Electronic Supplementary Material (ESI) for RSC Advances.

O_2-Mediated C(sp^2)−X Bonds Oxygenation: Autoxidative Carbon-Heteroatom Bonds Formation Using Activated Alkenes as Linkage

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Supporting Information

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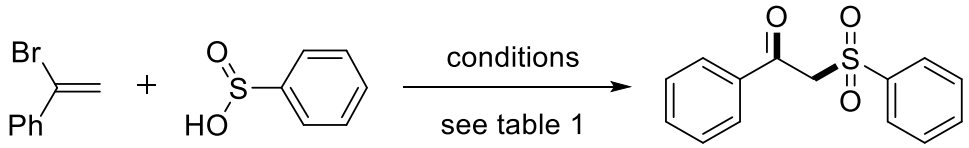
General information

All reactions were run under a dry air atmosphere with a dry air balloon fitted on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. All the solvents were purified according to the solvents handbook. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Sulfinic acids[1], α-bromostyrene derivatives and α-chlorostyrene derivatives were all prepared following literature procedures.[2] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. IR spectra were recorded on a Mettler Toledo React IR TM 15 spectrometer using a diamond comb. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR. ^{1}H and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H) and $CDCl_3$ (77.16 ppm for ^{13}C), respectively.

Experimental section

1) Impact of reaction parameters.

Table S1. Impact of reaction parameters on O_2-mediated C(sp2)−X bonds oxygenation.[a]



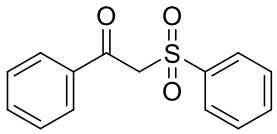
1a **2a** **3aa**

entry	solvent	condition	temp. / °C	additive	yield of **3aa** (%)[b]
1	$CHCl_3$	air	45	-	N.D.[c]

2	$CHCl_3$	air	45	pyridine	85[c]
3	$CHCl_3$	air	r.t.	pyridine	84
4	$CHCl_3$	air	r.t.	pyridine	63[d]
5	CH_2Cl_2	air	r.t.	pyridine	89
6	THF	air	r.t.	pyridine	95
7	MeCN	air	r.t.	pyridine	49
8	DMF	air	r.t.	pyridine	74
9	THF	N_2	r.t.	pyridine	0
10	THF	O_2	r.t.	pyridine	61
11	**THF**	**air**	**r.t.**	pyridine	**95[e]**

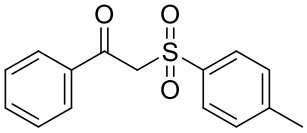
[a]Unless otherwise noted, all reactions were carried out using **1a** (0.20 mmol), **2a** (0.60 mmol), and pyridine (0.28 mmol) in solvent (4.0 mL) at room temperature for 1 h. [b]Isolated yield. [c]**2a** (0.80 mmol). [d]**2a** (0.40 mmol). [e]Pyridine (0.24 mmol).

2) Procedure and analytical data of compounds 3aa-5.

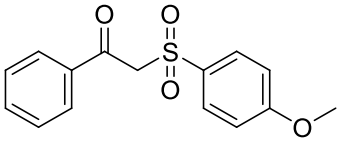


1-phenyl-2-(phenylsulfonyl)ethanone (3aa).[3a] Typical procedure: To an oven-dried Schlenk tube was added benzenesulfinic acid (0.60 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Pyridine (0.24 mmol), α-bromostyrene (0.20 mmol), and THF (4.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was vigorously stirred at room temperature for 1 h. Thereafter, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product **3aa**. Isolated yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.80 (m, 4H), 7.71-7.58 (m, 2H), 7.58-7.50 (m, 2H), 7.50-7.40 (m, 2H), 4.75 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 138.8, 135.7, 134.5, 134.3,

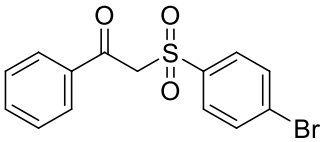
129.3(2), 129.2(7), 128.9, 128.6, 63.4.



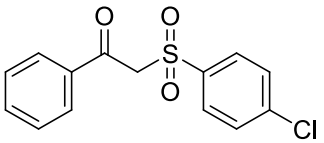
1-phenyl-2-tosylethanone (3ab).[3a] The synthesis procedure is the same as for **3aa**. the yield was determined by ^{1}H NMR by using dibromomethane as internal standard: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.87 (m 2H) , 7.76 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 145.5, 135.9, 135.8, 134.4, 130.0, 129.4, 129.0, 128.7, 63.7, 21.8.



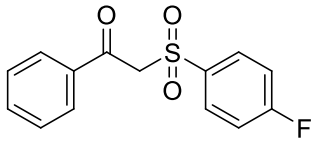
2-((4-methoxyphenyl)sulfonyl)-1-phenylethanone(3ac).[3b] The synthesis procedure is the same as for **3aa**. Isolated yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.90 (m, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.66-7.58 (m, 1H), 7.52-7.44 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.72 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 164.2, 135.9, 134.4, 131.0, 130.3, 129.4, 128.9, 114.5, 63.9, 55.8.



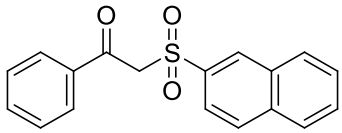
2-((4-bromophenyl)sulfonyl)-1-phenylethanone (3ad).[3a] The synthesis procedure is the same as for **3aa**. Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.88 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 137.7, 135.6, 134.7, 132.6, 130.3, 129.9, 129.4, 129.1, 63.4.



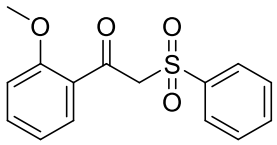
2-((4-chlorophenyl)sulfonyl)-1-phenylethanone (3ae).[3c] The synthesis procedure is the same as for **3aa**. Isolated yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55-7.46 (m, 4H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 141.2, 137.2, 135.7, 134.7, 130.3, 129.7, 129.4, 129.1, 63.4.



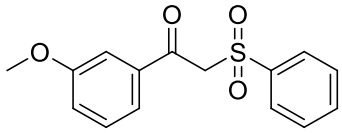
2-(4-fluorophenylsulfonyl)-1-phenylethanone (3af).[3b] The synthesis procedure is the same as for **3aa**. Isolated yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.85 (m, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.25-7.14 (m, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 166.2 (d, *1JCF* = 258.0 Hz), 135.7, 134.8(d, *4JCF* = 3.0 Hz), 134.6, 131.8 (d, *3JCF* = 9.8 Hz), 129.3, 129.0, 116.6 (d, *2JCF* = 22.8 Hz), 63.5.



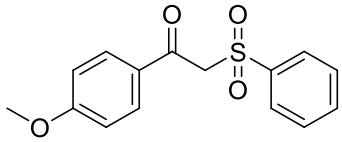
2-(naphthalen-2-ylsulfonyl)-1-phenylethanone (3ag).[3a] Typical procedure: To an oven-dried Schlenk tube equipped with a stir bar was added 2-naphthylsulfinic acid (0.80 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. Then, pyridine (0.32 mmol), α-bromostyrene (0.20 mmol), and THF (4.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at room temperature for 8 h. Thereafter, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product. Isolated yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.05-7.84 (m, 6H), 7.67 (t, *J* = 7.6 Hz, 1H), 7,64-7.55 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 4.82 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 135.9, 135.8, 135.6, 134.4, 132.1, 130.8, 129.7, 129.6(5), 129.6(3), 129.4, 129.0, 128.1, 127.9, 123.1, 63.8.



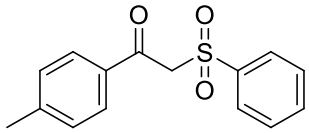
1-(2-methoxyphenyl)-2-(phenylsulfonyl)ethanone (3ba).[3c] The synthesis procedure is the same as for **3aa**. Isolated yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.91-7.83 (m, 2H), 7.66 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.54-7.46 (m, 3H), 7.03-6.95 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.95 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 159.1, 139.8, 135.4, 133.9, 131.4, 129.0, 128.6, 126.4, 121.1, 111.8, 67.5, 55.8.



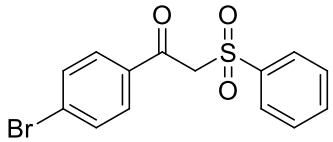
1-(3-methoxyphenyl)-2-(phenylsulfonyl)ethanone (3ca).[3b] The synthesis procedure is the same as for **3aa**. Isolated yield: 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.87 (m, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.52-7.47 (m, 1H), 7.43 (t, *J* = 2.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H),7.19-7.11 (m, 1H), 4.73 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 160.1, 138.9, 137.1, 134.3, 129.9, 129.3, 128.7, 122.2, 121.3, 113.1, 63.6, 55. 6.



1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (3da).[3b] The synthesis procedure is the same as for **3aa**. Isolated yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2H), 7.90-7.86 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.01-6.86 (m, 2H), 4.69 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3, 164.7, 138.9, 134.3, 132.0, 129.3, 129.0, 128.7, 114.2, 63.6, 55.8.

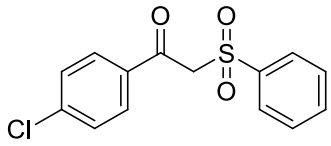


2-(phenylsulfonyl)-1-(p-tolyl)ethanone (3ea).[3d] The synthesis procedure is the same as for **3aa**. Isolated yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.28-7.25 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 145.7, 138.9, 134.3, 133.4, 129.7, 129.5, 129.3, 128.7, 63.5, 21.9.

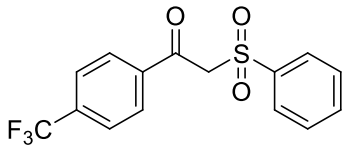


1-(4-bromophenyl)-2-(phenylsulfonyl)ethanone (3fa).[3a] The synthesis procedure is the same as for **3aa**. Isolated yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.85 (m, 2H), 7.81 (d, *J* = 8.4 Hz,

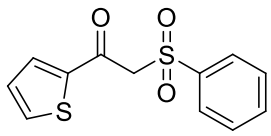
2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 138.5, 134.4, 132.3, 130.8, 130.1, 129.3, 128.5, 63.5.



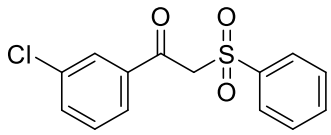
1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanone (3ga).[3b] The synthesis procedure is the same as for **3aa**. Isolated yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.81 (m, 4H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0, 141.3, 138.6, 134.5, 134.1, 130.9, 129.4, 129.3, 128.7, 63.7.



2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethanone (3ha).[3d] The synthesis procedure is the same as for **3aa**. Isolated yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.94-7.84 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.68 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.55 (tt, *J* = 7.8, 1.6 Hz, 2H), 4.79 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 138.5, 138.3, 135.6 (q, *2JCF* = 32.9 Hz), 134.7, 129.9, 129.5, 128.7, 126.1 (q, *3JCF* = 3.7 Hz), 123.5(q, *1JCF* = 274.0 Hz), 63.9.

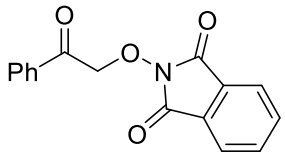


2-(phenylsulfonyl)-1-(thiophen-2-yl)ethanone (3ia).[3e] The synthesis procedure is the same as for **3aa**. Isolated yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.81 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.75 (d, *J* = 4.8, 0.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 4.4 Hz, 1H), 4.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 143.3, 138.6, 136.6, 135.3, 134.5, 129.4, 128.8(4), 128.7(6), 64.8.



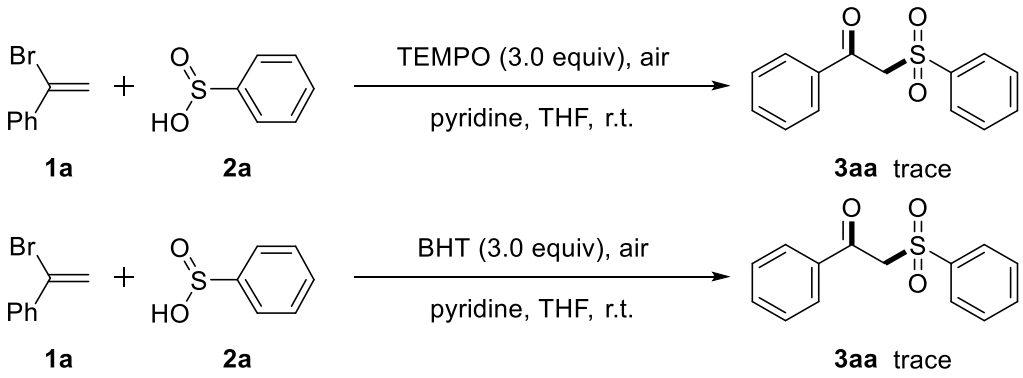
1-(3-chlorophenyl)-2-(phenylsulfonyl)ethan-1-one (3ja).[3f] Typical procedure: To an oven-dried Schlenk tube was added benzenesulfinic acid (0.80 mmol), and a balloon filled with dry air was

connected to the Schlenk tube through the side arm and purged one time. Pyridine (0.32 mmol), α-bromostyrene (0.20 mmol), and MeCN (4.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was vigorously stirred at 60 °C for 6 h. Thereafter, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product **3ja** in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.79 (m, 4H), 7.72-7.64 (m, 1H), 7.61-7.52 (m, 3H), 7.47-7.40 (m, 1H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 138.6, 137.3, 135.4, 134.6, 134.4, 130.3, 129.4, 129.3, 128.7, 127.7, 63.7.



