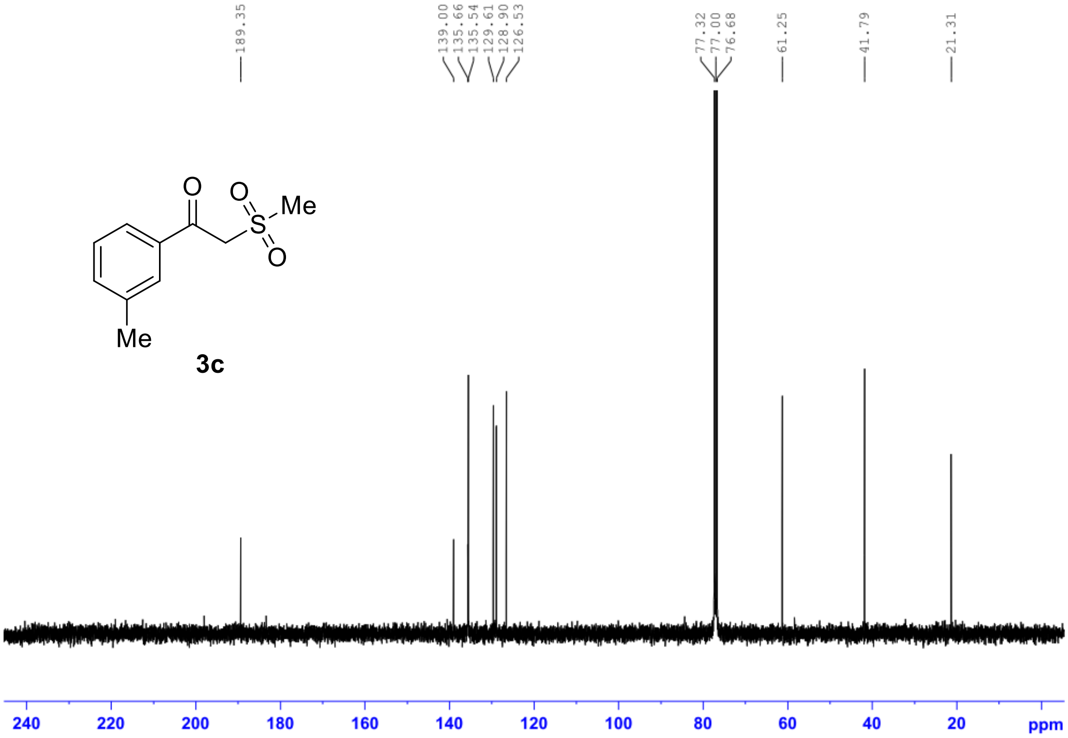
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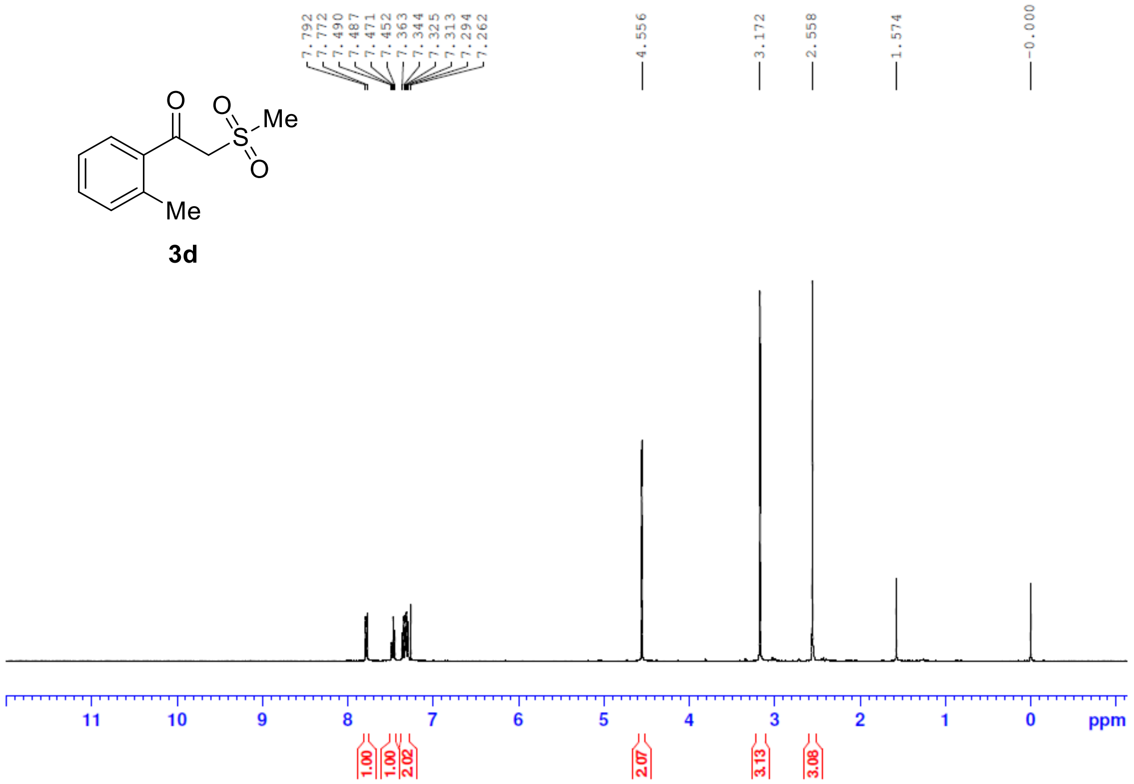
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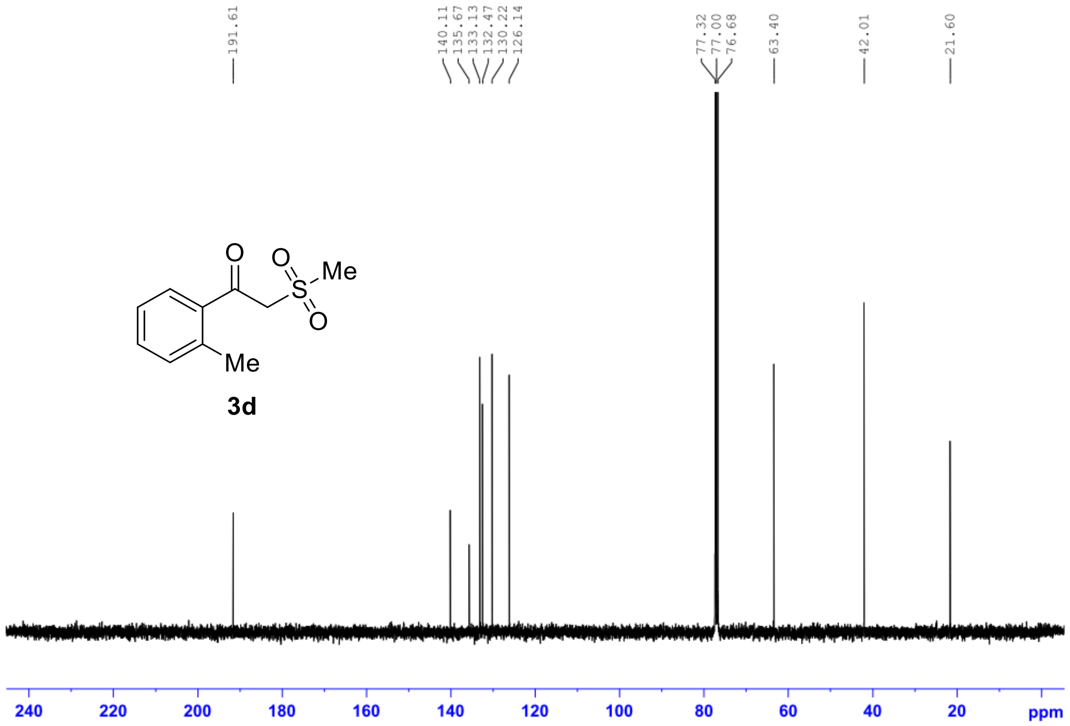
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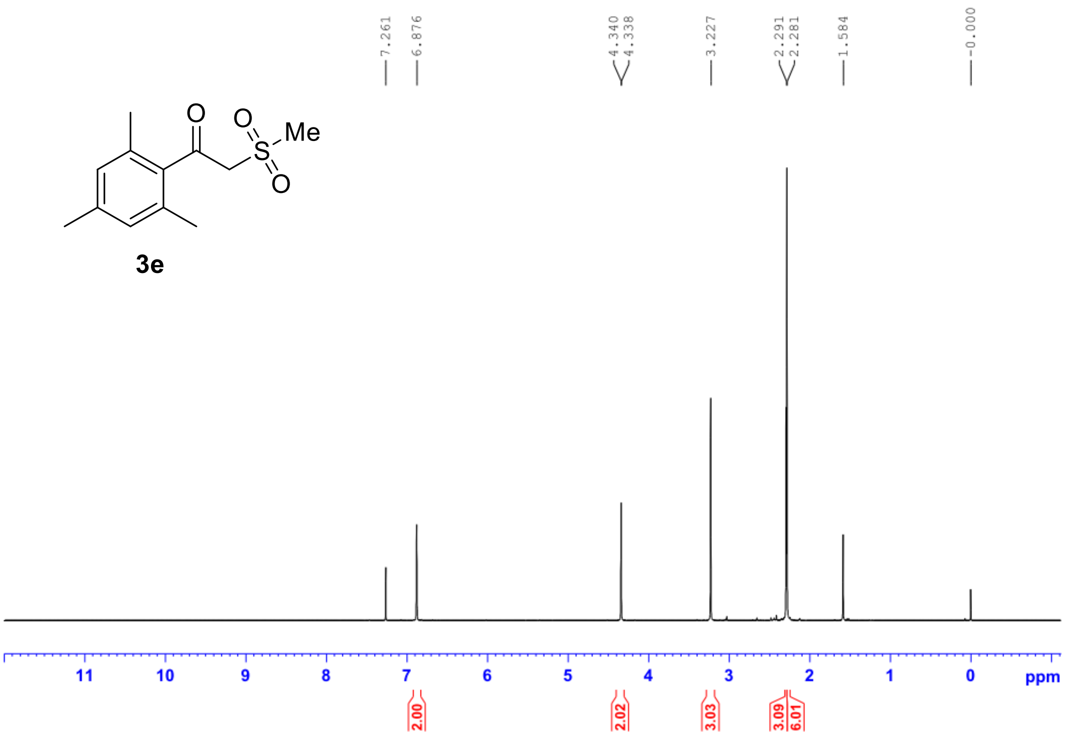
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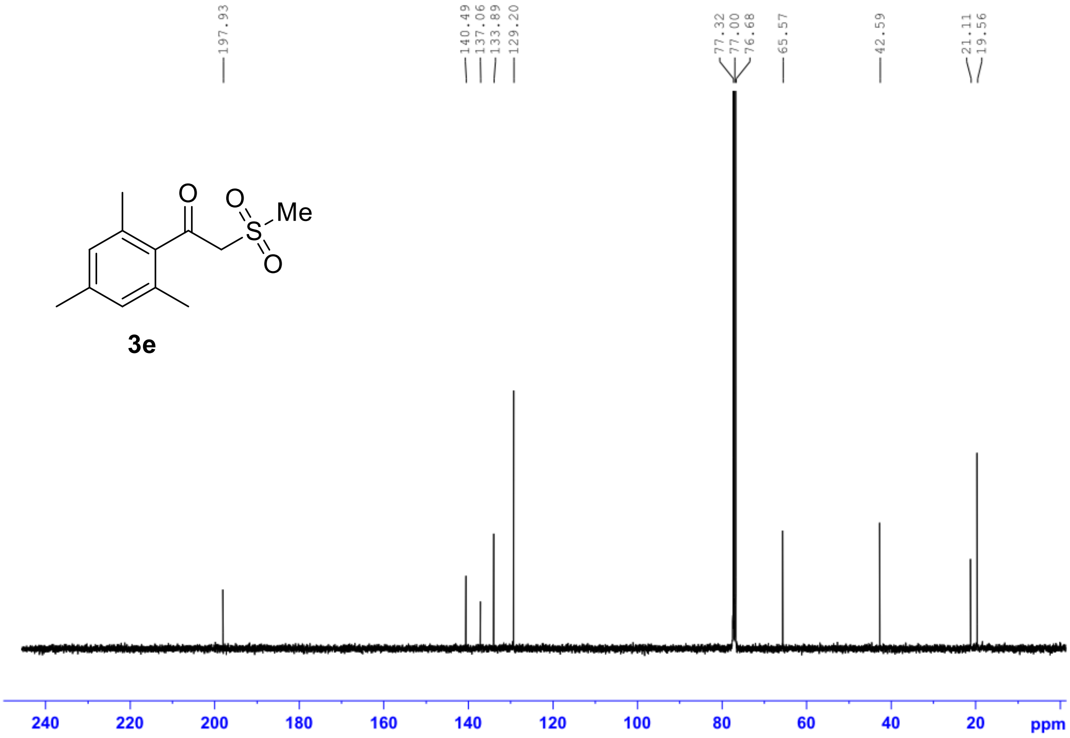
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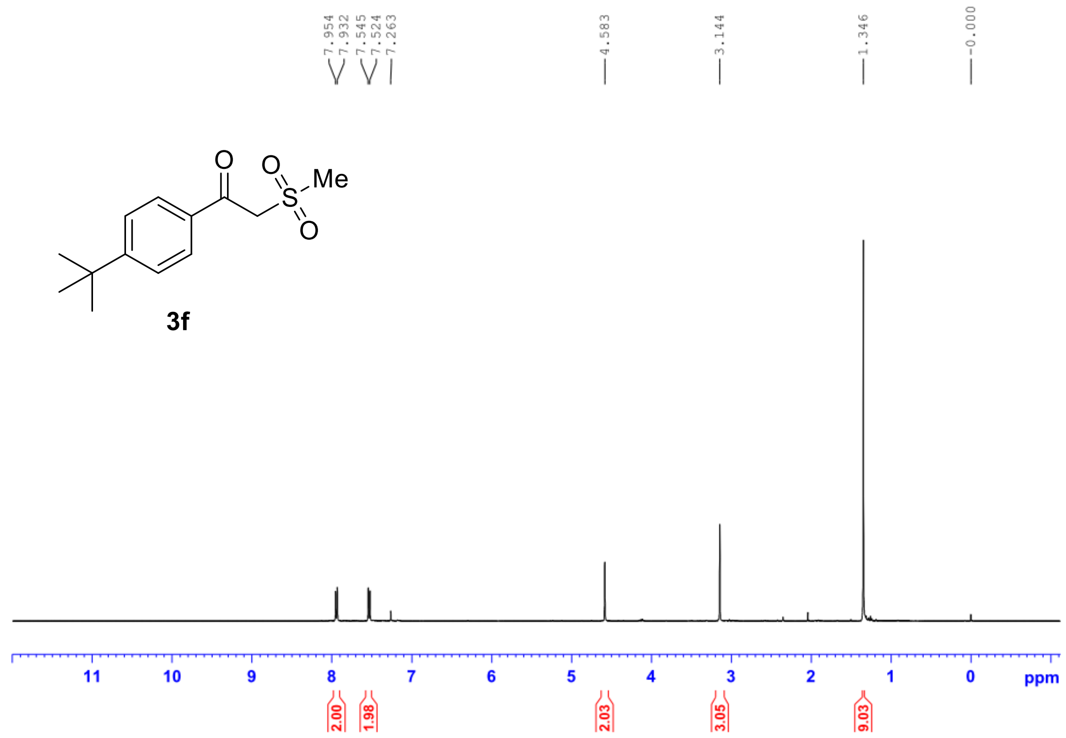
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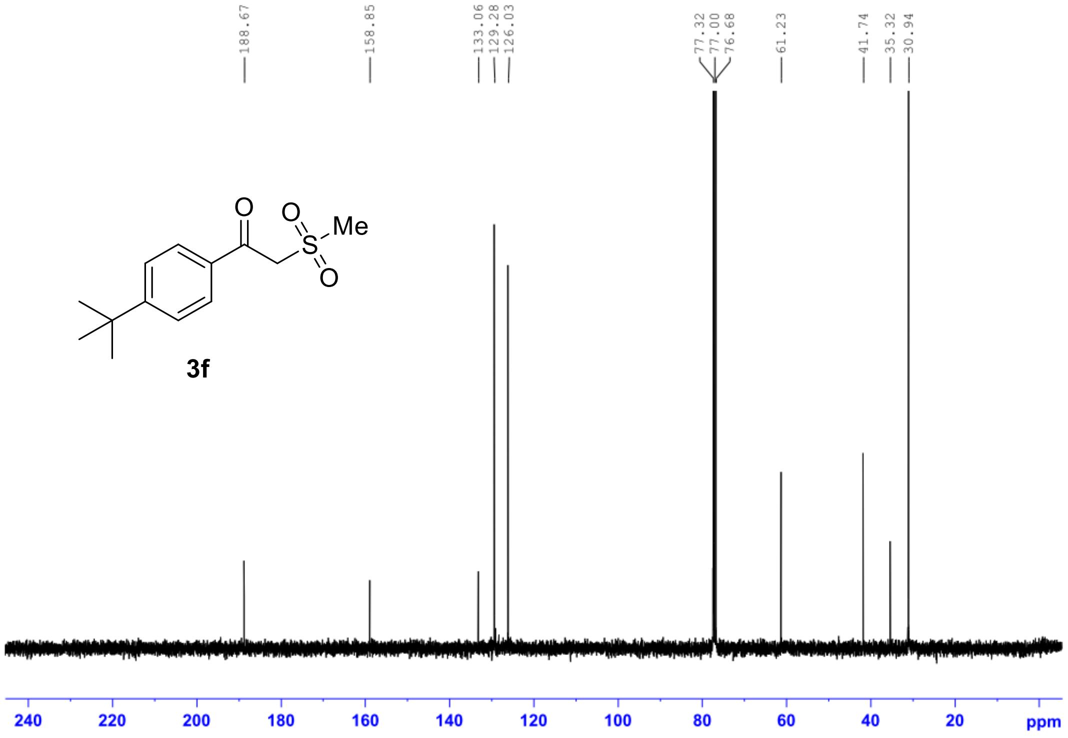
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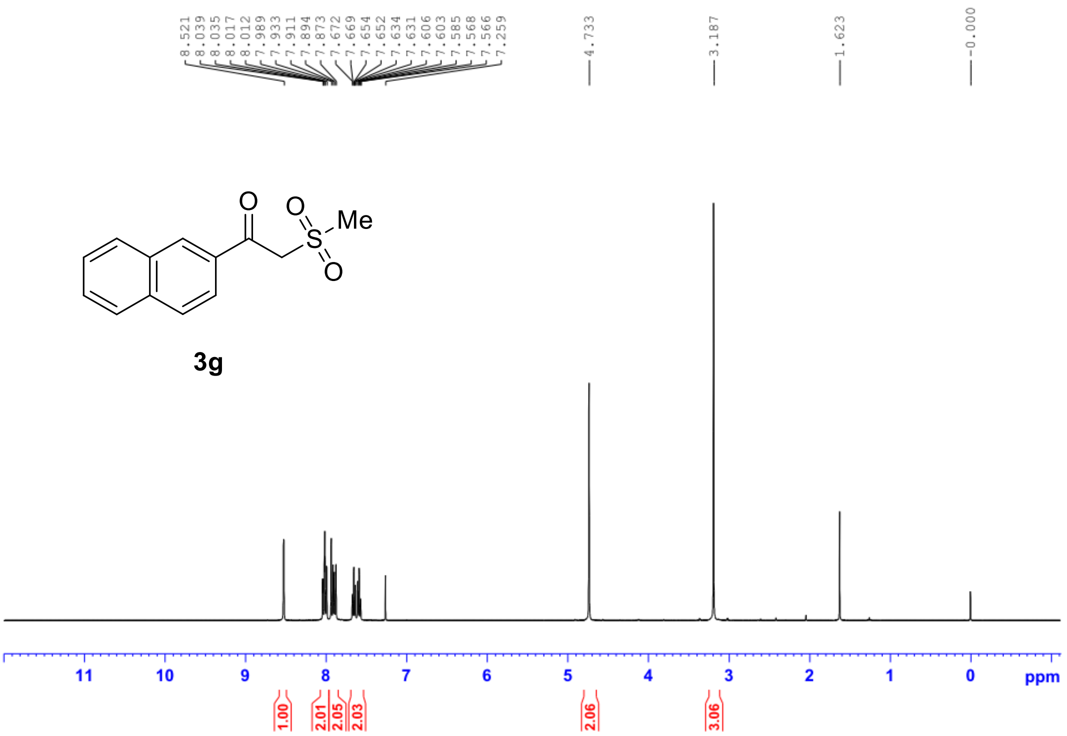
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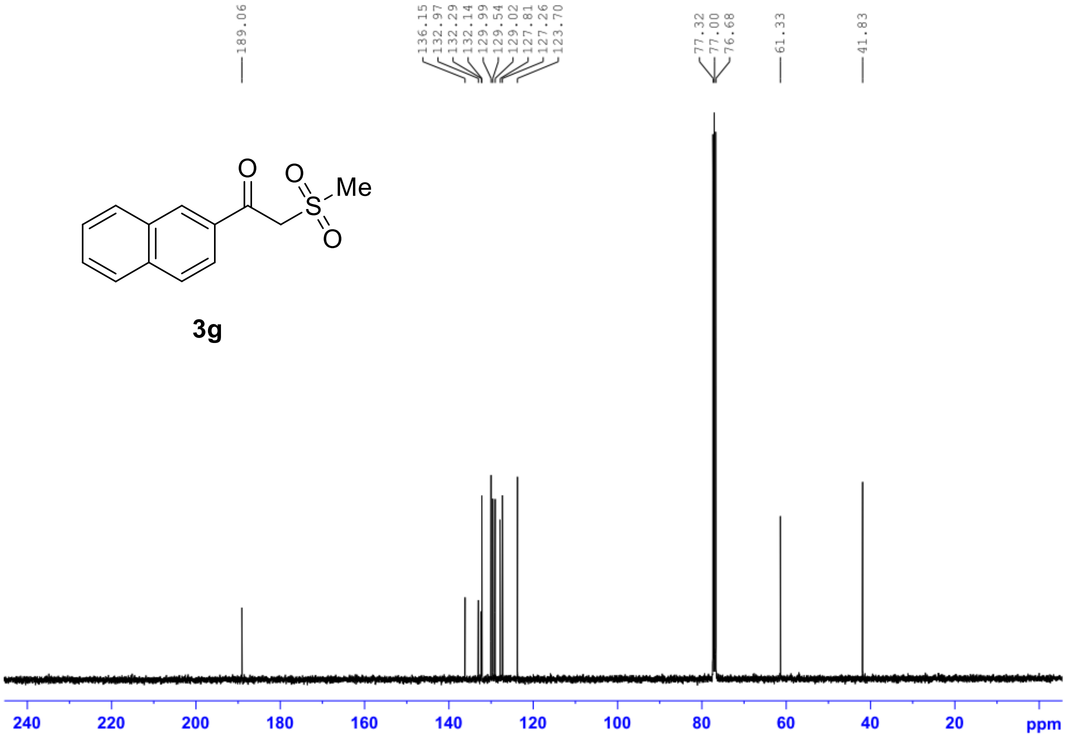
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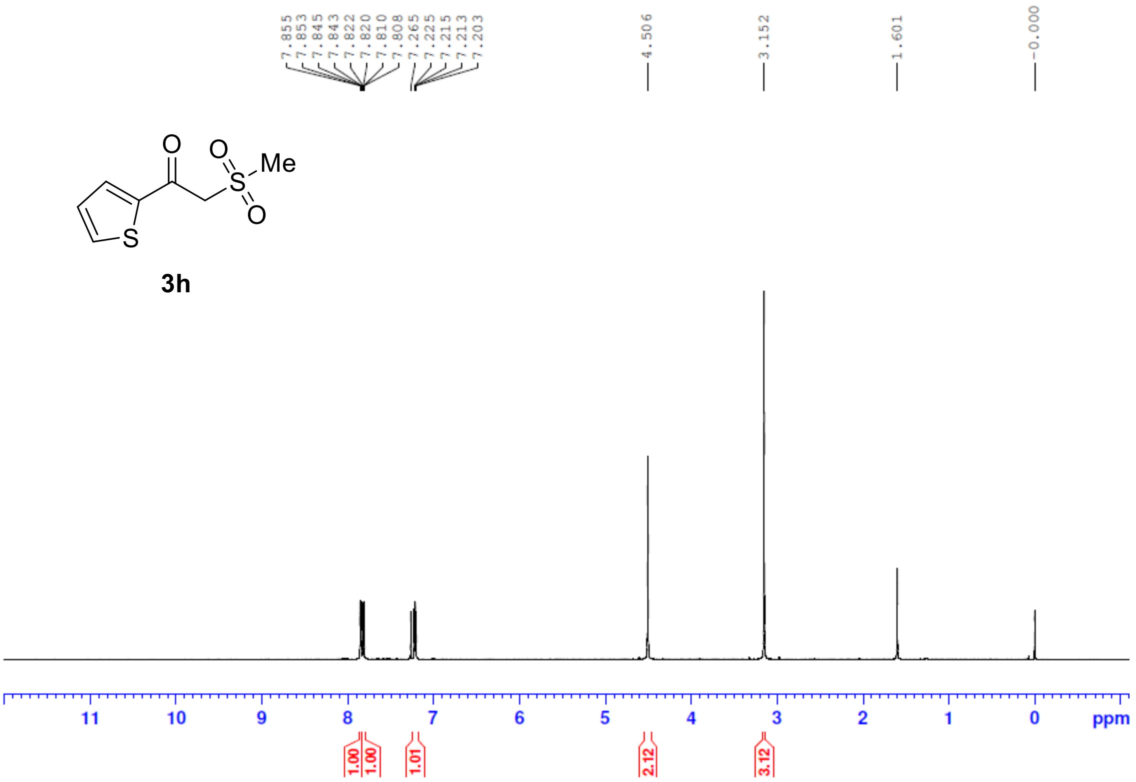
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7.808
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7.225
7.215
7.213
7.203
4.506
3.152
1.601
-0.000
O
O
S
Me
O
S
3h
11
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6
5
4
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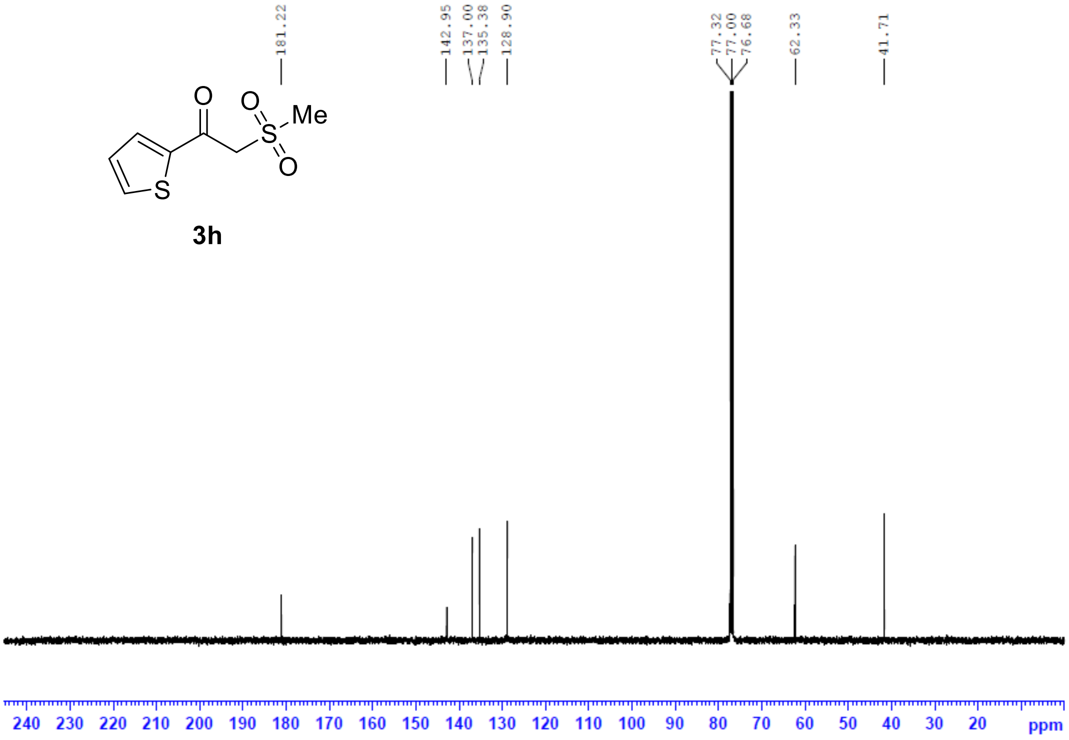
1.00
1.01
2.12
3.12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76.68
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41.71
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O
S
Me
O
S
3h
240
230
220
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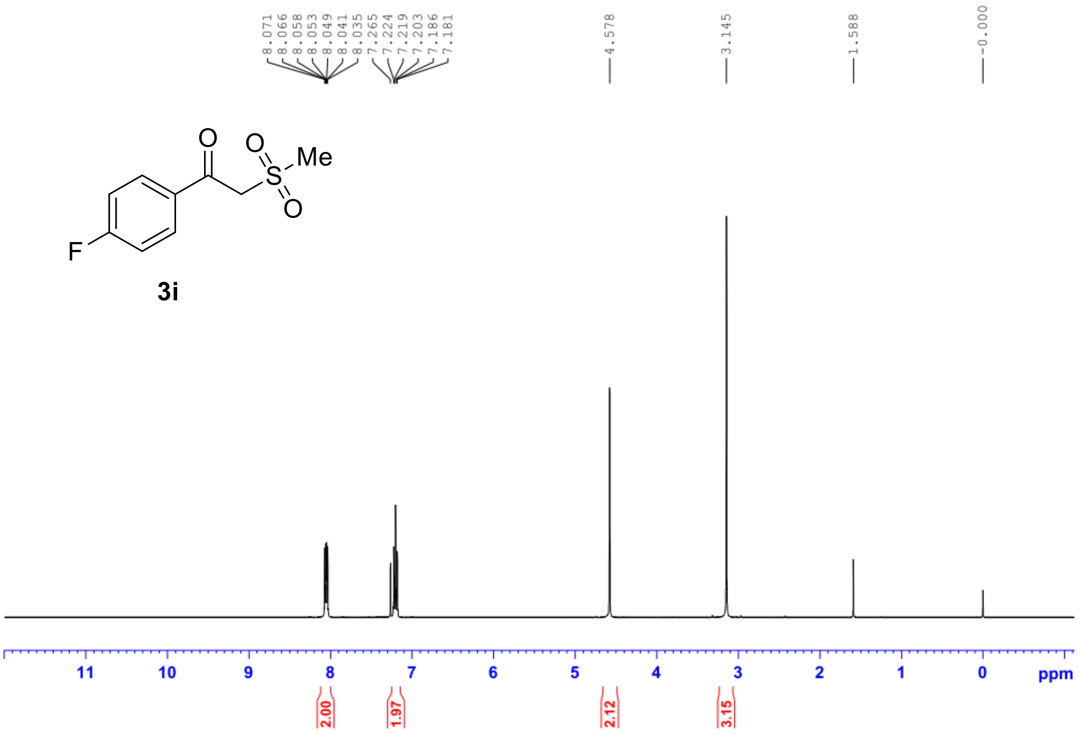
ppm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8.035
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7.219
7.203
7.186
7.181
4.578
3.145
1.588
-0.000
O
O
Me
S
O
F
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7
6
5
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ppm
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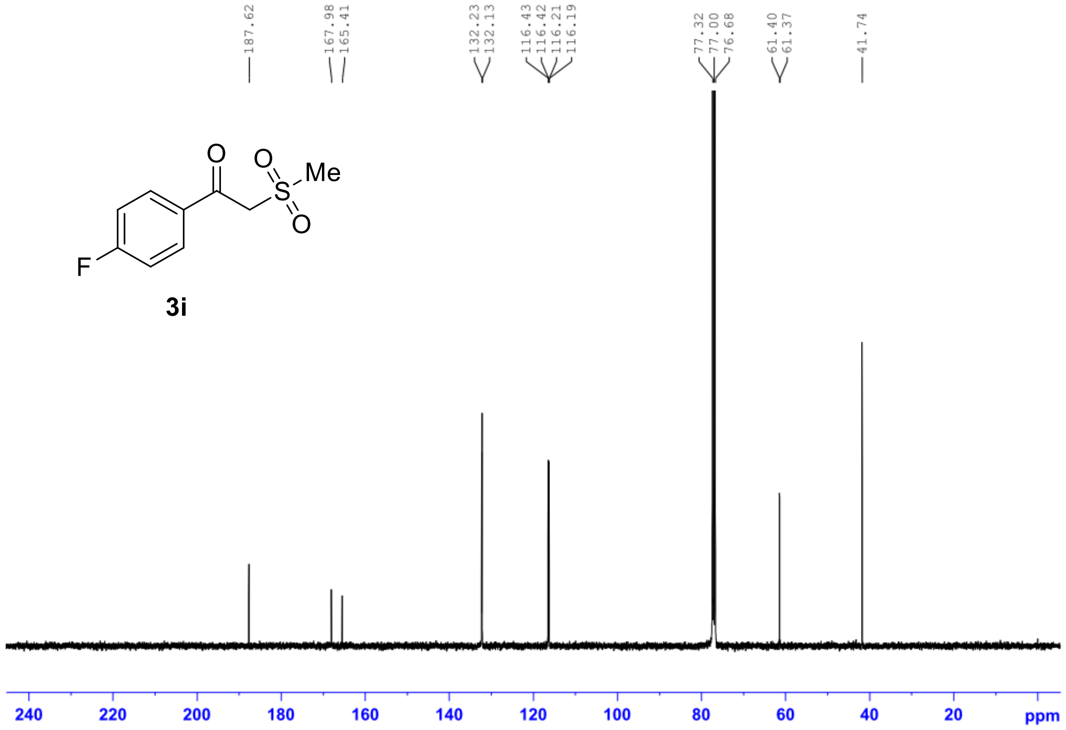
3.15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116.21
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61.40
61.37
41.74
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O
F
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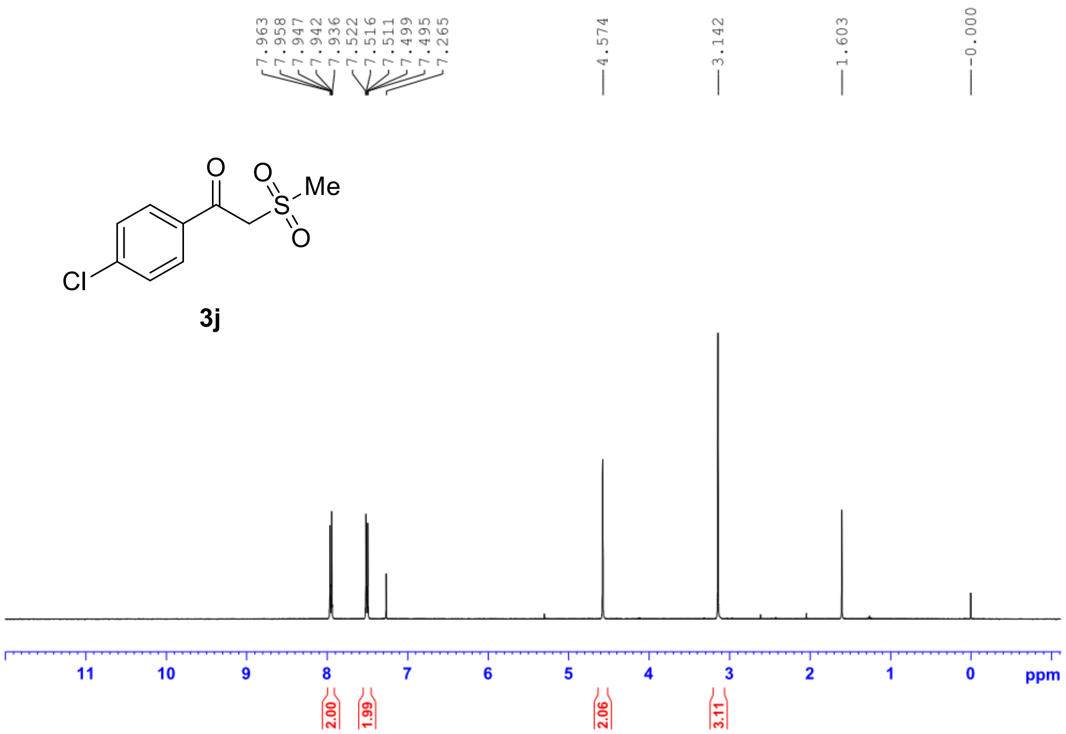
20
ppm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7.495
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4.574
3.142
1.603
-0.000
O
O
S
Me
O
Cl
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7
6
5
4
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ppm
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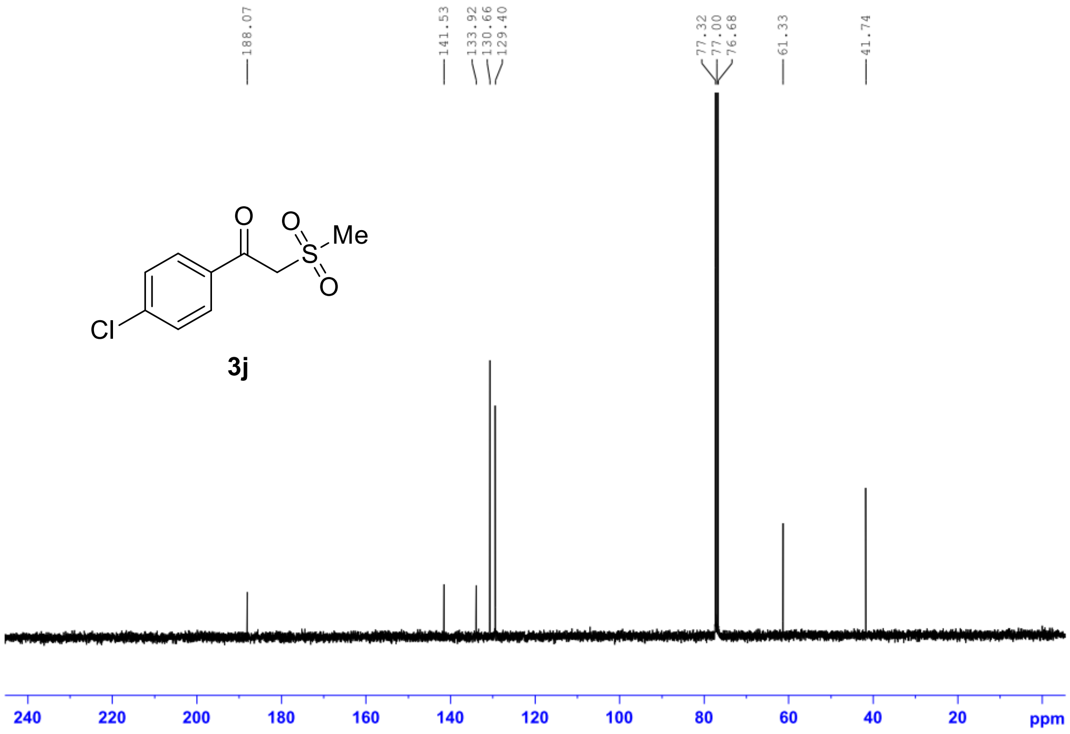
1.99
2.06
3.11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141.53
