Supplementary Information

Copper-catalyzed direct oxysulfonylation of alkenes with dioxygen and sulfonylhydrazides leading to β-ketosulfones

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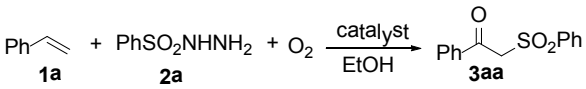
1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. $^{18}O_2$ (97%) was purchased from Beijing Gaisi Chemical Gases Center. $H_2{}^{18}O$ (98%) was purchased from ICON ISOTOPE Company. All solvents were dried according to standard procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200 - 300 mesh).

2. Optimization of reaction conditions

Table S1. The reaction of **1a** and **2a** in different conditions[a]



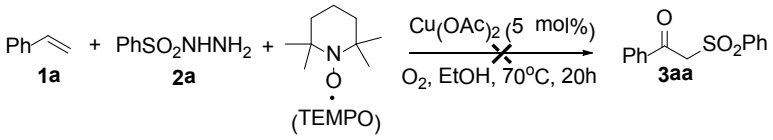
Entry	Catalyst	Temperature	Ratio **1a :2a**	yield (%)[b]
1	-	70	1.5:1	24
2	$Pd(OAc)_2$(5 mol%)	70	1.5:1	25
3	$FeBr_3$(5 mol%)	70	1.5:1	25
4	$AgNO_3$(5 mol%)	70	1.5:1	39
5	$RuCl_3$(5 mol%)	70	1.5:1	30
6	$Co(OAc)_2$(5 mol%)	70	1.5:1	48
7	$In(OAc)_3$(5 mol%)	70	1.5:1	28
8	$Zn(OTf)_2$(5 mol%)	70	1.5:1	29
9	$Cu(OAc)_2$ (5 mol%)	70	1.5:1	70
10	$Cu(OAc)_2$ (5 mol%)	rt	1.5:1	44
11	$Cu(OAc)_2$ (5 mol%)	50	1.5:1	58
12	$Cu(OAc)_2$ (5 mol%)	70	1:1	61
13	$Cu(OAc)_2$ (5 mol%)	70	1:1.5	63
14	$Cu(OAc)_2$ (5 mol%)	70	1:2	62
15	$Cu(OAc)_2$ (2 mol%)	70	1.5:1	52
16	$Cu(OAc)_2$ (10 mol%)	70	1.5:1	69
17	$Cu(OAc)_2$ (20 mol%)	70	1.5:1	56

[a] Reaction conditions: styrene **1a** (0.5-0.75 mmol), phenylsulfonohydrazide **2a** (0.5-1 mmol), catalyst (2-20 mol %), EtOH (3.0 mL), rt-70 °C, 20 h, O_2 (balloon). [b] Isolated yields based on **2a** except for entries 13-14.

3. General procedure for copper catalyzed oxysulfonylation of alkenes with dioxygen and sulfonylhydrazides to form β-ketosulfones

To a mixture of alkene (0.75 mmol), sulfonylhydrazide (0.5 mmol), $Cu(OAc)_2$ (0.025 mmol, 5 mol%), and EtOH (3 mL) in a 25 mL round-bottomed flack at room temperature under O_2 (balloon). The reaction vessel was allowed to stir at 70 °C for 20 h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products.

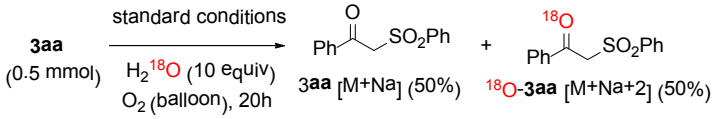
4. Preliminary mechanistic studies with TEMPO



To a mixture of styrene (0.75 mmol), phenylsulfonohydrazide (0.5 mmol), TEMPO (0.6 mmol), $Cu(OAc)_2$ (0.025 mmol, 5 mol%) in EtOH (3 mL) at room temperature under O_2 (balloon). The reaction vessel was allowed to stir for 20 h at 70 °C. After the reaction, the solution was concentrated in vacuum, no desired product was detected.

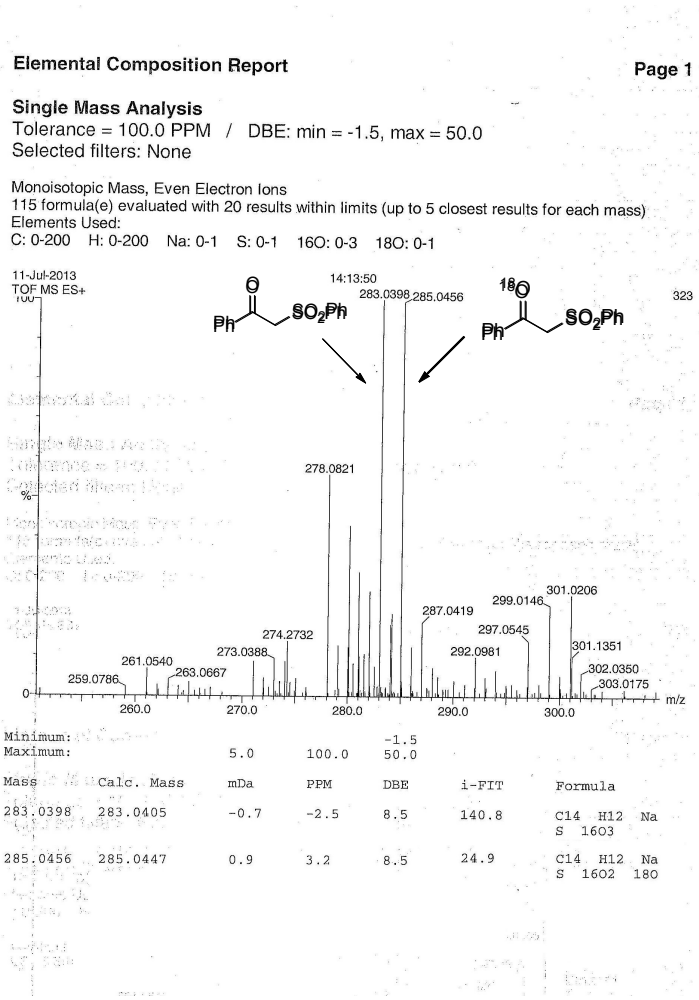
5. Labeling experiments

5.1 Oxygen scrambling experiment of ^{16}O-3aa with $H_2{}^{18}O$ (10 equiv).

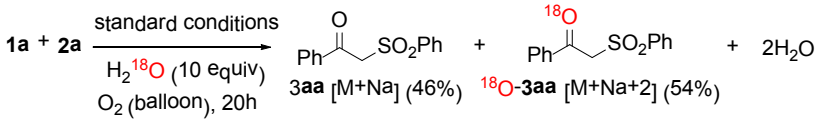


To a mixture of product **3aa** (130 mg, 0.5 mmol), $Cu(OAc)_2$ (0.025 mmol, 5 mol%), and $H_2{}^{18}O$ (5 mmol, 10 equiv) in EtOH (2 mL) at room temperature under O_2 (balloon). The reaction vessel was allowed to stir at 70 °C for 20h. After the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1) as an eluent. The products were measured by HRMS.

The HRMS spectra of products was listed as bellow.

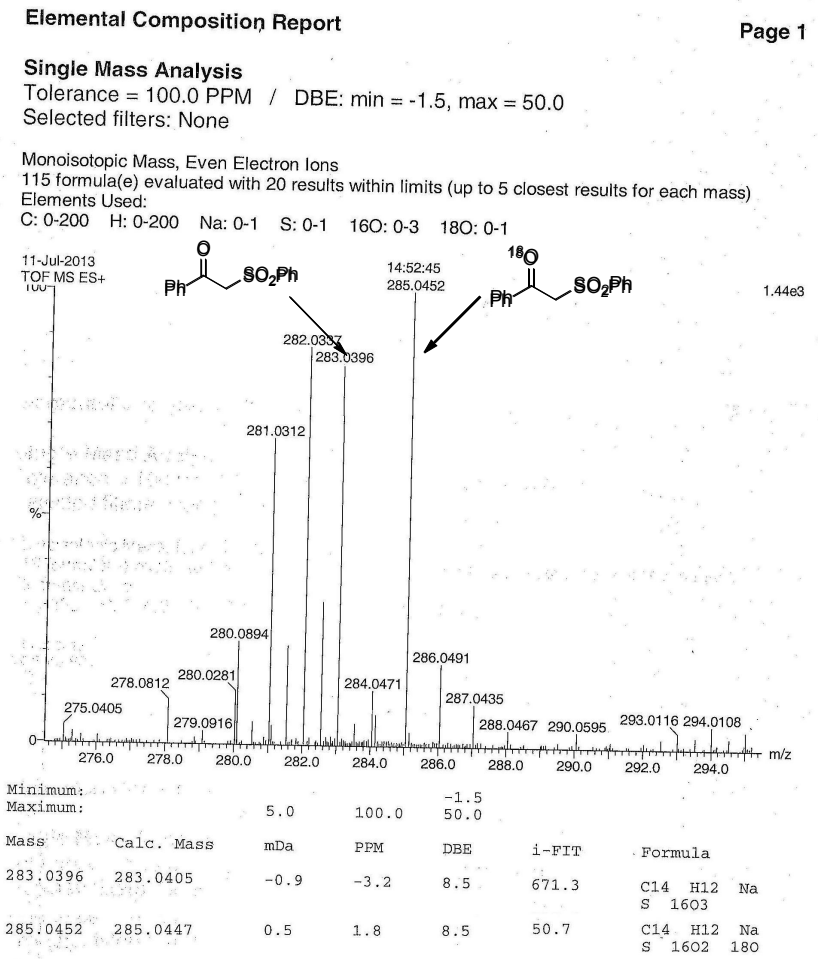


5.2 Copper catalyzed oxysulfonylation of styrene (1a) with phenylsulfonohydrazide (2a) in the presence of $H_2{}^{18}O$ (10 equiv) under O_2.

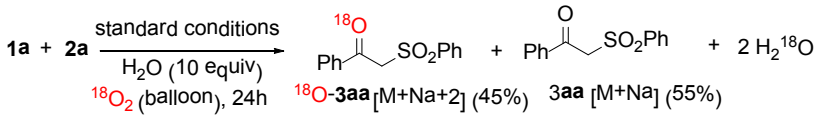


To a mixture of styrene **1a** (0.75 mmol), phenylsulfonohydrazide **2a** (0.5 mmol), $Cu(OAc)_2$ (0.025 mmol, 5 mol%), and $H_2{}^{18}O$ (5 mmol, 10 equiv) in EtOH (2 mL) at room temperature under O_2 (balloon). The reaction vessel was allowed to stir at 70 °C for 20 h. After the reaction, the resulting mixture was concentrated under vacuum. Then, the residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1) as an eluent to give the products in 64% yield. The products were measured by HRMS.

The HRMS spectra of products was listed as bellow.



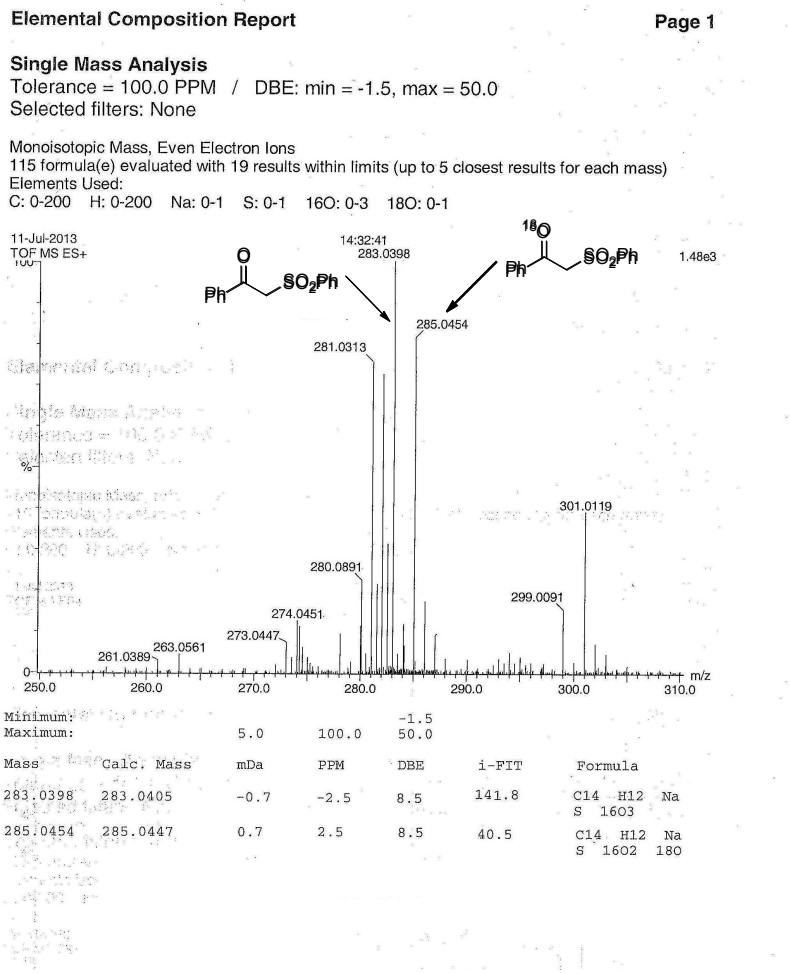
5.3 Copper catalyzed oxysulfonylation of styrene (1a) with phenylsulfonohydrazide (2a) in the presence of H_2O (10 equiv) under $^{18}O_2$.



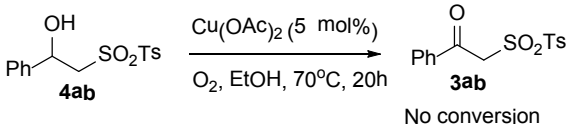
To a mixture of styrene **1a** (0.75 mmol), phenylsulfonohydrazide **2a** (0.5 mmol), $Cu(OAc)_2$ (0.025 mmol, 5 mol%) and H_2O (5 mmol, 10 equiv) in EtOH (2 mL) at room temperature under $^{18}O_2$ (balloon). The reaction vessel was allowed to stir at 70 °C for 20

h. Then, the reaction solution was submitted to flash chromatographic separation on a short silica gel using petroleum ether/ethyl acetate (4:1) as an eluent to give the products in 63% yield. The products were measured by HRMS.

The HRMS spectra of products was listed as bellow.

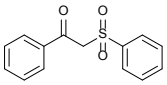


6. The reaction of β-hydroxysulfone (4ab) in standard conditions

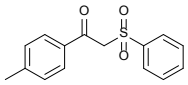


β-Hydroxysulfone **4ab** (0.1 mmol) was added to a mixture of $Cu(OAc)_2$ (5 mol %), in EtOH (2 mL) at room temperature under O_2 (balloon). The reaction mixture was stirred at 70 °C for 24 h. Then, the solution was concentrated in vacuum, no β-ketosulfone **3ab** was detected.

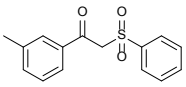
7. Characterization data of β-ketosulfones 3aa-3af, 4ab

2-Phenyl-1-(piperidin-1-yl)ethanone (3aa) 

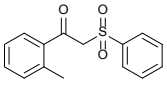
Compound **3aa** was obtained in 70% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.97-7.91 (m, 4H), 7.69-7.62 (m, 2H), 7.57 (t, J = 7.7 Hz, 2H), 7.50 (t, J = 7.7 Hz, 2H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 188.0, 138.8, 135.8, 134.4, 134.2, 129.3, 129.2, 128.9, 128.6, 63.5; HRMS calc. for $C_{14}H_{12}O_3SNa$ $(M+H)^+$, 261.0585; found, 261.0581.

2-(phenylsulfonyl)-1-p-tolylethanone (3ba) 

Compound **3ba** was obtained in 70% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.91 (d, J = 7.3 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.5, 145.6, 138.9, 134.2, 133.4, 129.6, 129.5, 129.2, 128.6, 63.5, 21.8; HRMS calc. for $C_{15}H_{14}O_3SNa$ $(M+Na)^+$, 297.0561; found, 297.0558.

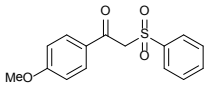
2-(phenylsulfonyl)-1-m-tolylethanone (3ca) 

Compound **3ca** was obtained in 69% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.92 (dd, J_1 = 1.2 Hz, J_2 = 8.2 Hz, 2H), 7.74 (d, J = 9.2 Hz, 2H), 7.70-7.66 (m, 1H), 7.56 (t, J = 7.7 Hz, 2H), 7.44 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 4.75 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 188.1, 138.9, 138.8, 135.8, 135.2, 134.2, 129.7, 129.2, 128.7, 128.6, 126.6, 63.5, 21.3; HRMS calc. for $C_{15}H_{14}O_3SNa$ $(M+Na)^+$, 297.0561; found, 297.0559.