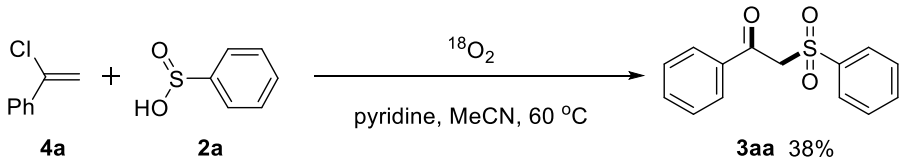
2-(2-oxo-2-phenylethoxy)isoindoline-1,3-dione (5).[3g] Typical procedure: To an oven-dried Schlenk tube equipped with a stir bar was added NHPI (0.80 mmol), and a balloon filled with O_2 was connected to the Schlenk tube through the side arm and purged one time. Then, pyridine (0.32 mmol), α-bromostyrene (0.20 mmol), and MeCN (4.0 mL) were successively injected in the reaction tube with magnetic stirring. The reaction mixture was allowed to stir at 80 °C for 6 h. Thereafter, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product. Isolated yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.89-7.83 (m, 2H), 7.79-7.74 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 5.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 163.2, 134.8, 134.5, 134.2, 129.0, 128.9, 128.4, 123.9, 78.6.

3) Radical trapping experiments.



Typical procedure for Radical trapping experiments: To an oven-dried Schlenk tube equipped with a stir bar were added benzenesulfinic acid (0.6 mmol), TEMPO or BHT (0.6 mmol). A balloon filled with dry air was then connected to the Schlenk tube through the side arm and the dry air was purged once. Then, pyridine (0.24 mmol), α-bromostyrene (0.2 mmol) and THF (4.0 mL) were successively injected in the reaction tube and the reaction mixture was stirred at room temperature for 1 h. Thereafter, the reaction mixture was analyzed by TLC and GC-MS.

4) Labeling experiments.

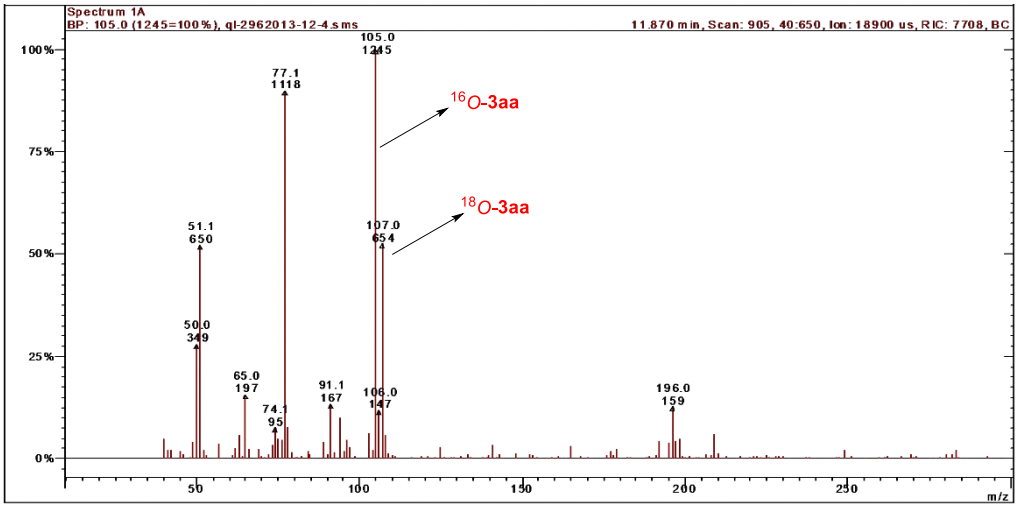


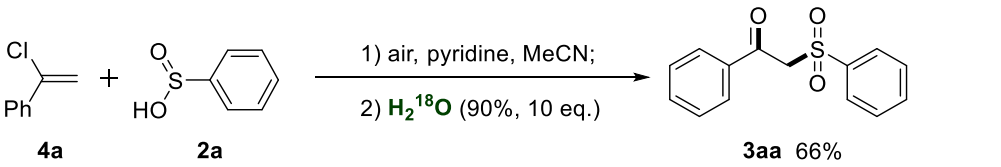
4a **2a** **3aa** 38%

^{18}O**-3aa**: 34.4%; ^{16}O**-3aa** = 65.6%

Typical procedure for $^{18}O_2$ labeling experiments: To a 15.0 mL oven-dried Schlenk tube equipped with a stir bar were added benzenesulfinic acid (0.80 mmol) and MeCN (4.0 mL), which was degassed the air by the method of freeze-pump-thaw cycle for 6 times. When the solvent is frozen, opened the stopcock to vacuum and pumped off the atmosphere for 10 minutes, after then, $^{18}O_2$ was purged to the tube and the solvent was thawed to liquid. Thereafter, sealed the flask. Then, pyridine (0.32 mmol), α-chlorostyrene (0.2 mmol), and MeCN (4.0 mL) were successively injected in the reaction tube and the reaction mixture was stirred at 60 °C for 6 h. After the reaction, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product **3aa** in 38% yield with 34.4% of which was labelled.

The EI-MS spectral of **3aa**



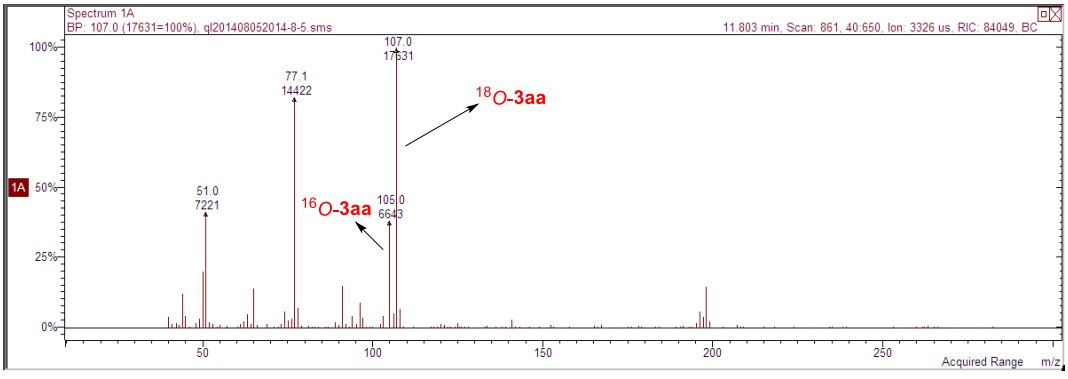


4a **2a** **3aa** 66%

^{18}O-**3aa**: 27.4%; ^{16}O-**3aa** = 72.6%

Typical procedure for $H_2{}^{18}O$ labeling experiments: To an oven-dried Schlenk tube equipped with a stir bar was added benzenesulfinic acid (0.8 mmol), and a balloon filled with dry air was connected to the Schlenk tube through the side arm and the dry air was purged one time. Then, pyridine (0.32 mmol), α-chlorostyrene (0.2 mmol), and MeCN (4.0 mL) were successively injected in the reaction tube and the reaction mixture was stirred at 60 °C for 6 h. Thereafter, $H_2{}^{18}O$ (2.0 mmol) was added and the reaction mixture was allowed to stir at 60 °C for another 6 h. After the reaction, the solvent was evaporated and the crude product was separated on a silica gel column with petroleum ether and ethyl acetate as eluent to afford the desired product **3aa** in 67% yield with 72.6% of which was labelled.

The EI-MS spectral of **3aa**



5) ReactIR experiments.

The reaction between 1a (α-bromostyrene) and 2a (benzenesulfinic acid) under different oxygen pressure (balloon): an oven-dried three-necked reaction vessel were equipped with a stir bar and **2a** (0.6 mmol), the operando IR probe was inserted through an adapter into the middle neck, the other two necks were capped by septa for injections and a balloon (O_2/N_2 under different ration). After evacuation under vacuum and flushing with gas (O_2/N_2) through the balloon for three times, CH_2Cl_2 (4.0 mL) was added to the vessel via a springe and the reaction was monitored by operando IR at room temperature (stirring speed: 1000 r/min). Afterwards, pyridine (0.24 mmol) and **1a** (0.2 mmol) were added and the reaction mixture was stirred vigorously at RT for 1 h. After the reaction, the reaction mixture was analyzed by ^1H NMR analysis using dibromomethane as internal standard. The yields are 95% (O_2/N_2 = 1:2), 99% (O_2/N_2 = 1:3), 99% (O_2/N_2 = 1:4).

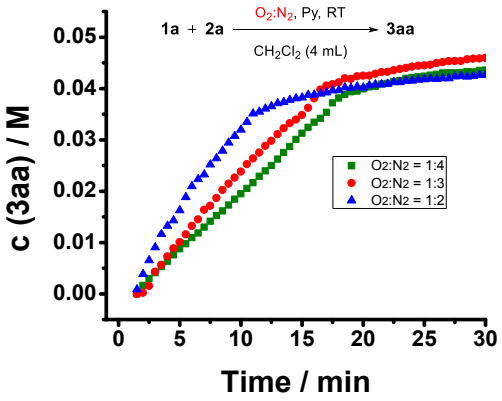


Figure 1. The kinetic profiles of the reaction of **1a** (0.2 mmol), **2a** (0.6 mmol) and pyridine (0.24 mmol) in CH_2Cl_2 (4.0 mL) at room temperature under different oxygen pressure (balloon), 1000 r/min (stirring speed).

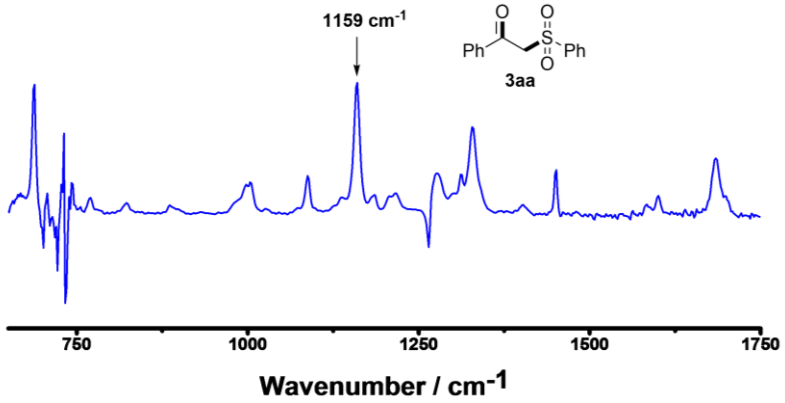


Figure 2. The Characteristic IR band of the **3aa** (in CH_2Cl_2).