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76.68
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41.74
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Me
O
Cl
3j
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200
180
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140
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60
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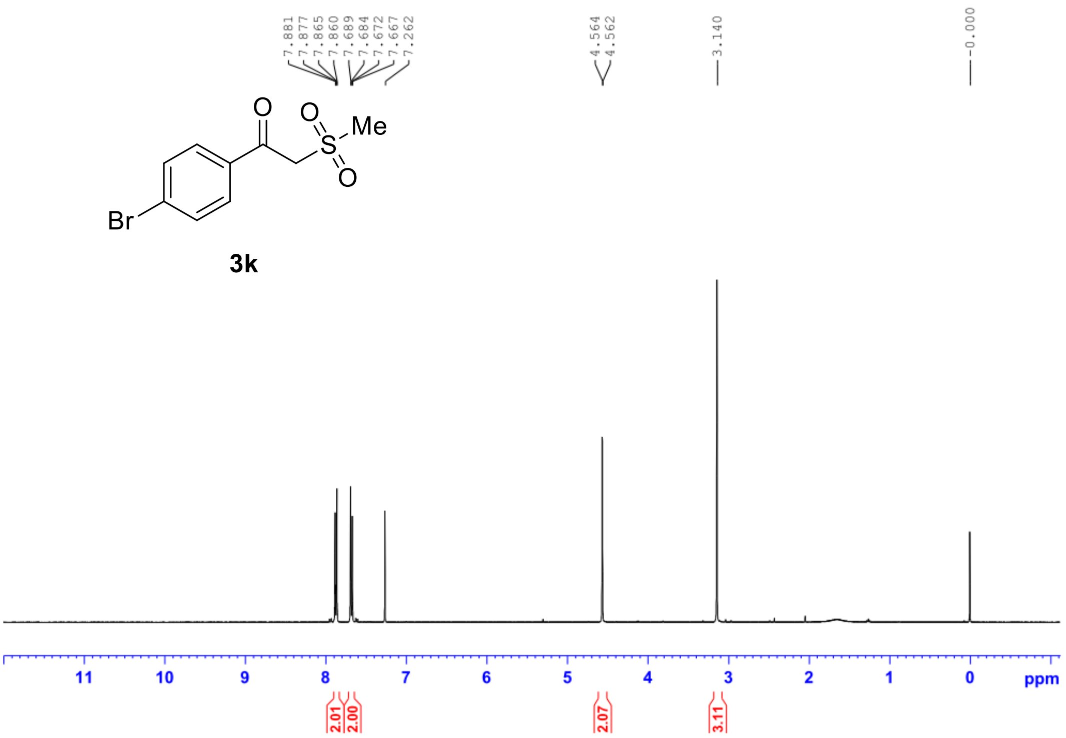
ppm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7.667
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4.562
3.140
-0.000
O
O
Me
S
O
Br
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10
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7
6
5
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ppm
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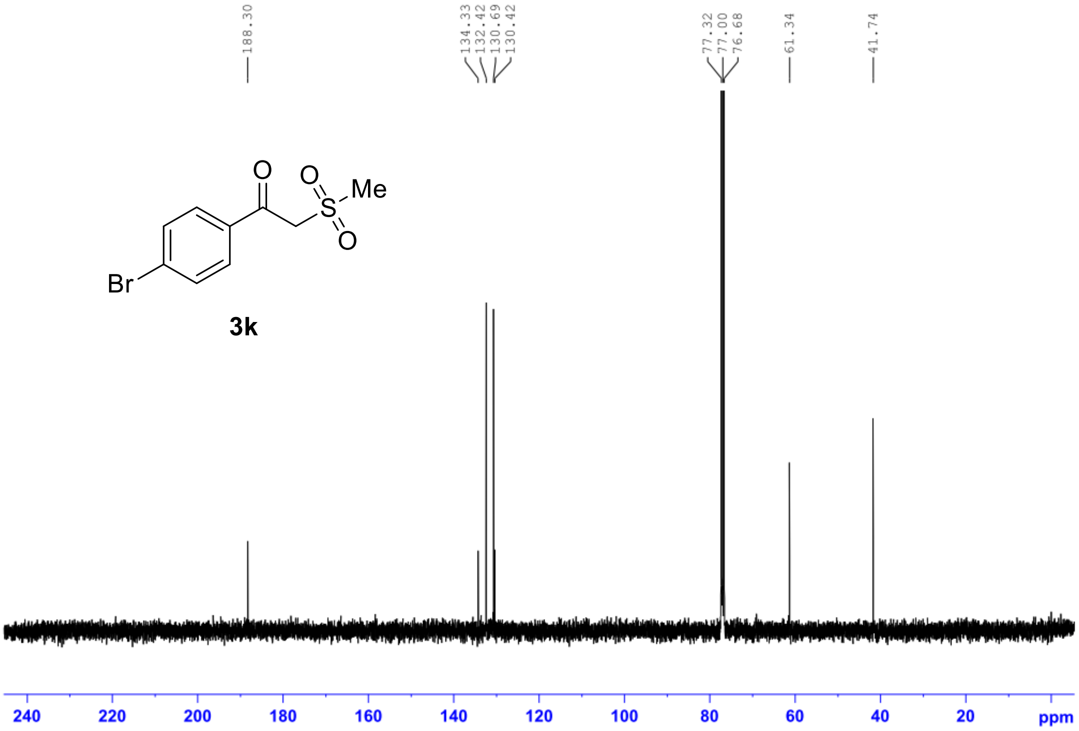
3.11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Br
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120
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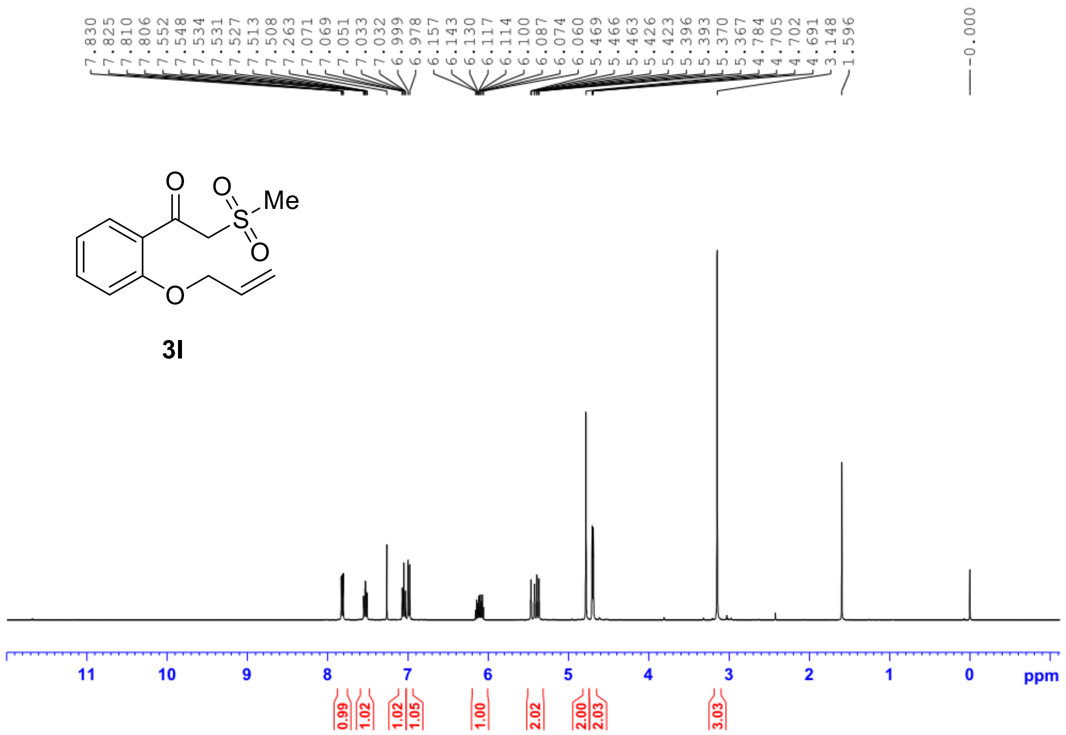
60
40
20
ppm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7.527
7.513
7.508
7.263
7.071
7.069
7.051
7.033
7.032
6.999
6.978
6.157
6.143
6.130
6.117
6.114
6.100
6.087
6.074
6.060
5.469
5.466
5.463
5.426
5.423
5.396
5.393
5.370
5.367
4.784
4.705
4.702
4.691
3.148
1.596
0.000
O
O
S
Me
O
O
3l
11
10
9
8
7
6
5
4
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ppm
0.99
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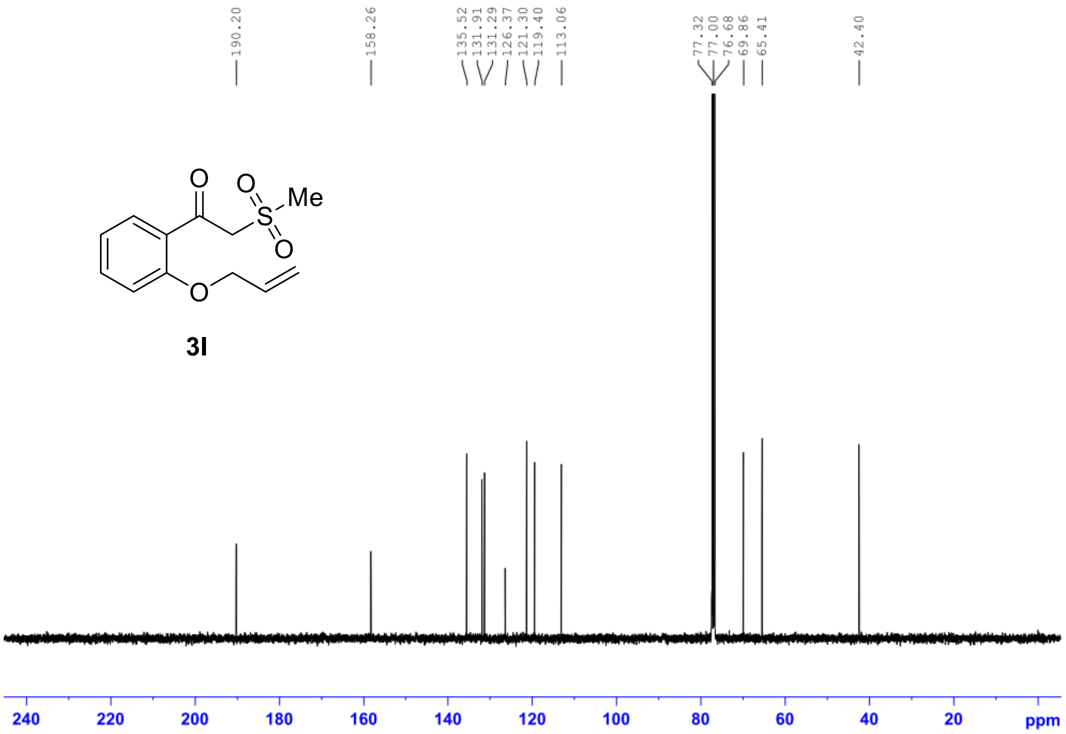
1.02
1.05
1.00
2.02
2.00
2.03
3.03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126.37
121.30
119.40
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77.32
77.00
76.68
69.86
65.41
42.40
O
O
S
Me
O
O
3l
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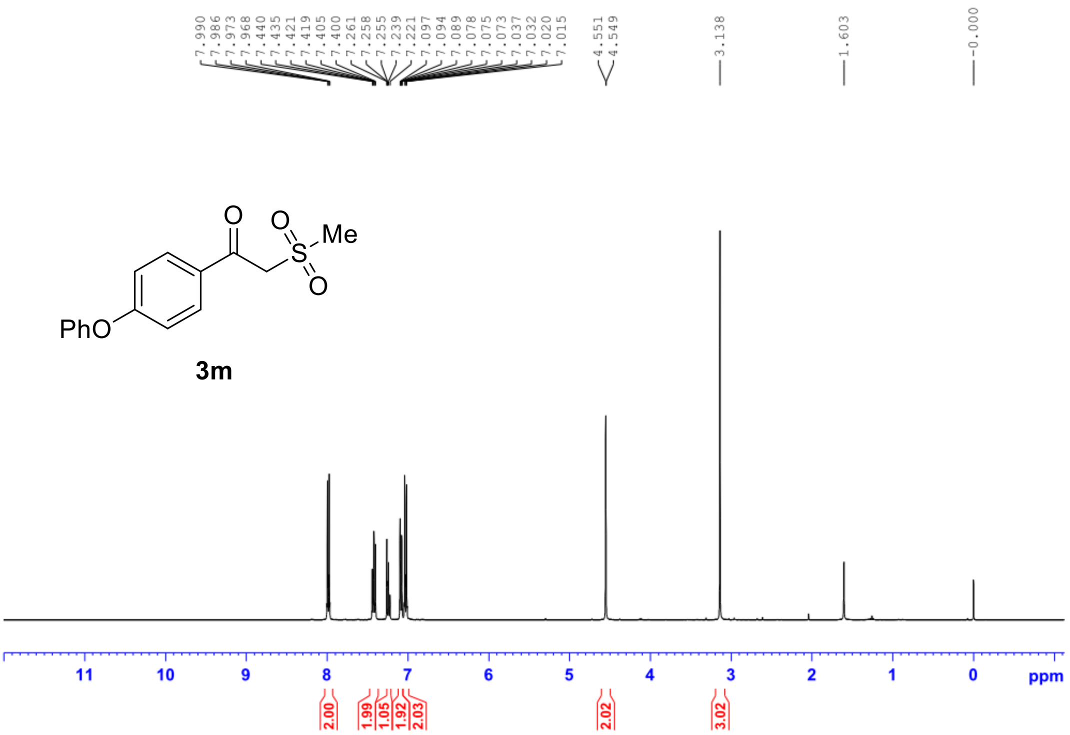
200
180
160
140
120
100
80
60
40
20
ppm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7.405
7.400
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7.258
7.255
7.239
7.221
7.097
7.094
7.089
7.078
7.075
7.073
7.037
7.032
7.020
7.015
4.551
4.549
3.138
1.603
-0.000
O
O
S
Me
O
PhO
3m
11
10
9
8
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5
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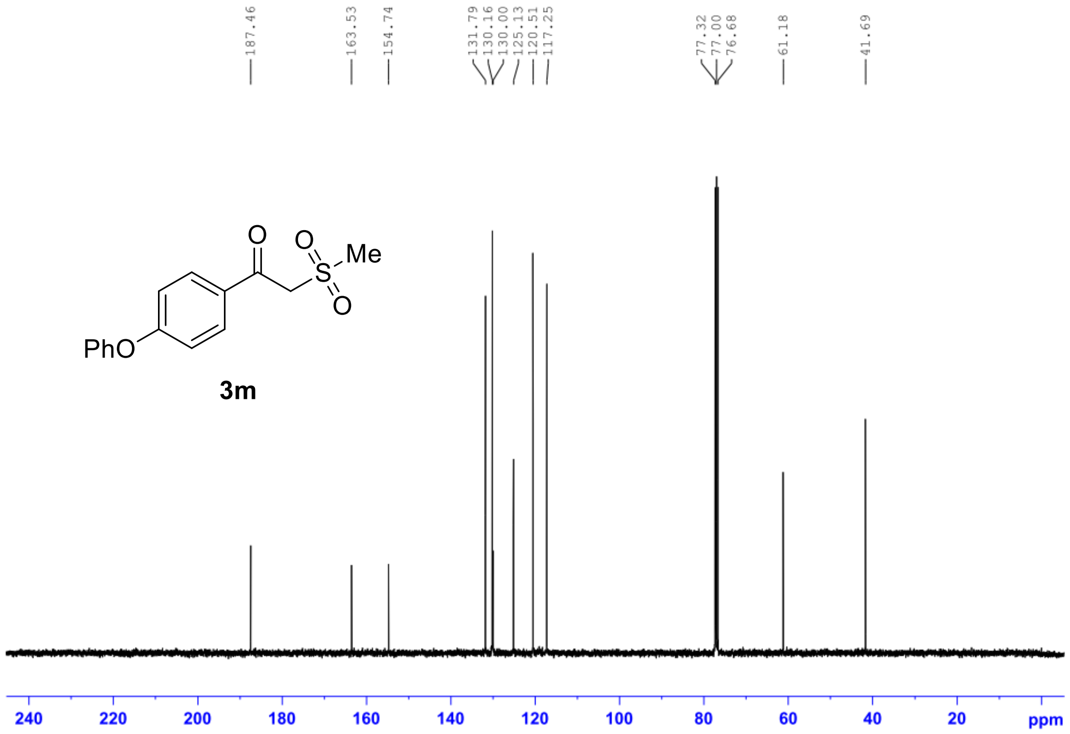
2.02
3.02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120.51
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77.32
77.00
76.68
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41.69
O
O
S
Me
O
PhO
3m
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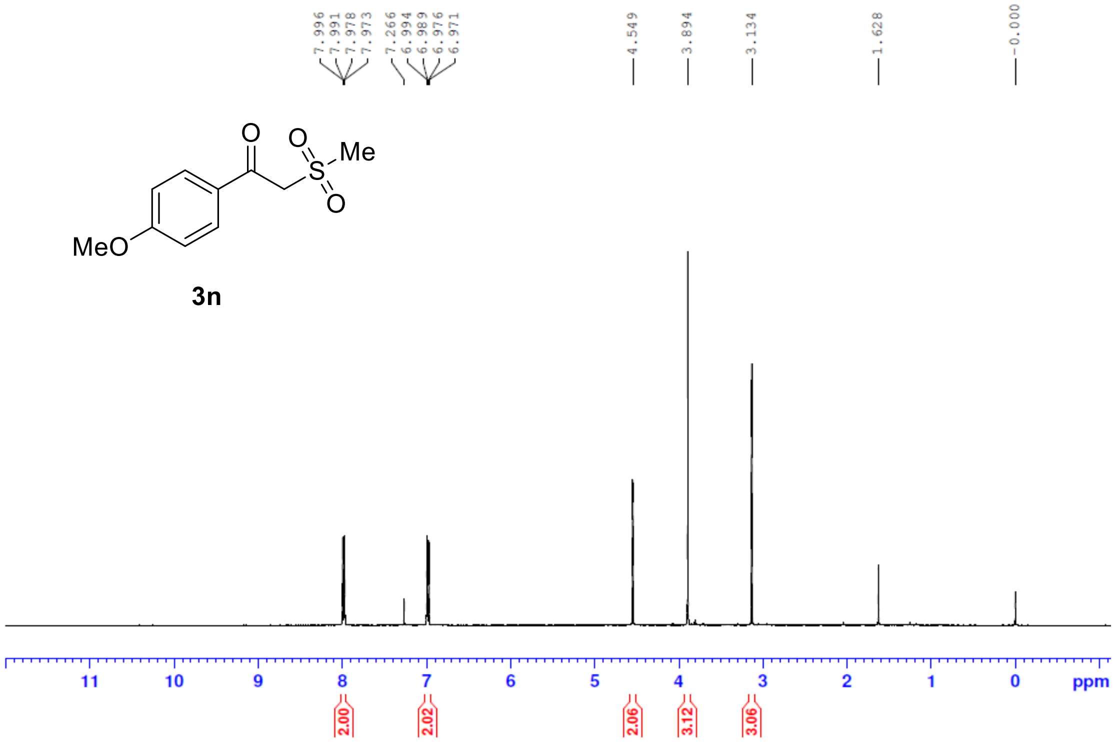
220
200
180
160
140
120
100
80
60
40
20
ppm