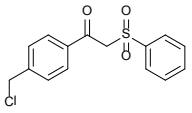
2-(phenylsulfonyl)-1-o-tolylethanone (3da) 

Compound **3da** was obtained in 64% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.89 (d, J = 7.3 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.30-7.26 (m, 2H), 4.73 (s, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 190.4, 140.0, 139.1, 135.7, 134.1, 132.8, 132.3, 130.3, 129.2, 128.5, 125.9, 65.5, 21.5; HRMS calc. for $C_{15}H_{14}O_3SNa$

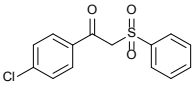
$(M+Na)^+$, 297.0561; found, 297.0565.

1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (3ea) 

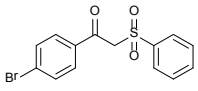
Compound **3ea** was obtained in 52% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.93 (dd, J_1 = 8.2 Hz, J_2 = 16.6 Hz, 4H), 7.68 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.71 (s, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 186.1, 164.6, 138.9, 134.1, 131.9, 129.2, 128.9, 128.6, 114.1, 63.5, 55.6; HRMS calc. for $C_{15}H_{14}O_4SNa$ $(M+Na)^+$, 313.0510; found, 313.0510.

1-(4-(chloromethyl)phenyl)-2-(phenylsulfonyl)ethanone (3fa) 

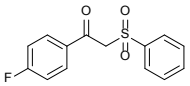
Compound **3fa** was obtained in 60% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.95 (d, J = 8.3 Hz, 2H), 7.90 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 2H), 7.70-7.66 (m, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.75 (s, 2H), 4.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.4, 143.8, 138.7, 135.6, 134.3, 129.8, 129.3, 128.9, 128.6, 63.6, 45.0; HRMS calc. for $C_{15}H_{13}O_3SClNa$ $(M+Na)^+$, 331.0172; found, 331.0171.

1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanone (3ga) 

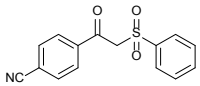
Compound **3ga** was obtained in 67% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.92-7.89 (m, 4H), 7.70 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 186.9, 141.1, 138.6, 134.4, 134.1, 130.7, 129.3, 129,2, 128.5, 63.6; HRMS calc. for $C_{14}H_{11}O_3ClSNa$ $(M+Na)^+$, 317.0015; found, 317.0013.

1-(4-bromophenyl)-2-(phenylsulfonyl)ethanone (3ha) 

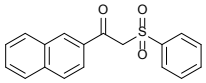
Compound **3ha** was obtained in 72% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.90 (d, J = 7.3 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.58 (t, J = 7.7 Hz, 2H), 4.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.1, 138.6, 134.5, 134.4, 132.3, 130.8, 130.0, 129.3, 128.5, 63.6; HRMS calc. for $C_{14}H_{11}O_3BrSNa$ $(M+Na)^+$, 360.9510; found, 360.9510.

1-(4-fluorophenyl)-2-(phenylsulfonyl)ethanone (3ia) 

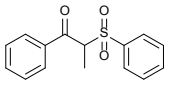
Compound **3ia** was obtained in 54% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.01 (dd, J_1 = 5.3 Hz, J_2 = 8.8 Hz, 2H), 7.91 (d, J = 7.4 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.18 (t, J = 7.9 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 186.4, 167.8, 165.2, 138.7, 134.3, 132.3, 132.2, 129.3, 128.5, 116.2, 116.0, 63.6; HRMS calc. for $C_{14}H_{11}O_3FSNa$ $(M+Na)^+$, 301.0311; found, 301.0309.

4-(2-(phenylsulfonyl)acetyl)benzonitrile (3ja) 

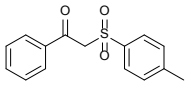
Compound **3ja** was obtained in 50% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.08 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 4.77 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.0, 138.5, 138.5, 134.6, 132.6, 129.7, 129.4, 128.5, 117.6, 117.5, 63.8; HRMS calc. for $C_{15}H_{11}O_3NSNa$ $(M+Na)^+$, 308.0357; found, 308.0364.

1-(naphthalen-2-yl)-2-(phenylsulfonyl)ethanone (3ka) 

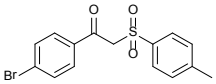
Compound **3ka** was obtained in 53% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.49 (s, 1H), 8.01-7.89 (m, 6H), 7.67 (t, J = 7.4 Hz, 2H), 7.62-7.55 (m, 3H), 4.89 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.8, 138.8, 136.1, 134.2, 133.1, 132.3, 132.1, 130.0, 129.4, 129.2, 128.9, 128.6, 127.8, 127.2, 123.9, 63.7; HRMS calc. for $C_{18}H_{14}O_3SNa$ $(M+Na)^+$, 333.0561; found, 333.0174.

1-phenyl-2-(phenylsulfonyl)propan-1-one (3la) 

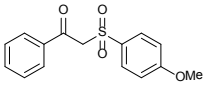
Compound **3la** was obtained in 61% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.98 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 2H), 7.81 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 2H), 7.69-7.61 (m, 2H), 7.56-7.48 (m, 4H), 5.19 (q, J = 6.9 Hz, 1H), 1.60 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 192.5, 136.3, 136.2, 134.2, 134.1, 129.8, 129.1, 128.9, 128.8, 65.0, 13.2; HRMS calc. for $C_{15}H_{14}O_3SNa$ $(M+Na)^+$, 297.0561; found, 244.1131.

1-phenyl-2-tosylethanone (3ab) 

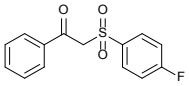
Compound **3ab** was obtained in 71% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.96 (d, J = 7.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.74 (s, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 188.2, 145.4, 135.8, 135.8, 134.3, 129.8, 129.3, 128.9, 128.6, 63.6, 21.7; HRMS calc. for $C_{15}H_{14}O_3SNa$ $(M+Na)^+$, 297.0561; found, 297.0564.

1-(4-bromophenyl)-2-tosylethanone (3hb) 

Compound **3hb** was obtained in 68% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.84 (dd, J_1 = 1.9 Hz, J_2 = 6.8 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.69 (s, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.3, 145.6, 135.6, 134.5, 132.2, 130.8, 129.9, 129.9, 128.6, 63.8, 21.7; HRMS calc. for $C_{15}H_{13}O_3BrSNa$ $(M+Na)^+$, 374.9666; found, 374.9662.

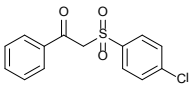
2-(4-methoxyphenylsulfonyl)-1-phenylethanone (3ac) 

Compound **3ac** was obtained in 63% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.96 (d, J = 7.2 Hz, 2H), 7.82 (d, J = 9.0 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.9 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 4.73 (s, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 188.3, 164.2, 135.9, 134.3, 130.9, 130.3, 129.3, 128.8, 114.4, 63.8, 55.7; HRMS calc. for $C_{15}H_{14}O_4SNa$ $(M+Na)^+$, 313.0510; found, 313.0509.

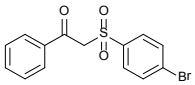
2-(4-fluorophenylsulfonyl)-1-phenylethanone (3ad) 

Compound **3ad** was obtained in 55% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.96-7.93 (m, 4H), 7.67-7.63 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 8.1 Hz, 2H), 4.77 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 188.0, 167.4, 164.9, 135.7, 134.5, 131.7, 131.6, 129.3, 128.9, 116.7, 116.4, 63.5; HRMS calc.

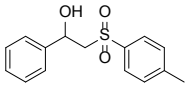
for $C_{14}H_{11}O_3FSNa$ $(M+Na)^+$, 301.0311; found, 301.0310.

2-(4-chlorophenylsulfonyl)-1-phenylethanone (3ae) 

Compound **3ae** was obtained in 72% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.96 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.56-7.50 (m, 4H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.9, 141.1, 137.2, 135.6, 134.5, 130.2, 129.5, 129.3, 129.0, 63.4; HRMS calc. for $C_{14}H_{11}O_3ClSNa$ $(M+Na)^+$, 317.0015; found, 317.0014.

2-(4-bromophenylsulfonyl)-1-phenylethanone (3af) 

Compound **3af** was obtained in 60% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.95 (dd, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 187.9, 137.7, 135.6, 134.5, 132.5, 130.2, 129.8, 129.3, 129.0, 63.3; HRMS calc. for $C_{14}H_{11}O_3BrSNa$ $(M+Na)^+$, 360.9510; found, 360.9516.

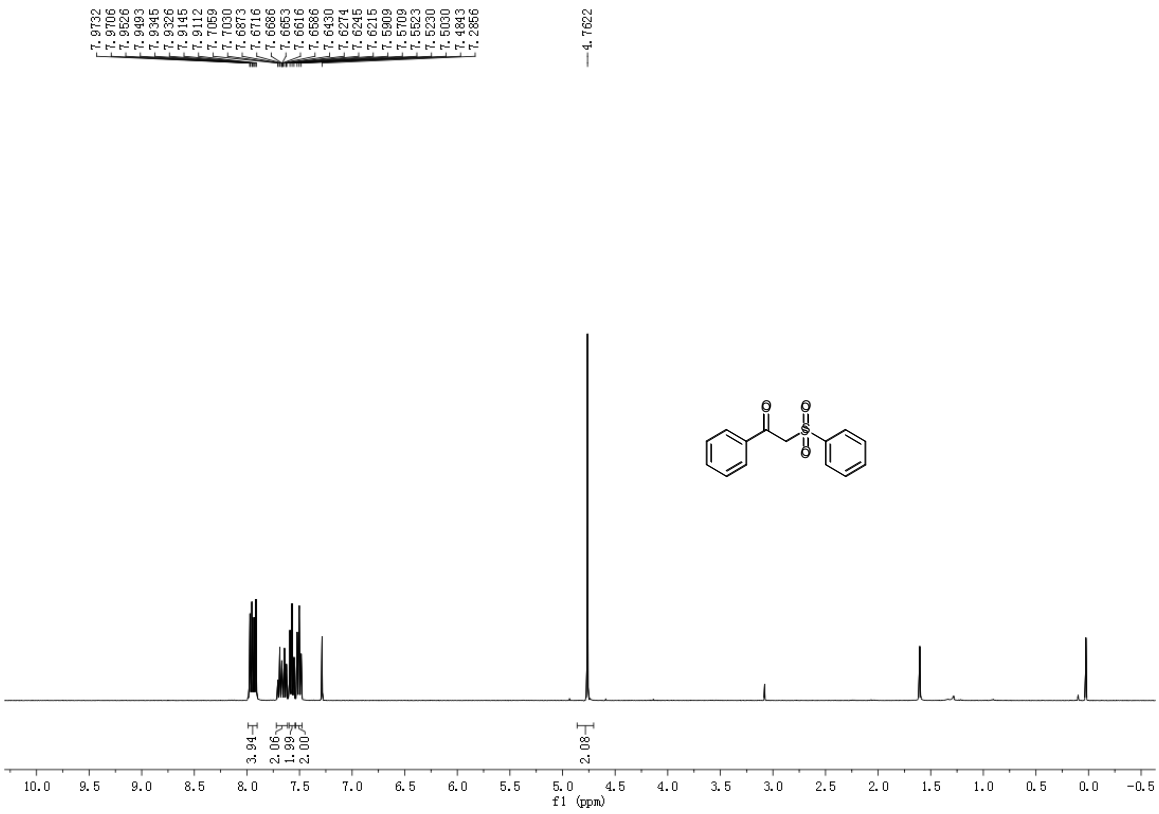
1-phenyl-2-tosylethanol[1] 

Compound **4ab** was obtained in 9% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.85 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.34-7.28 (m, 5H), 5.27 (d, J = 9.0 Hz, 1H), 3.77 (s, 1H), 3.50 (dd, J_1 = 10.1 Hz, J_2 = 14. 4 Hz, 1H), 3.33 (dd, J_1 = 1.8 Hz, J_2 = 14.4 Hz, 1H), 2.49 (s, 3H); MS (ESI$^+$): $[M+H]^+$ 277.1, $[M+Na]^+$ 299.1.

Reference

[1] (a) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu, A. W. Lei, *Angew. Chem., Int. Ed.,* 2013, **52**, 7156; (b) T. Taniguchi, A. Idota, H. Ishibashi, *Org. Biomol. Chem.* 2011, **9**, 3151; (c) B. T. Cho, D. J. Kim, *Tetrahedron: Asymmetry*. 2001, **12**, 2043.