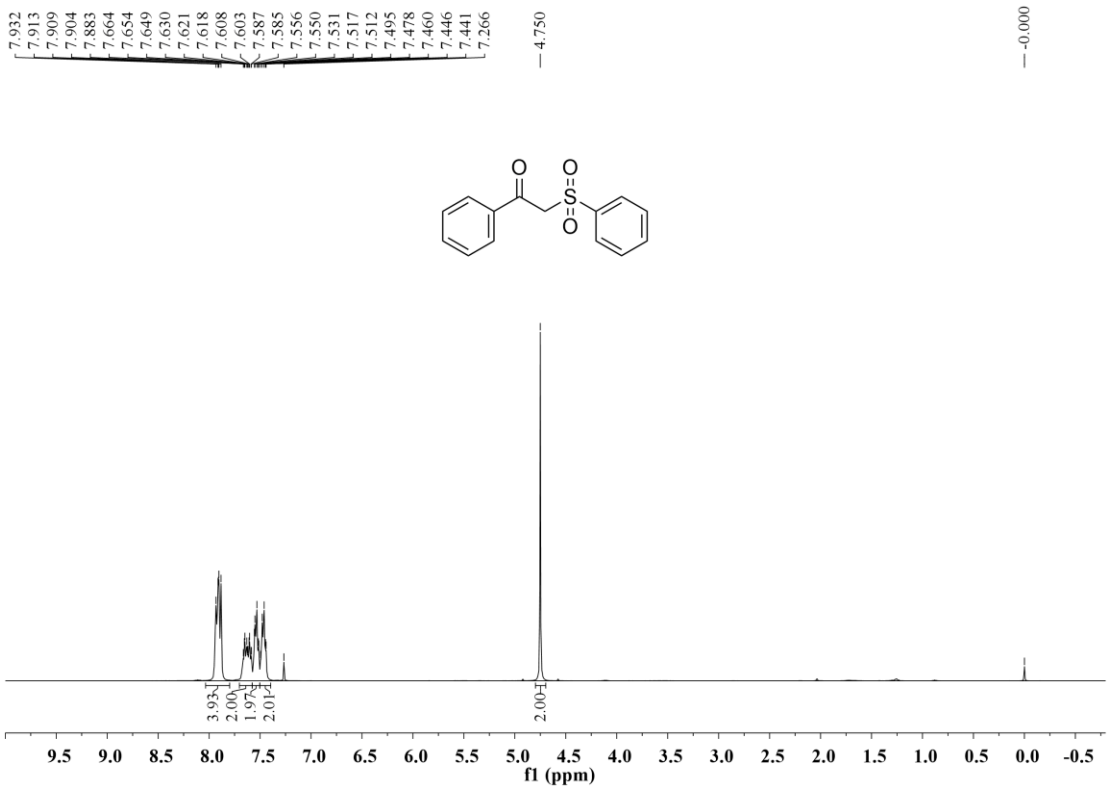
References

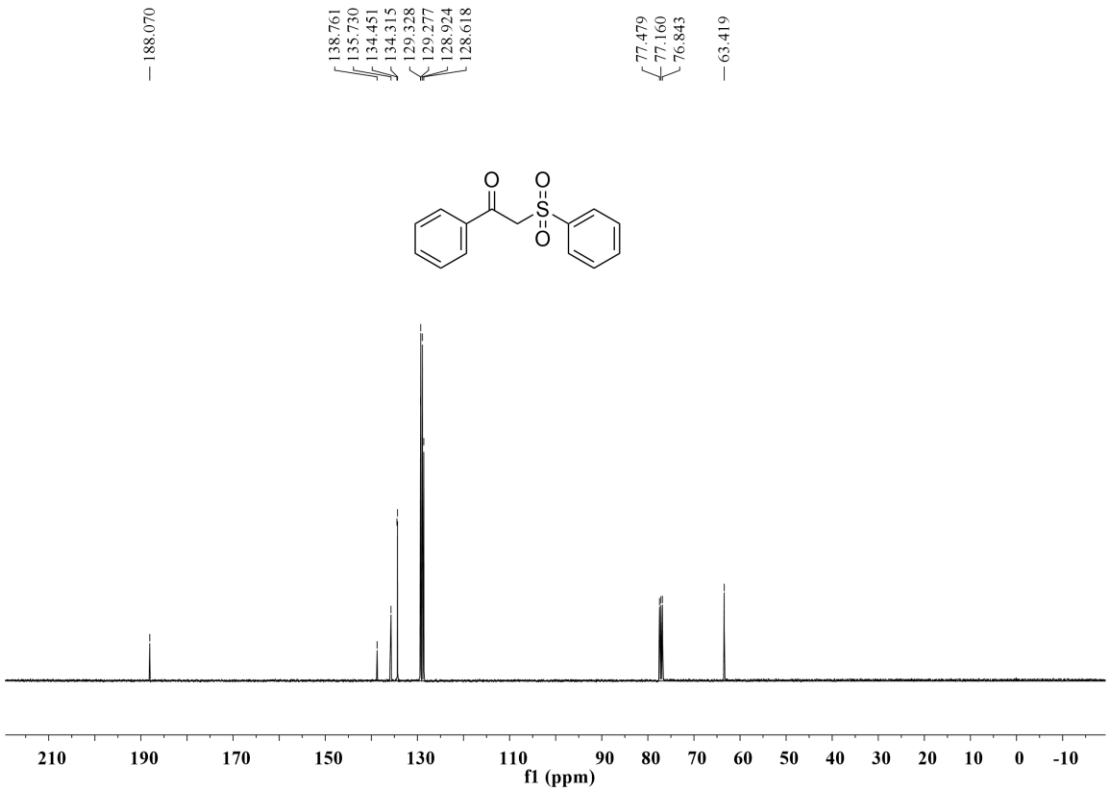
(1) S. Oae, H. Togo, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3802-3812.

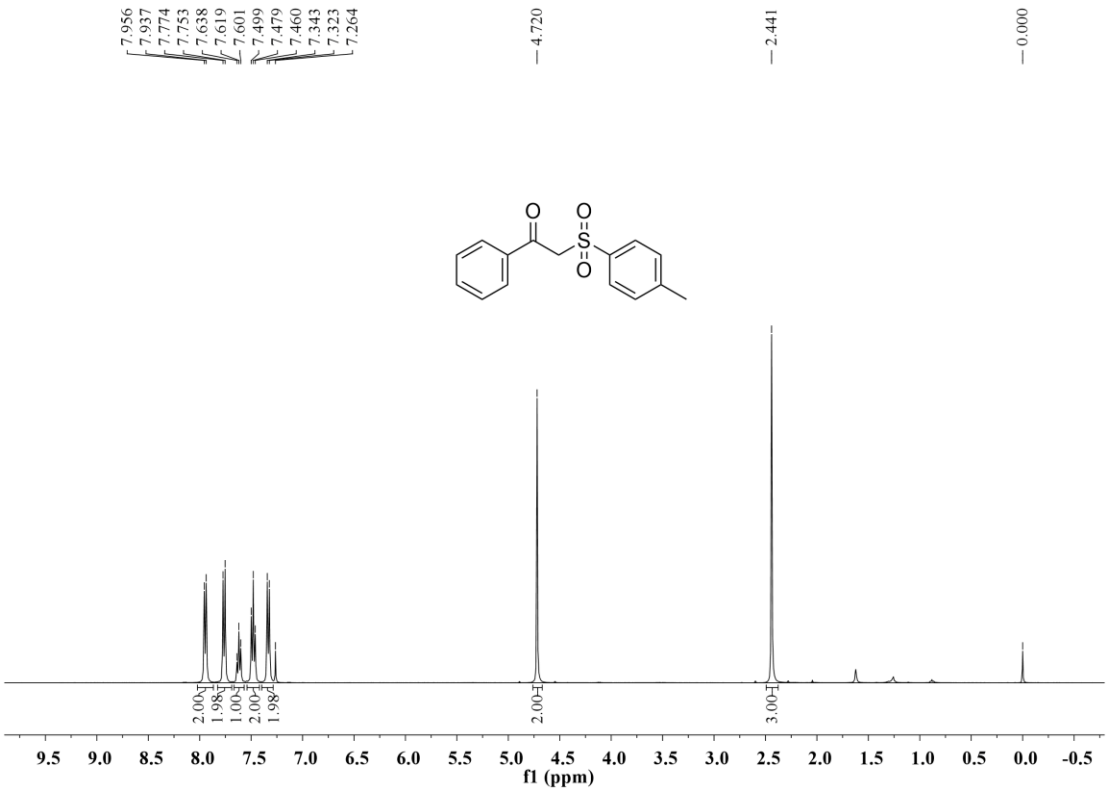
(2) a) A. Lilienkampf, M. P. Johansson, K. Wähälä, *Org. Lett.* **2003**, *5*, 3387-3390; b) A. K. Macharla, R. Chozhiyath Nappunni, N. Nama, *Tetrahedron Lett.* **2012**, *53*, 1401-1405; c) P. B. Silveira, A. L. Monteiro, *Journal of Molecular Catalysis A: Chemical* **2006**, *247*, 1-6; d) M. Kodomari, T. Nagaoka, Y. Furusawa, *Tetrahedron Letters* **2001**, *42*, 3105-3107; e) T. Takeda, R. Sasaki, S. Yamauchi, T. Fujiwara, *Tetrahedron* **1997**, *53*, 557-566; f) A. Hamze, J.-D. Brion, M. Alami, *Org. Lett.* **2012**, *14*, 2782-2785.

(3) a) H. Loghmani-Khouzani, M. R. Poorheravi, M. M. M. Sadeghi, L. Caggiano, R. F. W. Jackson, *Tetrahedron* **2008**, *64*, 7419-7425; b) G. C. Tsui, Q. Glenadel, C. Lau, M. Lautens, *Org. Lett.* **2010**, *13*, 208-211; c) Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang, A. Lei, *J. Am. Chem. Soc.* **2013**, *135*, 11481-11484; d) J. Xiang, M. Ipek, V. Suri, M. Tam, Y. Xing, N. Huang, Y. Zhang, J. Tobin, T. S. Mansour, J. McKew, *Bioorg. Med. Chem.* **2007**, *15*, 4396-4405; e) J. Yang, H. Li, M. Li, J. Peng, Y. Gu, *Adv. Synth. Catal.* **2012**, *354*, 688-700; f) J. Xuan, Z.-J. Feng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, *Chem.--Eur. J.* **2014**, *20*, 3045-3049; g) S. X. Wang, X. W. Li, J. T. Li, *Ultrason. Sonochem.* **2008**, *15*, 33-36.