3n

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7.991
7.978
7.973
7.266
6.994
6.989
6.976
6.971
4.549
3.894
3.134
1.628
-0.000
O
O
S
Me
O
MeO
11
10
9
8
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6
5
4
3
2
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ppm
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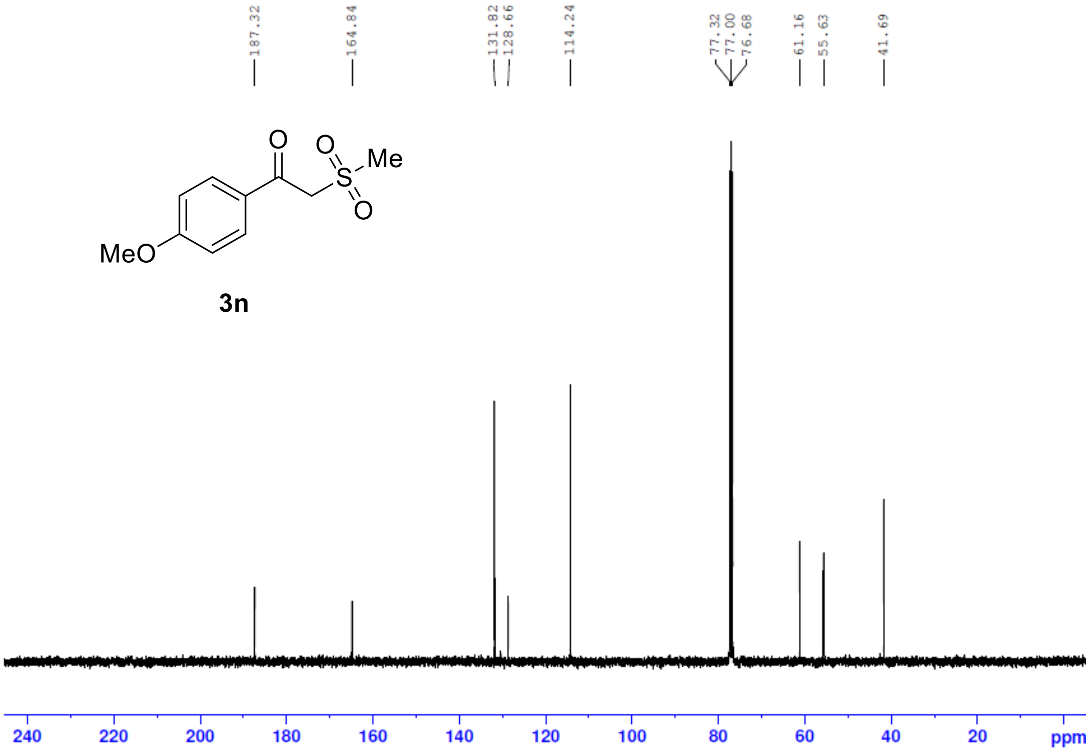
2.06
3.12
3.06