8. Copies of NMR Spectra for 3aa−3af, 4ab

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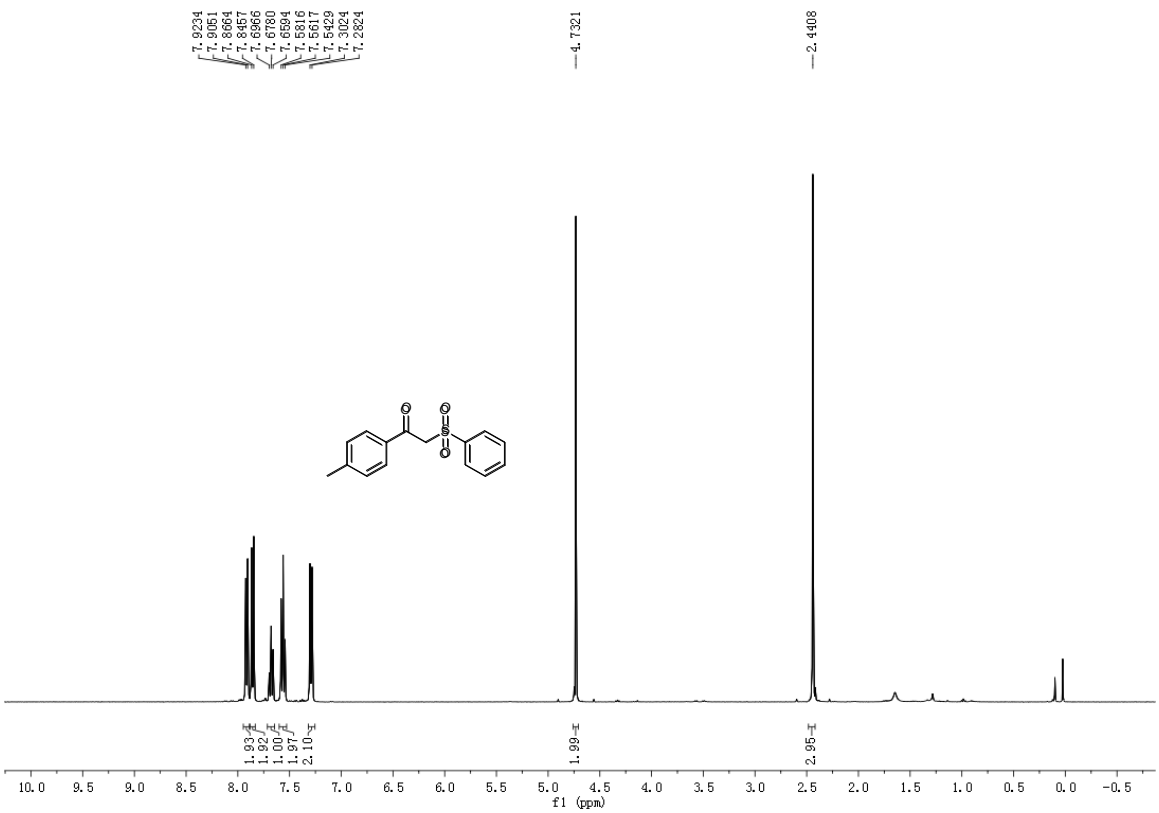
135.78
134.36
134.22
129.28
129.21
128.87
128.59
77.37
77.05
76.73
63.47
f1 (ppm)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7.3024
7.2824
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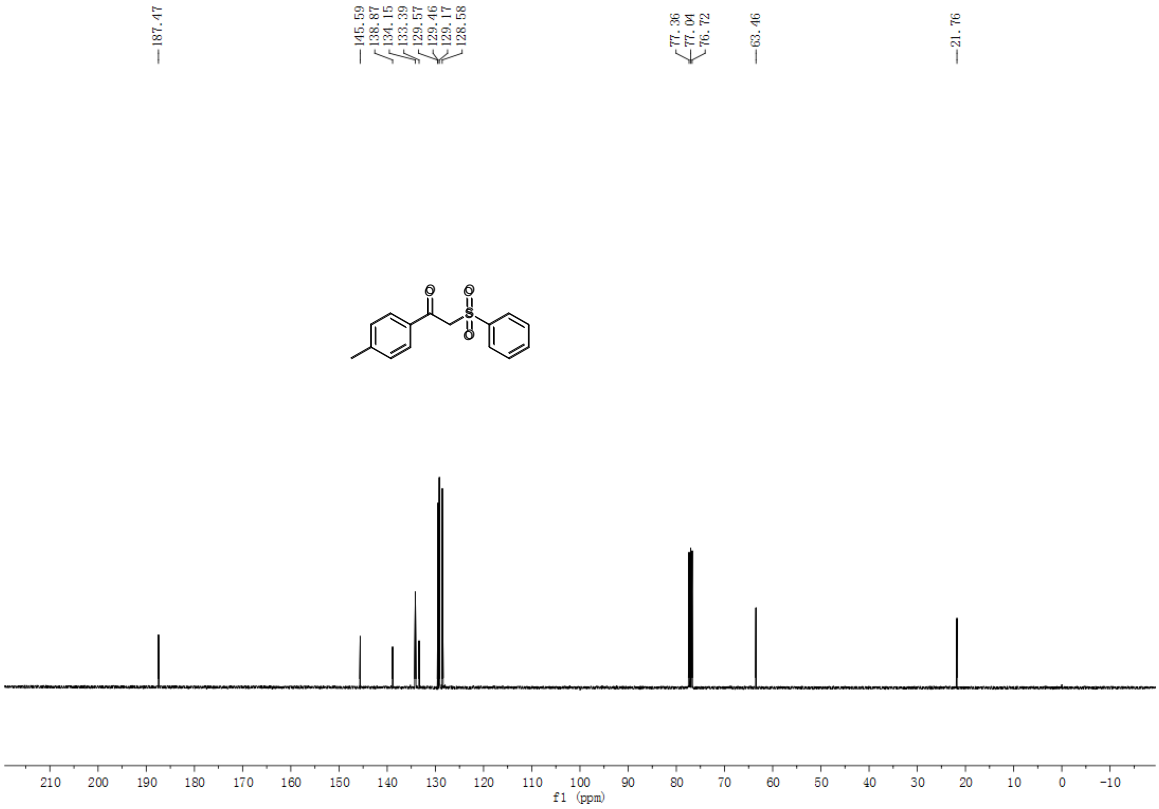
1.93
1.92
1.00
1.97
2.10
1.99
2.95
f1 (ppm)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134.15
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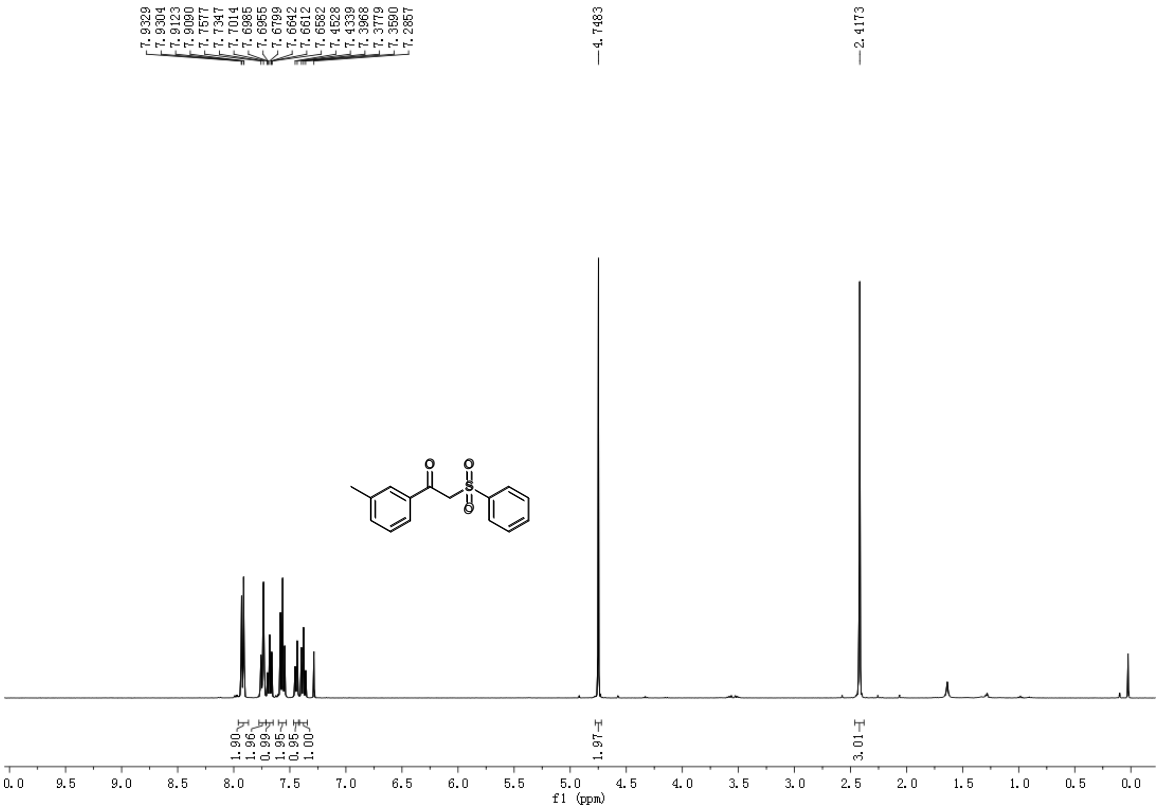
129.17
128.58
77.36
77.04
76.72
63.46
21.76
f1 (ppm)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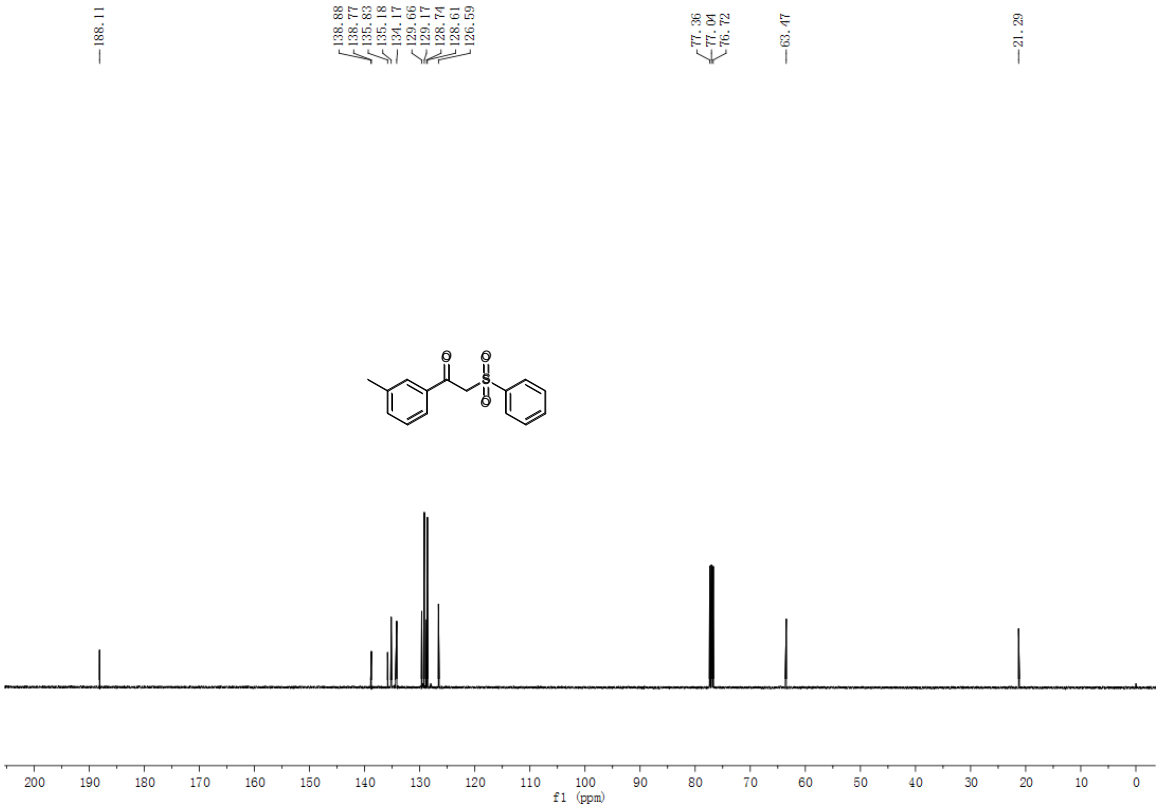
7.6955
7.6799
7.6642
7.6612
7.6582
7.4528
7.4339
7.3968
7.3779
7.3590
7.2857
4.7483
2.4173
1.90
1.96
0.99
1.95
0.95
1.00
1.97
3.01
f1 (ppm)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138.77
135.63
135.18
134.17
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129.17
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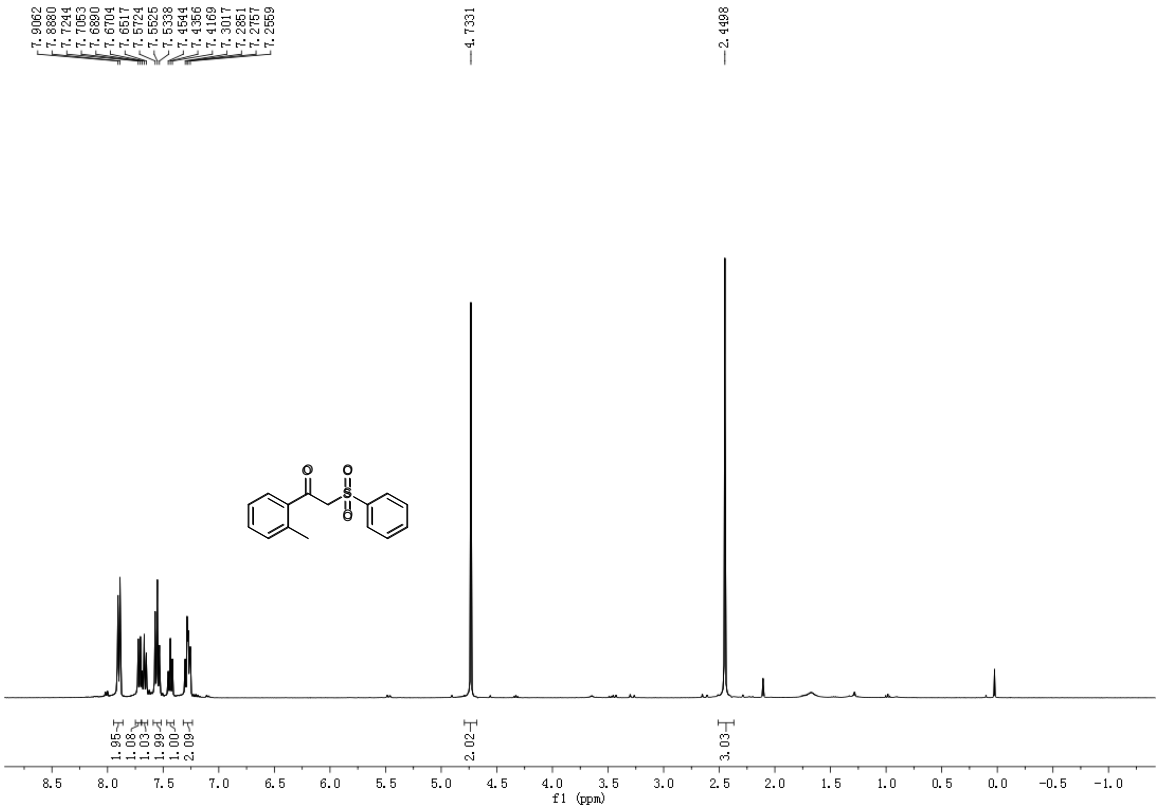
128.61
126.59
77.36
77.04
76.72
63.47
21.29
f1 (ppm)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7.5525
7.5338
7.4544
7.4356
7.4169
7.3017
7.2851
7.2757
7.2569
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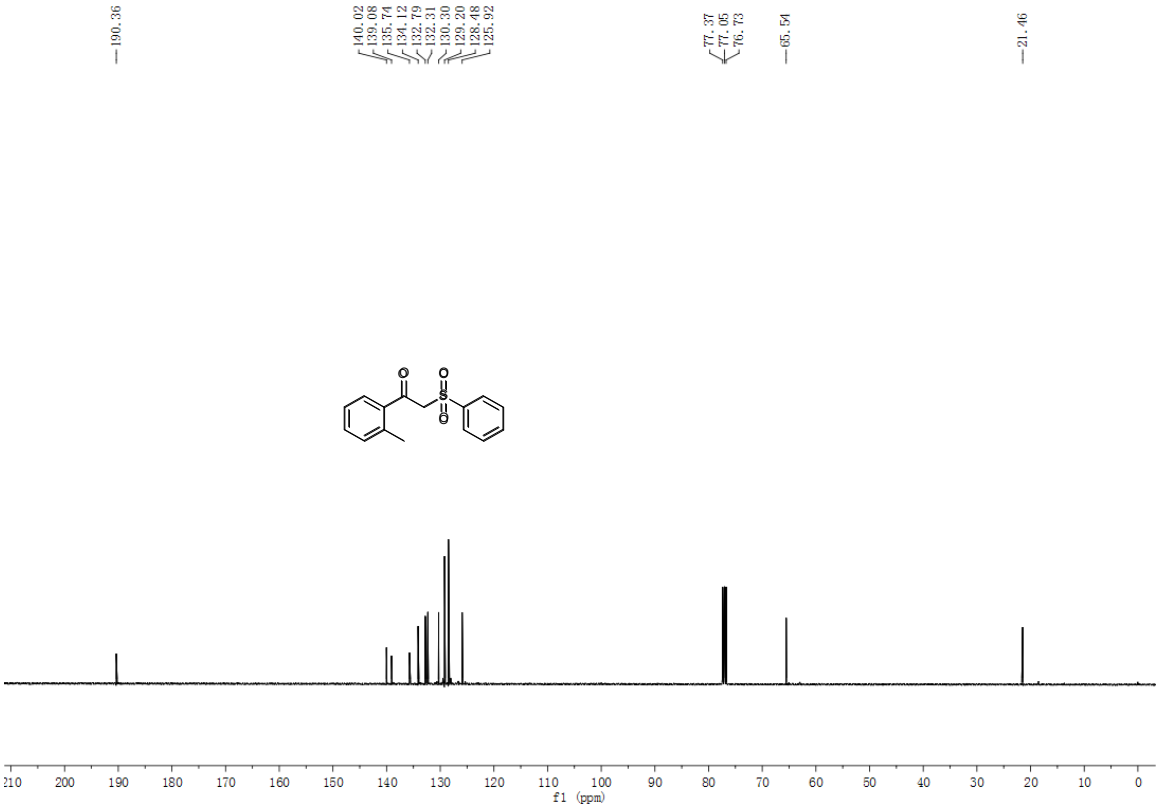
1.08
1.03
1.99
1.00
2.09
2.02
3.03
f1 (ppm)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140.02
139.08
135.74
134.12
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130.30
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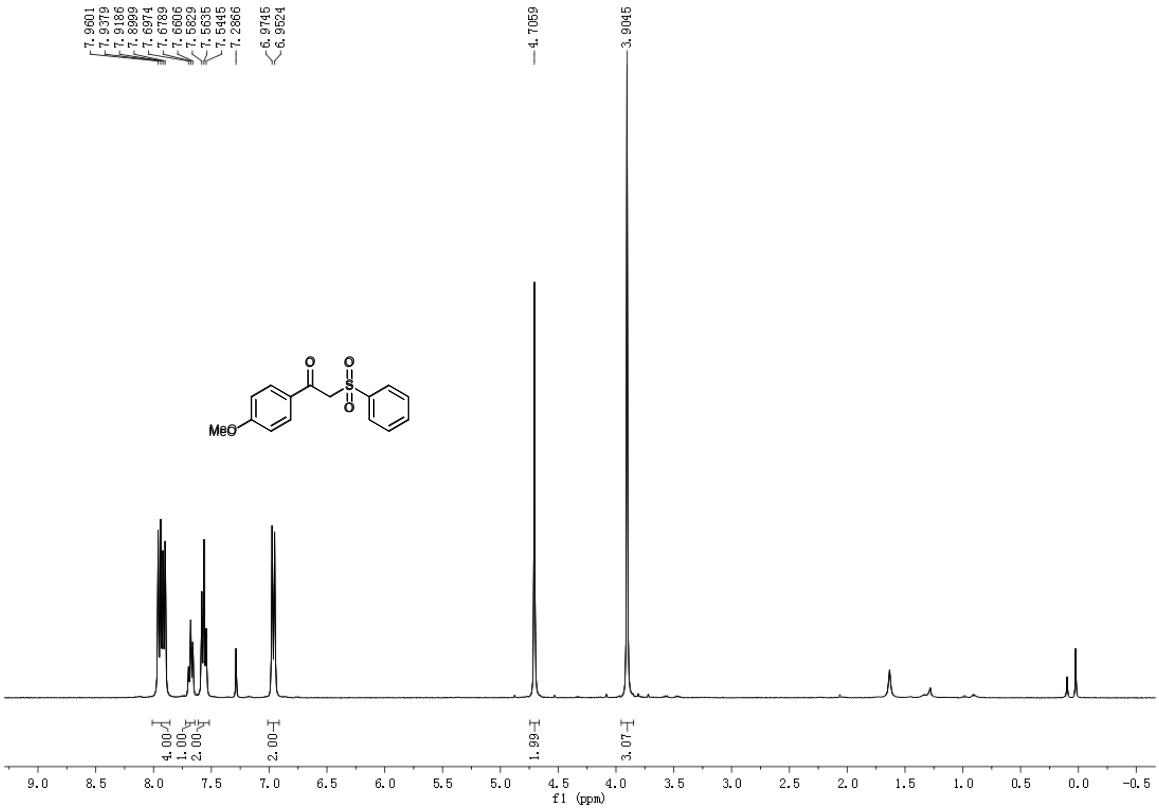
77.05
76.73
65.54
21.46
f1 (ppm)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7.5635
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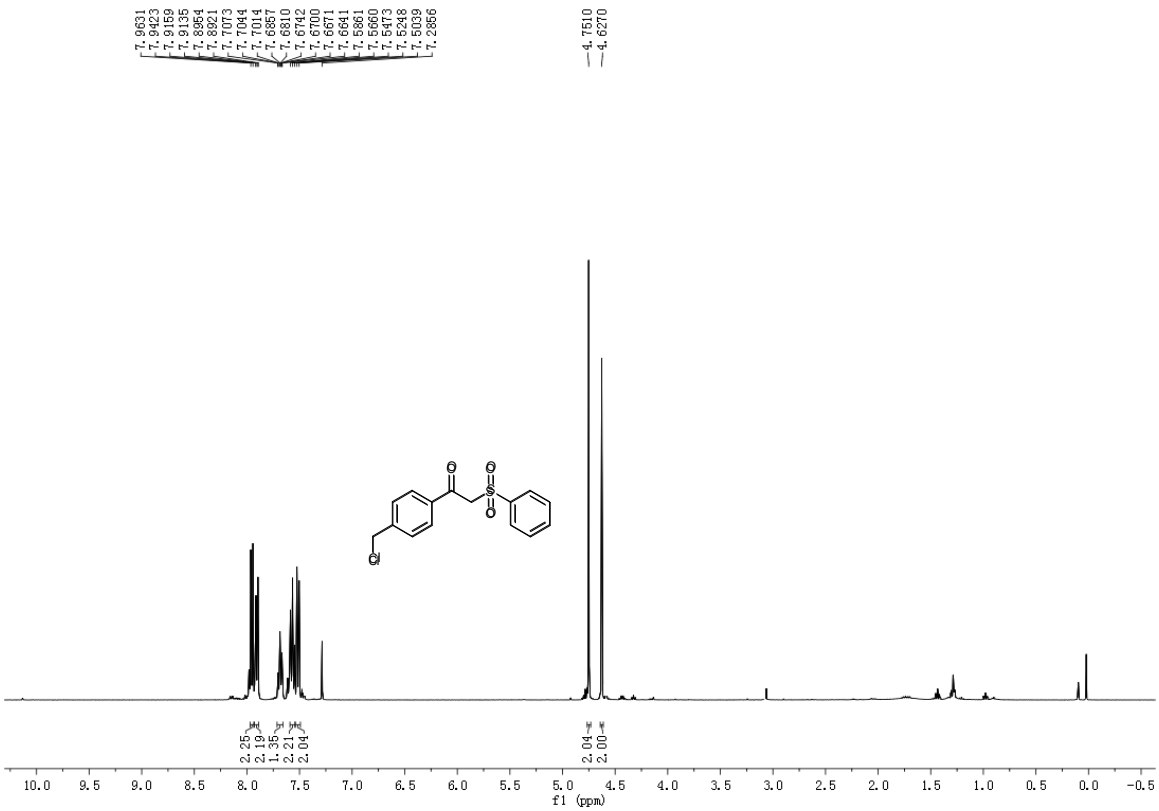
7.2866
6.9745
6.9524
4.7059
3.9045
MeO
4.00
1.00
2.00
2.00
1.99
3.07
f1 (ppm)