NMR Spectra of Products



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7.264
4.720
2.441
0.000
2.00
1.98
1.00
2.00
1.98
2.00
3.00
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
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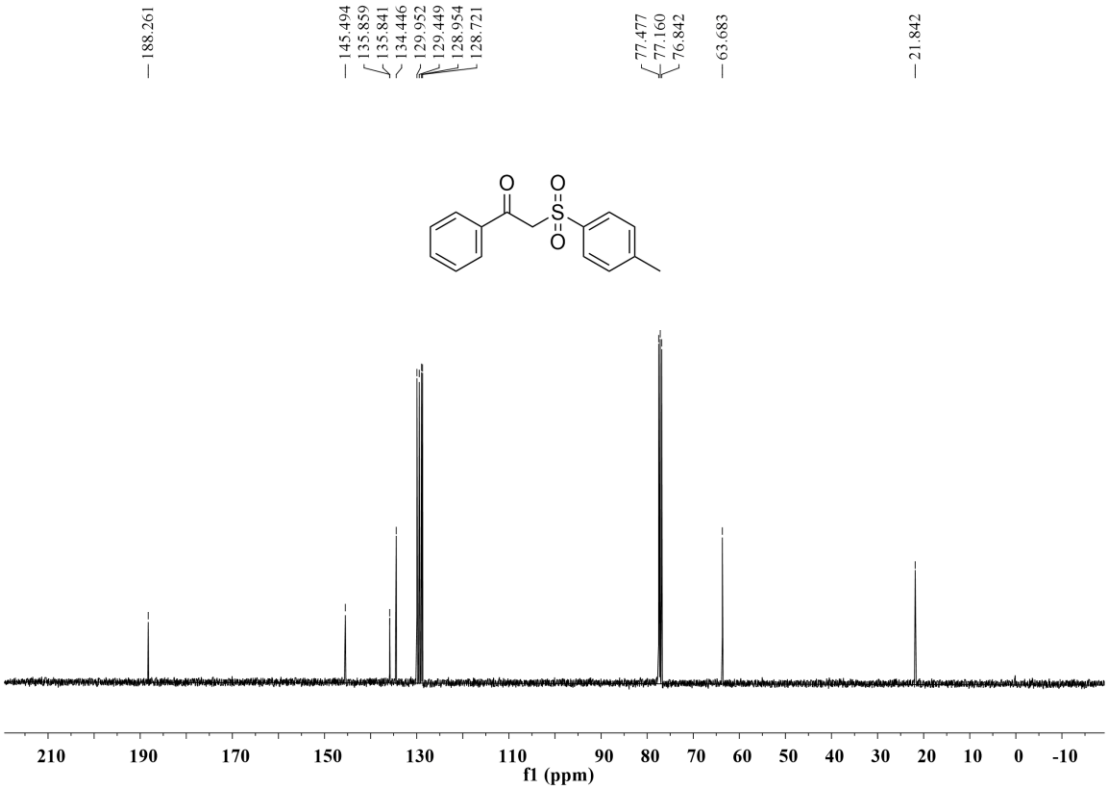
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63.683
21.842
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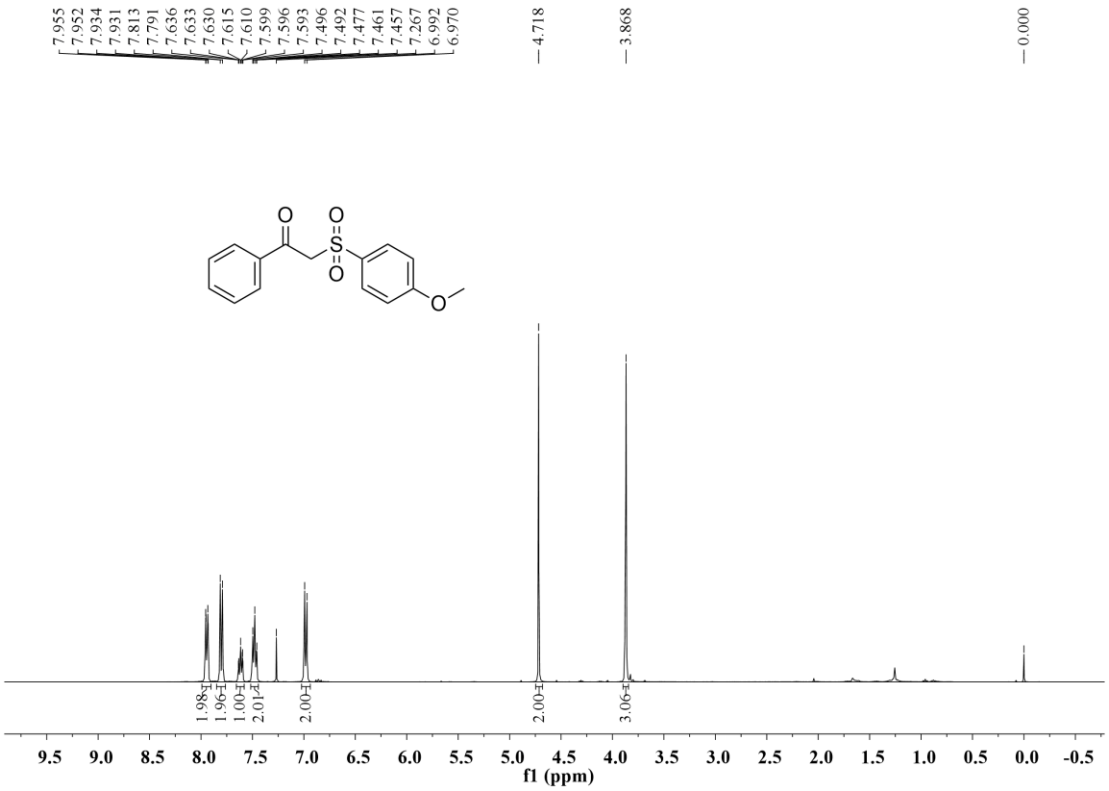
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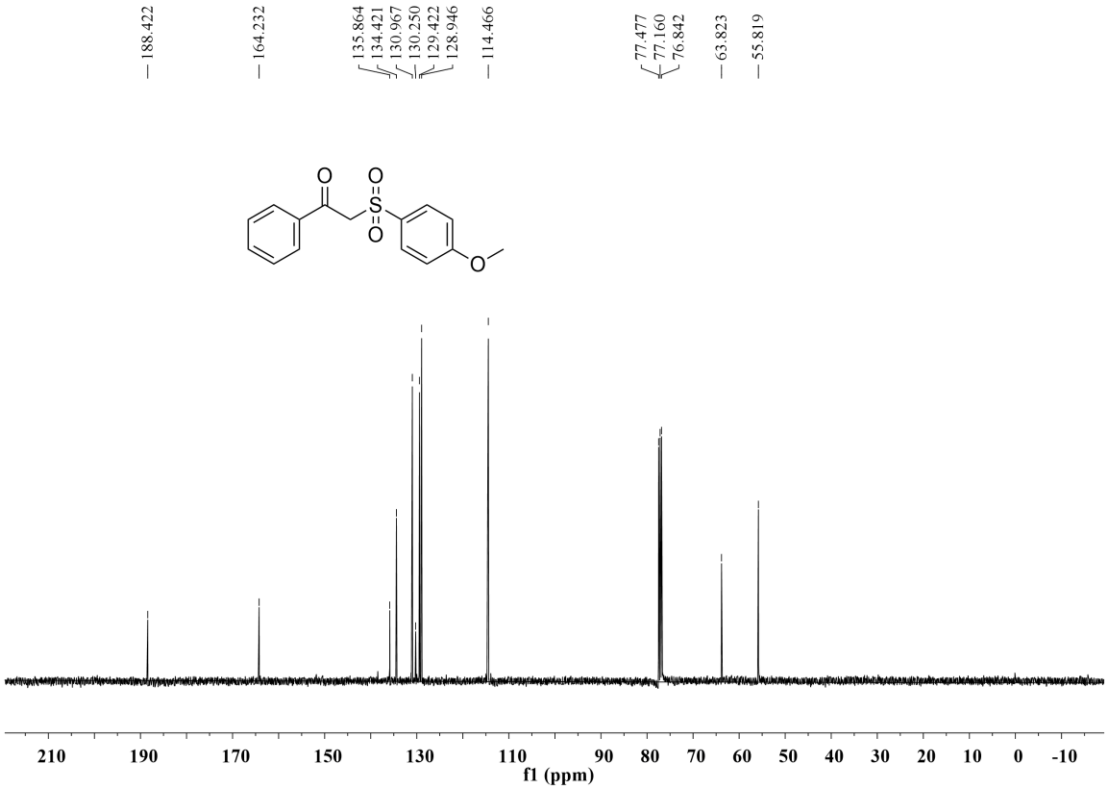
7.596
7.593
7.496
7.492
7.477
7.461
7.457
7.267
6.992
6.970
4.718
3.868
0.000
1.98
1.96
1.00
2.01
2.00
2.00
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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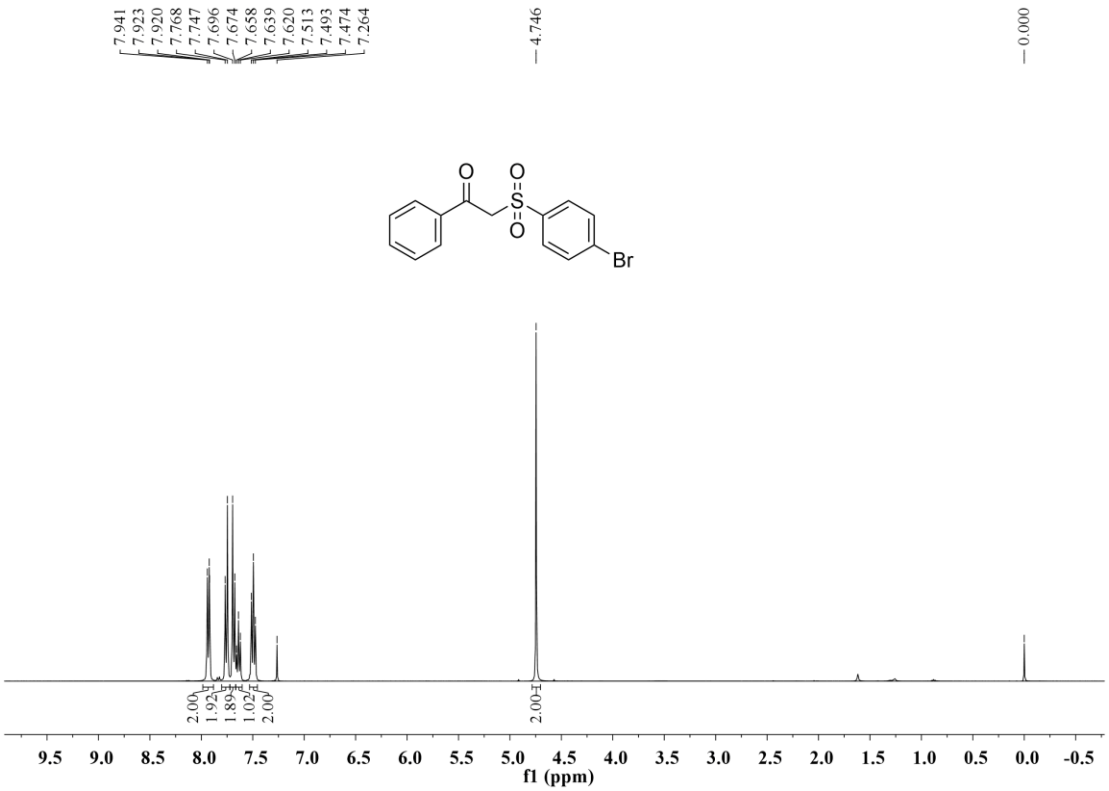
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7.474
7.264
4.746
0.000
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O
S
O
Br