3n

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114.24
77.32
77.00
76.68
61.16
55.63
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O
S
Me
O
MeO
240
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140
120
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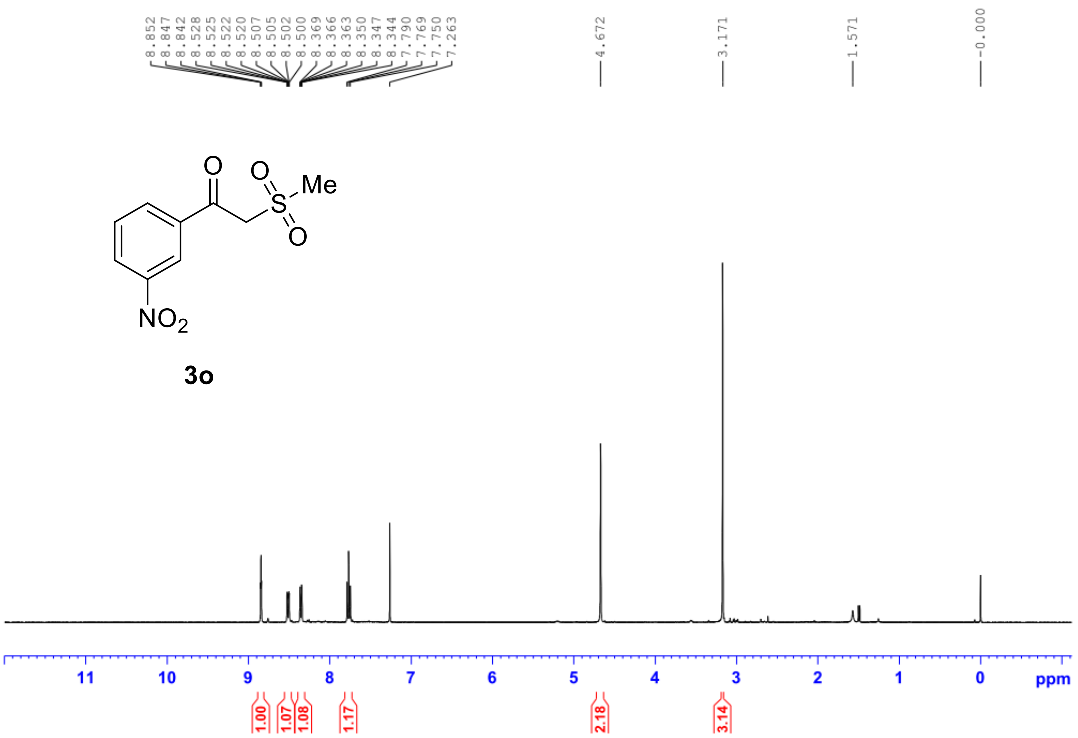
60
40
20
ppm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8.366
8.363
8.350
8.347
8.344
7.790
7.769
7.750
7.263
4.672
3.171
1.571
-0.000
O
O
S
Me
O
$NO_2$
3o
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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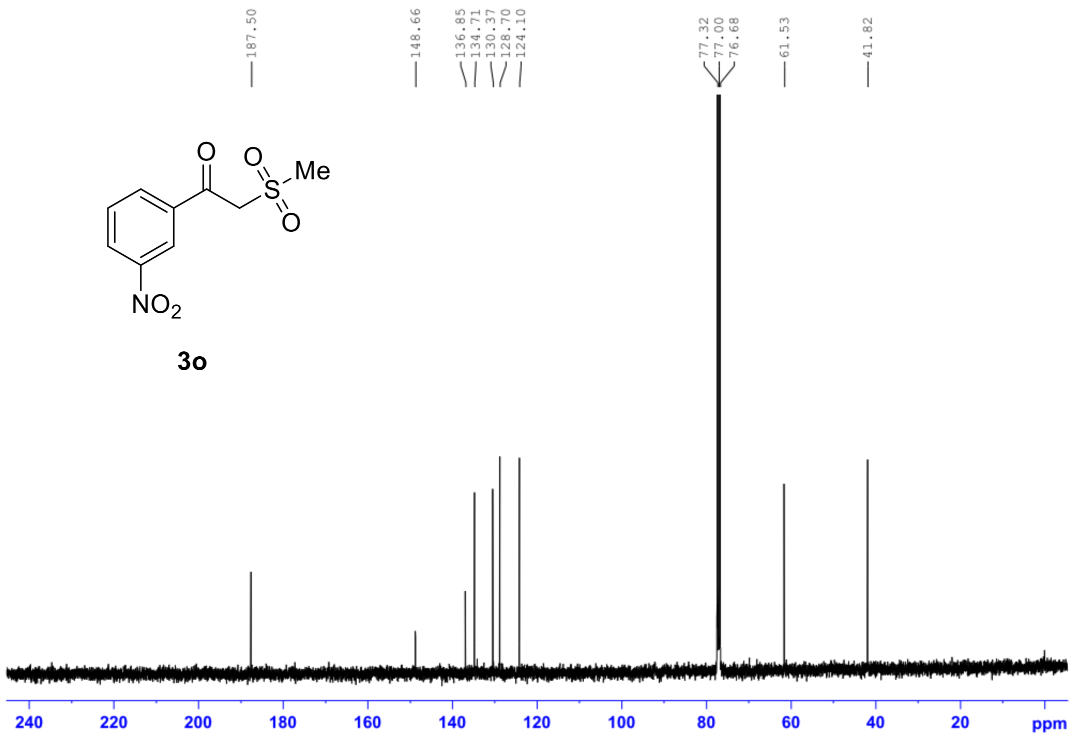
1.17
2.18
3.14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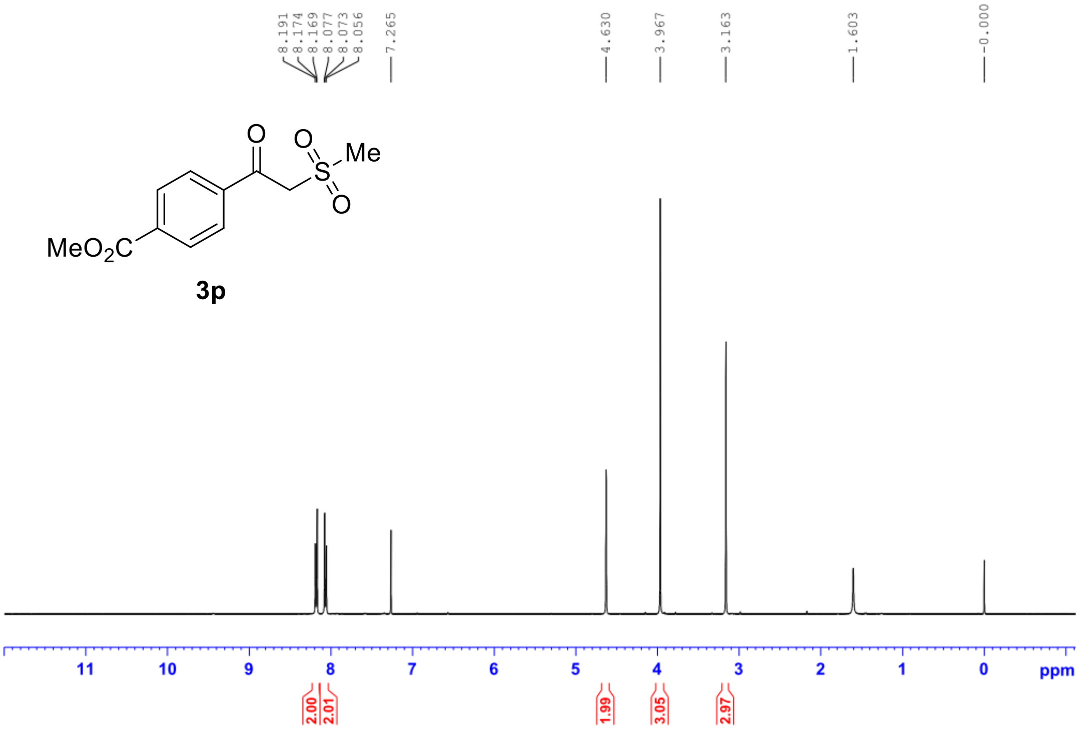
130.37
128.70
124.10
77.32
77.00
76.68
61.53
41.82
O
O
S
Me
O
$NO_2$
3o
240
220
200
180
160
140
120
100
80
60
40
20
ppm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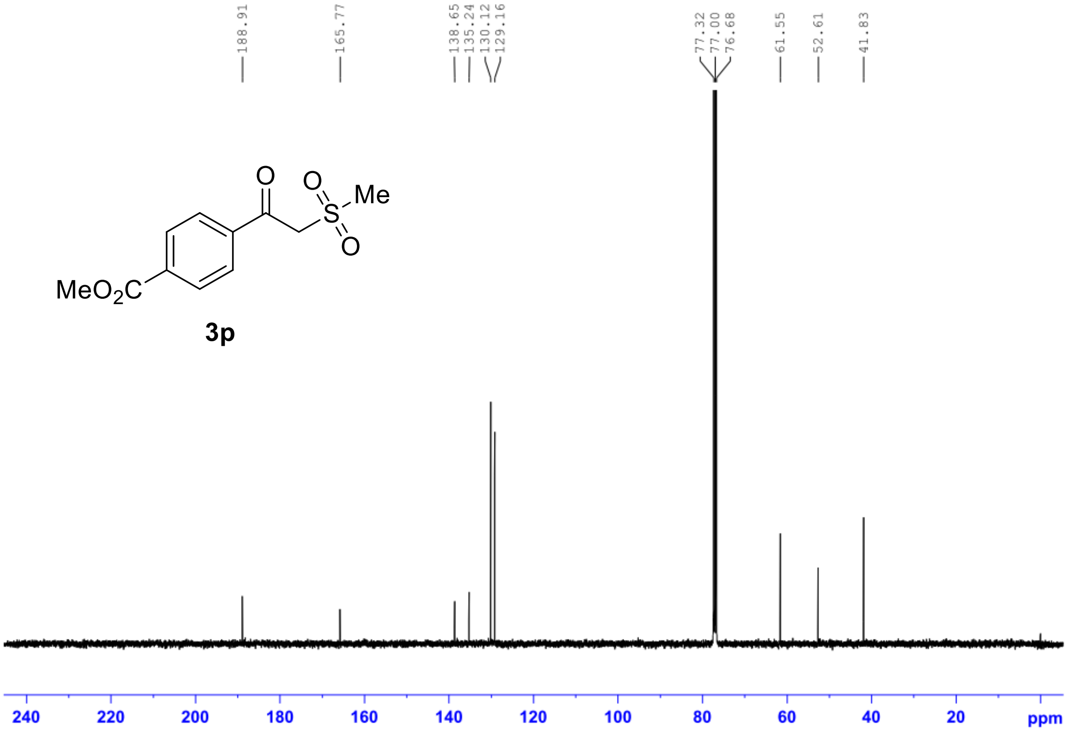
8.056
7.265
4.630
3.967
3.163
1.603
-0.000
O
O
S
Me
O
MeO$_2$C
3p
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
1.99
3.05
2.97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77.32
77.00
76.68
61.55
52.61
41.83
O
O
S
Me
O
MeO$_2$C
3p
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200
180
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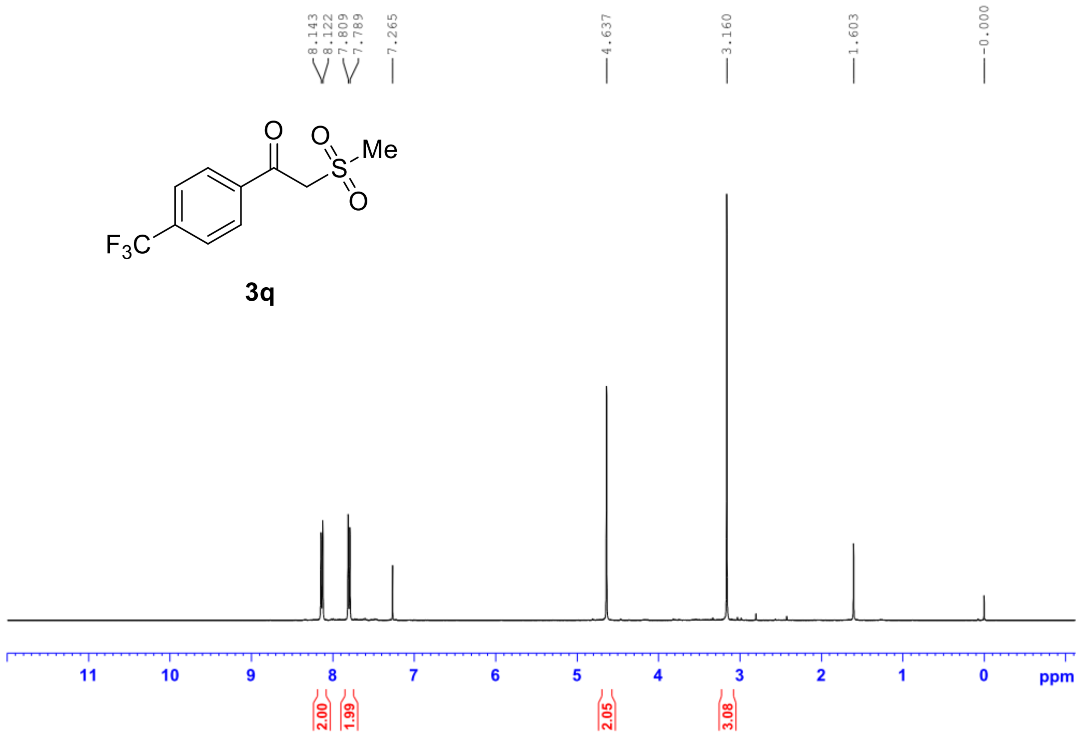
140
120
100
80
60
40
20
ppm



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1.603
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O
O
S
Me
O
F3C
3q
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10
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8
7
6
5
4
3
2
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ppm
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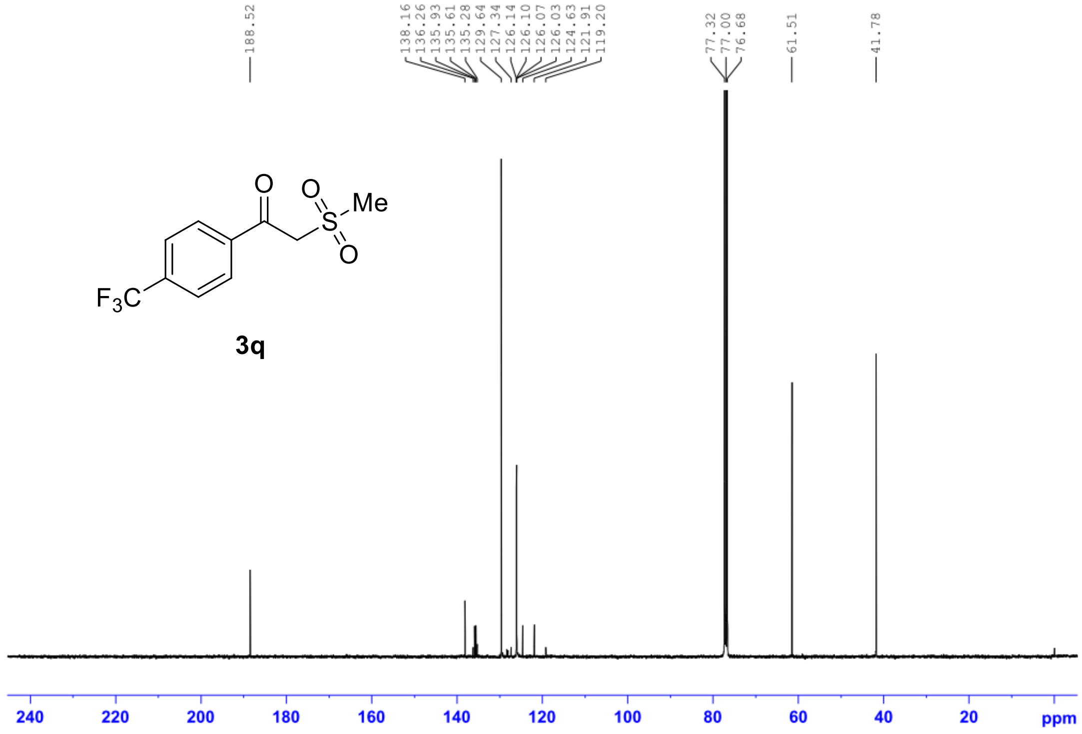
1.99
2.05
3.08



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126.10
126.07
126.03
124.63
121.91
119.20
77.32
77.00
76.68
61.51
41.78
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F3C
3q
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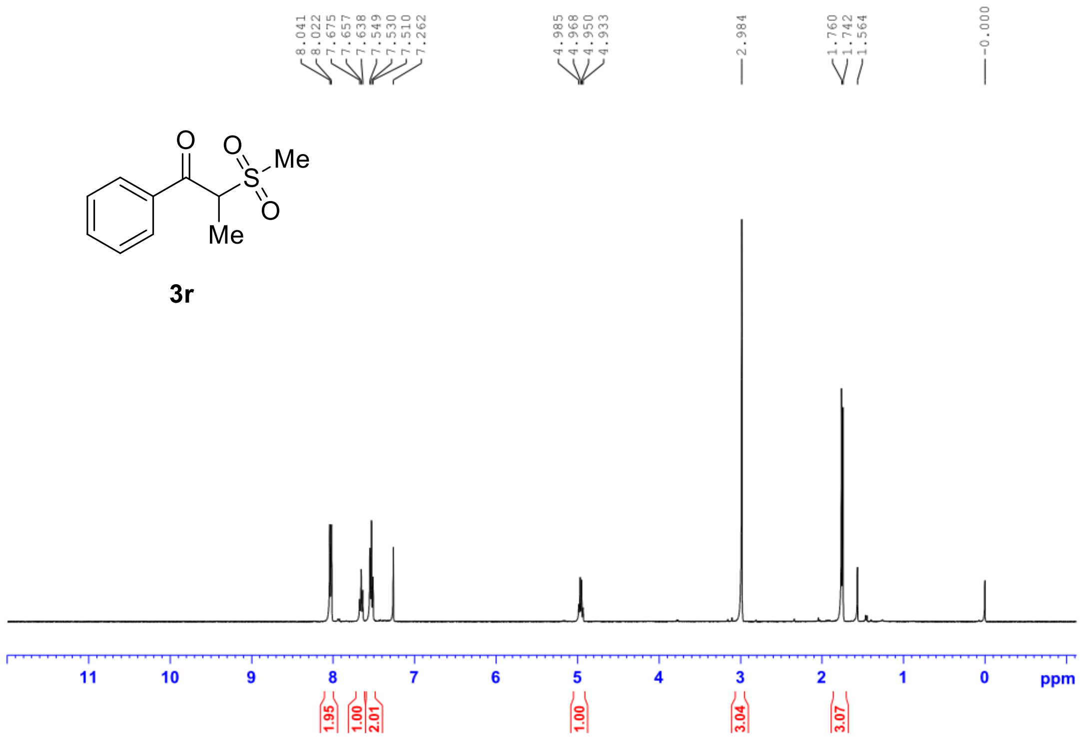
20
ppm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4.933
2.984
1.760
1.742
1.564
-0.000
O
O
S
Me
O
Me
3r
11
10
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1.00
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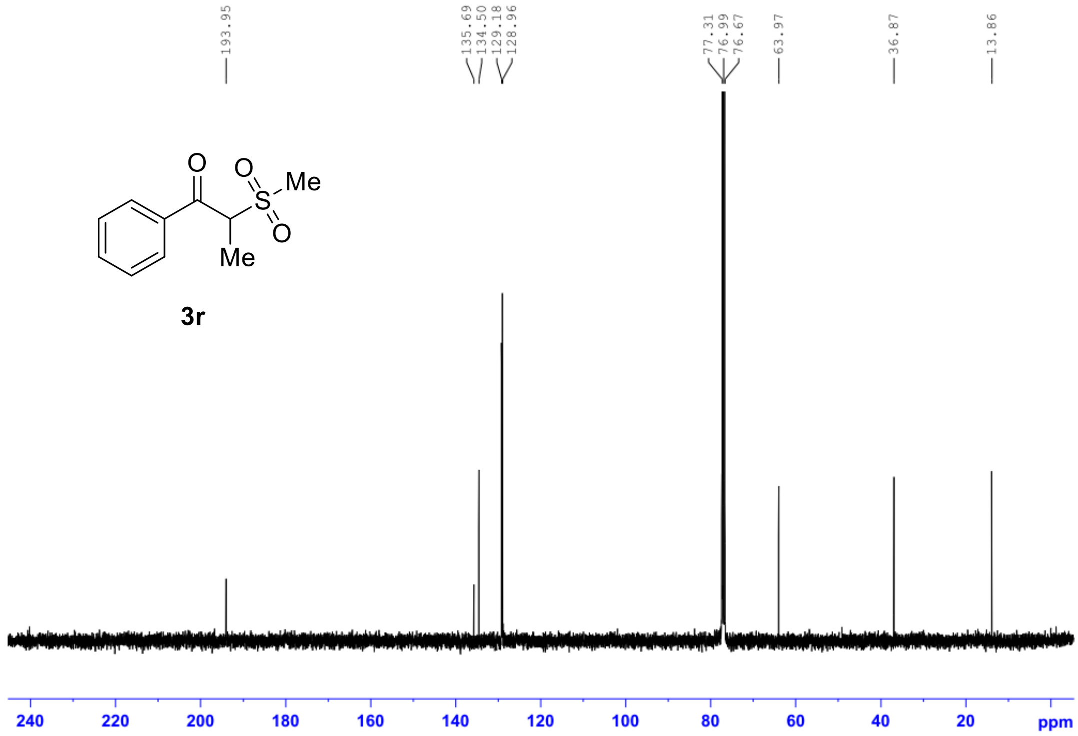
3.07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76.67
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36.87
13.86
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Me
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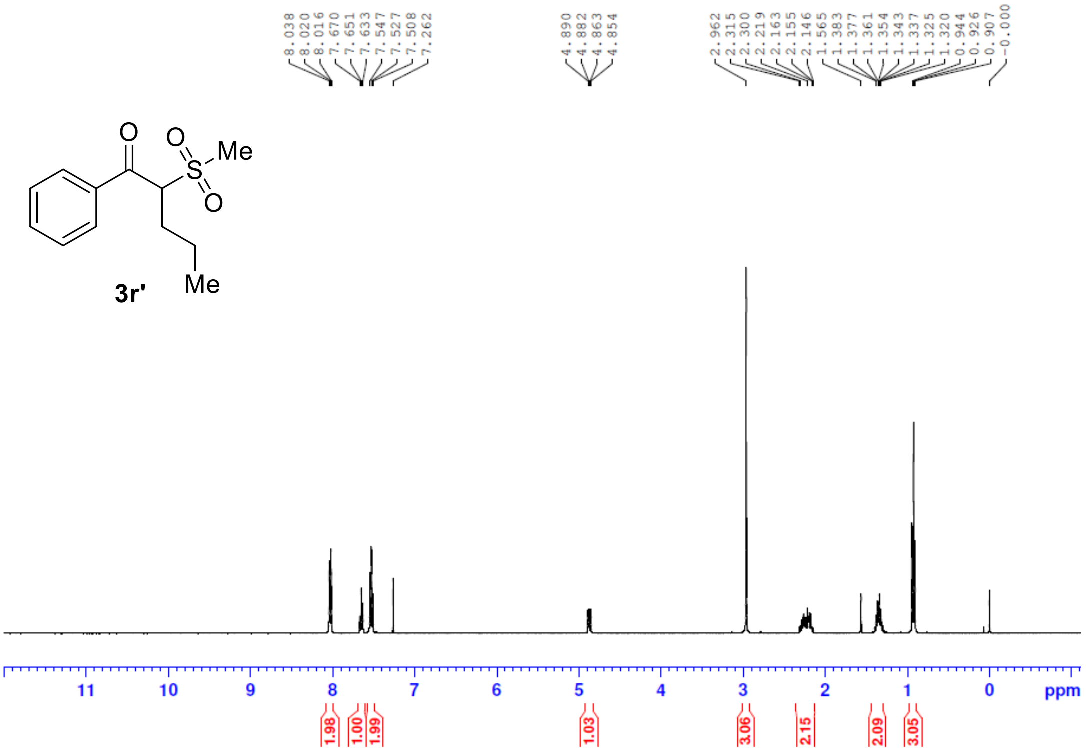
60
40
20
ppm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7.262
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4.863
4.854
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2.300
2.219
2.163
2.155
2.146
1.565
1.383
1.377
1.361
1.354
1.343
1.337
1.325
1.320
0.944
0.926
0.907
-0.000
O
O
S
Me
O
Me
3r'
11
10
9
8
7
6
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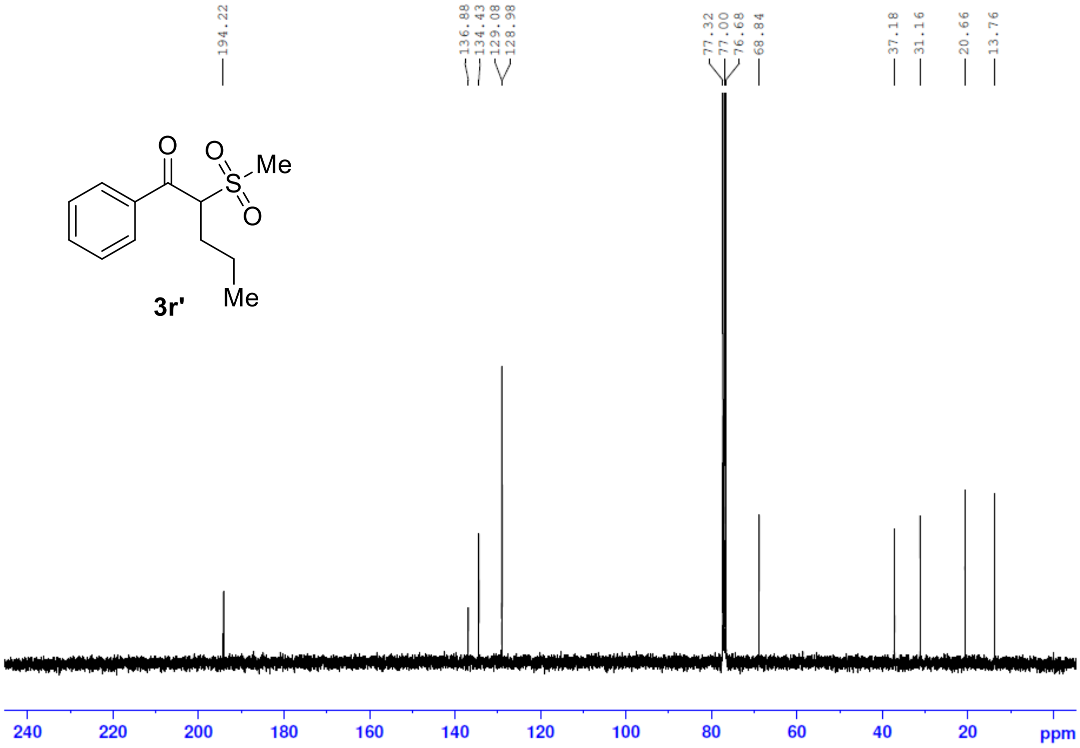
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13.76
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Me
O
Me
3r'
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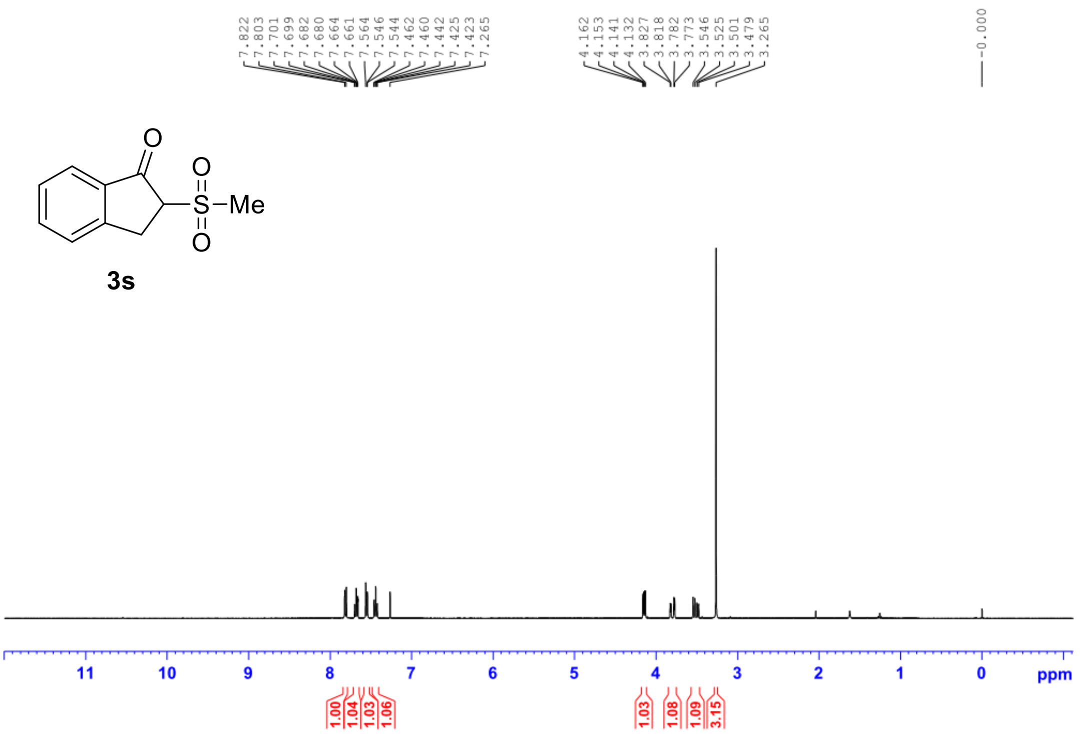
140
120
100
80
60
40
20
ppm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7.460
7.442
7.425
7.423
7.265
4.162
4.153
4.141
4.132
3.827
3.818
3.782
3.773
3.546
3.525
3.501
3.479
3.265
-0.000
O
O
S
Me
O
3s
11
10
9
8
7
6
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4
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1.06
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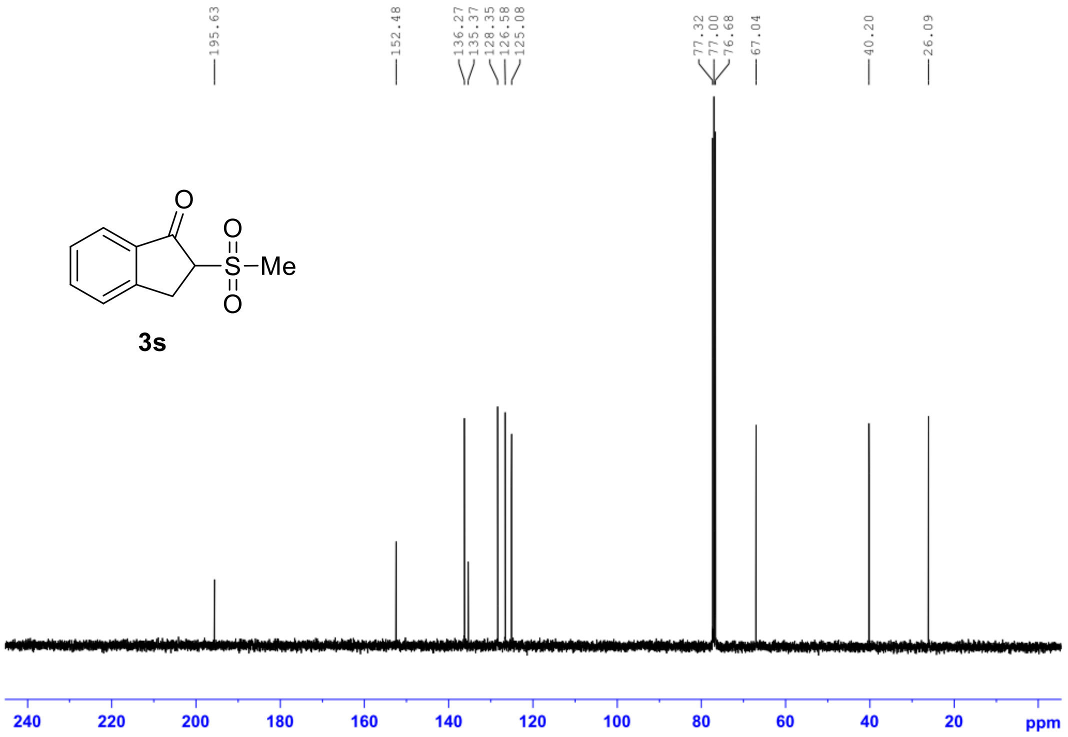
1.08
1.09
3.15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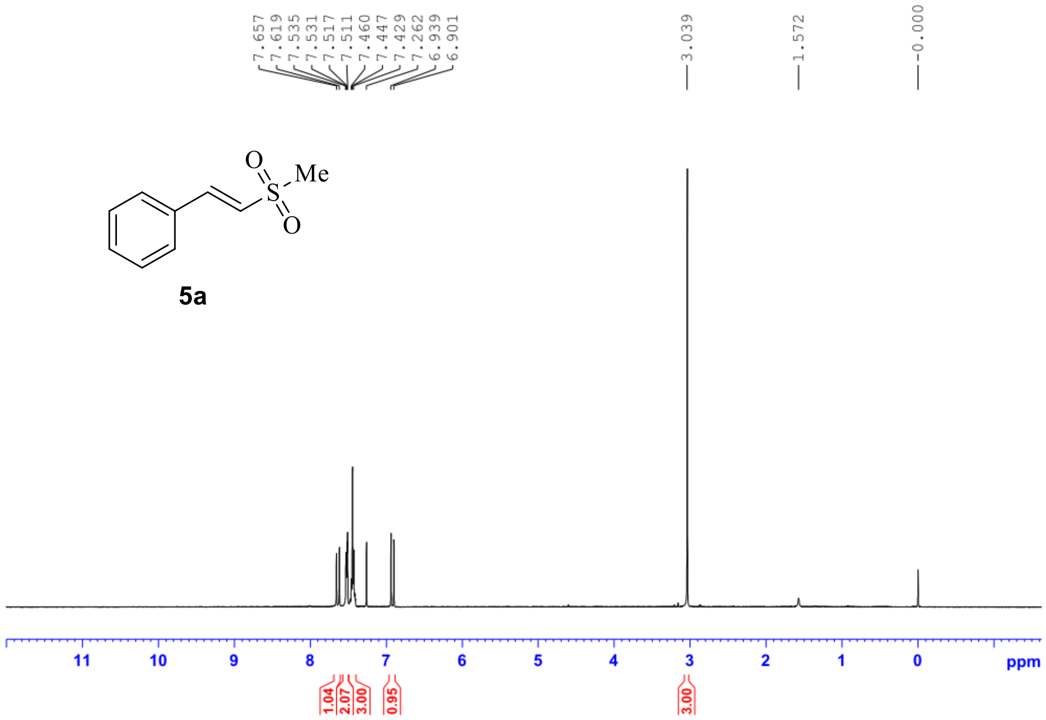
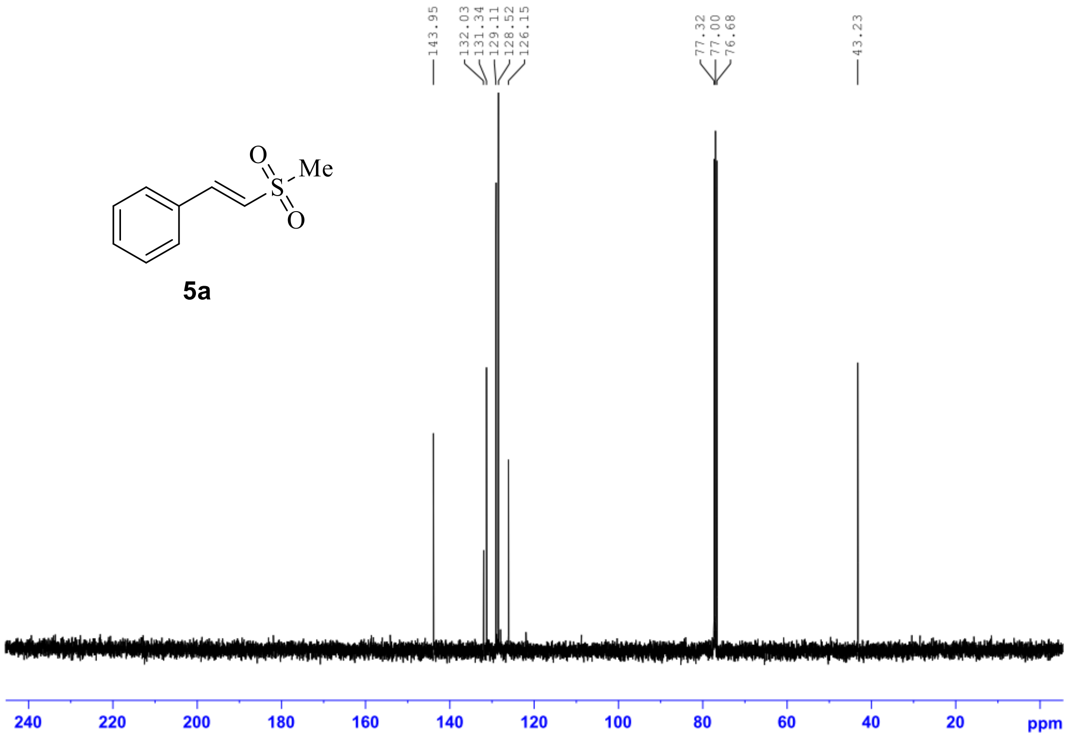
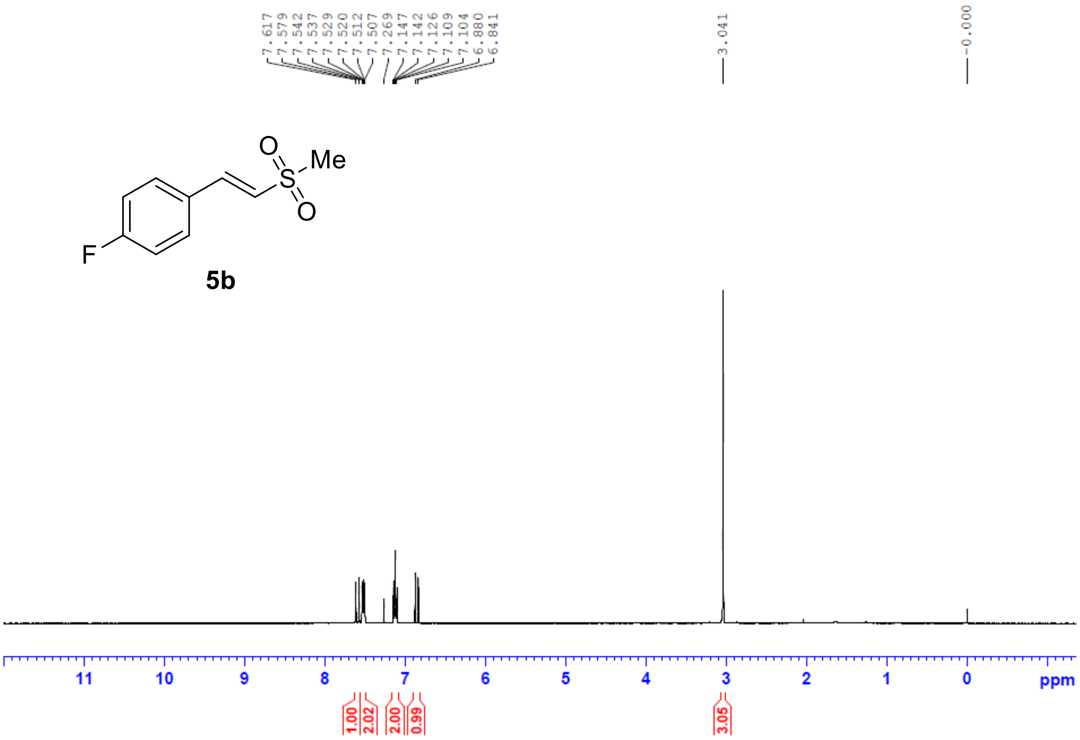
125.08
77.32
77.00
76.68
67.04
40.20
26.09
O
O
S
Me
O
3s
240
220
200
180
160
140
120
100
80
60
40
20
ppm