186.14
164.60
138.85
134.14
131.88
129.16
128.91
128.56
114.11
77.35
77.03
76.72
63.47
55.62
MeO
f1 (ppm)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7.6700
7.6671
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7.5660
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7.5248
7.5039
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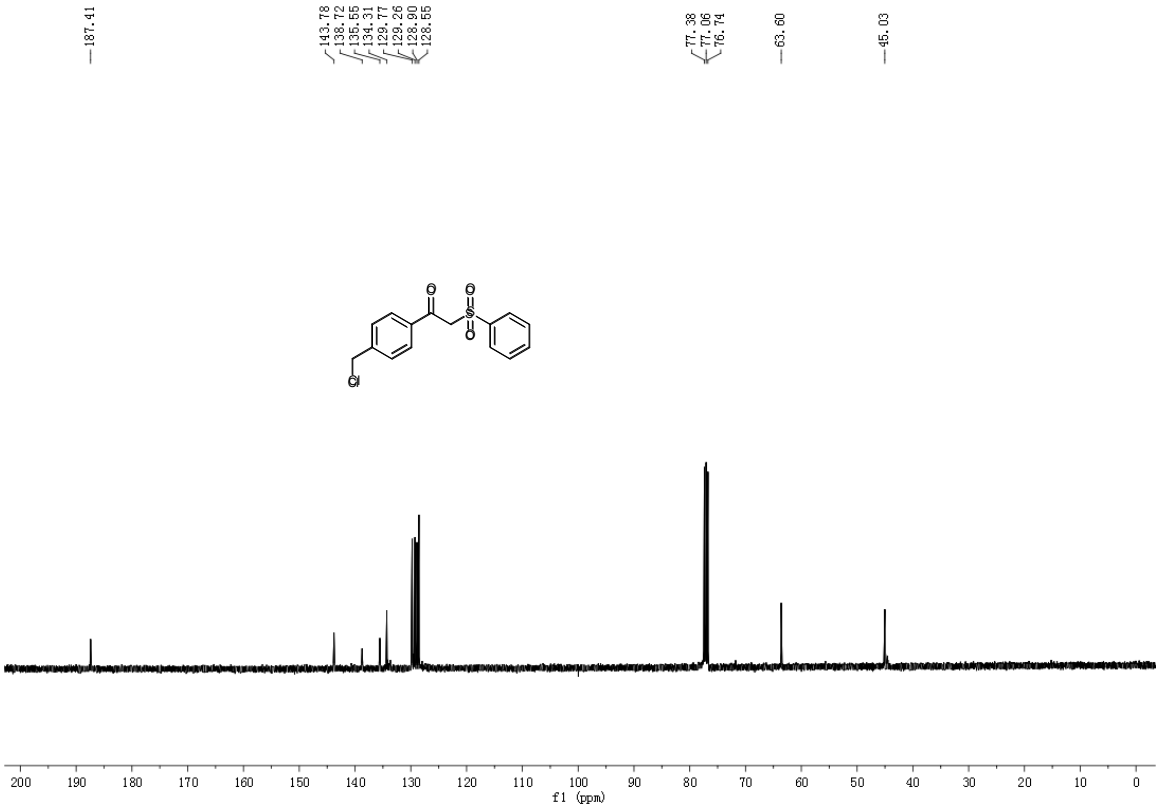
2.04
2.04
2.00
Cl
f1 (ppm)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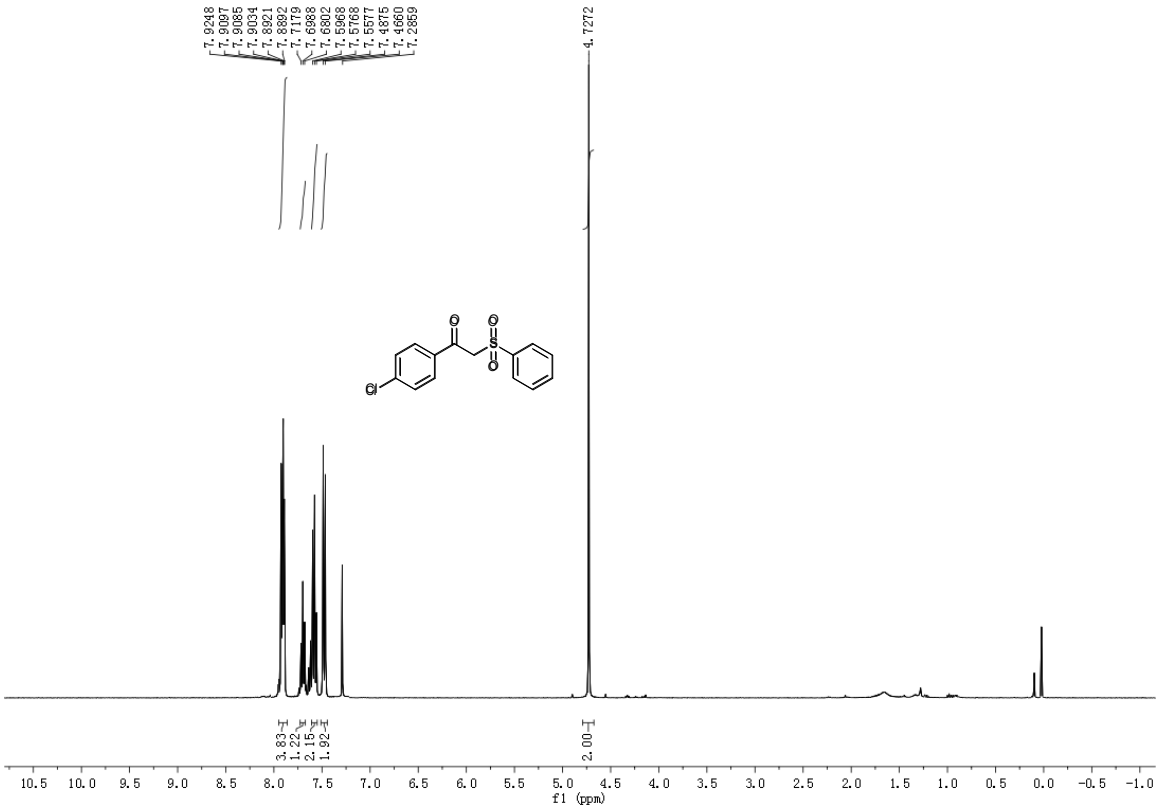
45.03
f1 (ppm)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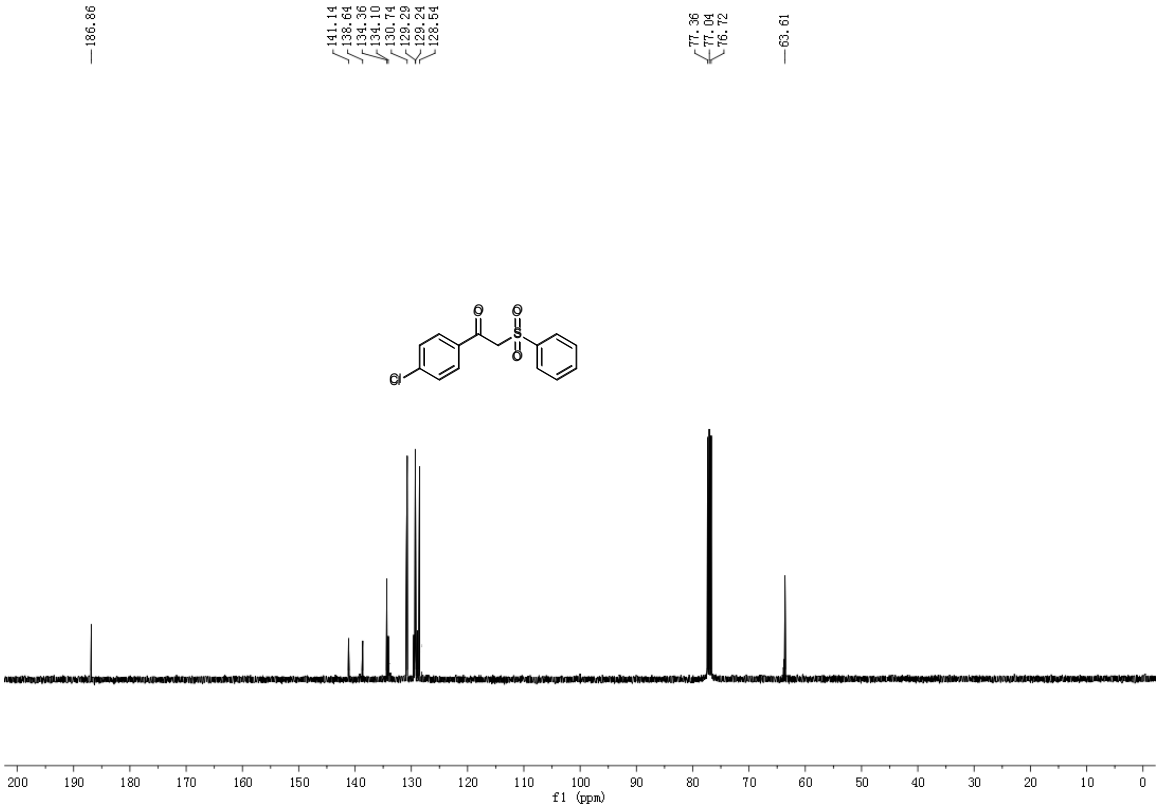
2.00
f1 (ppm)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77.36
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63.61
O
O
S
O
Cl
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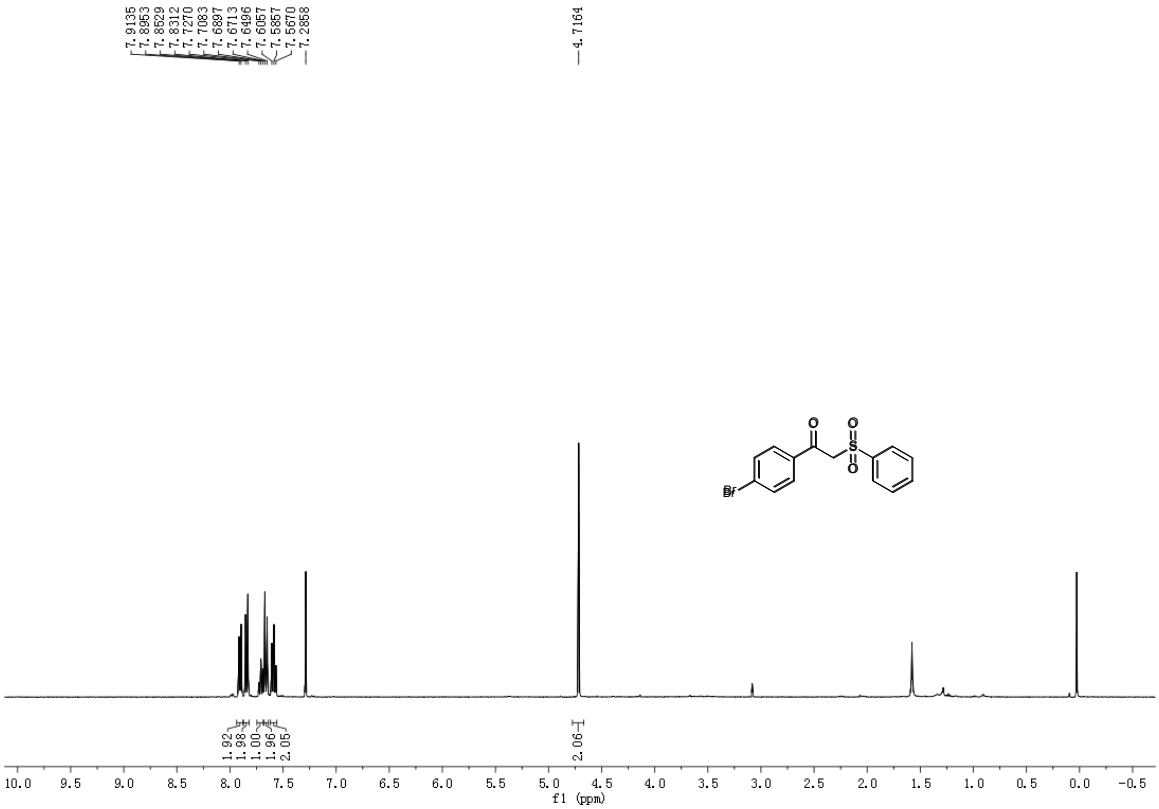
f1 (ppm)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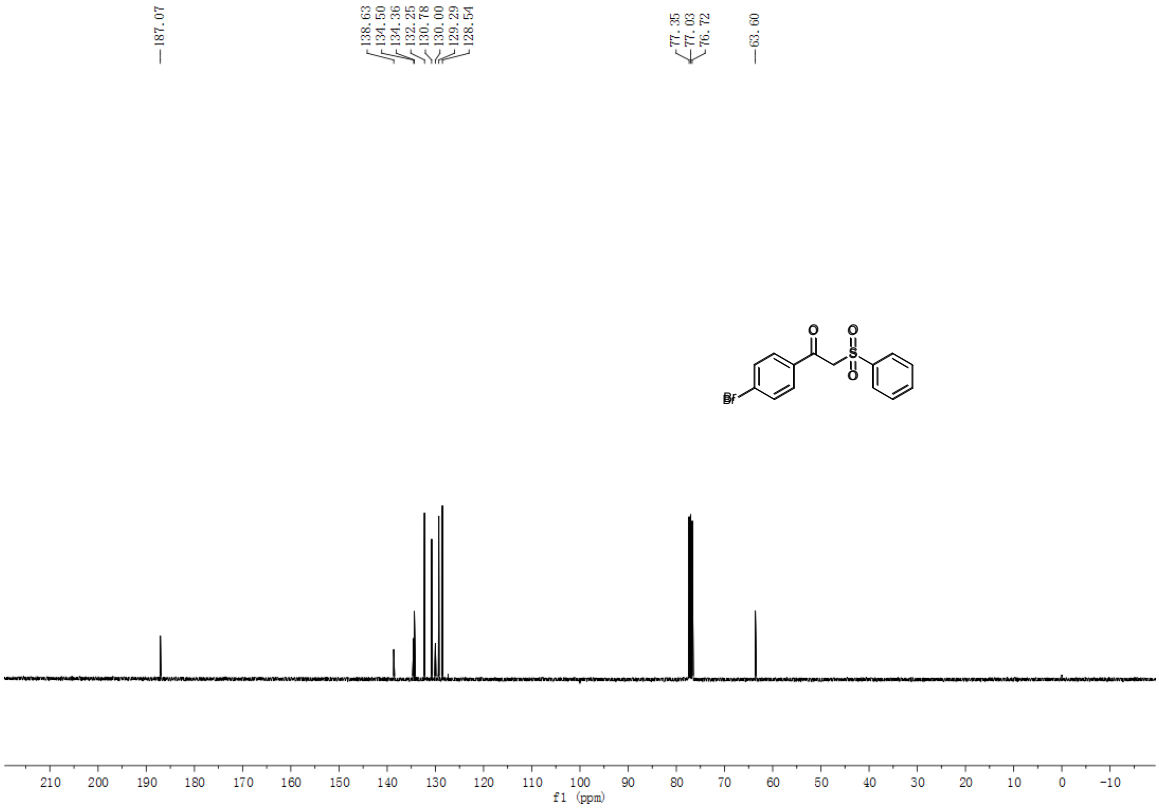
7.5670
7.2858
4.7164
O
O
S
O
Br
1.92
1.98
1.00
1.96
2.05
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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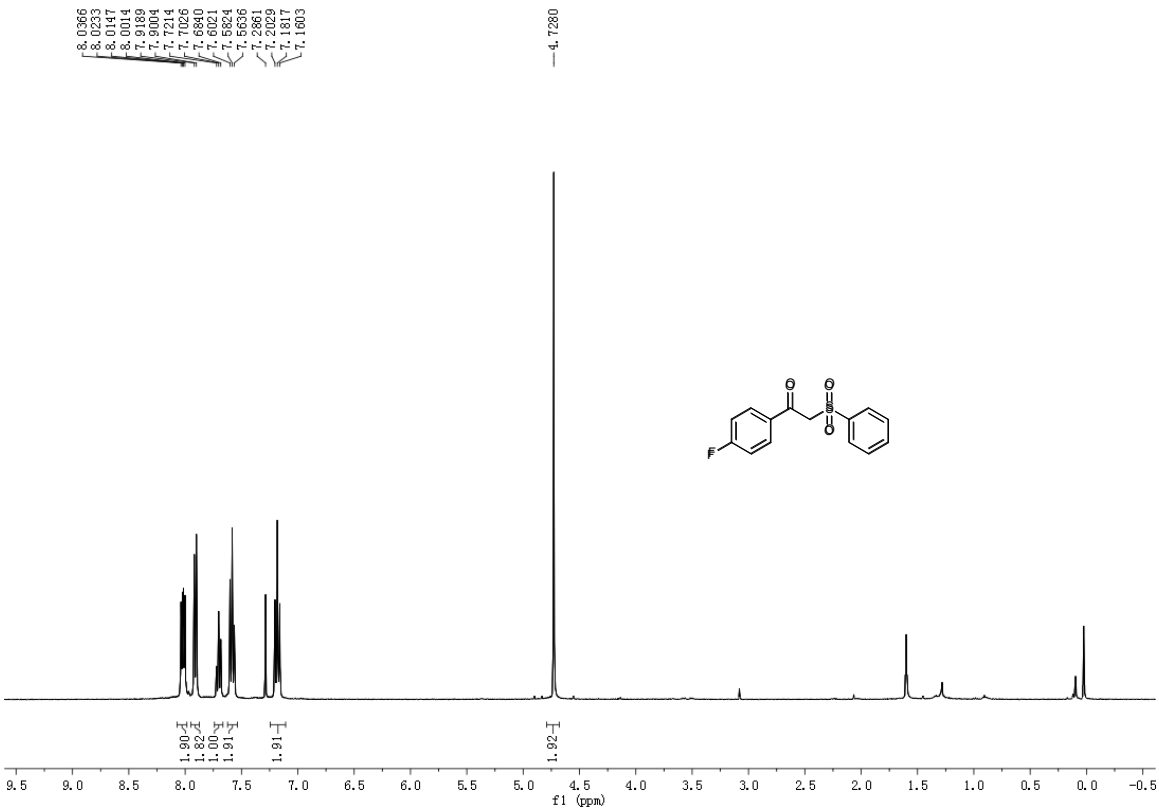
f1 (ppm)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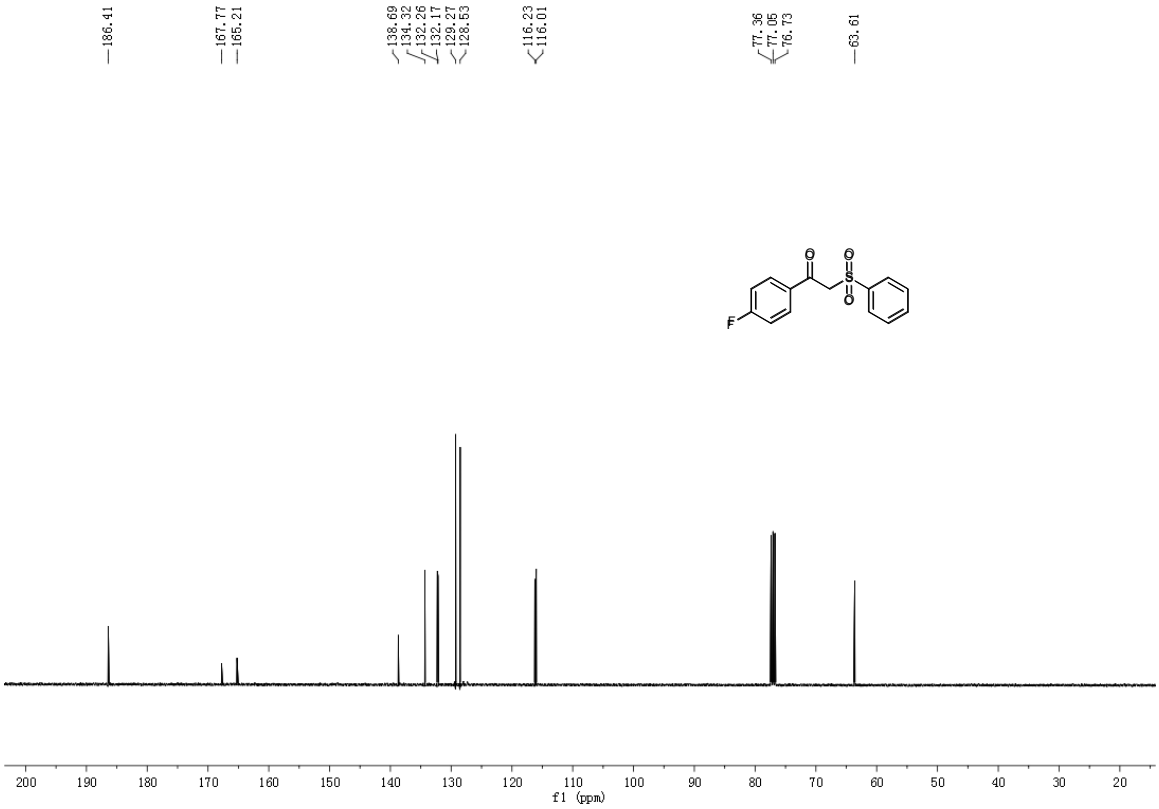