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1.92
1.89
1.02
2.00
2.00
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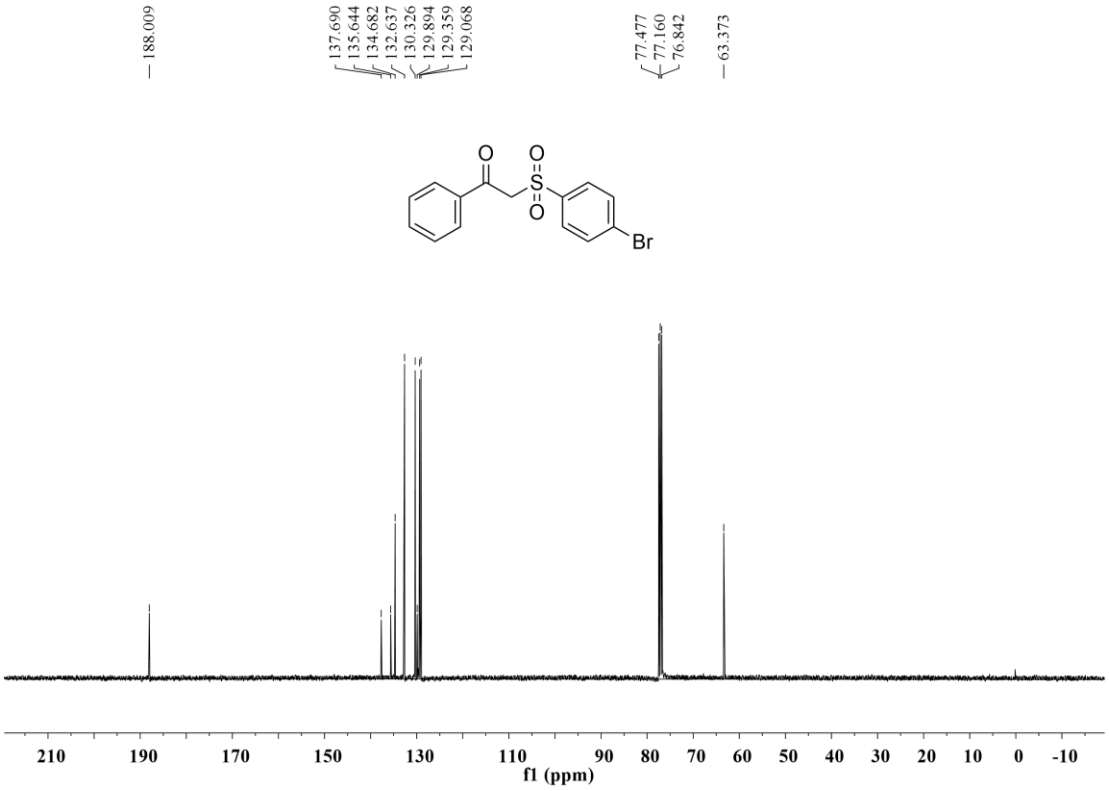
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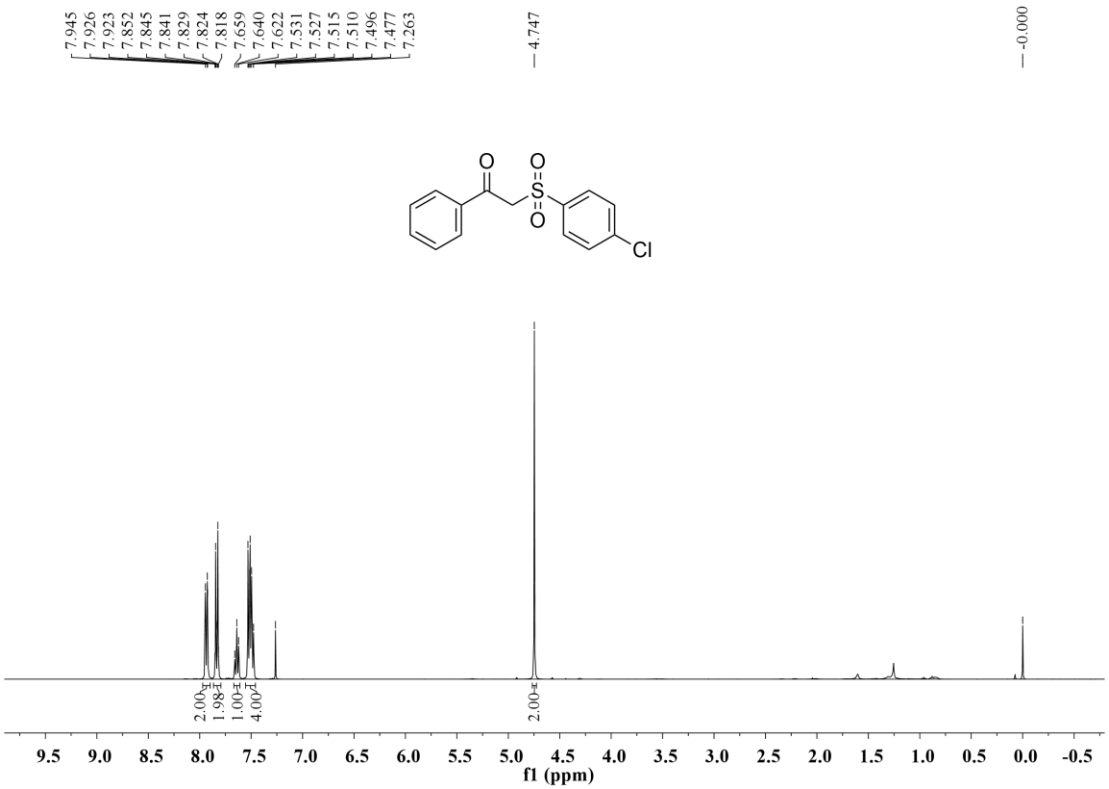
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7.622
7.531
7.527
7.515
7.510
7.496
7.477
7.263
4.747
-0.000
O
O
S
O
O
Cl
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1.98
1.00
4.00
2.00
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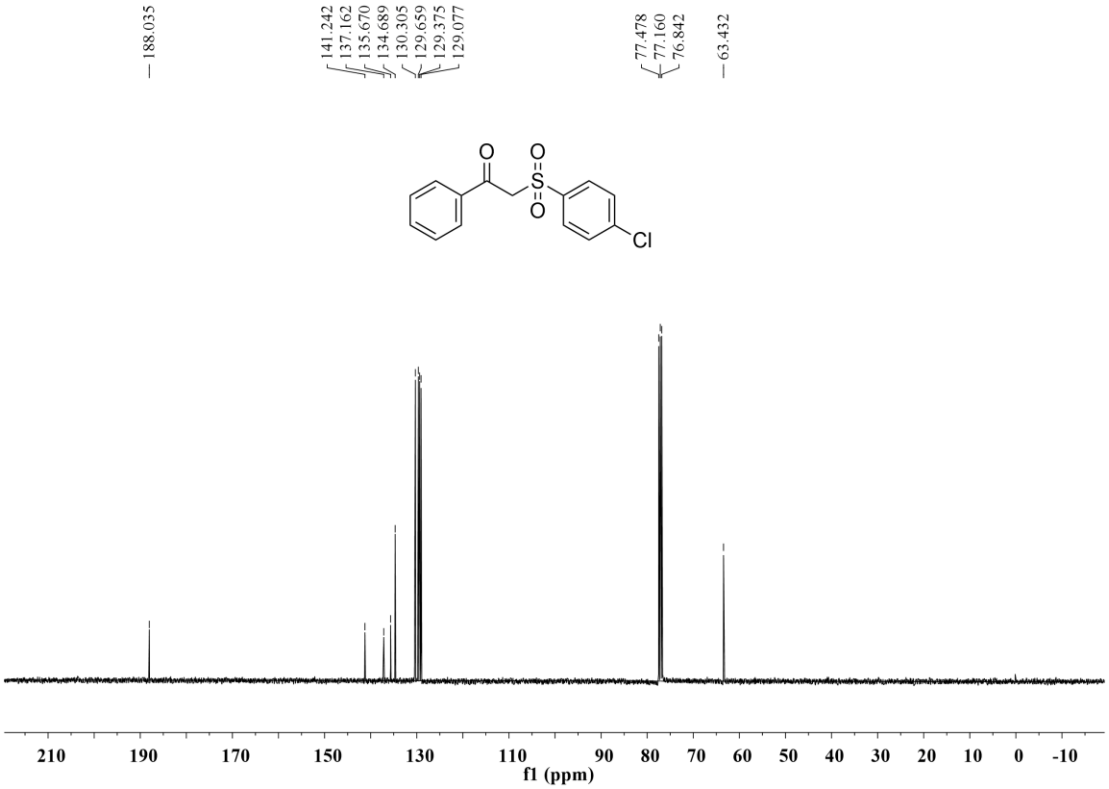
f1 (ppm)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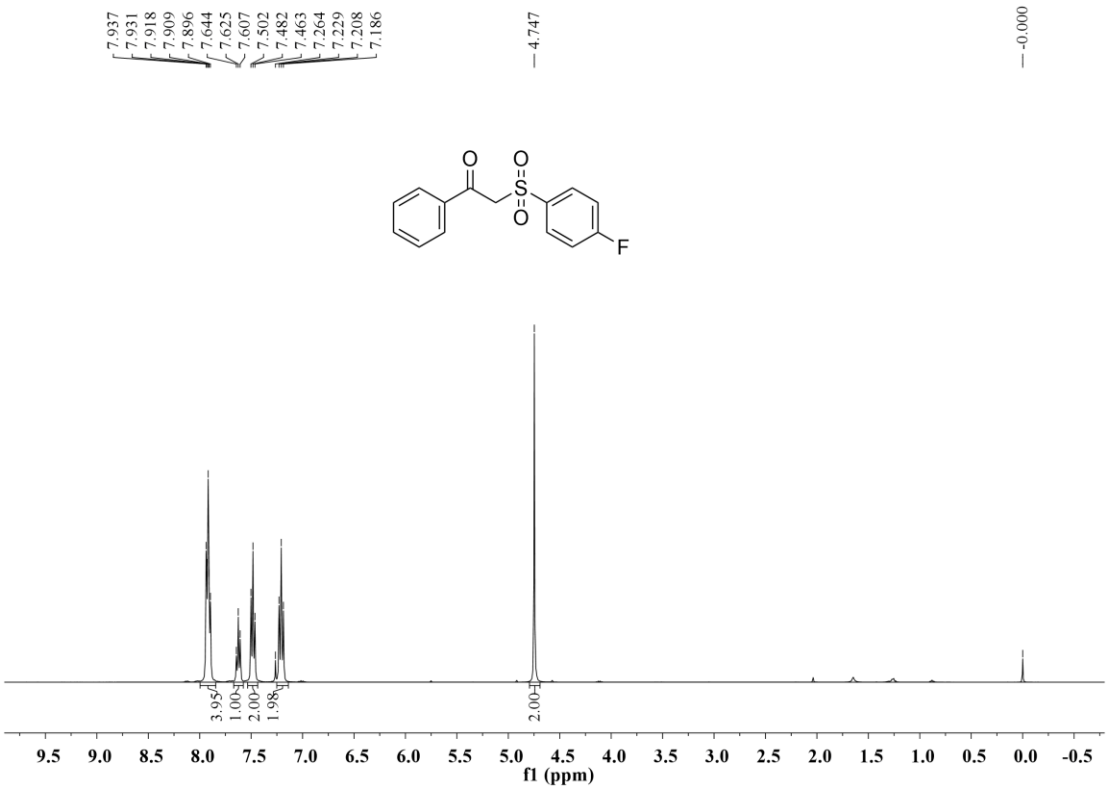
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7.186
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-0.000
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O
S
O
F
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2.00
1.98