## NMR Spetra for (*E*)-vinyl methyl sulfones







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7.507
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7.147
7.142
7.126
7.109
7.104
6.880
6.841
3.041
0.000
O
S
Me
O
F
5b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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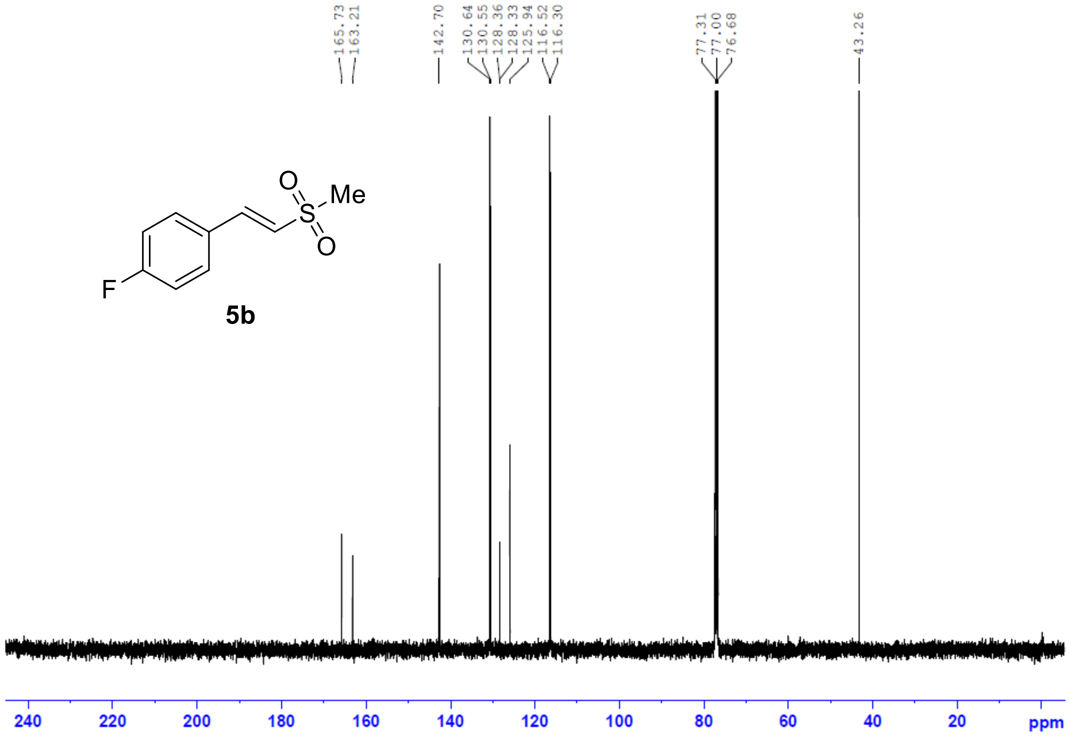
2.00
0.99
3.05



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128.33
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116.52
116.30
77.31
77.00
76.68
43.26
O
S
Me
O
F
5b
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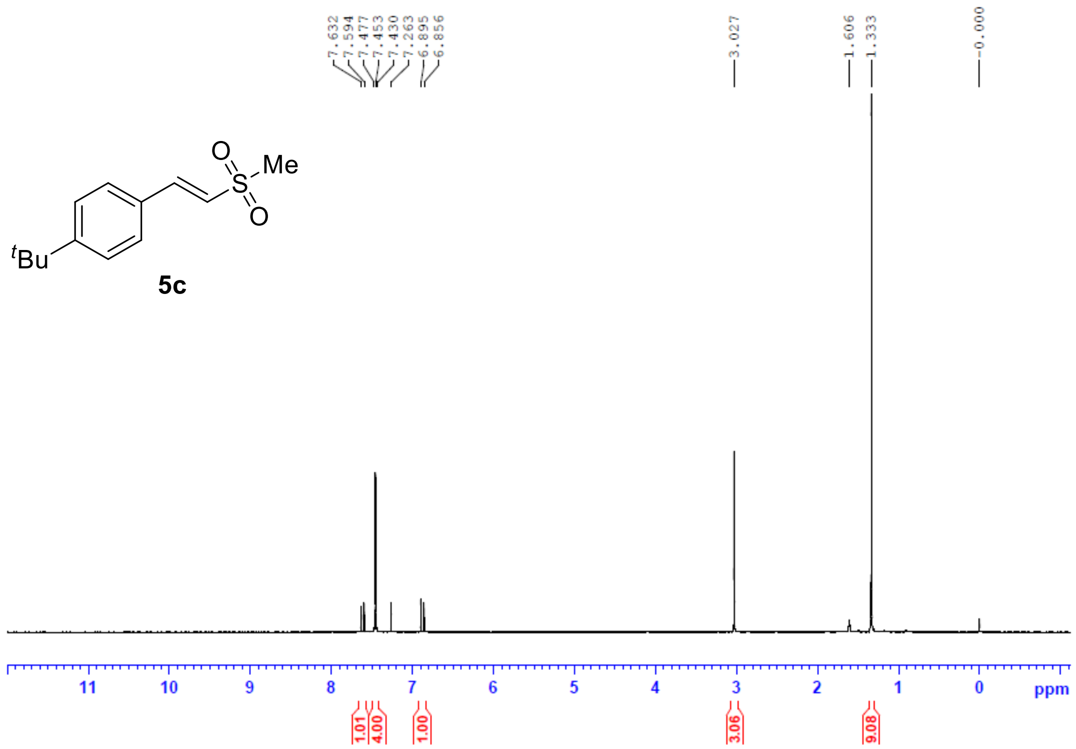
220
200
180
160
140
120
100
80
60
40
20
ppm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S
Me
O
tBu
5c
11
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4
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1
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ppm
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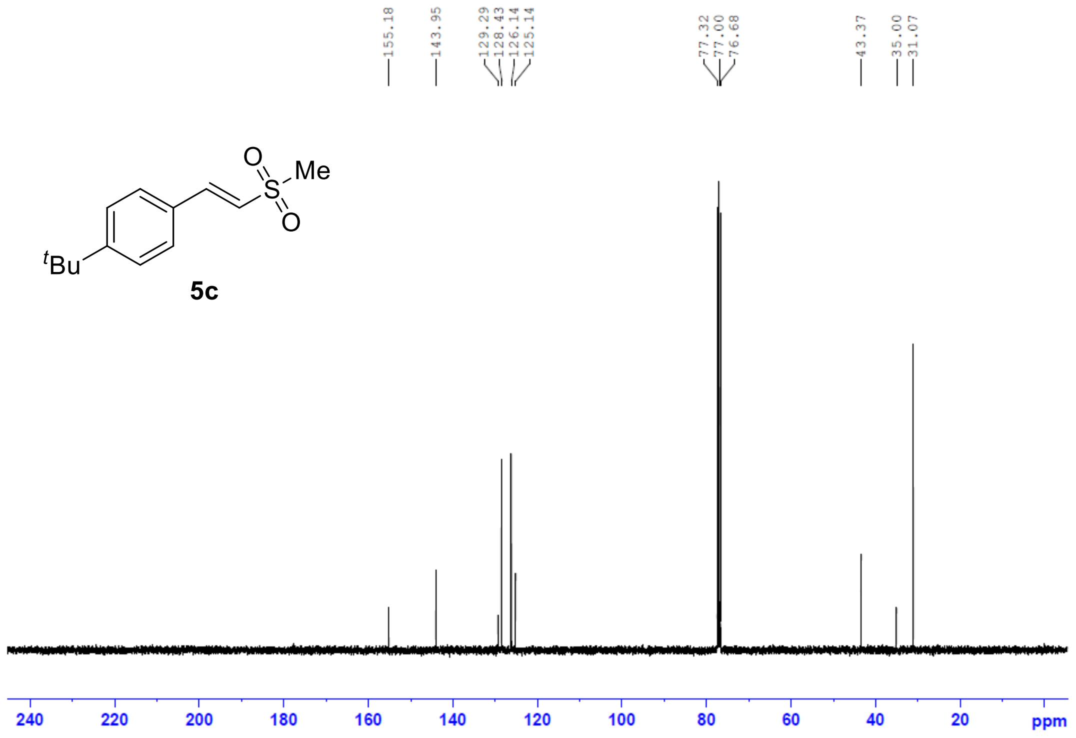
1.00
3.06
9.08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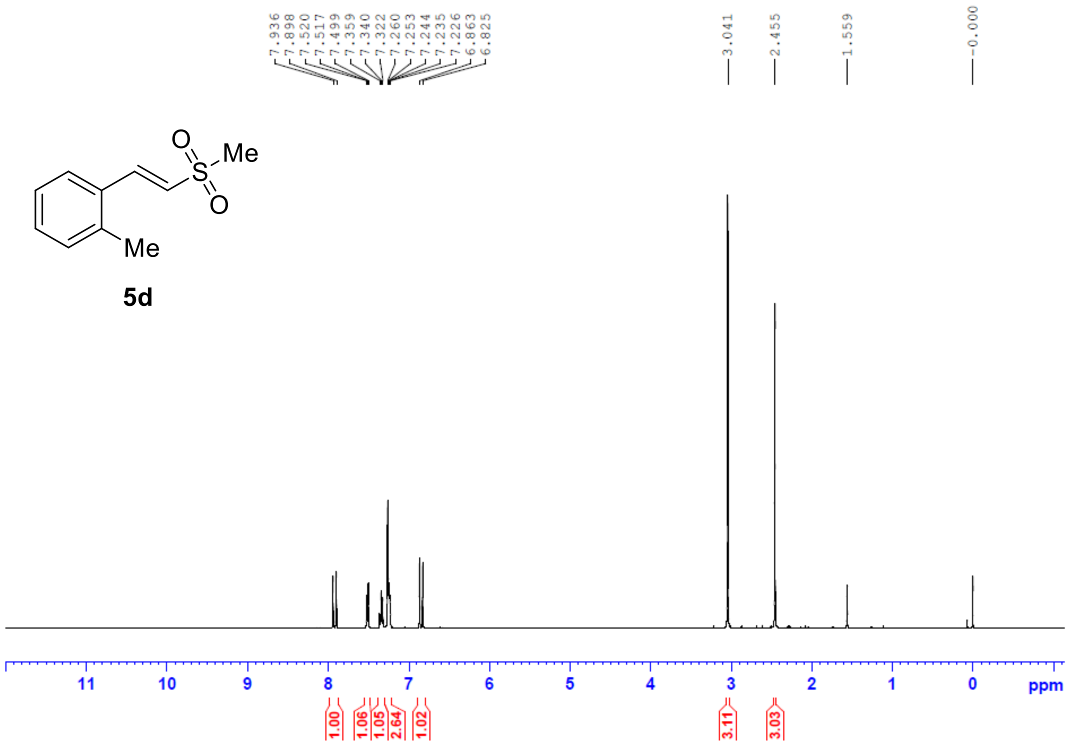
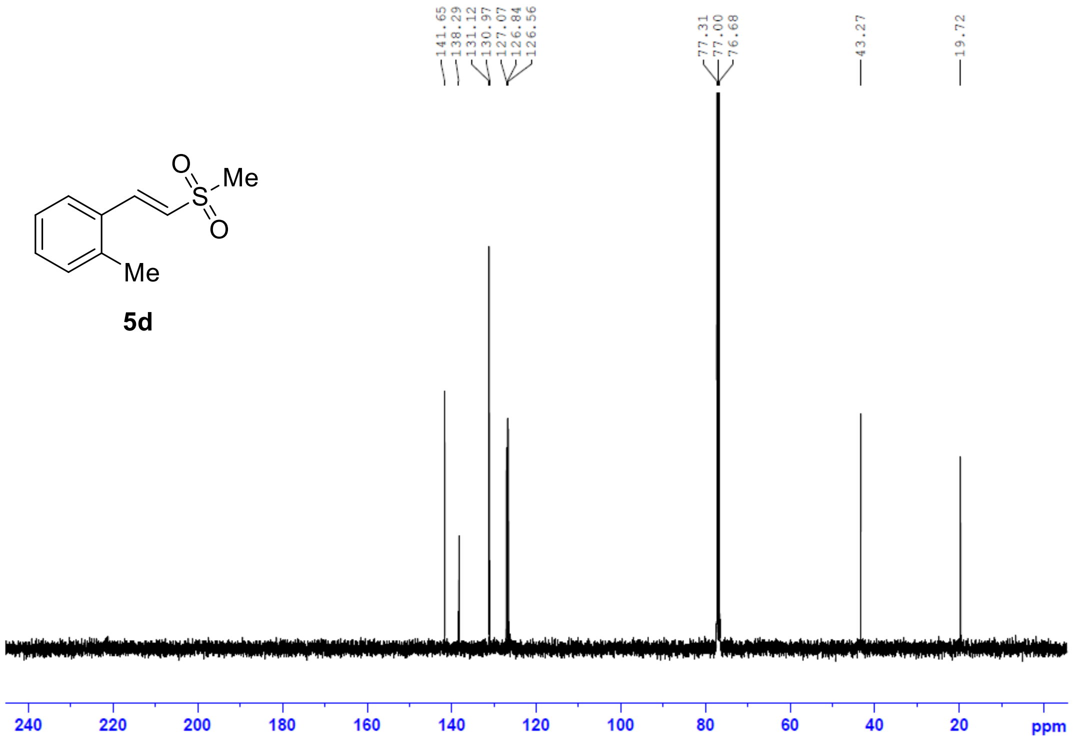
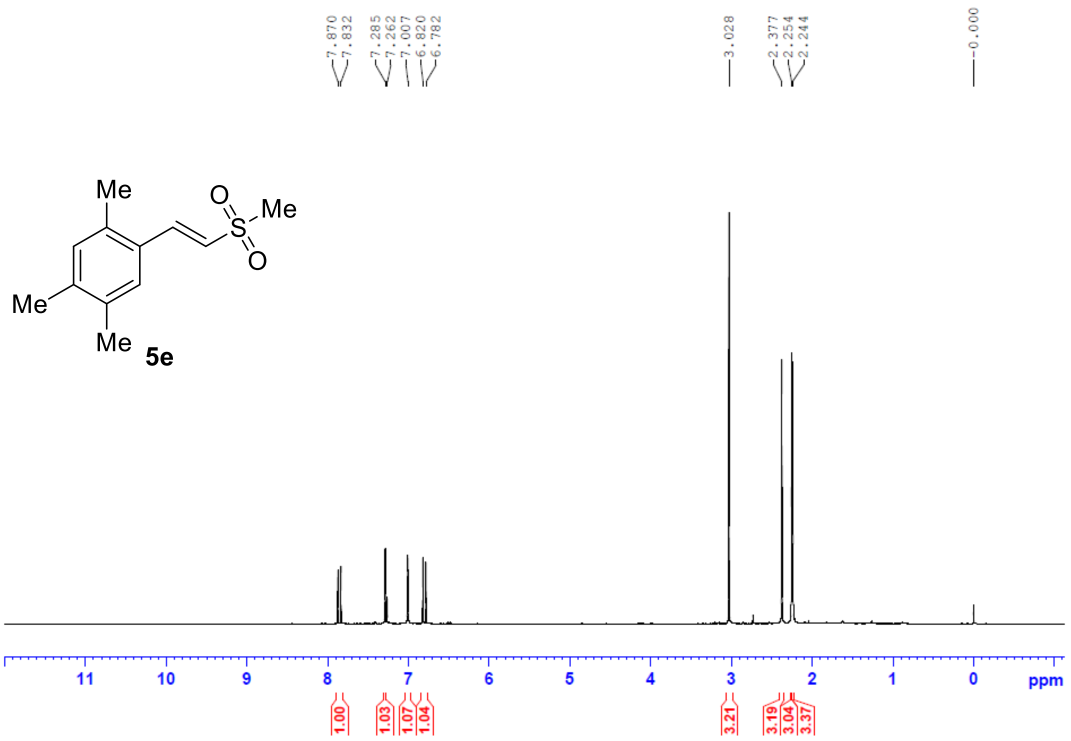
43.37
35.00
31.07
O
S
Me
O
tBu
5c
240
220
200
180
160
140
120
100
80
60
40
20
ppm