f1 (ppm)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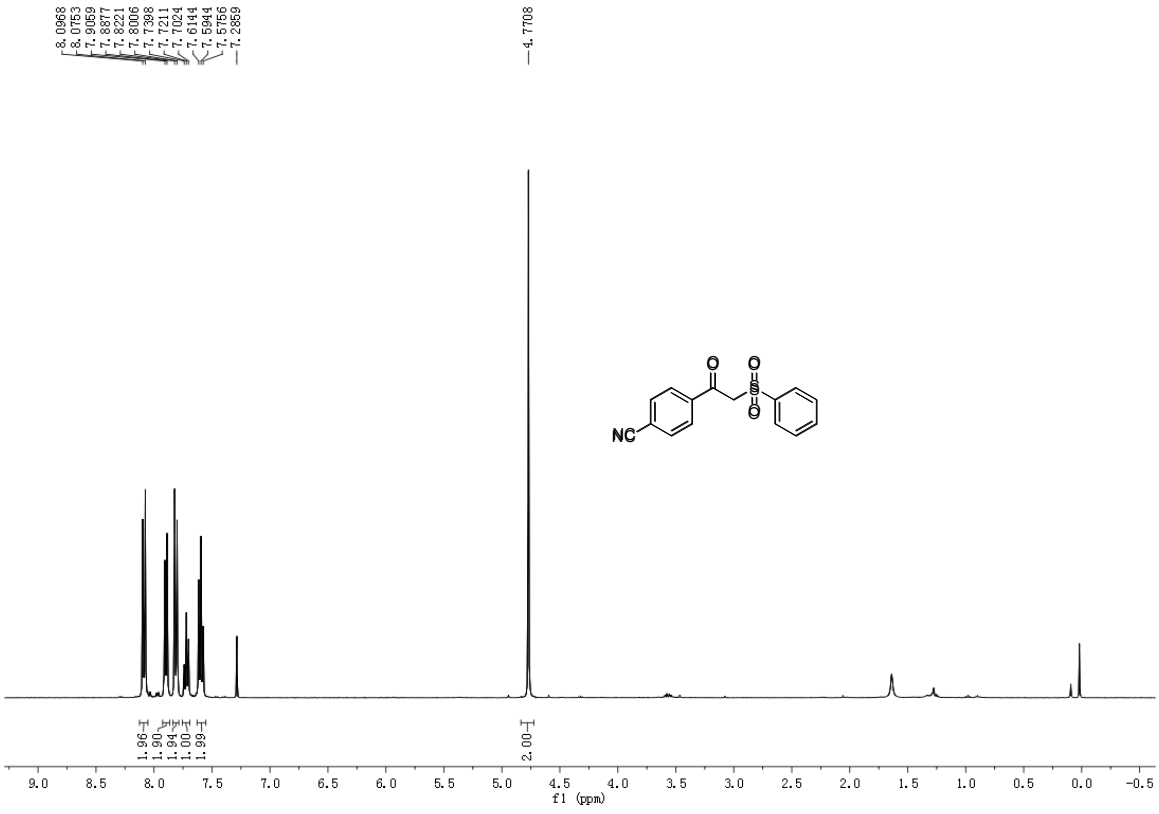
F
f1 (ppm)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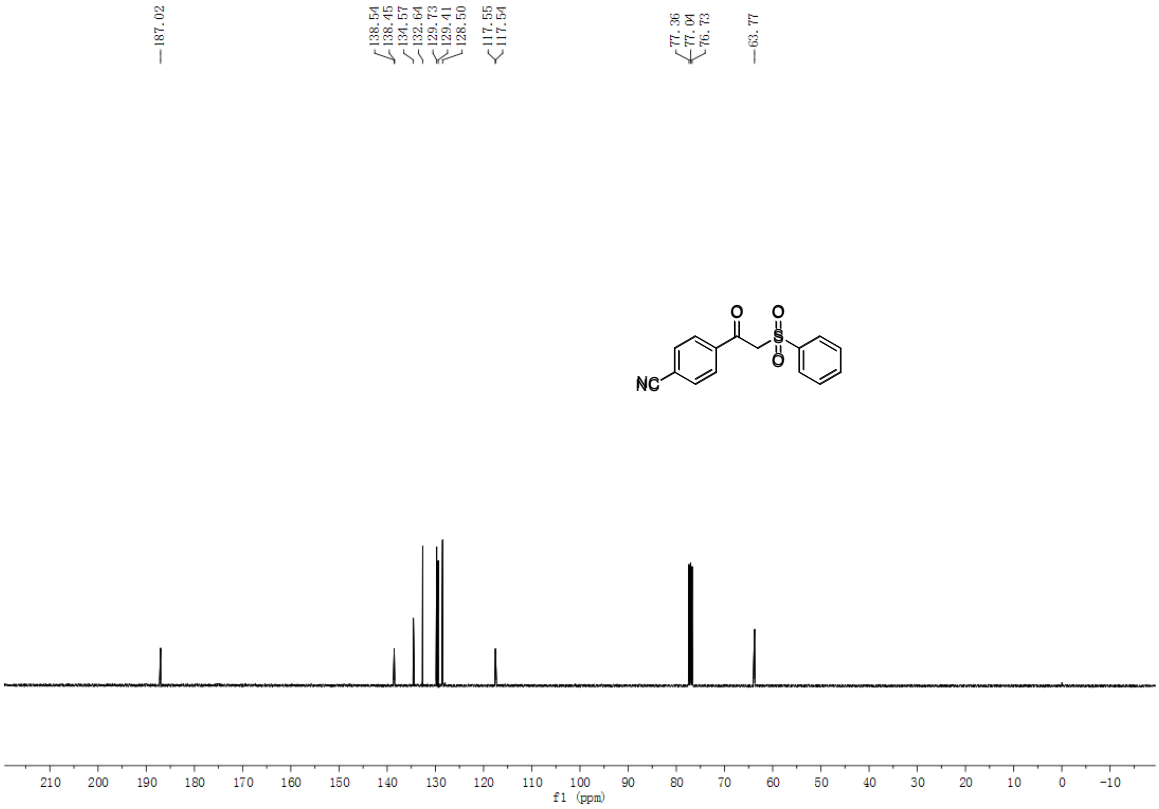
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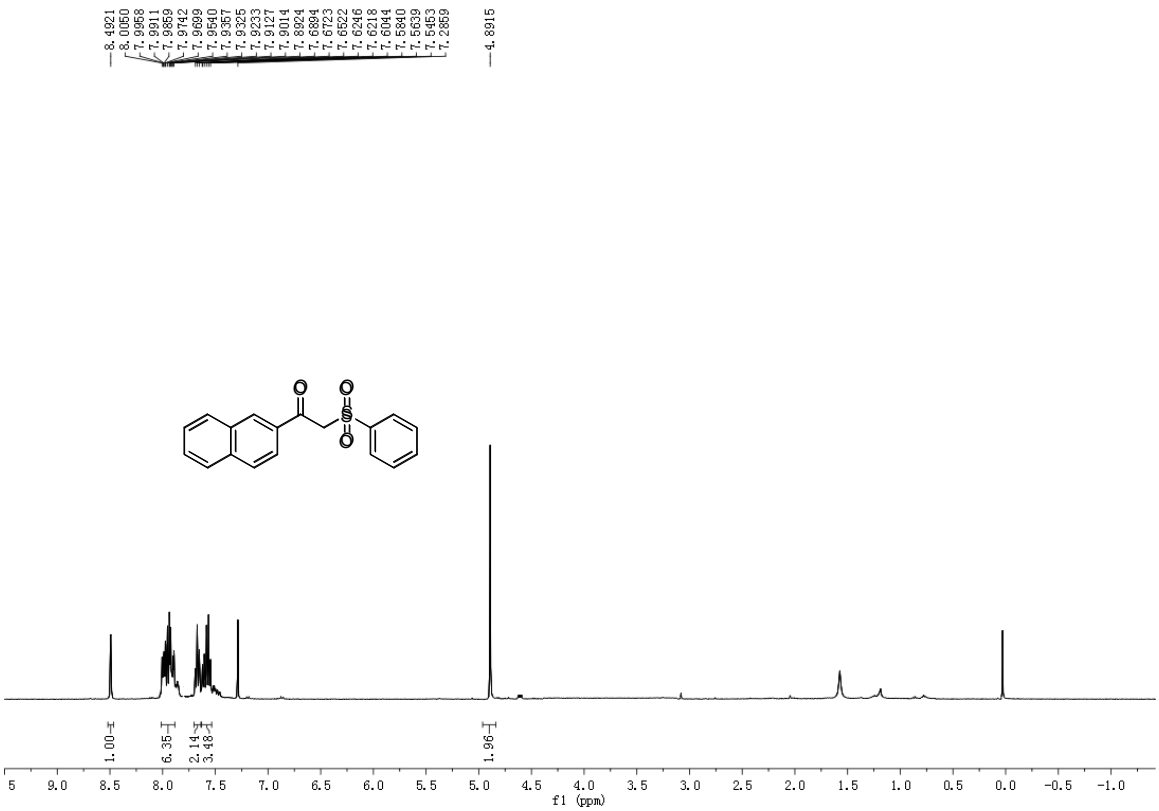
NC
f1 (ppm)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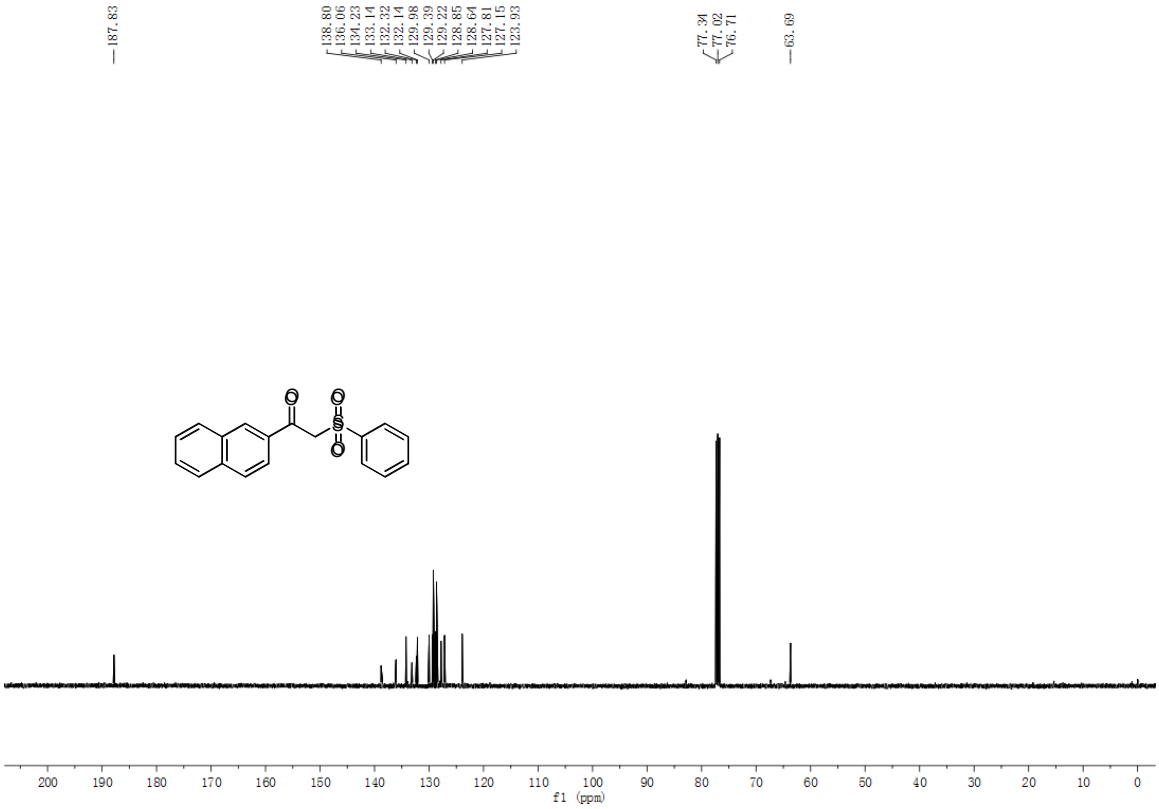
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132.14
129.98
129.39
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128.64
127.81
127.15
123.93
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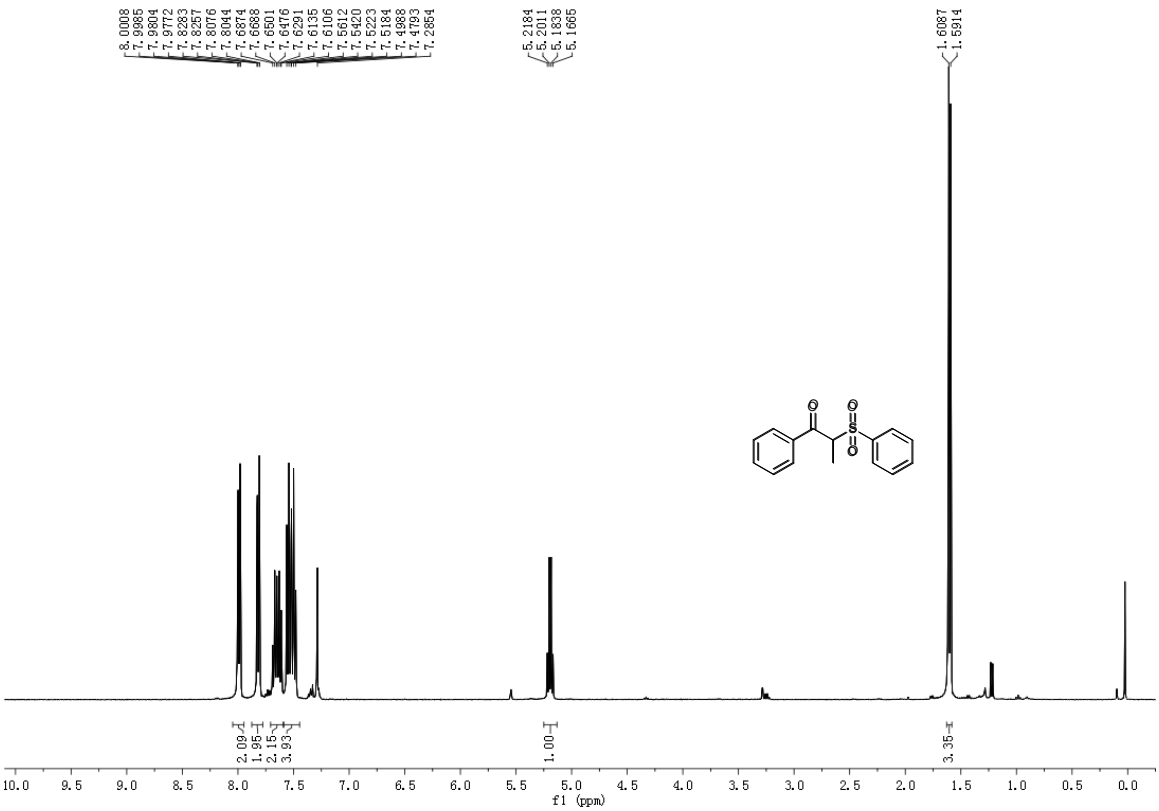
77.02
76.71
63.69
f1 (ppm)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7.6476
7.6291
7.6135
7.6106
7.5612
7.5420
7.5223
7.5184
7.4988
7.4793
7.2864
5.2184
5.2011
5.1838
5.1665
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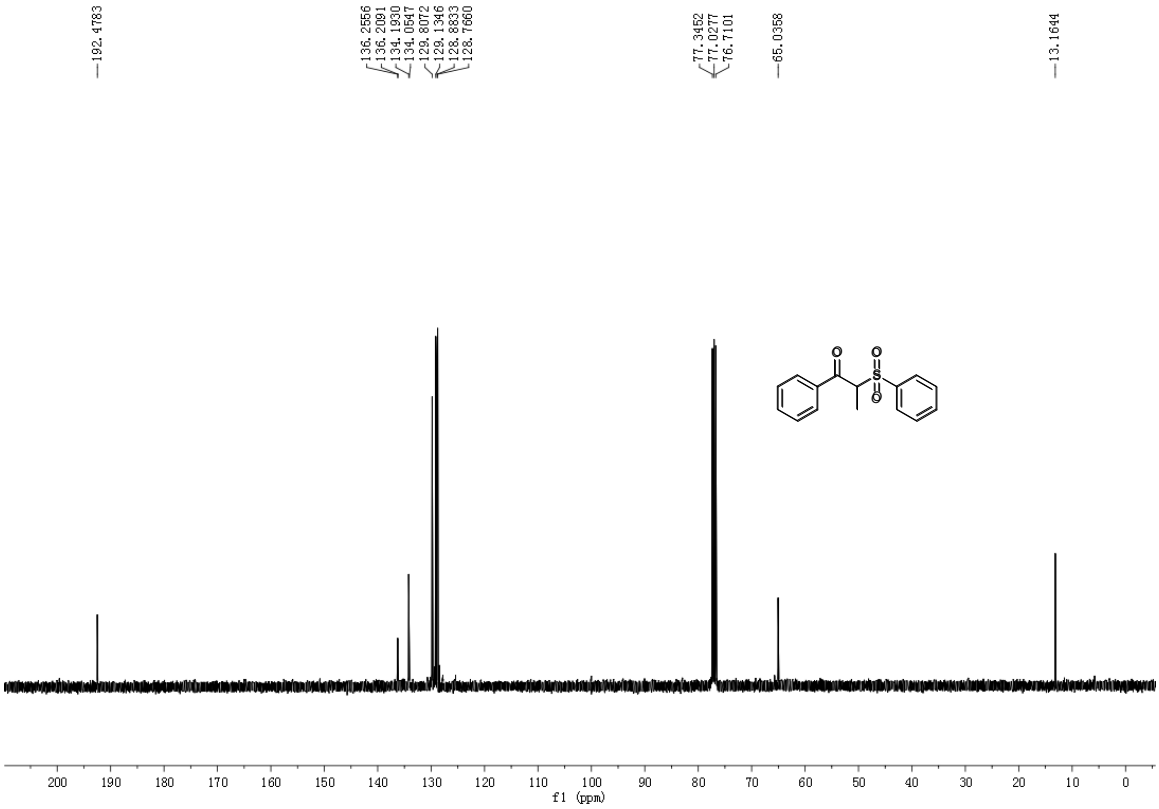
1.5914
2.09
1.95
2.15
3.93
1.00
3.35
f1 (ppm)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129.1346
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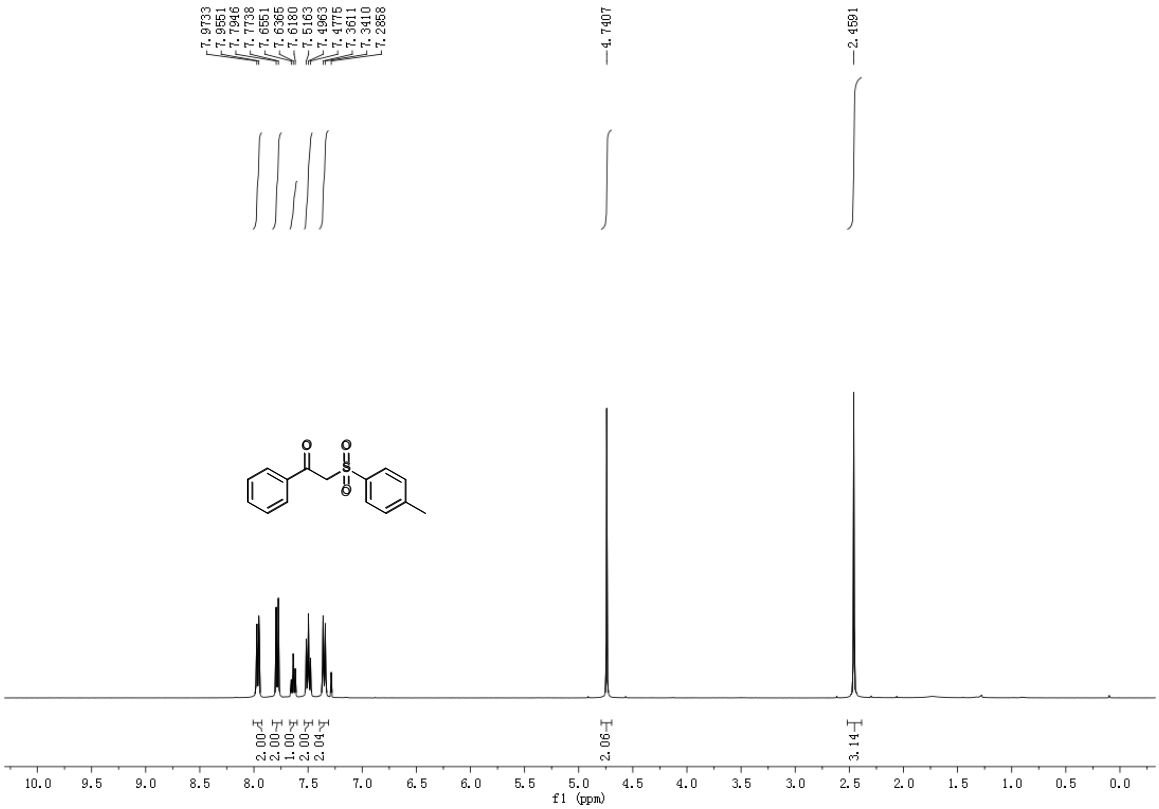
128.7660
77.3452
77.0277
76.7101
65.0368
13.1644