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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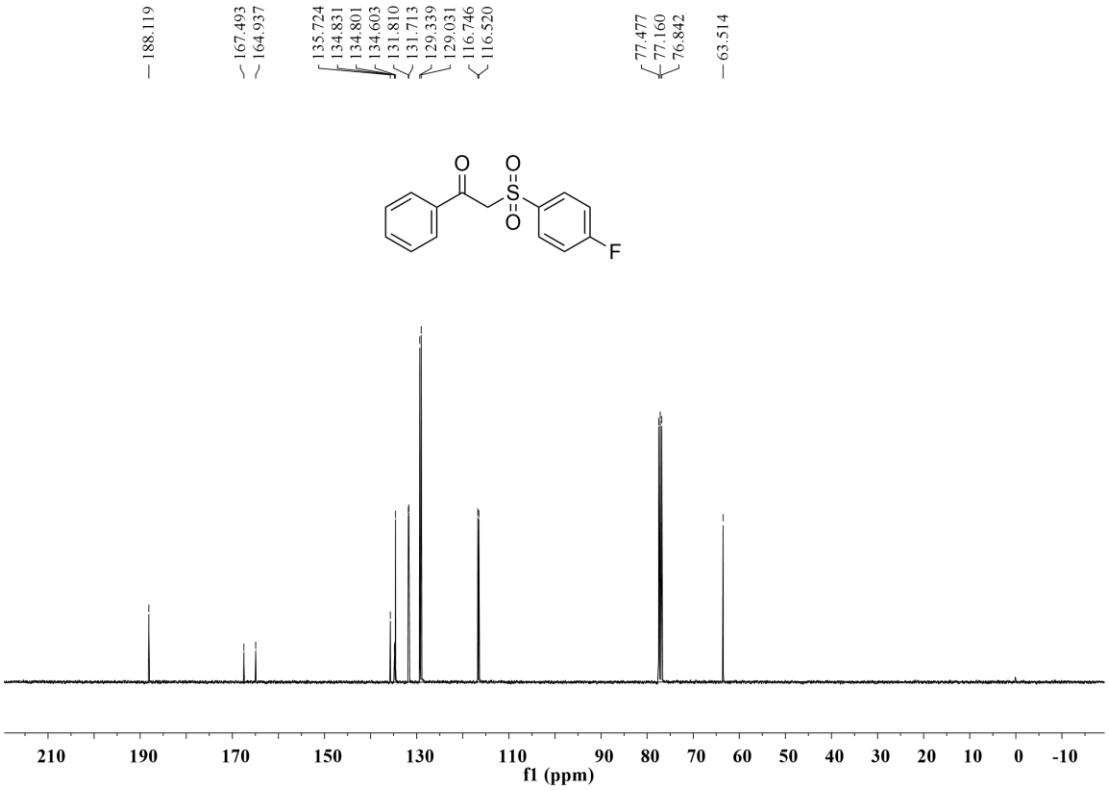
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116.520
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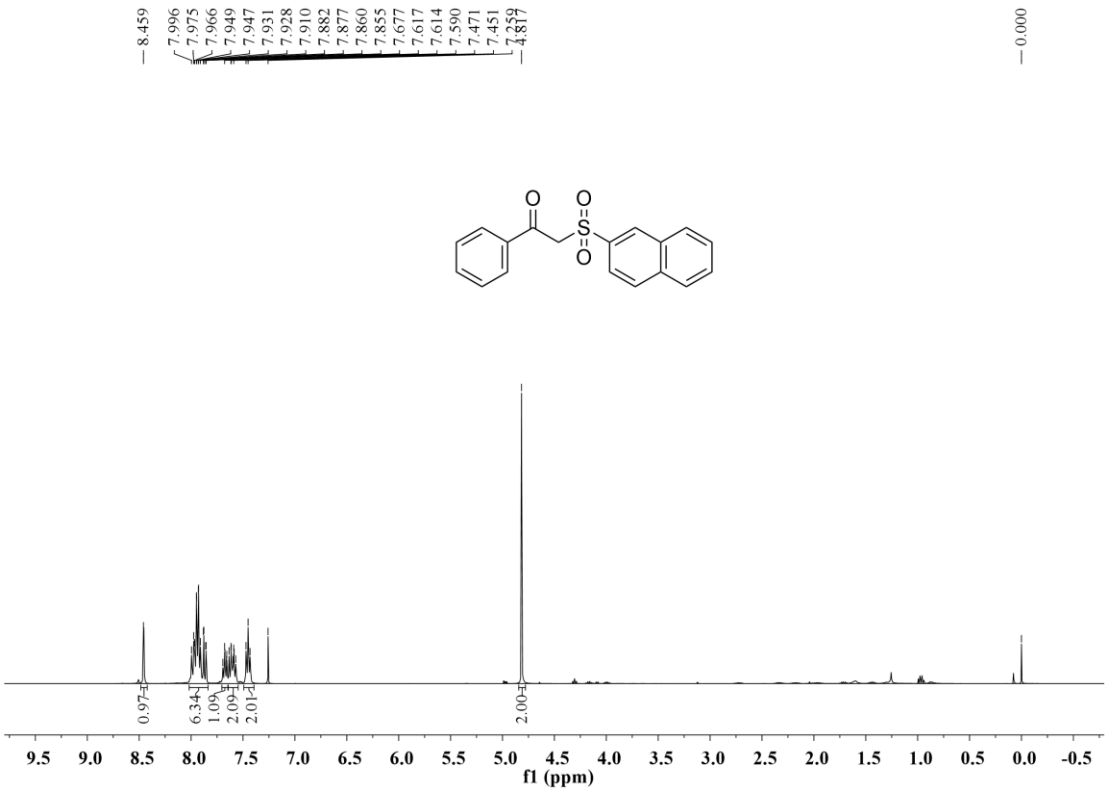
f1 (ppm)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7.855
7.677
7.617
7.614
7.590
7.471
7.451
7.259
4.817
0.000
O
O
S
O
0.97
6.34
1.09
2.09
2.01
2.00
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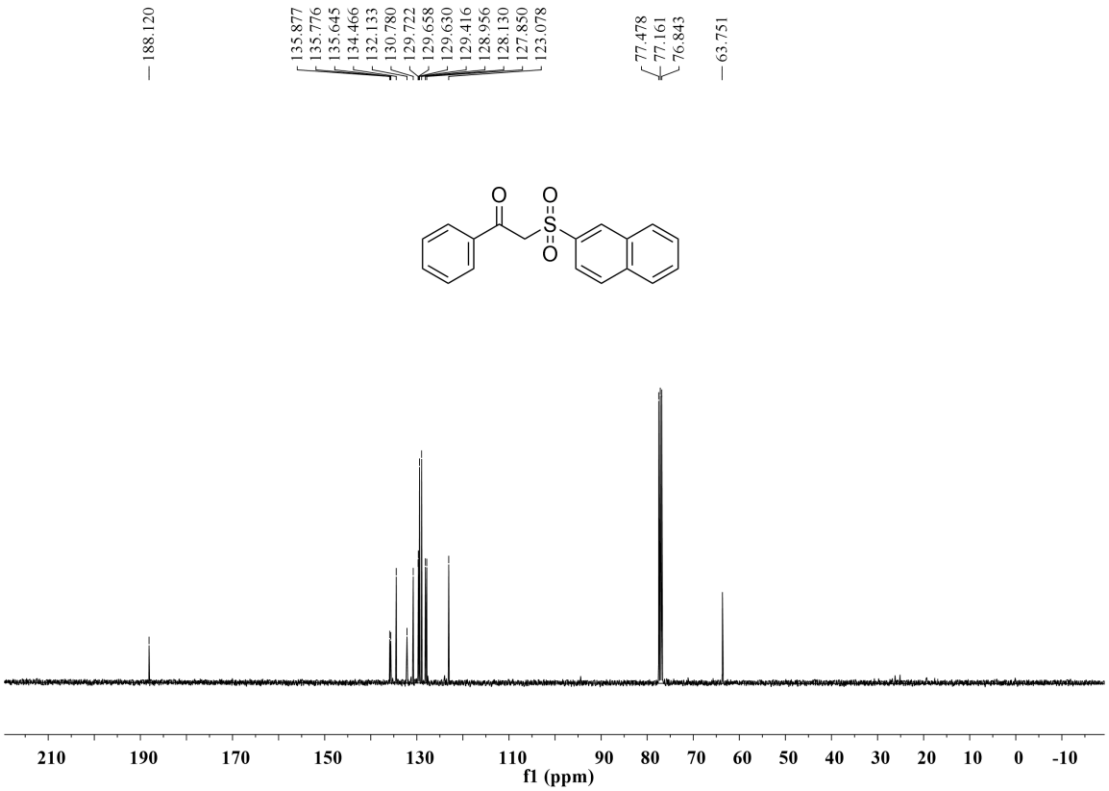
f1 (ppm)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S
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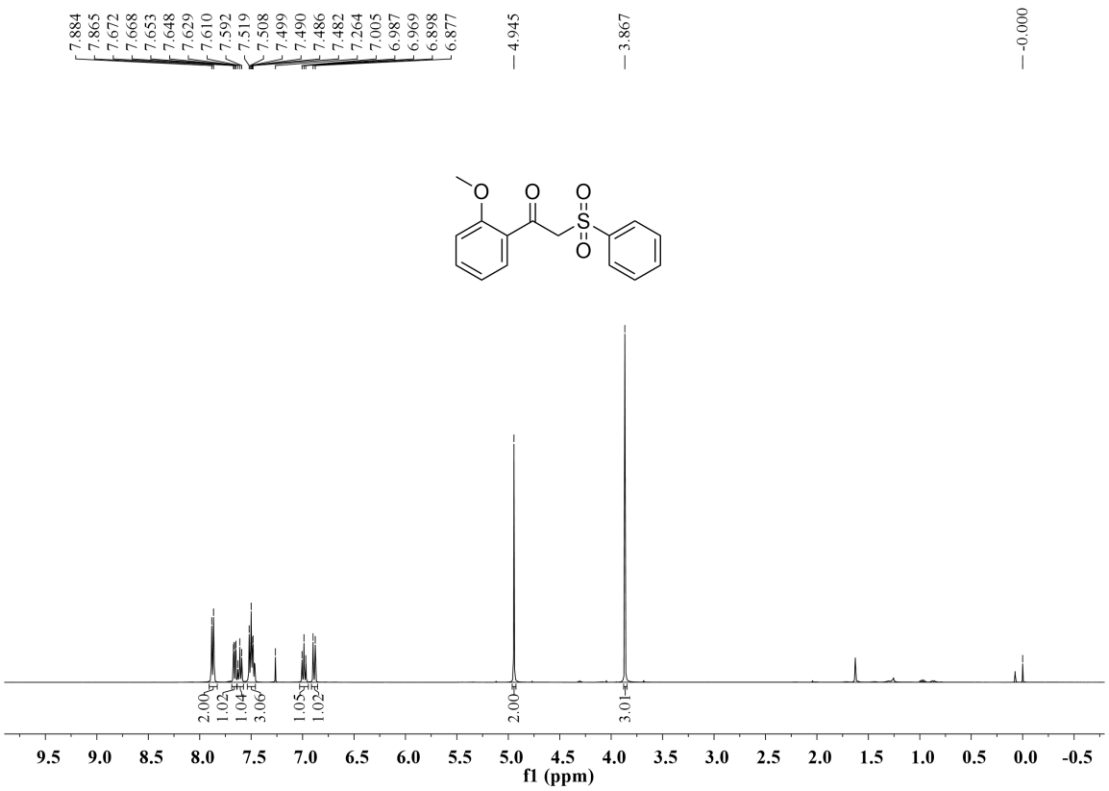
f1 (ppm)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7.482
7.264
7.005
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6.898
6.877
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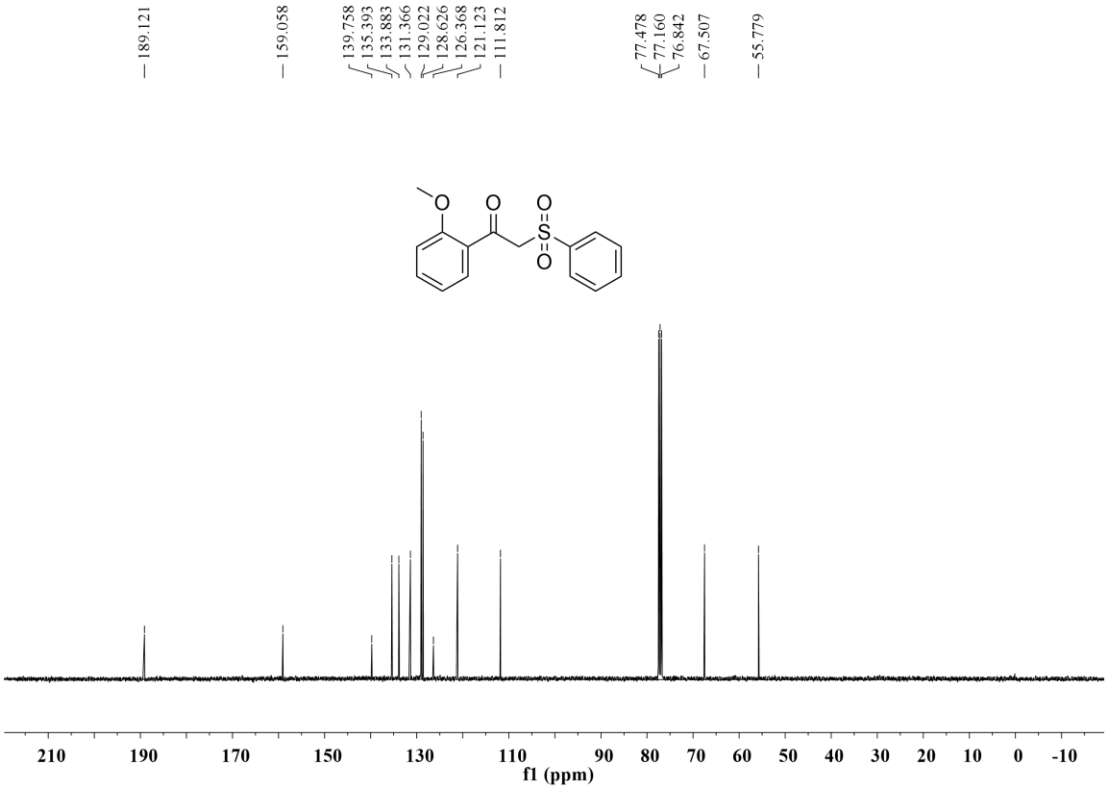
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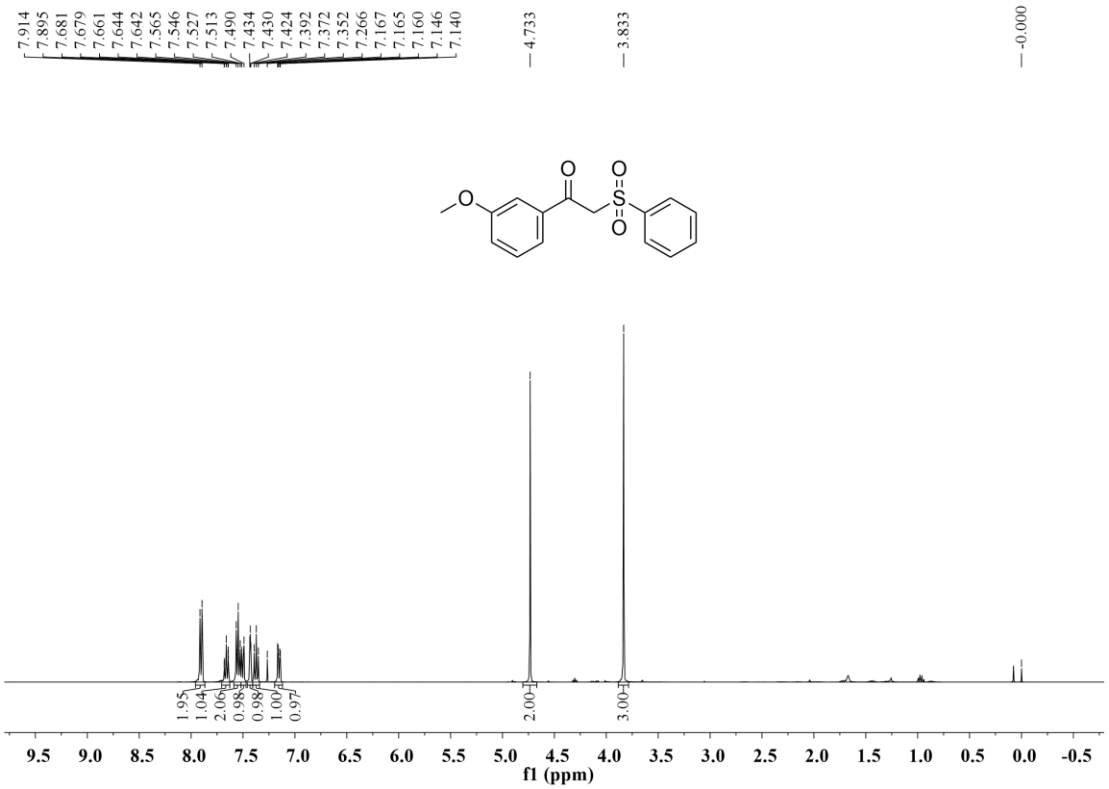