O
S
Me
O
Me
7.936
7.898
7.520
7.517
7.499
7.359
7.340
7.322
7.260
7.253
7.244
7.235
7.226
6.863
6.825
3.041
2.455
1.559
-0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
1.05
2.64
1.02
3.11
3.03

**5d**

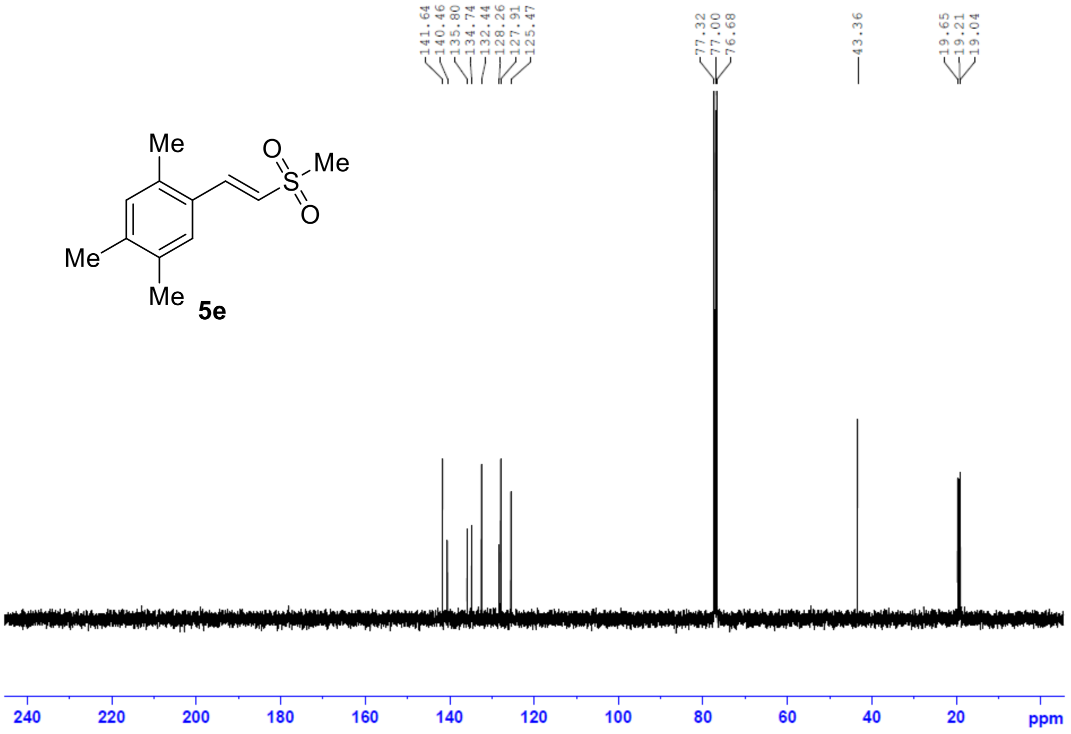

O
S
Me
O
Me
141.65
138.29
131.12
130.97
127.07
126.84
126.56
77.31
77.00
76.68
43.27
19.72
240
220
200
180
160
140
120
100
80
60
40
20
ppm

**5d**



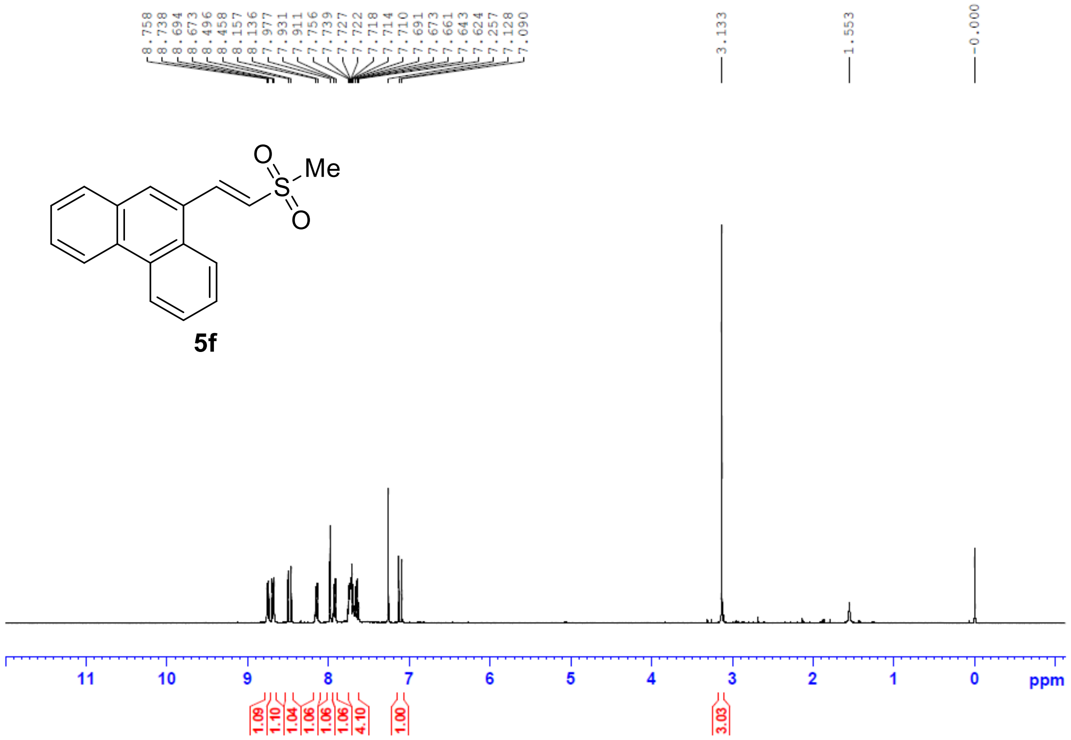
**5e**

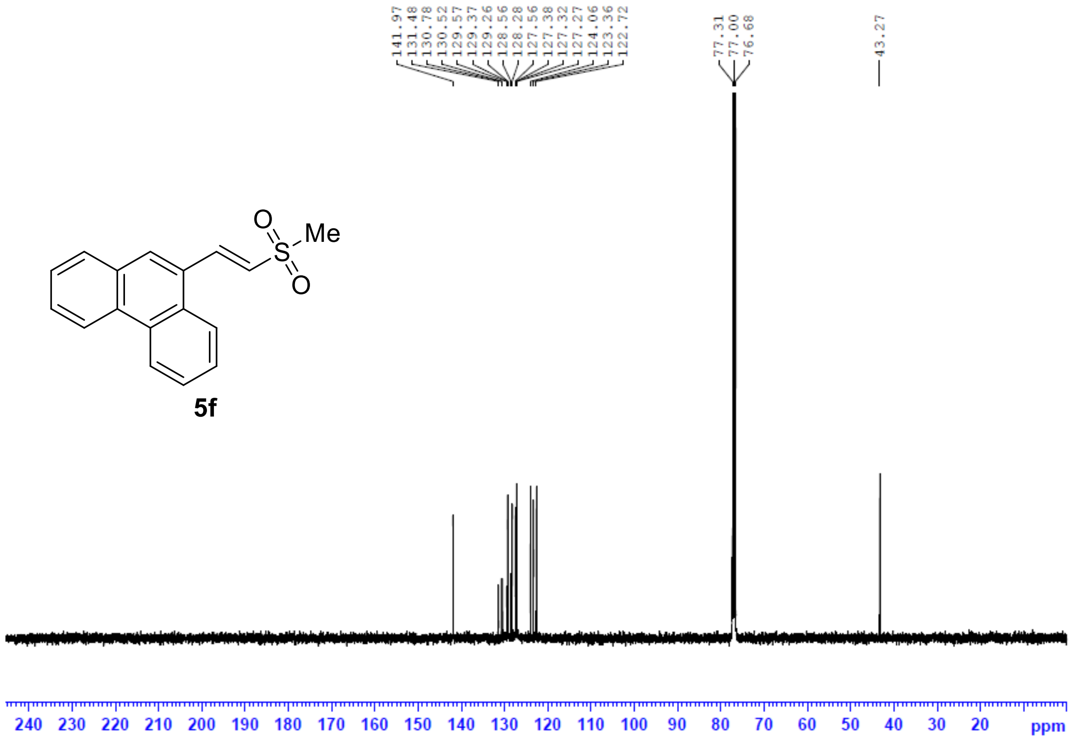
7.870
7.832
7.285
7.262
7.007
6.820
6.782
3.028
2.377
2.254
2.244
0.000
Me
O
S
Me
O
Me
Me
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.07
1.04
3.21
3.19
3.04
3.37

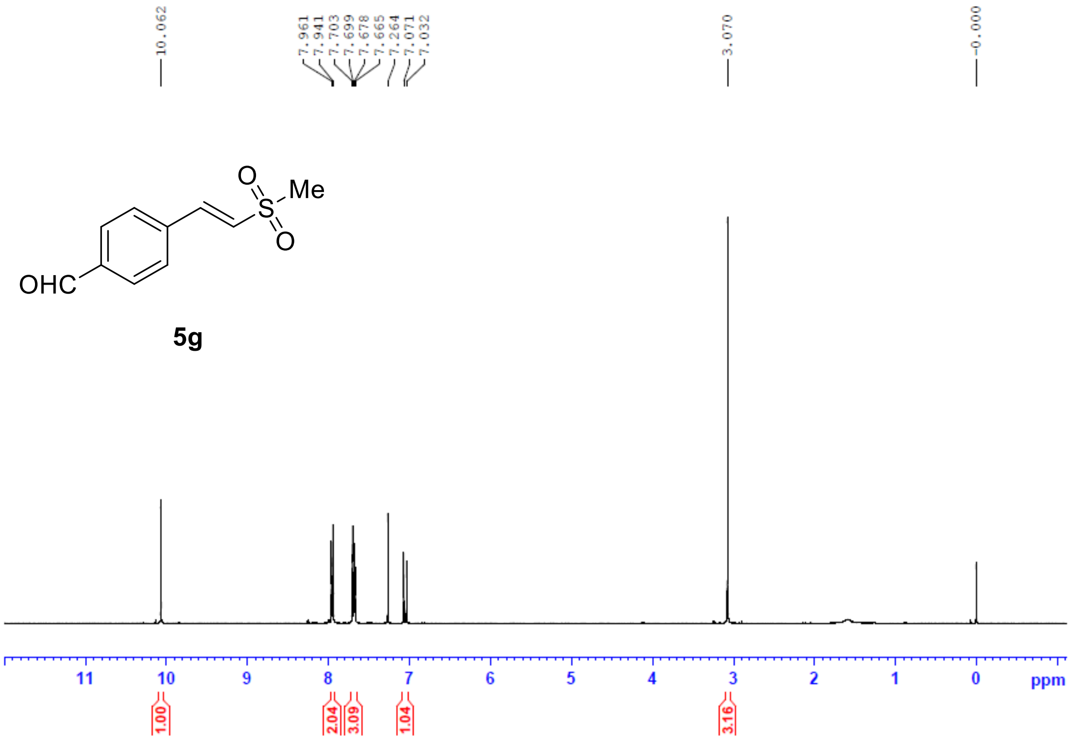


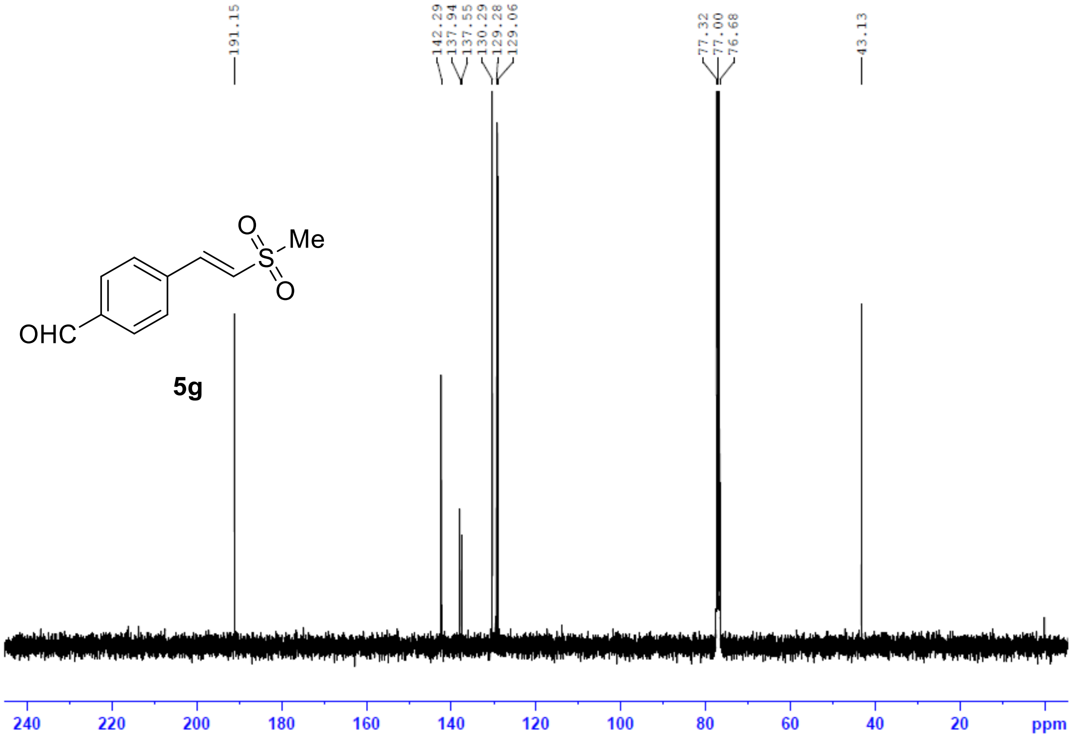
**5e**

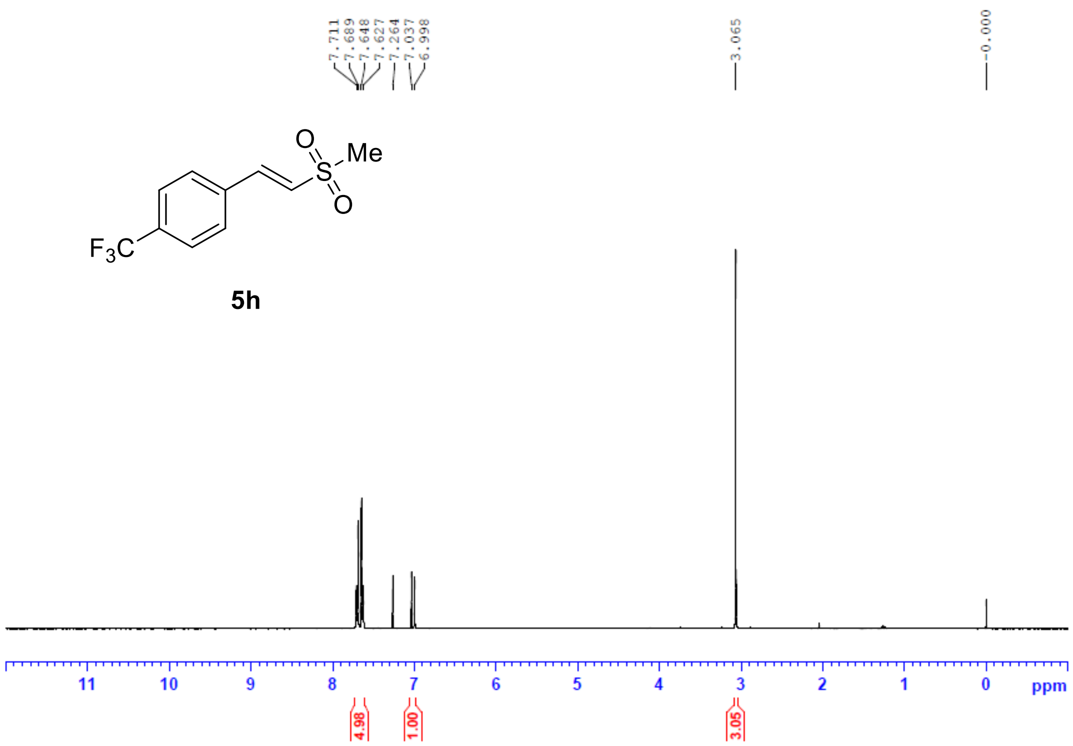
141.64
140.46
135.80
134.74
132.44
128.26
127.91
125.47
77.32
77.00
76.68
43.36
19.65
19.21
19.04
Me
O
S
Me
O
Me
Me
240
220
200
180
160
140
120
100
80
60
40
20
ppm

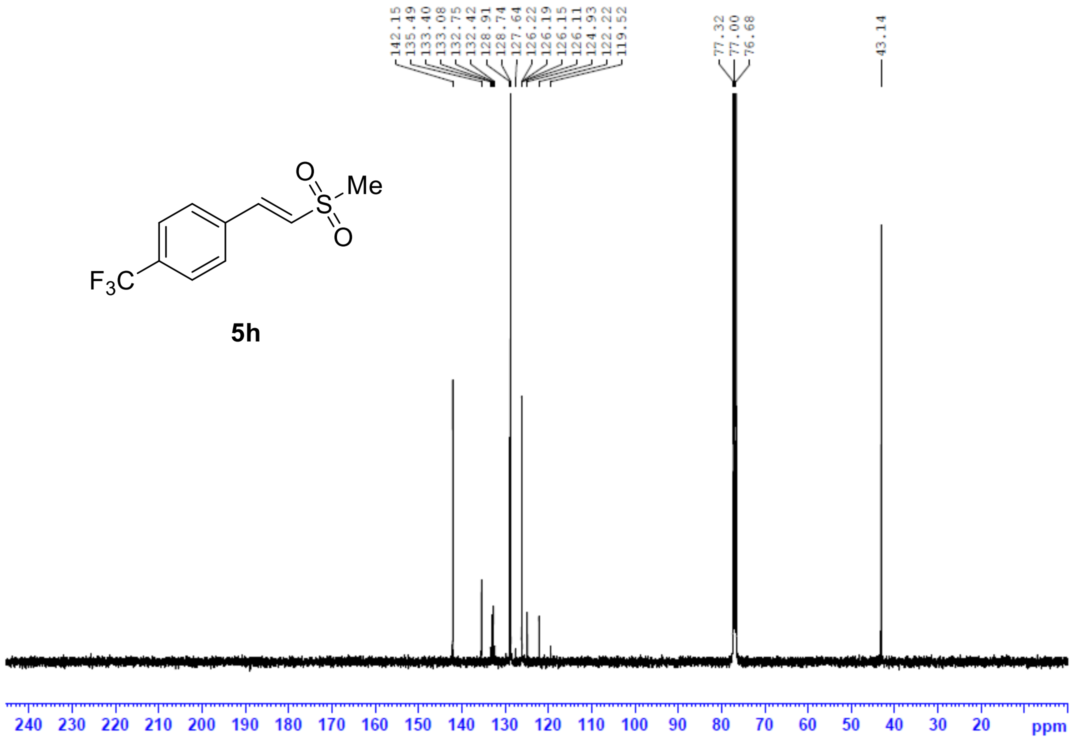

8.758
8.738
8.694
8.673
8.496
8.458
8.157
8.136
7.977
7.931
7.911
7.756
7.739
7.727
7.722
7.718
7.714
7.710
7.691
7.673
7.661
7.643
7.624
7.257
7.128
7.090
3.133
1.553
-0.000
O
S
Me
O
5f
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.09
1.10
1.04
1.06
1.06
1.06
4.10
1.00
3.03