f1 (ppm)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7.7946
7.7738
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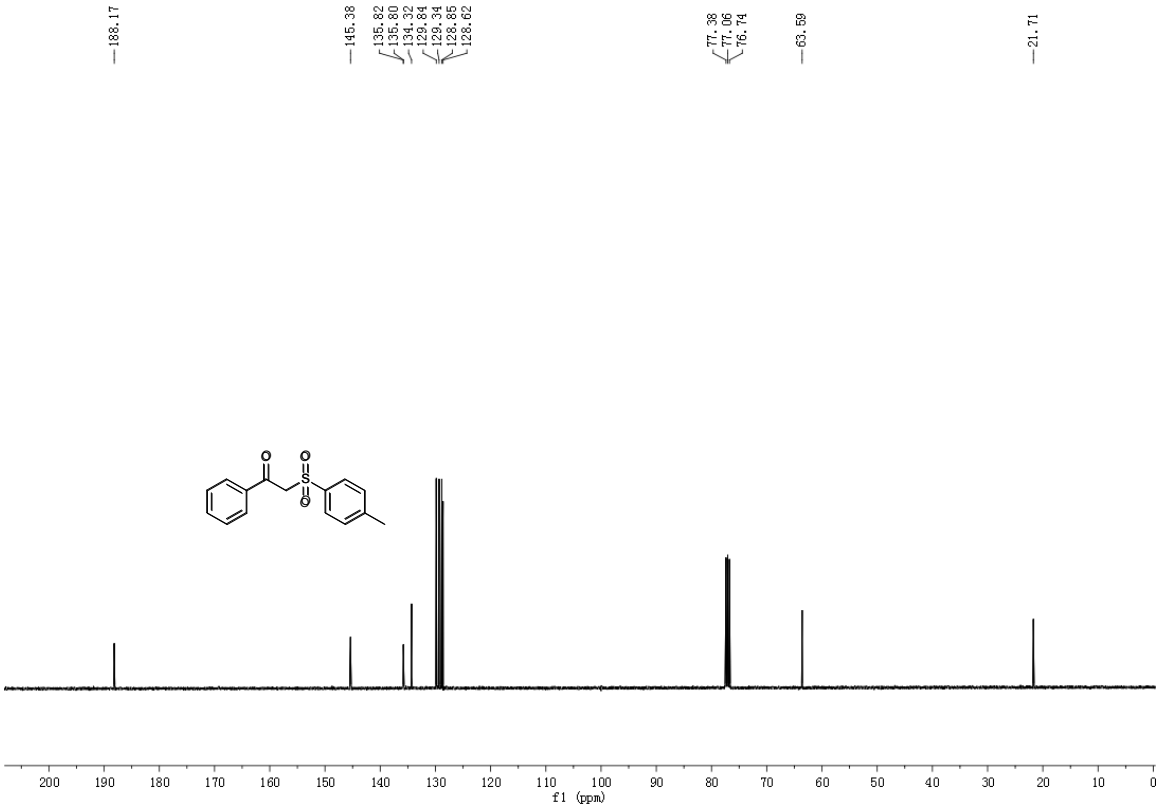
7.6180
7.5163
7.4963
7.4775
7.3611
7.3410
7.2858
4.7407
2.4591
2.00
2.00
1.00
2.00
2.04
2.06
3.14
f1 (ppm)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145.38
135.82
135.80
134.32
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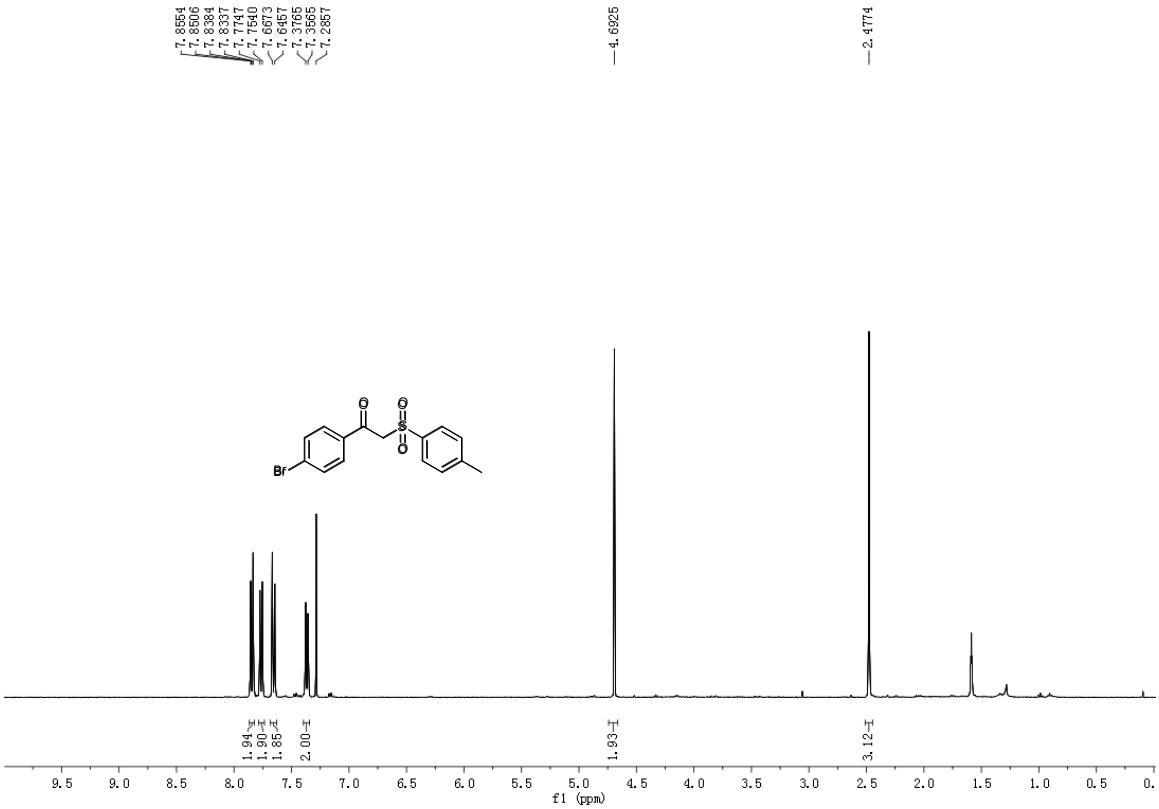
129.34
128.85
128.62
77.38
77.06
76.74
63.59
21.71
f1 (ppm)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7.8384
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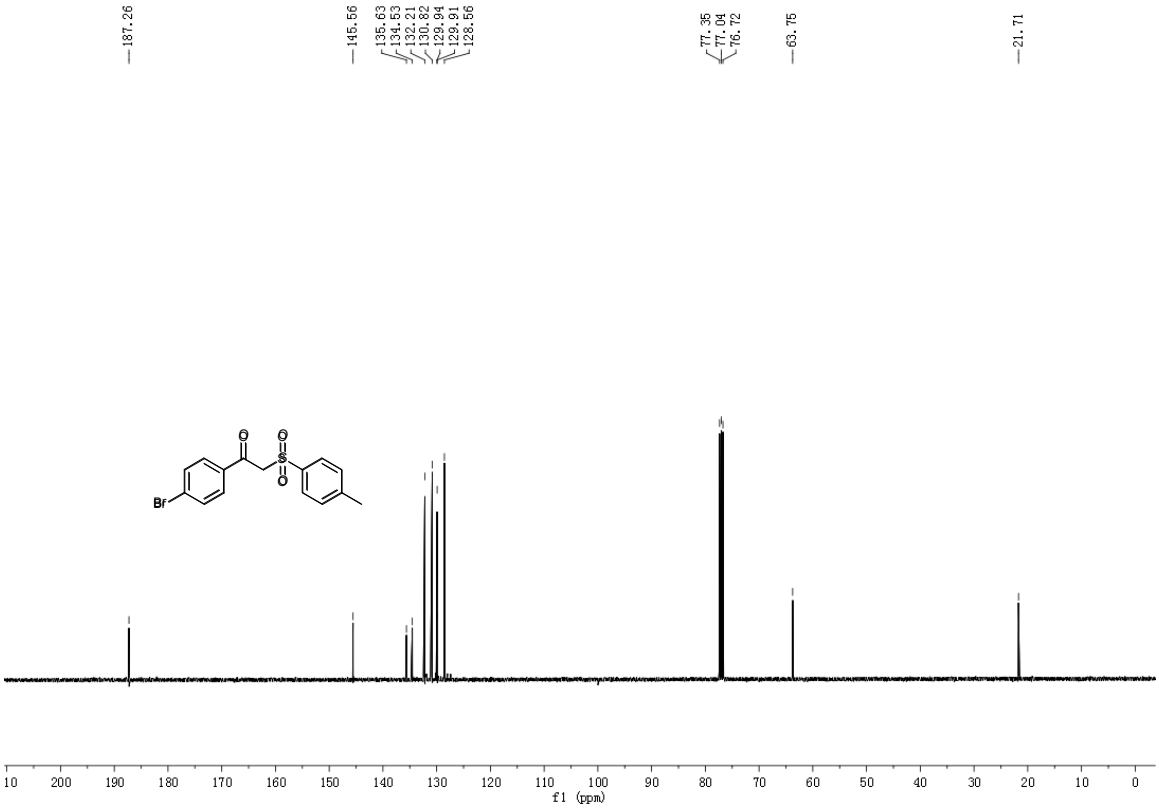
7.7747
7.7540
7.6673
7.6457
7.3765
7.3565
7.2867
4.6925
2.4774
Br
1.94
1.90
1.85
2.00
1.93
3.12
f1 (ppm)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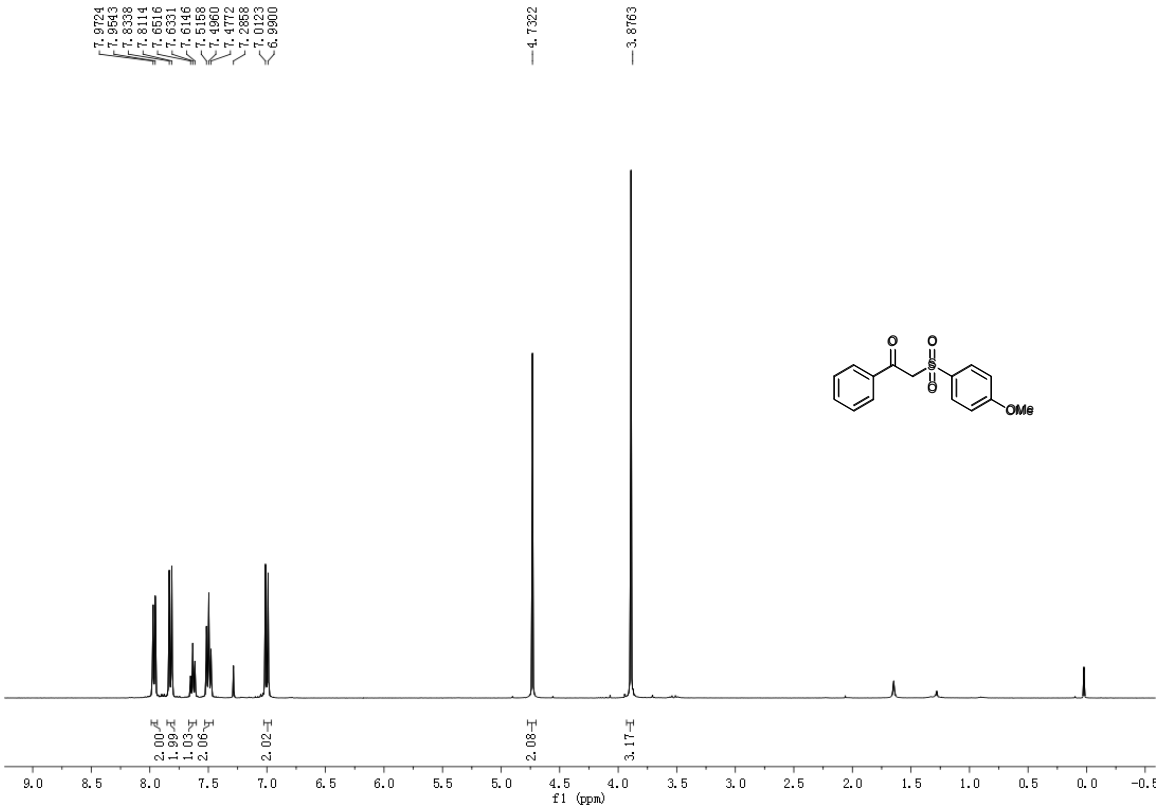
145.56
135.63
134.53
132.21
130.82
129.94
129.91
128.56
77.35
77.04
76.72
63.75
21.71
Br
f1 (ppm)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7.6331
7.6146
7.5158
7.4960
7.4772
7.2868
7.0123
6.9900
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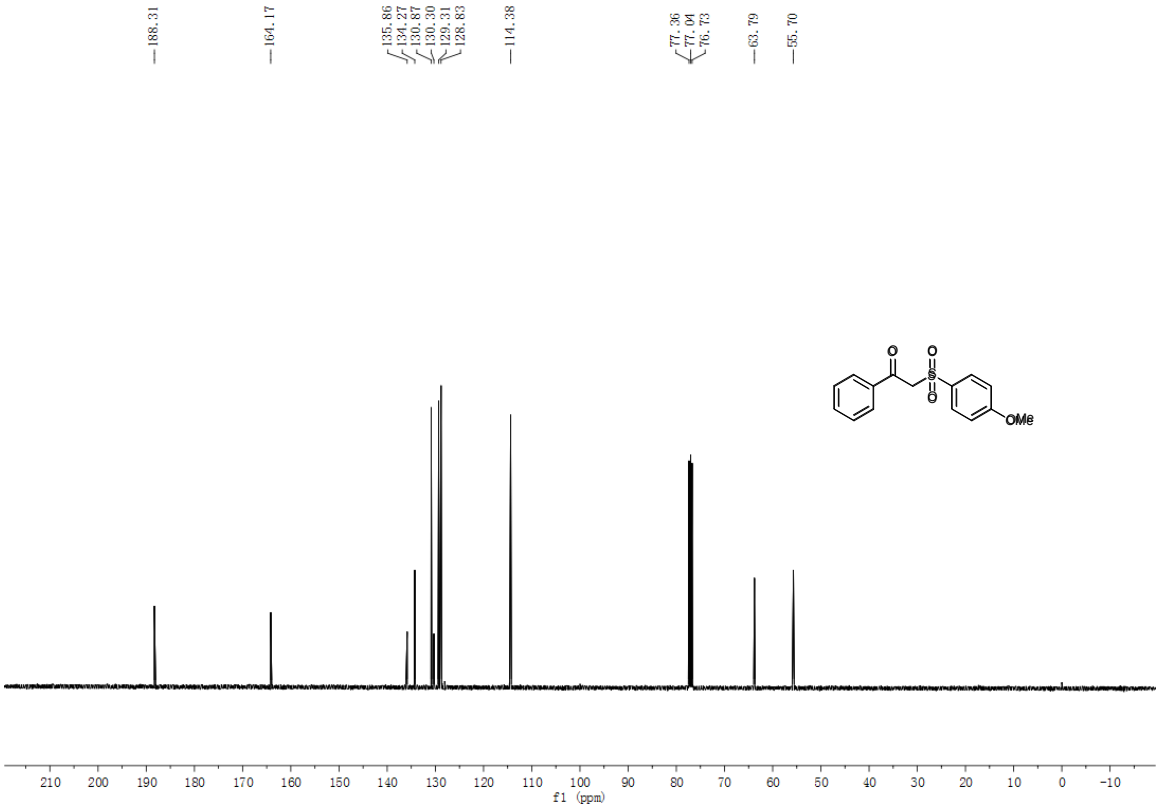
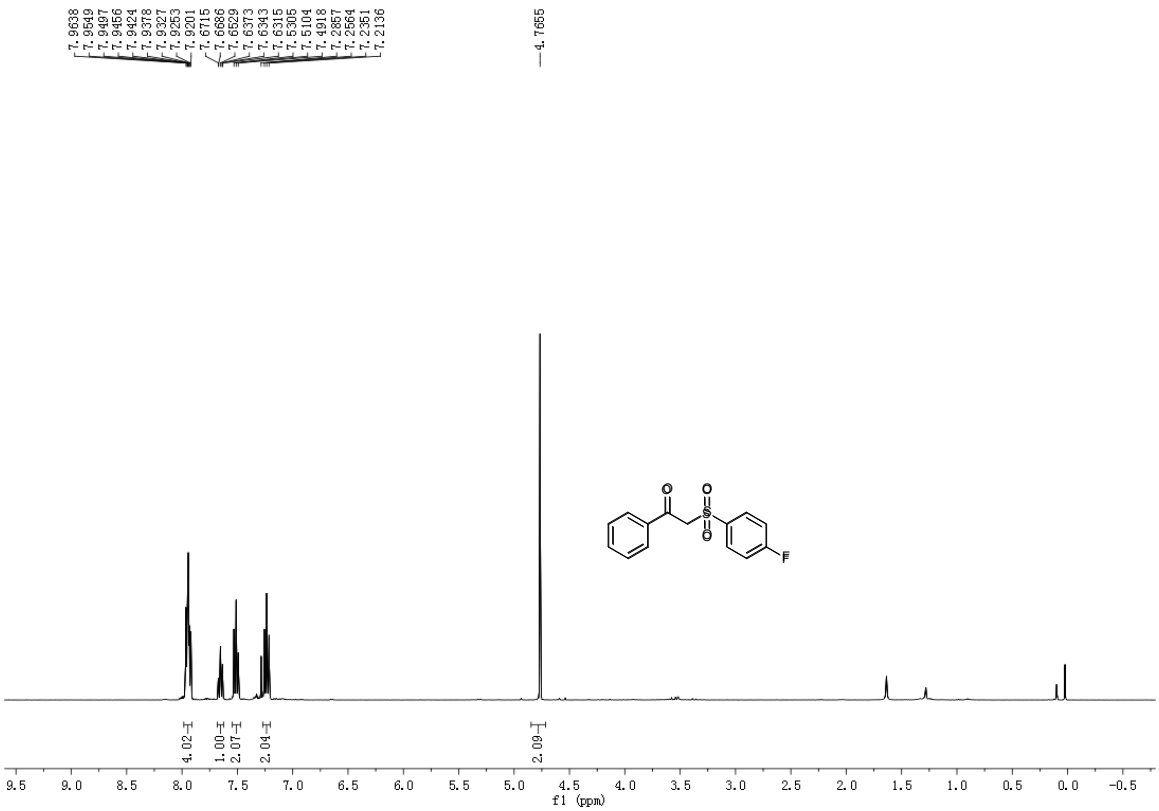
3.8763
OMe
2.00
1.99
1.03
2.06
2.02
2.08
3.17
f1 (ppm)