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4.733
3.833
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O
O
S
O
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3.00
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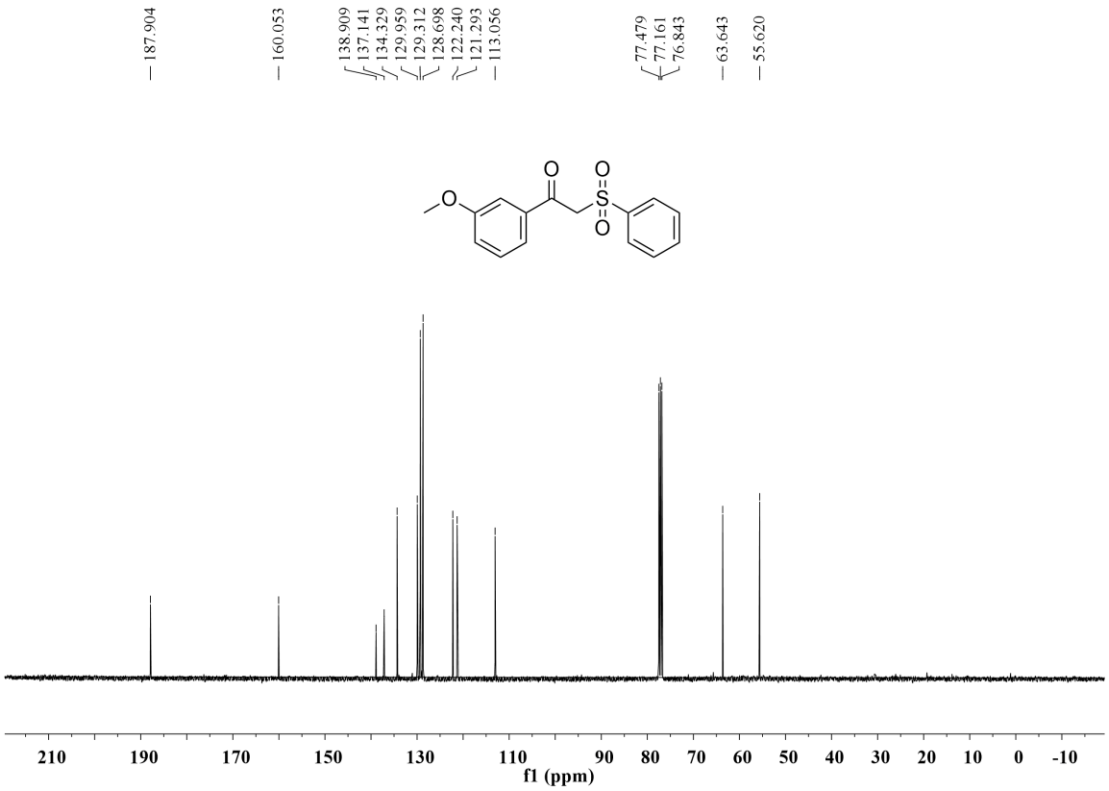
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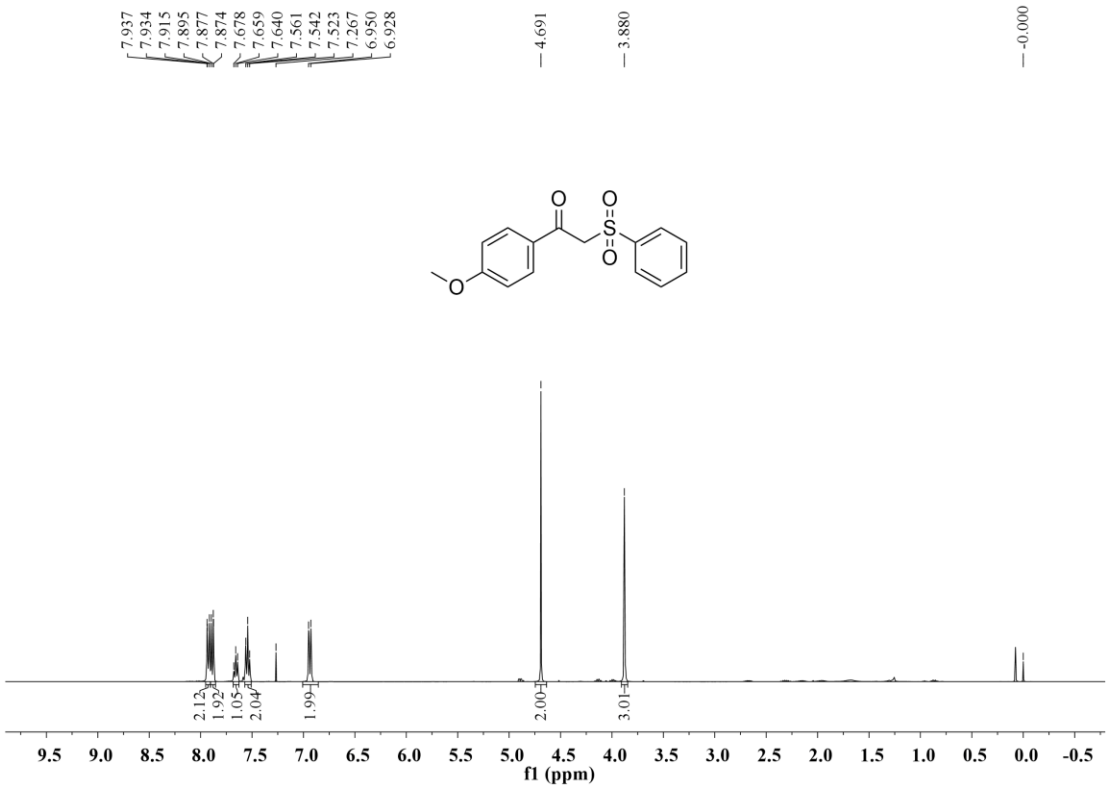
f1 (ppm)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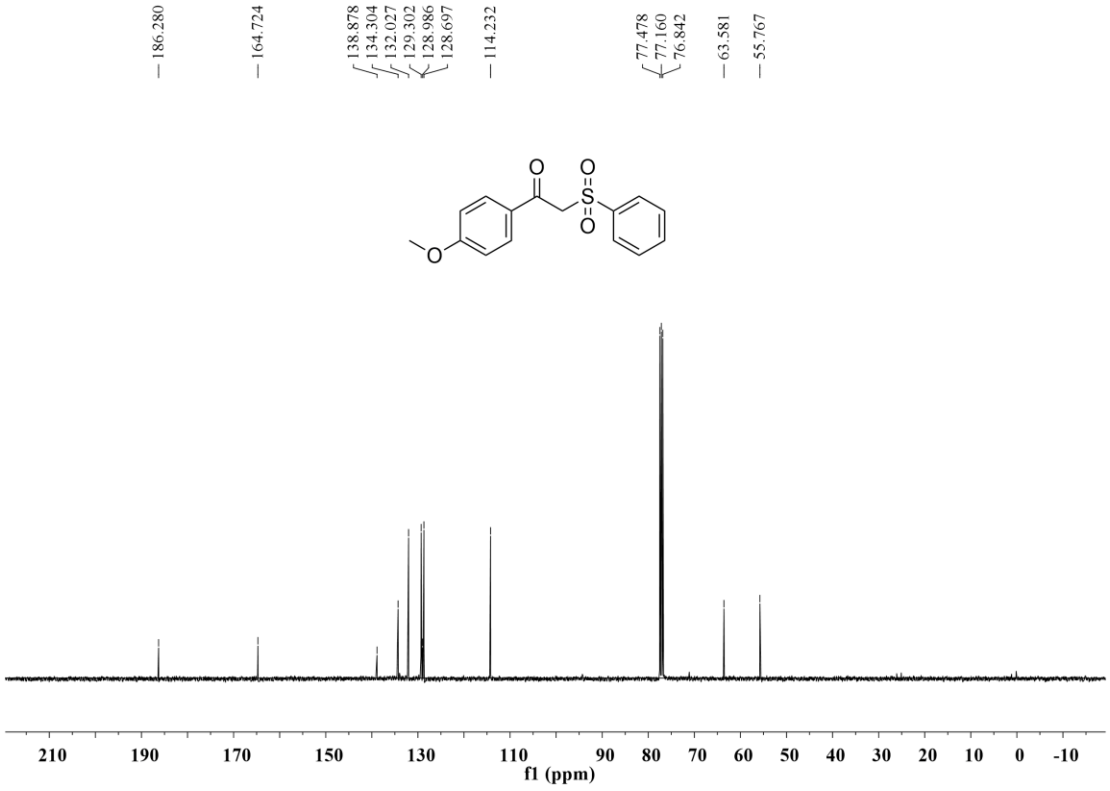
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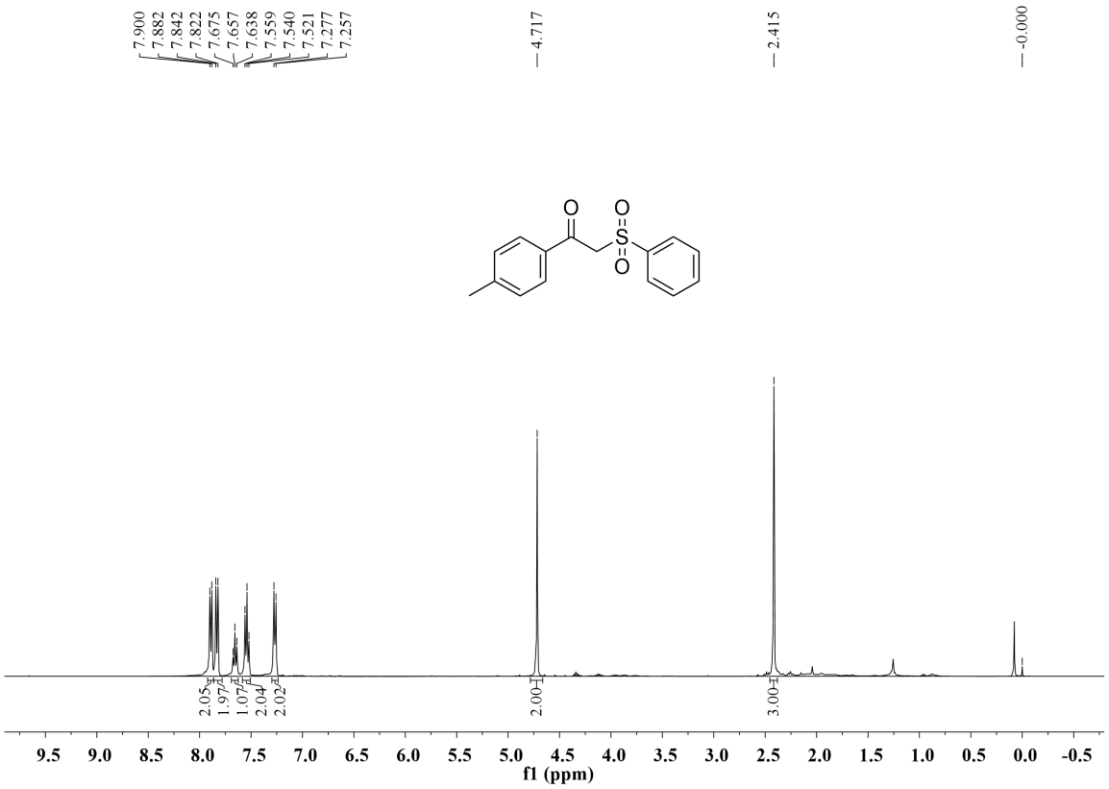
f1 (ppm)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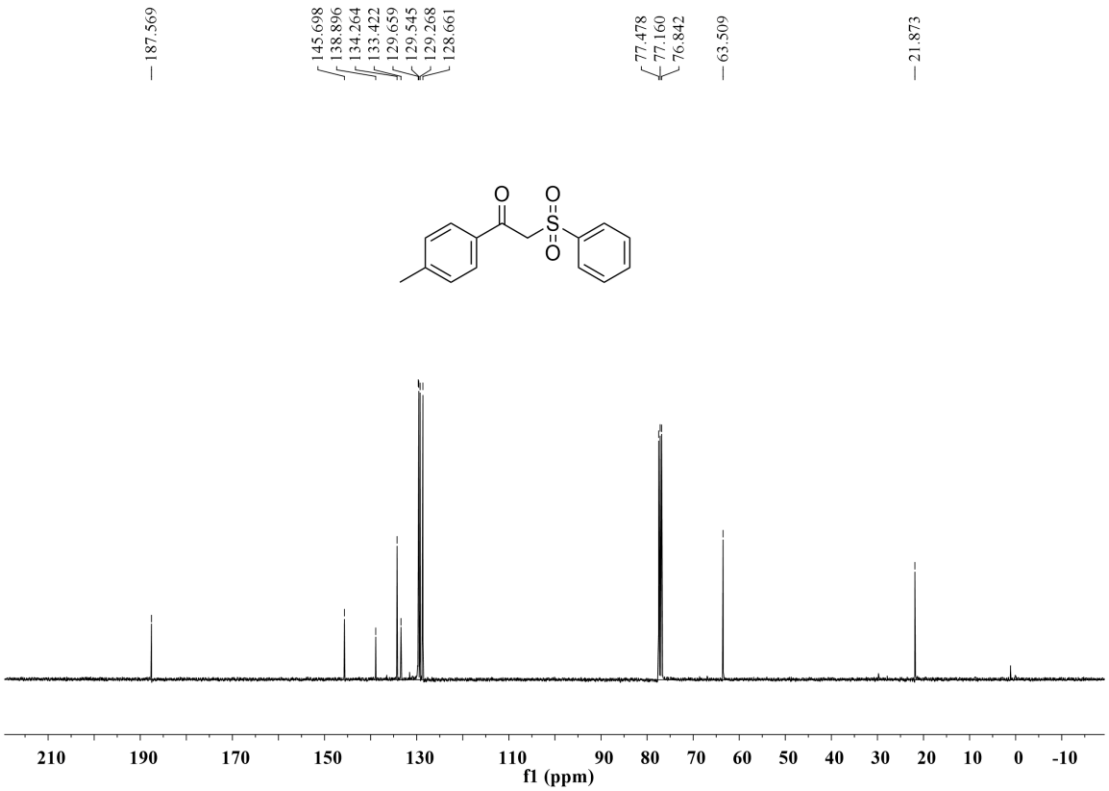
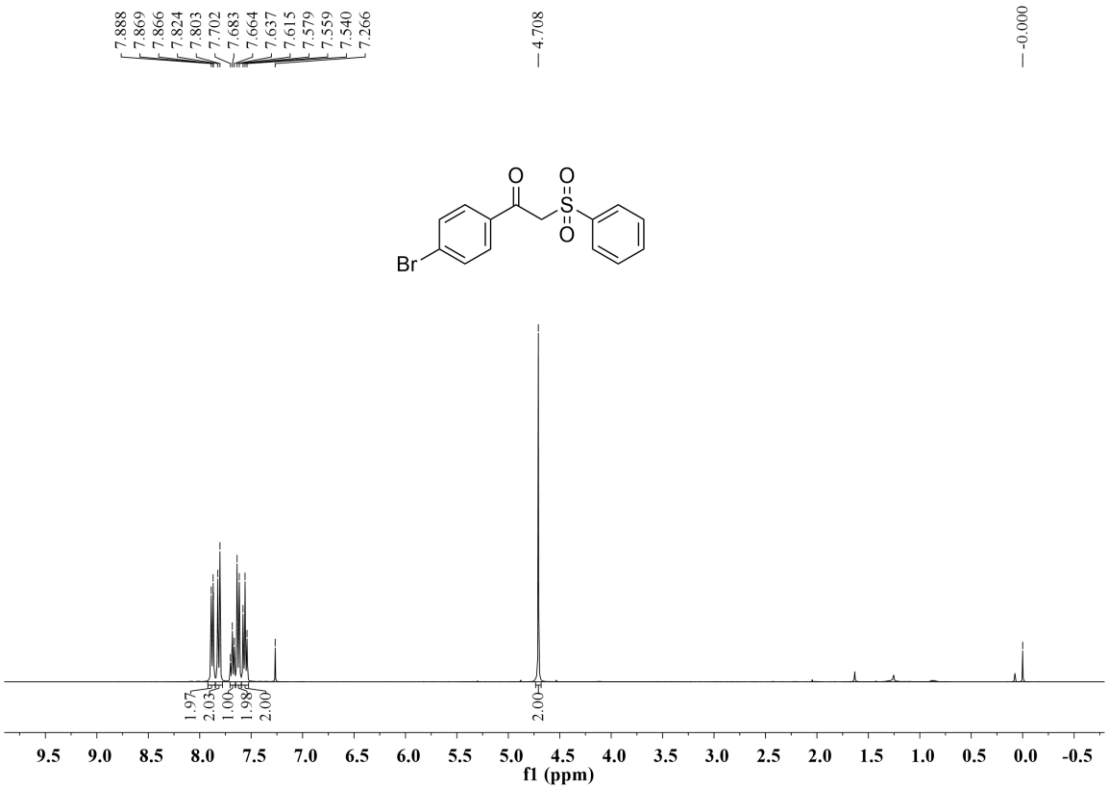
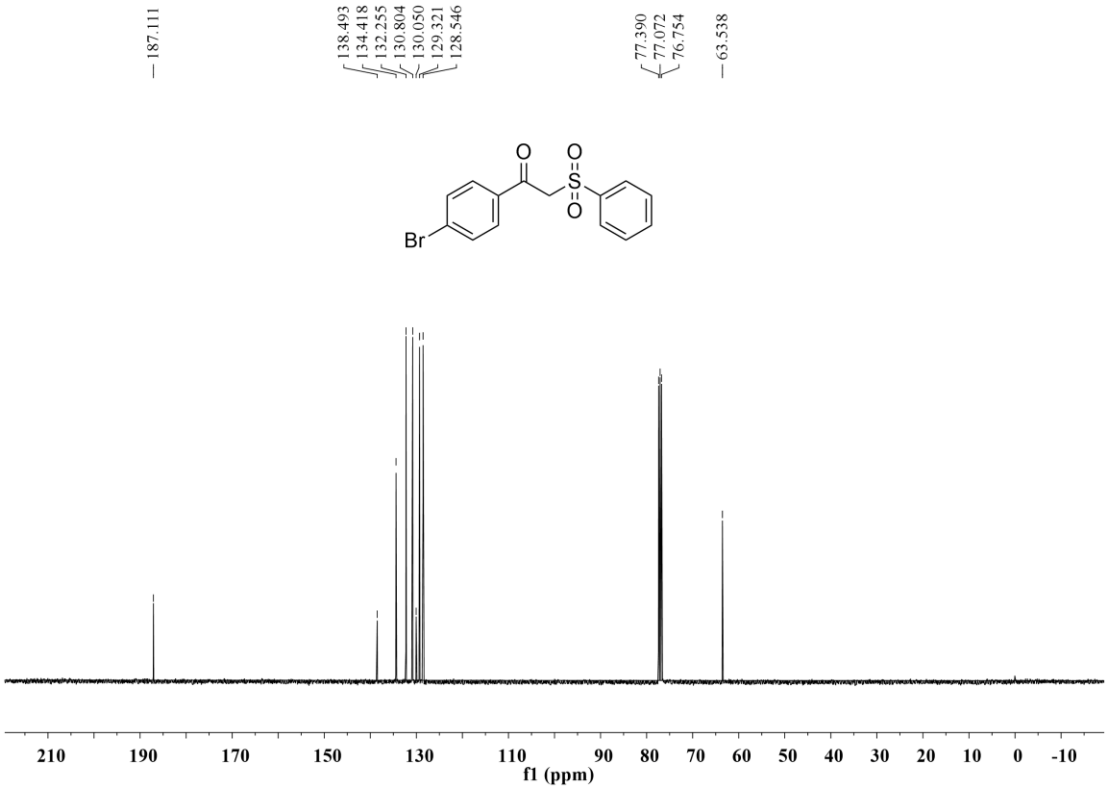
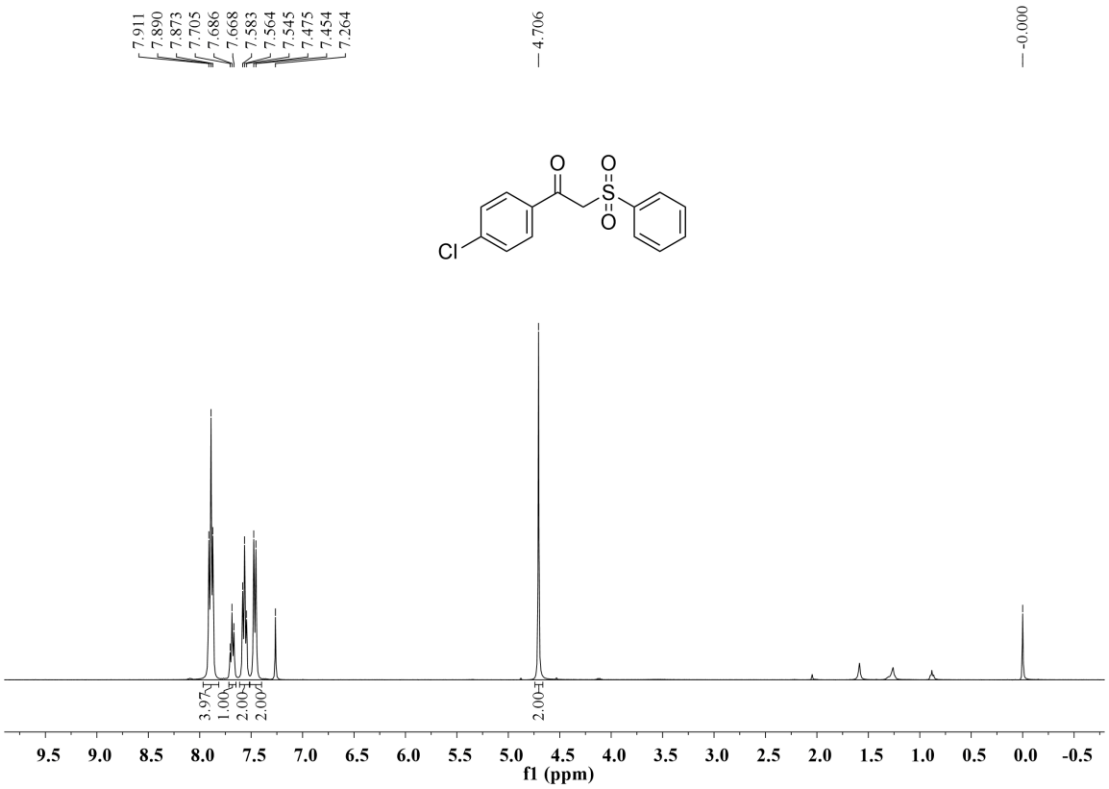
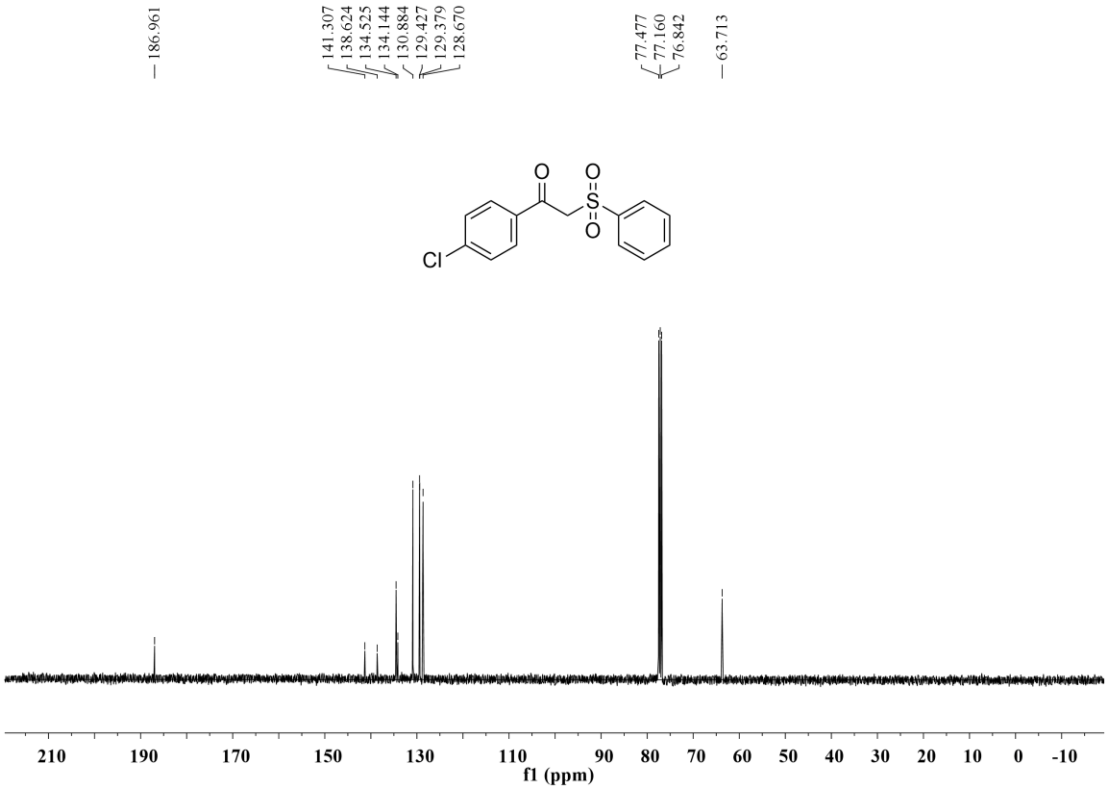
2.415
0.000
2.05
1.97
1.07
2.04
2.02
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