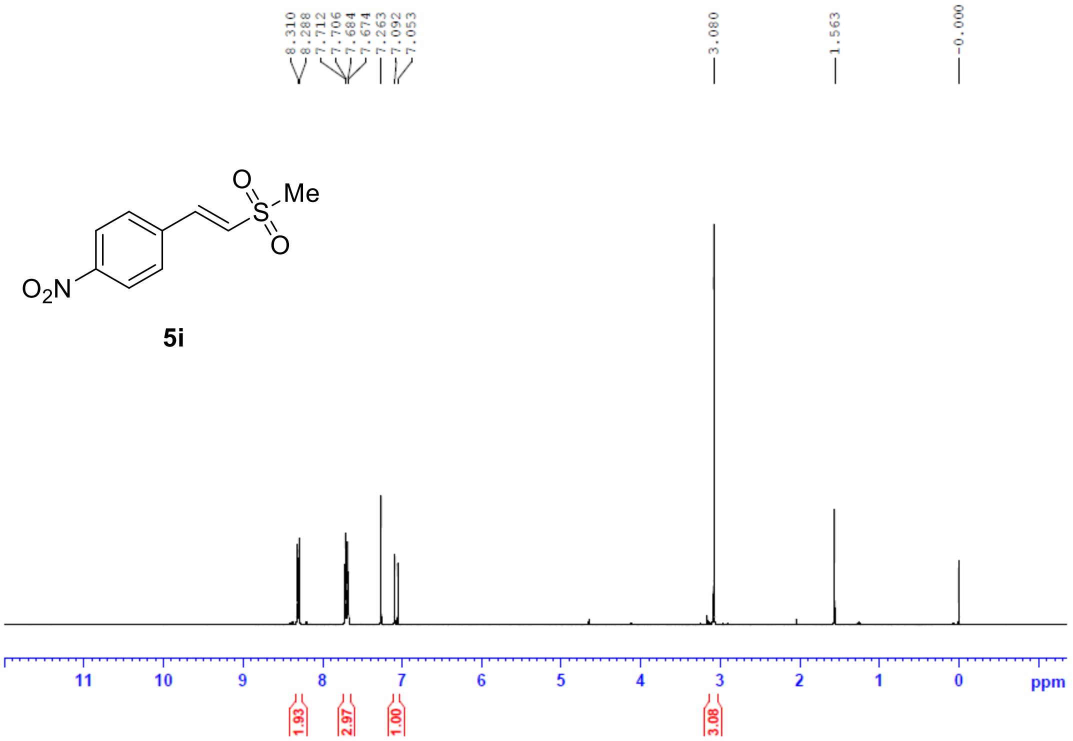

141.97
131.48
130.78
130.52
129.57
129.37
129.26
128.56
128.28
127.56
127.38
127.32
127.27
124.06
123.36
122.72
77.31
77.00
76.68
43.27
O
S
Me
O
5f
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


10.062
7.961
7.941
7.703
7.699
7.678
7.665
7.264
7.071
7.032
3.070
-0.000
O
S
O
Me
OHC
5g
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.04
3.09
1.04
3.16

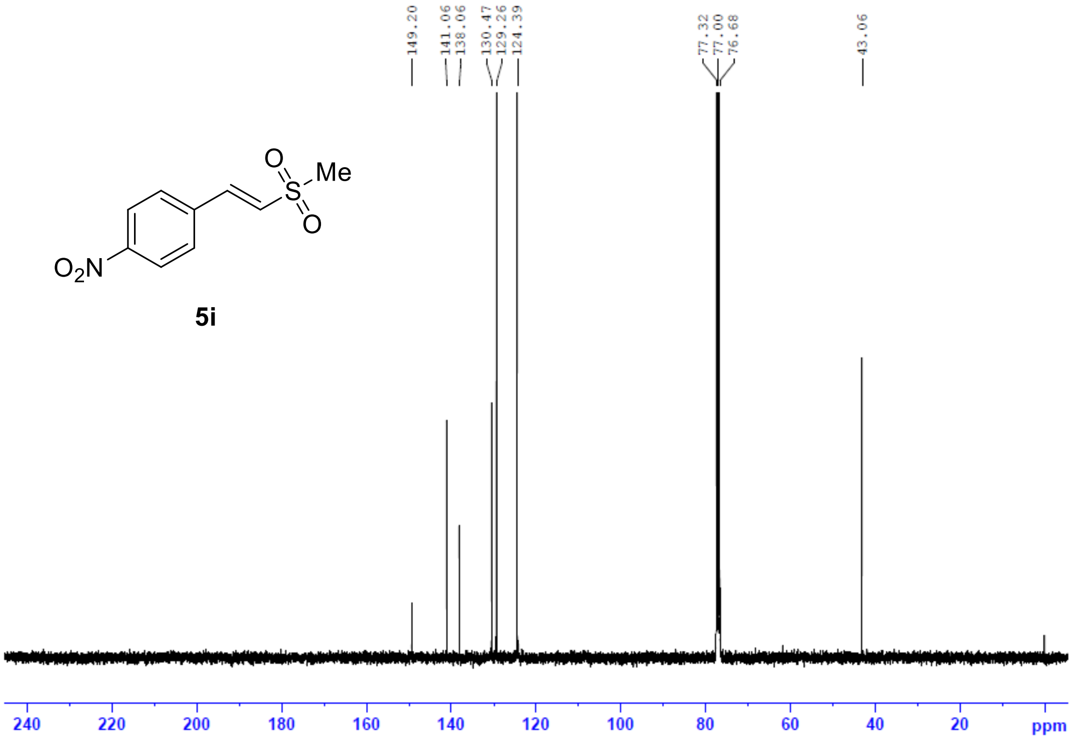

191.15
142.29
137.94
137.55
130.29
129.28
129.06
77.32
77.00
76.68
43.13
O
S
O
Me
OHC
5g
240
220
200
180
160
140
120
100
80
60
40
20
ppm


7.711
7.689
7.648
7.627
7.264
7.037
6.998
3.065
-0.000
O
S
Me
O
F3C
5h
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.98
1.00
3.05

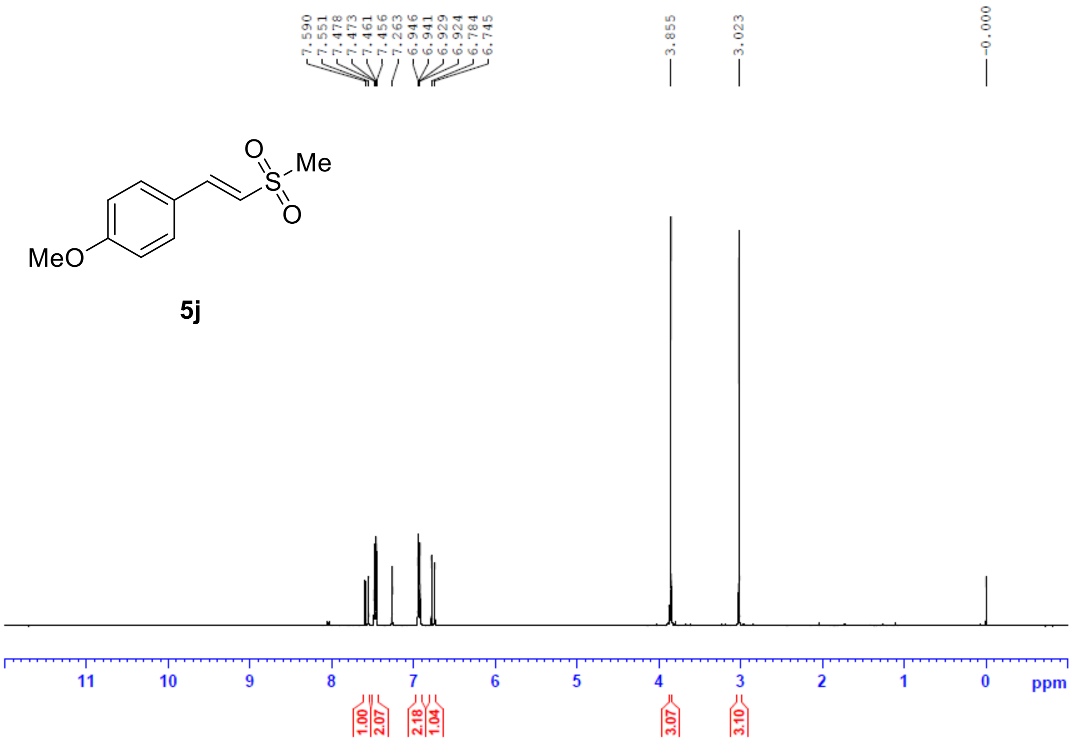

142.15
135.49
133.40
133.08
132.75
132.42
128.91
128.74
127.64
126.22
126.19
126.15
126.11
124.93
122.22
119.52
77.32
77.00
76.68
43.14
O
S
Me
O
F3C
5h
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

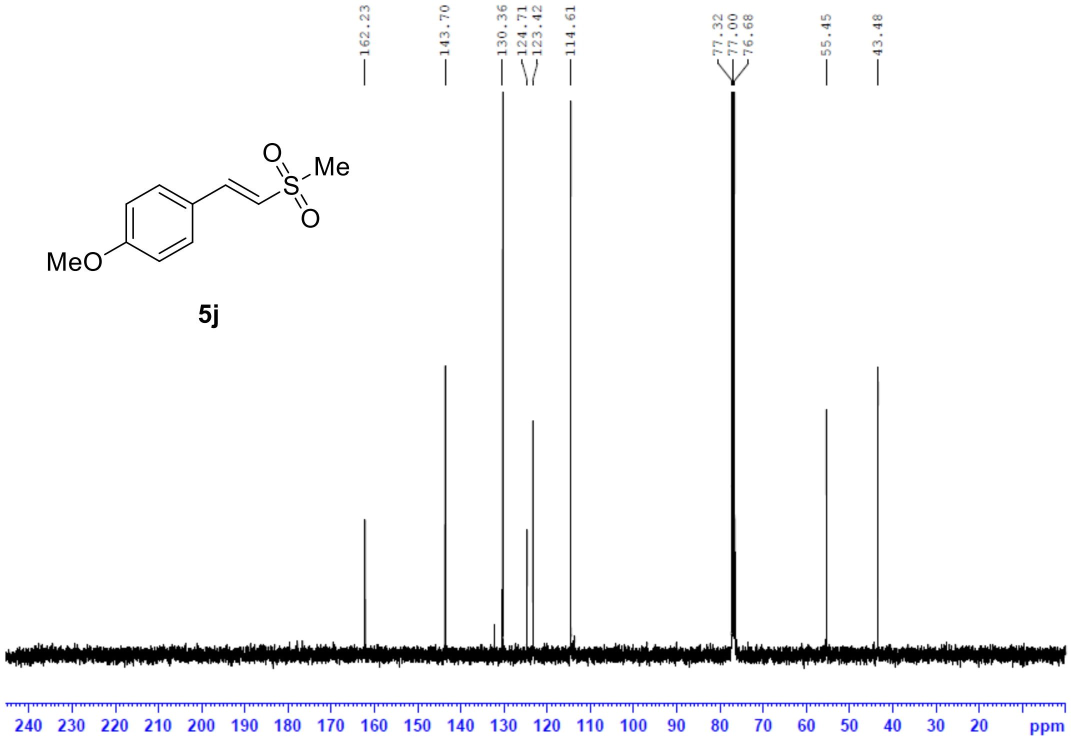


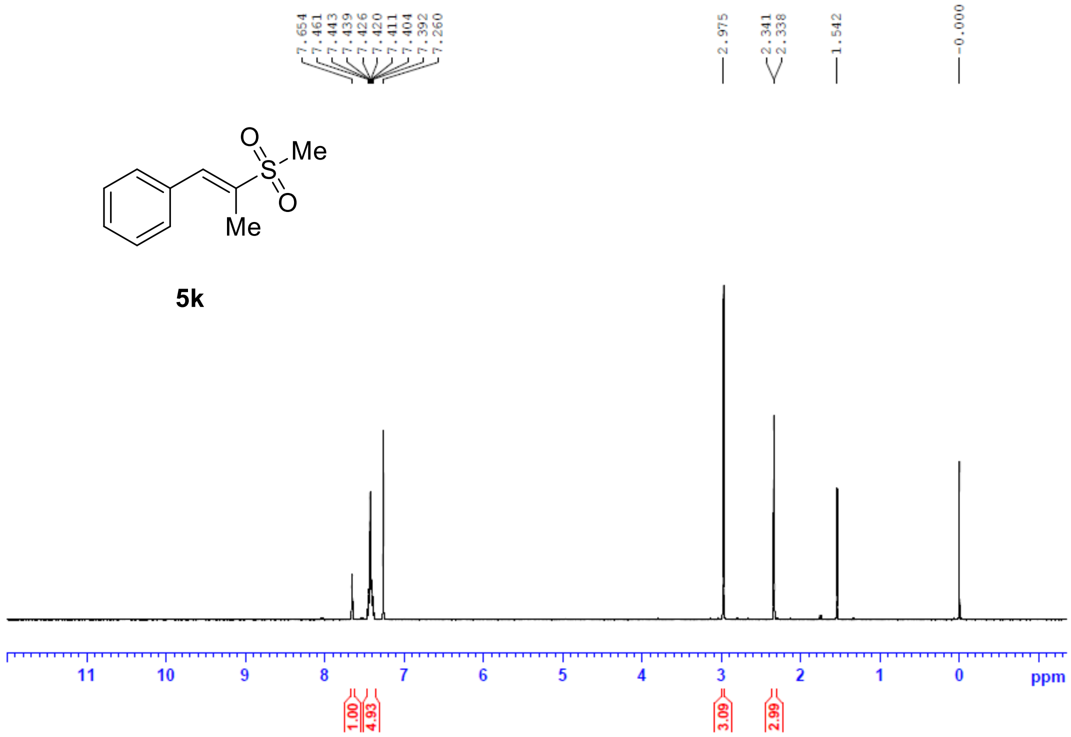
8.310
8.288
7.712
7.706
7.684
7.674
7.263
7.092
7.053
3.080
1.563
-0.000
O
Me
S
O
$O_2N$
5i
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
2.97
1.00
3.08



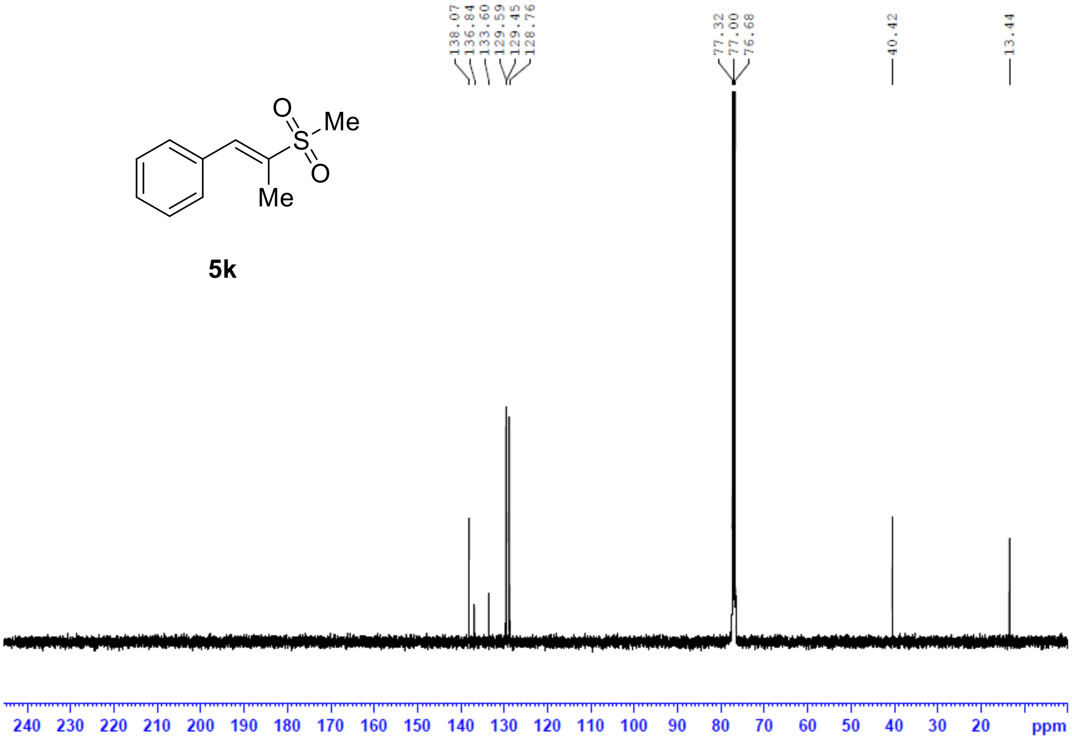
149.20
141.06
138.06
130.47
129.26
124.39
77.32
77.00
76.68
43.06
O
Me
S
O
$O_2N$
5i
240
220
200
180
160
140
120
100
80
60
40
20
ppm


7.590
7.551
7.478
7.473
7.461
7.456
7.263
6.946
6.941
6.929
6.924
6.784
6.745
3.855
3.023
-0.000
O
S
Me
O
MeO
5j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.07
2.18
1.04
3.07
3.10

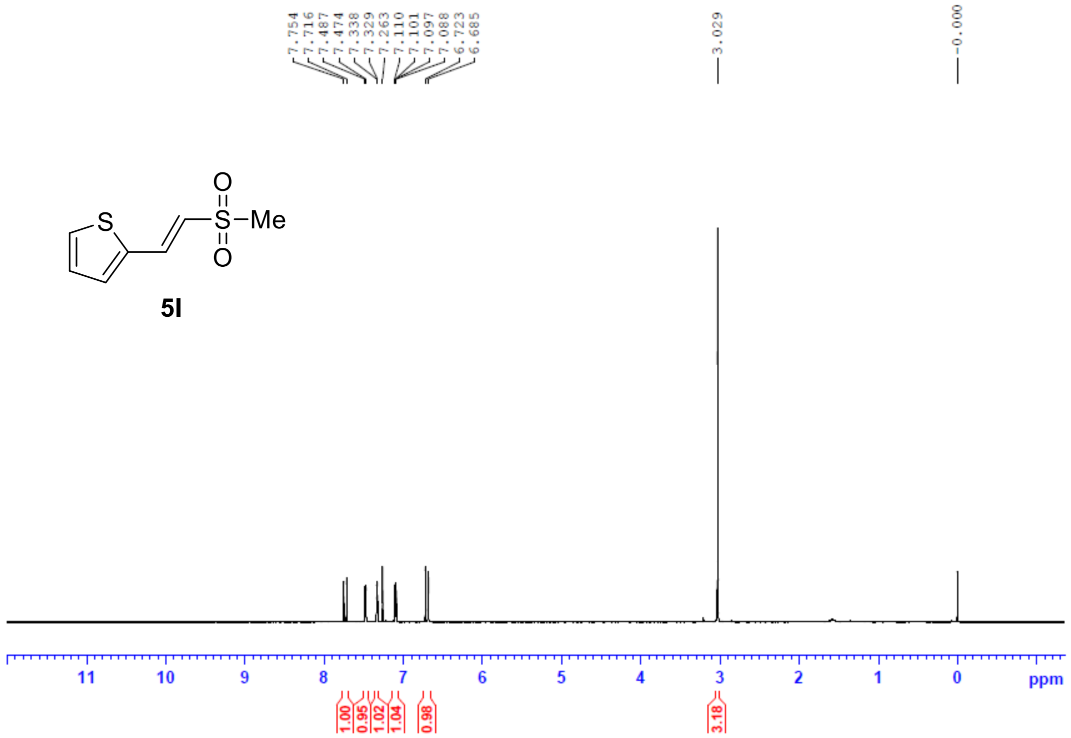

162.23
143.70
130.36
124.71
123.42
114.61
77.32
77.00
76.68
55.45
43.48
O
S
Me
O
MeO
5j
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

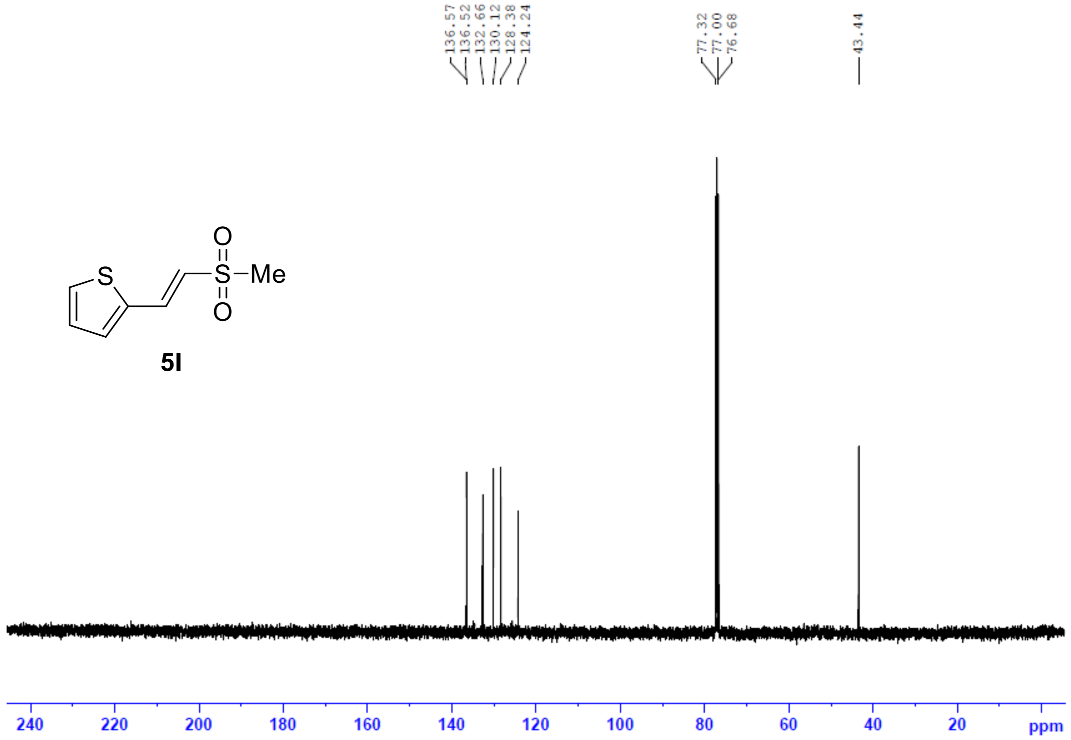

7.654
7.461
7.443
7.439
7.426
7.420
7.411
7.404
7.392
7.260
2.975
2.341
2.338
1.542
-0.000
O
S
Me
O
Me
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.93
3.09
2.99