188.31
164.17
135.86
134.27
130.87
130.30
129.31
128.83
114.38
77.36
77.04
76.73
63.79
55.70
OMe
f1 (ppm)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7.9424
7.9378
7.9327
7.9253
7.9201
7.6715
7.6686
7.6529
7.6373
7.6343
7.6315
7.5305
7.5104
7.4918
7.2857
7.2564
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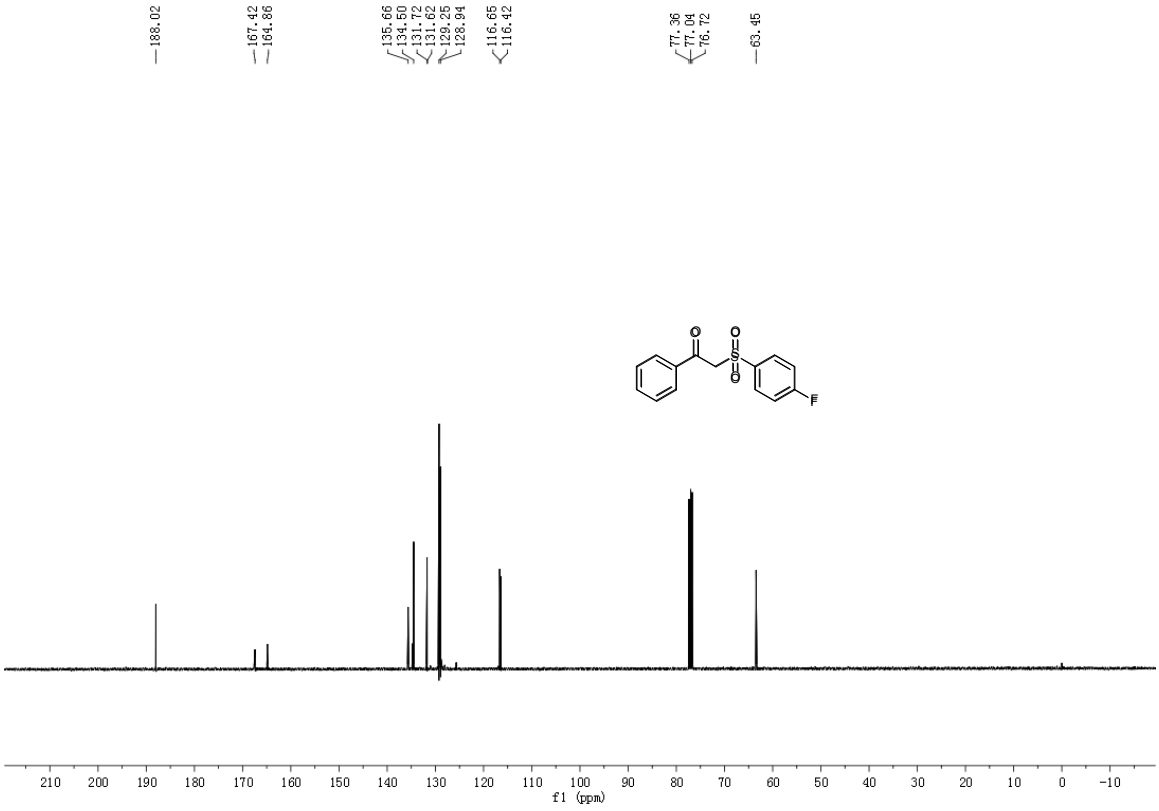
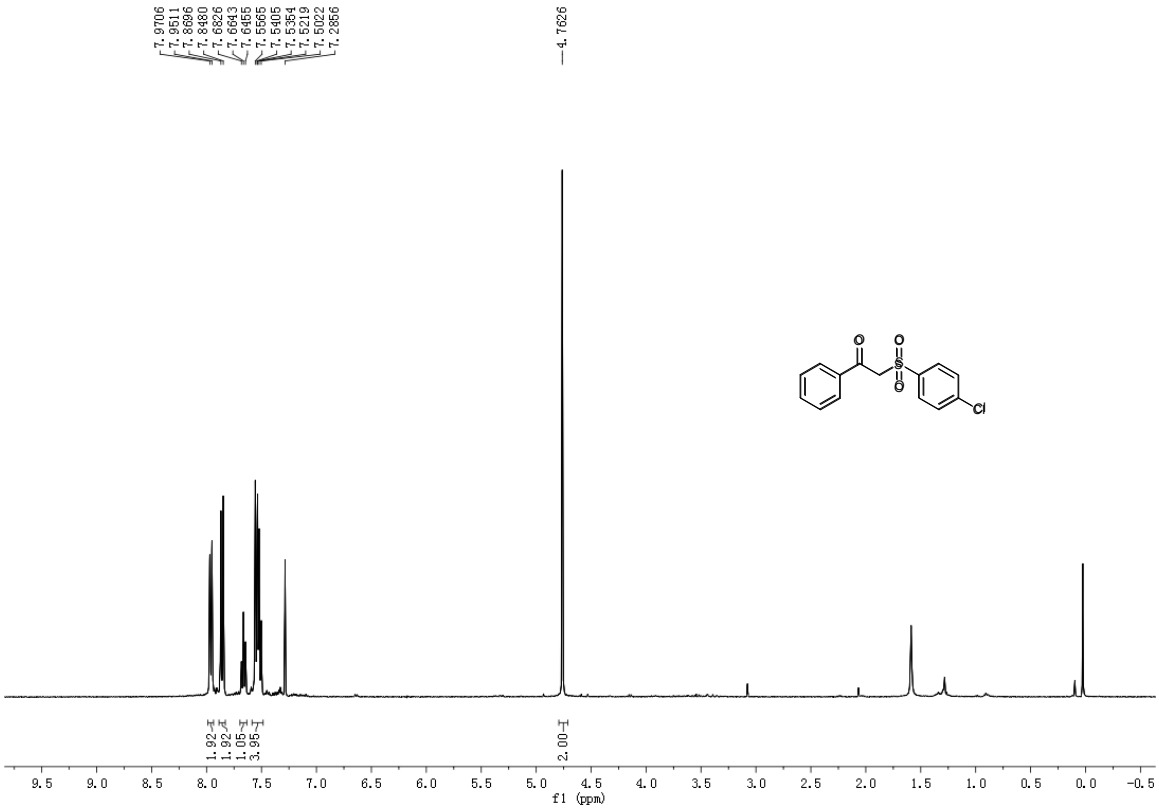
7.2136
4.7655
4.02
1.00
2.07
2.04
2.09
F
f1 (ppm)