**5k**

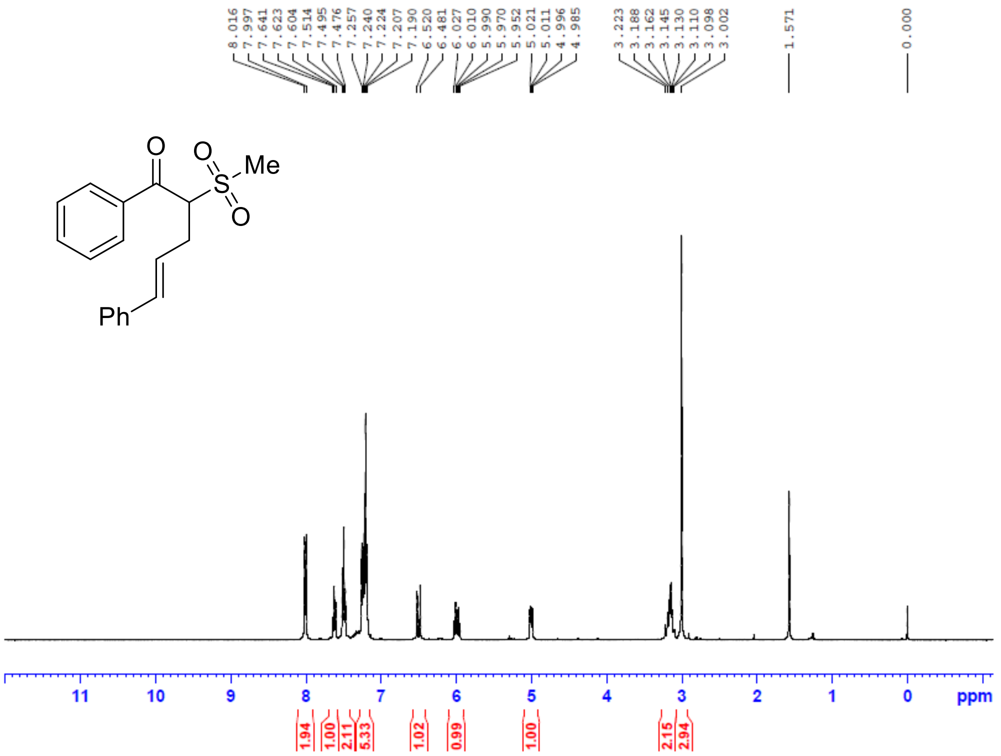

138.07
136.84
133.60
129.59
129.45
128.76
77.32
77.00
76.68
40.42
13.44
O
S
Me
O
Me
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

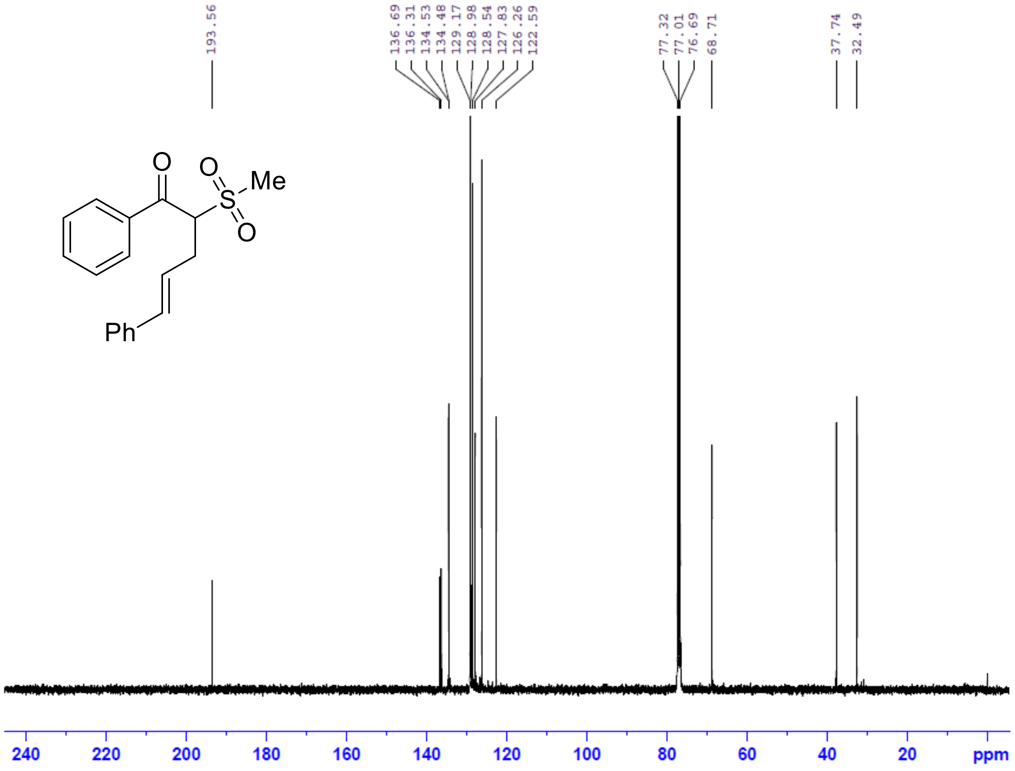
**5k**

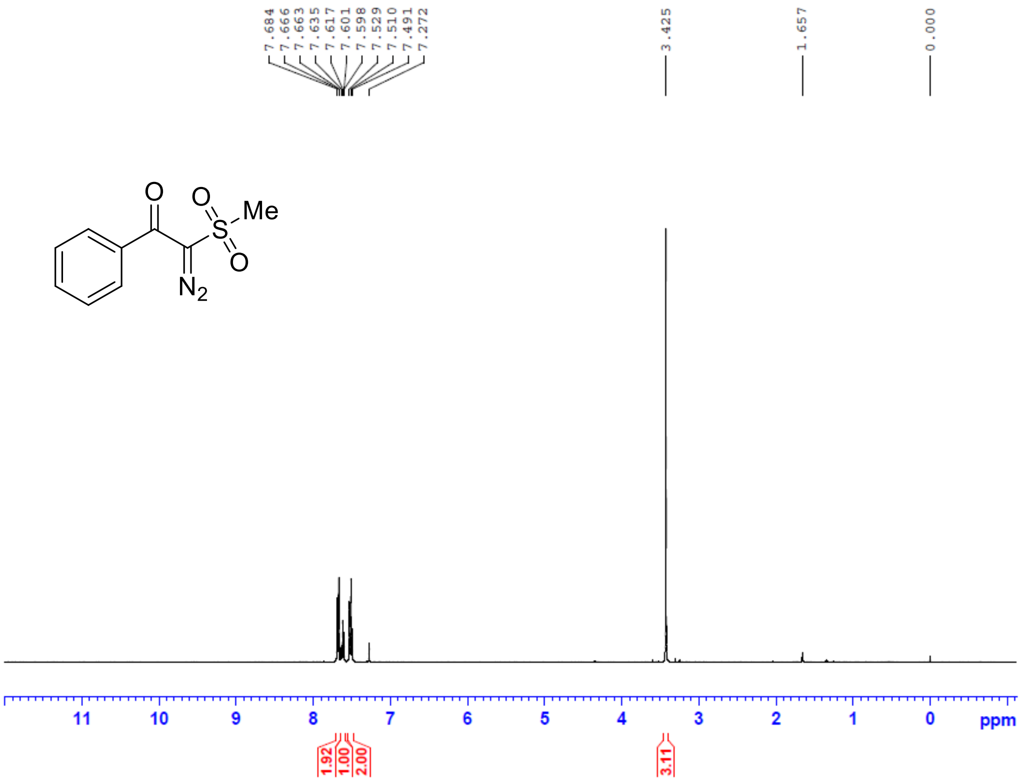

7.754
7.716
7.487
7.474
7.338
7.329
7.263
7.110
7.101
7.097
7.088
6.723
6.685
3.029
-0.000
S
O
S–Me
O
5l
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.95
1.02
1.04
0.98
3.18

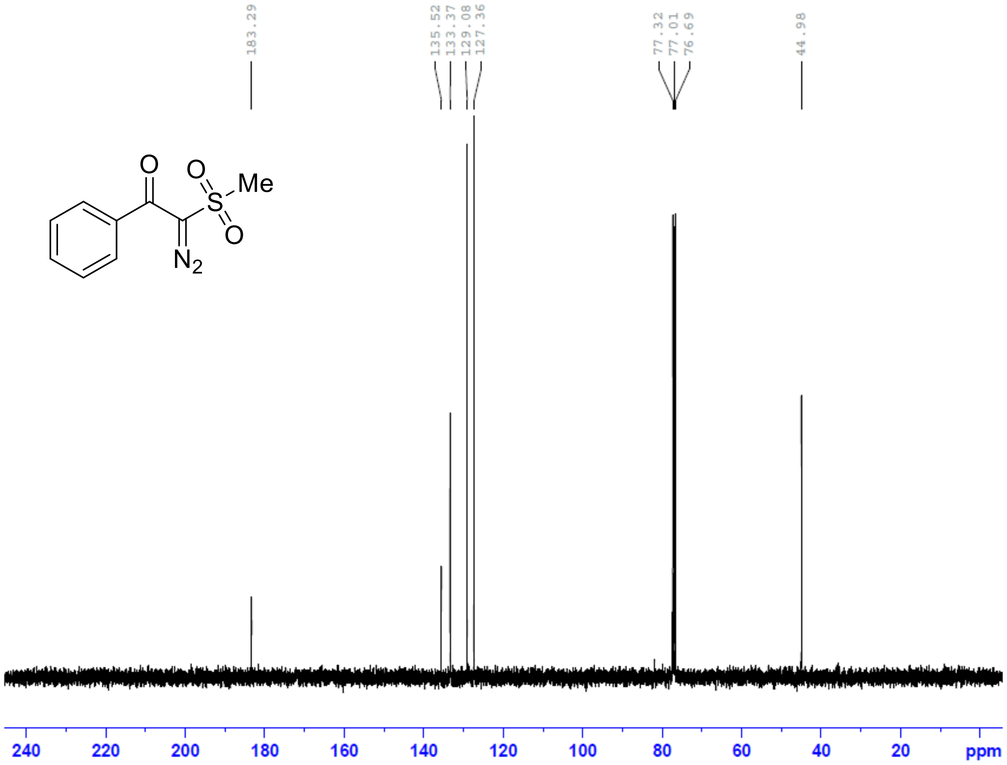

136.57
136.52
132.66
130.12
128.38
124.24
77.32
77.00
76.68
43.44
S
O
S–Me
O
5l
240
220
200
180
160
140
120
100
80
60
40
20
ppm

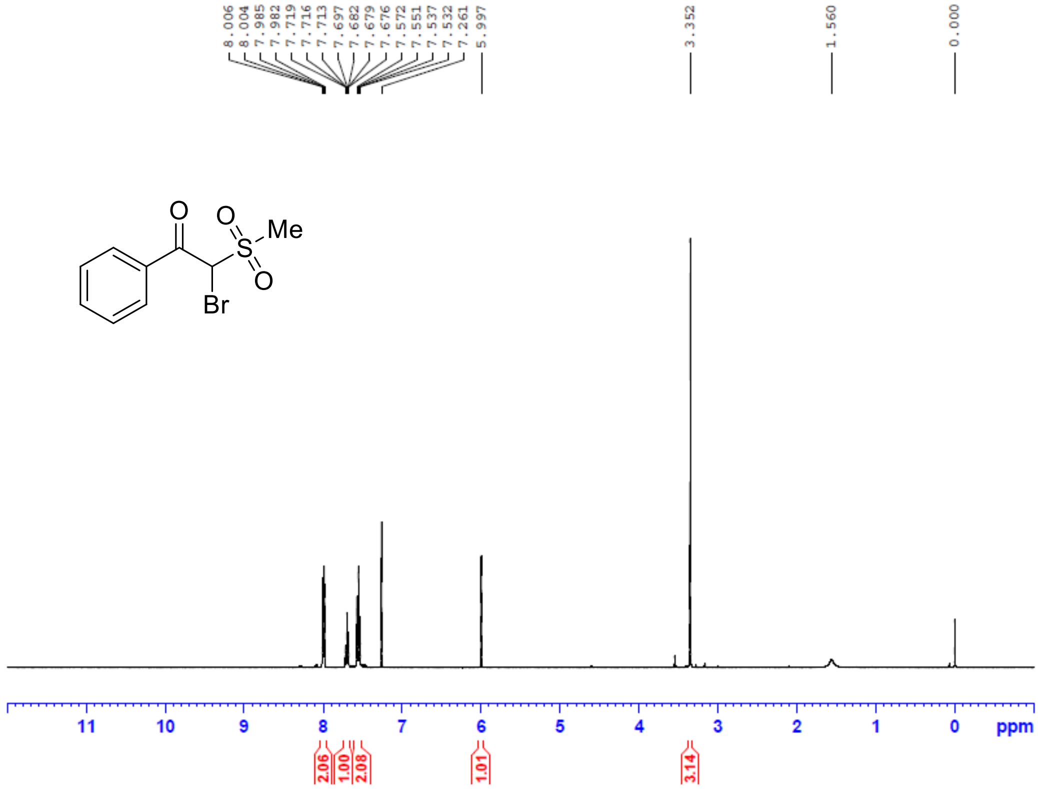
## NMR Spetra for transformations of methyl sulfones

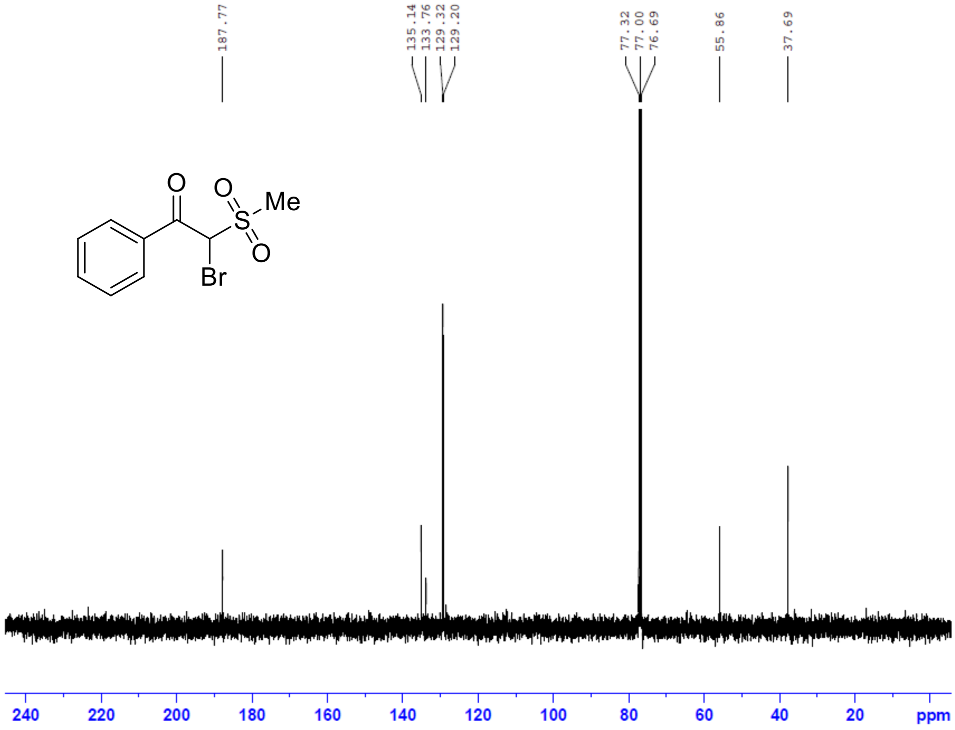


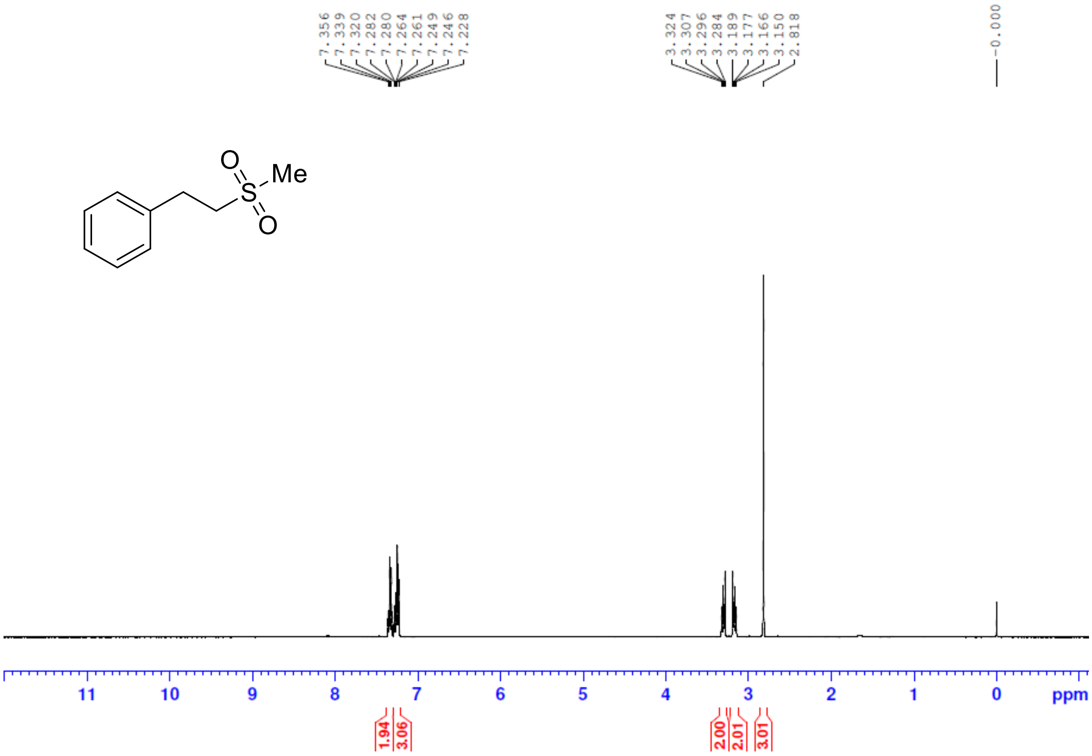


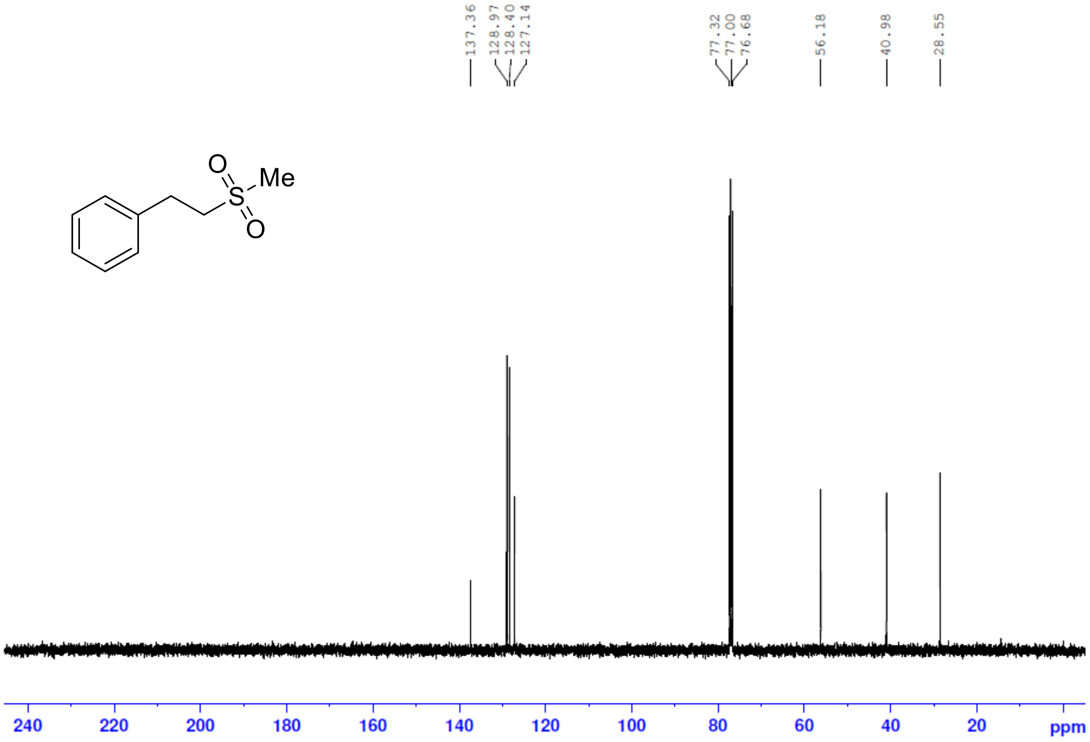

7.684
7.666
7.663
7.635
7.617
7.601
7.598
7.529
7.510
7.491
7.272
3.425
1.657
0.000
O
O
Me
S
O
N2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
1.00
2.00
3.11


183.29
135.52
133.37
129.08
127.36
77.32
77.01
76.69
44.98
O
O
Me
S
O
N2
240
220
200
180
160
140
120
100
80
60
40
20
ppm


8.006
8.004
7.985
7.982
7.719
7.716
7.713
7.697
7.682
7.679
7.676
7.572
7.551
7.537
7.532
7.261
5.997
3.352
1.560
0.000
O
O
S
Me
O
Br
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
1.00
2.08
1.01
3.14


187.77
135.14
133.76
129.32
129.20
77.32
77.00
76.69
55.86
37.69
O
O
S
Me
O
Br
240
220
200
180
160
140
120
100
80
60
40
20
ppm


7.356
7.339
7.320
7.282
7.280
7.264
7.261
7.249
7.246
7.228
3.324
3.307
3.296
3.284
3.189
3.177
3.166
3.150
2.818
-0.000
O
S
Me
O
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
3.06
2.00
2.01
3.01


137.36
128.97
128.40
127.14
77.32
77.00
76.68
56.18
40.98
28.55
O
S
Me
O
240
220
200
180
160
140
120
100
80
60
40
20
ppm