188.02
167.42
164.86
135.66
134.50
131.72
131.62
129.25
128.94
116.65
116.42
77.36
77.04
76.72
63.45
f1 (ppm)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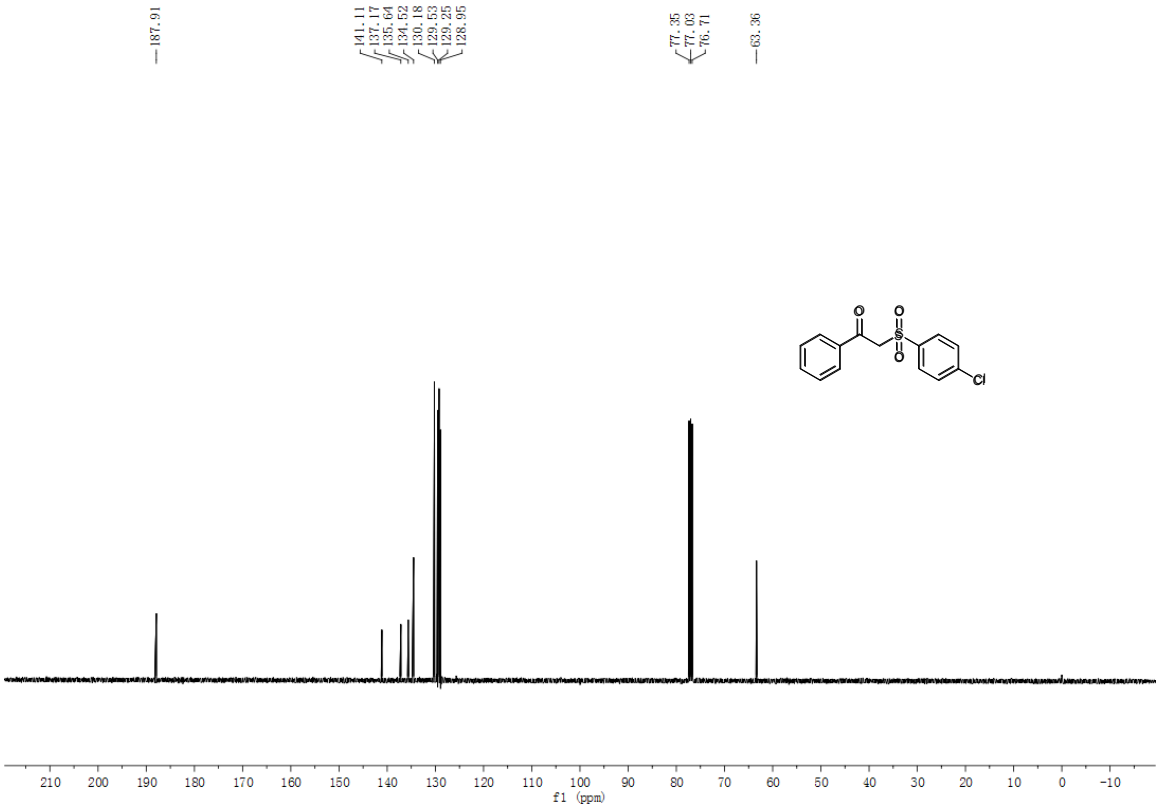
7.5405
7.5354
7.5219
7.5022
7.2856
4.7626
1.92
1.92
1.05
3.95
2.00
f1 (ppm)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141.11
137.17
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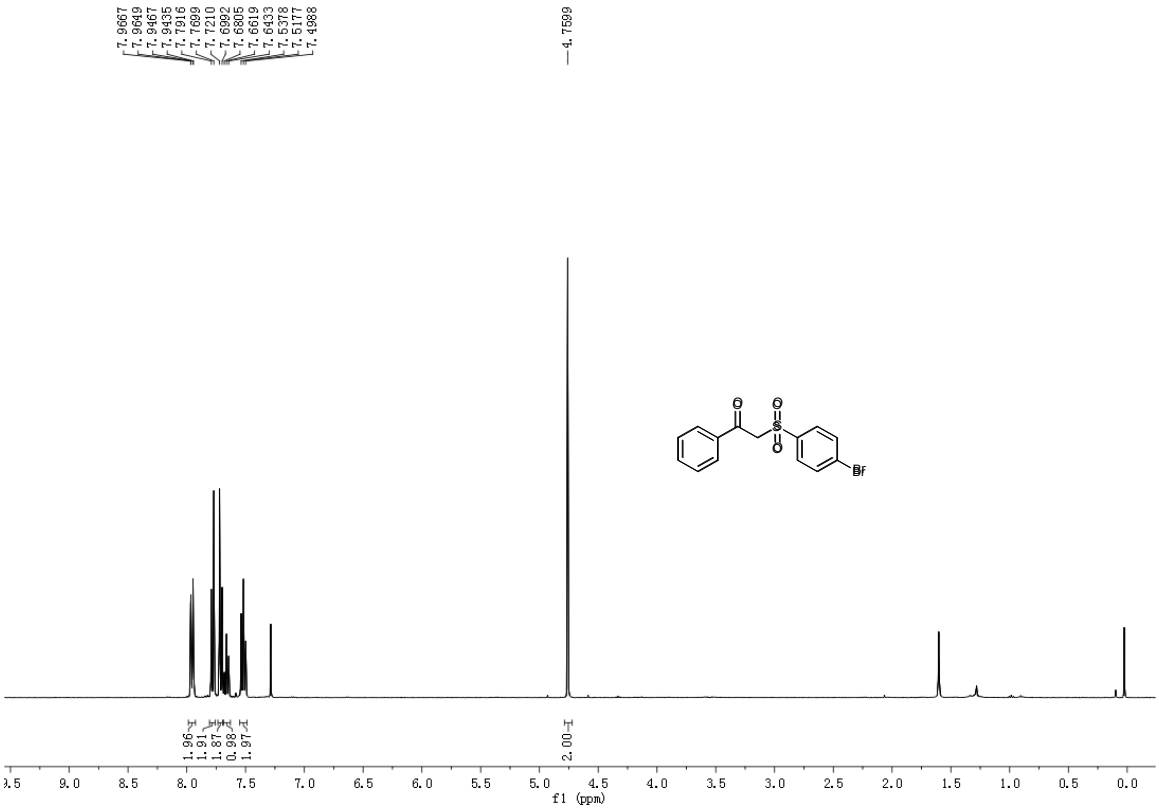
134.52
130.18
129.53
129.25
128.95
77.35
77.03
76.71
63.36
Cl
f1 (ppm)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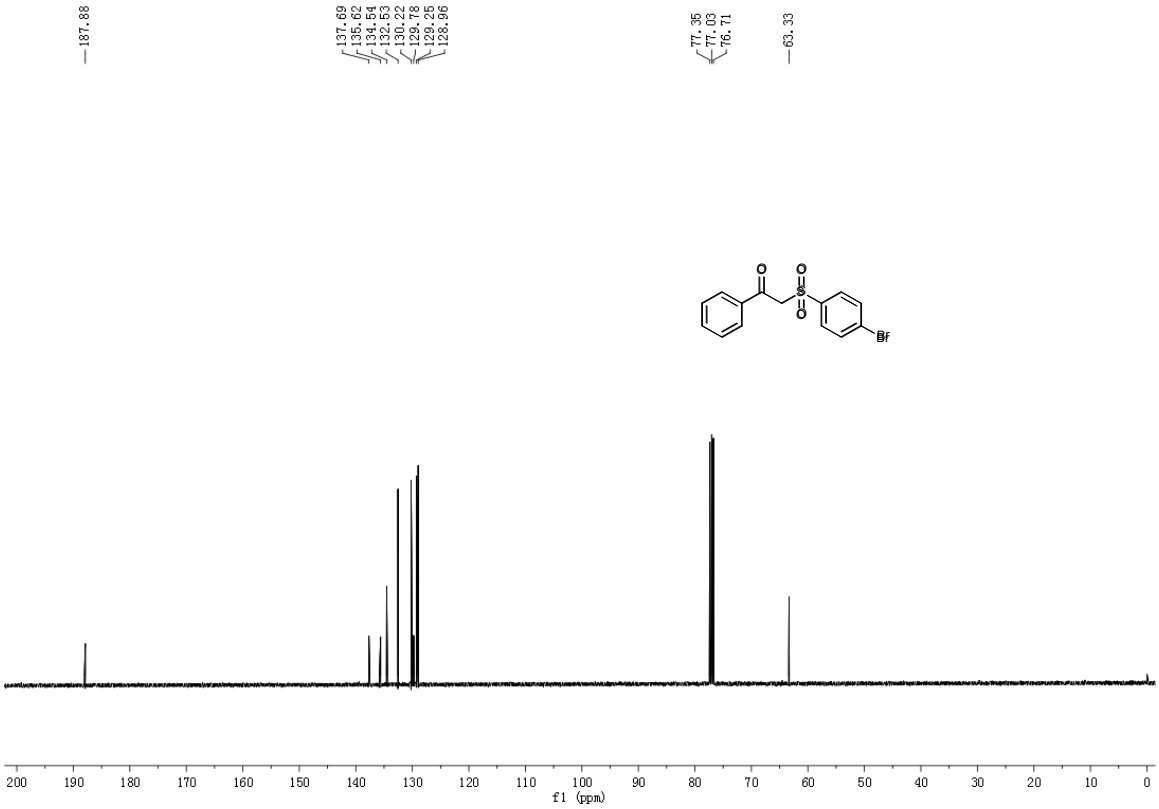
7.7210
7.6992
7.6805
7.6619
7.6433
7.5378
7.5177
7.4968
4.7599
Br
1.96
1.91
1.87
0.98
1.97
2.00
f1 (ppm)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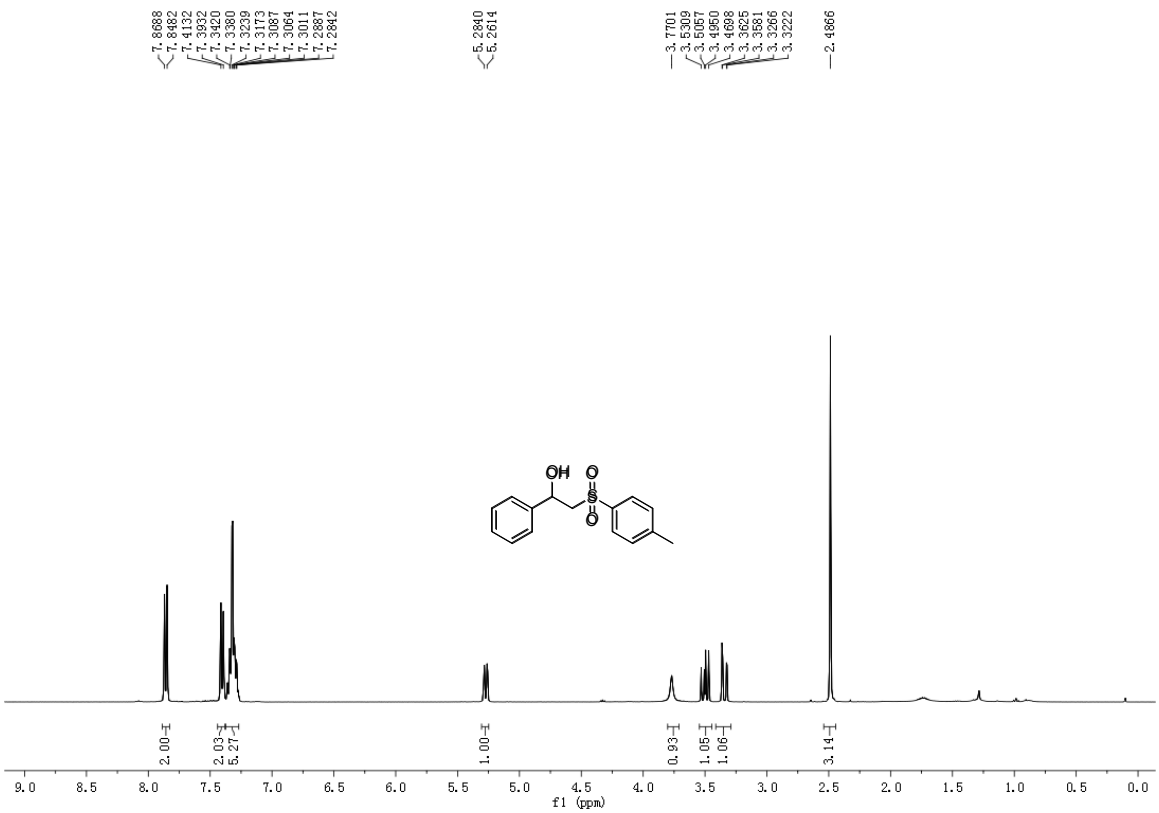
132.53
130.22
129.78
129.25
128.96
77.35
77.03
76.71
63.33
Br
f1 (ppm)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3.4698
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3.3581
3.3266
3.3222
2.4866
OH
2.00
2.03
5.27
1.00
0.93
1.05
1.06
3.14
f1 (ppm)