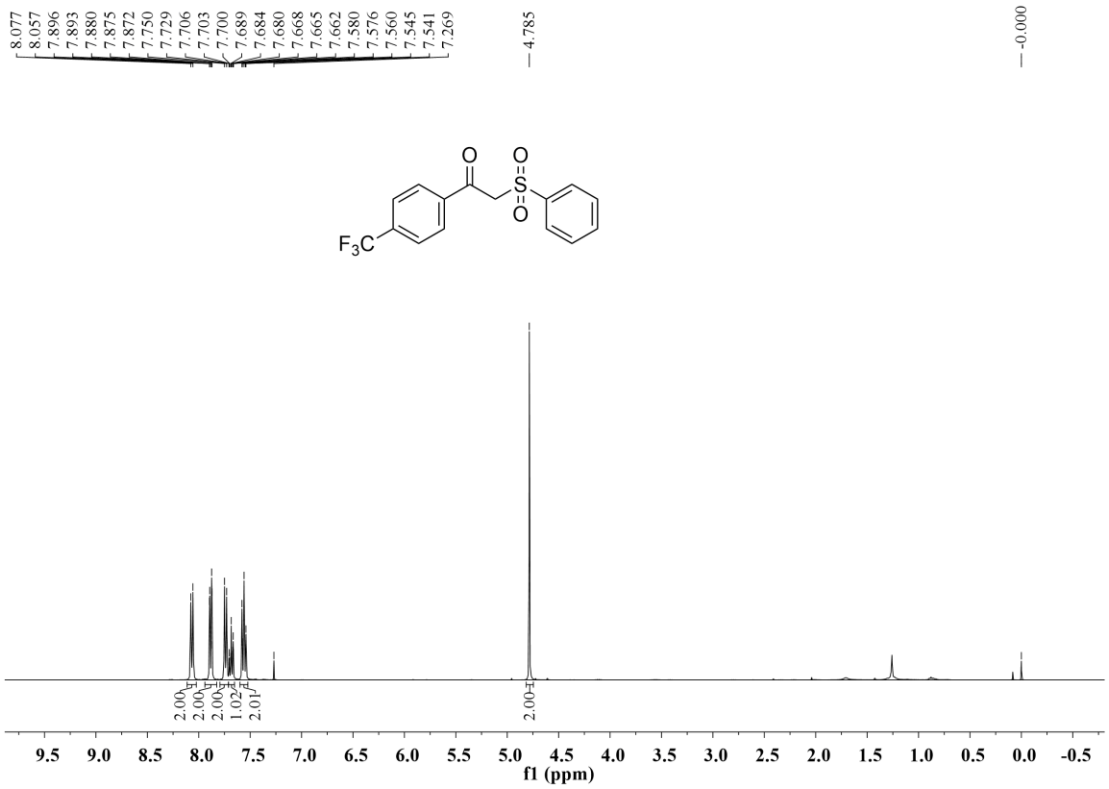

187.569
145.698
138.896
134.264
133.422
129.659
129.545
129.268
128.661
77.478
77.160
76.842
63.509
21.873
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

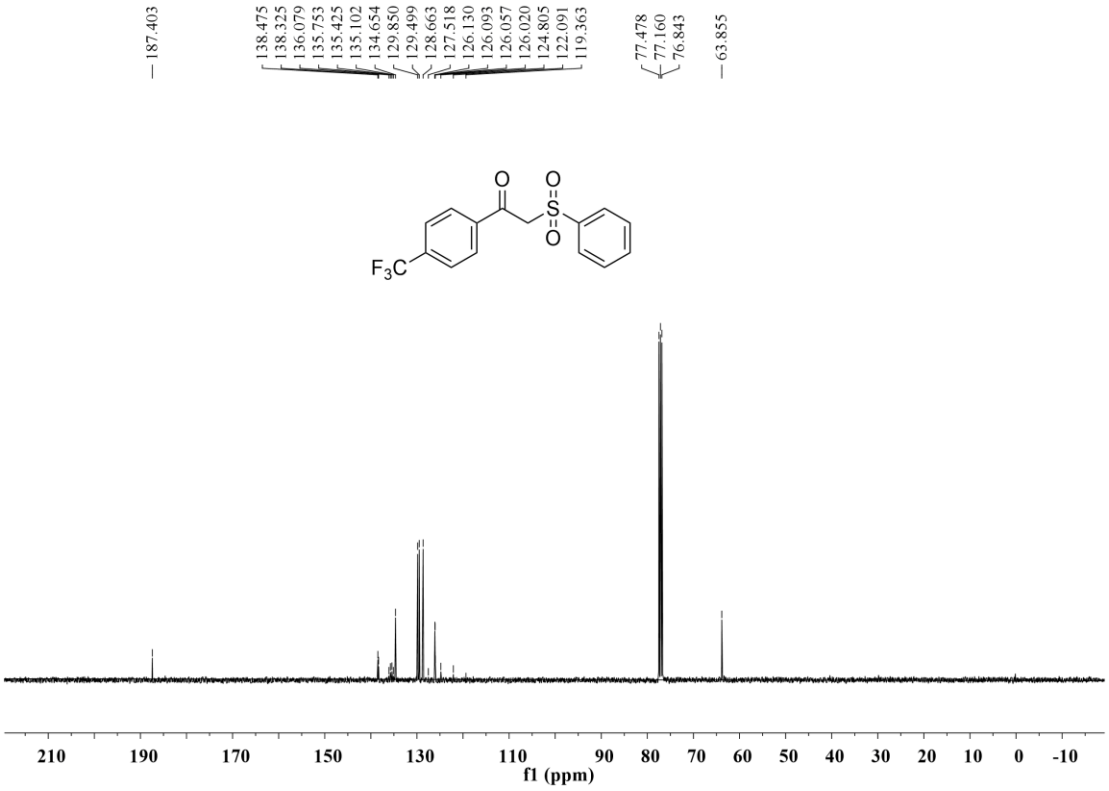

7.888
7.869
7.866
7.824
7.803
7.702
7.683
7.664
7.637
7.615
7.579
7.559
7.540
7.266
4.708
0.000
O
O
S
O
Br
1.97
2.03
1.00
1.98
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

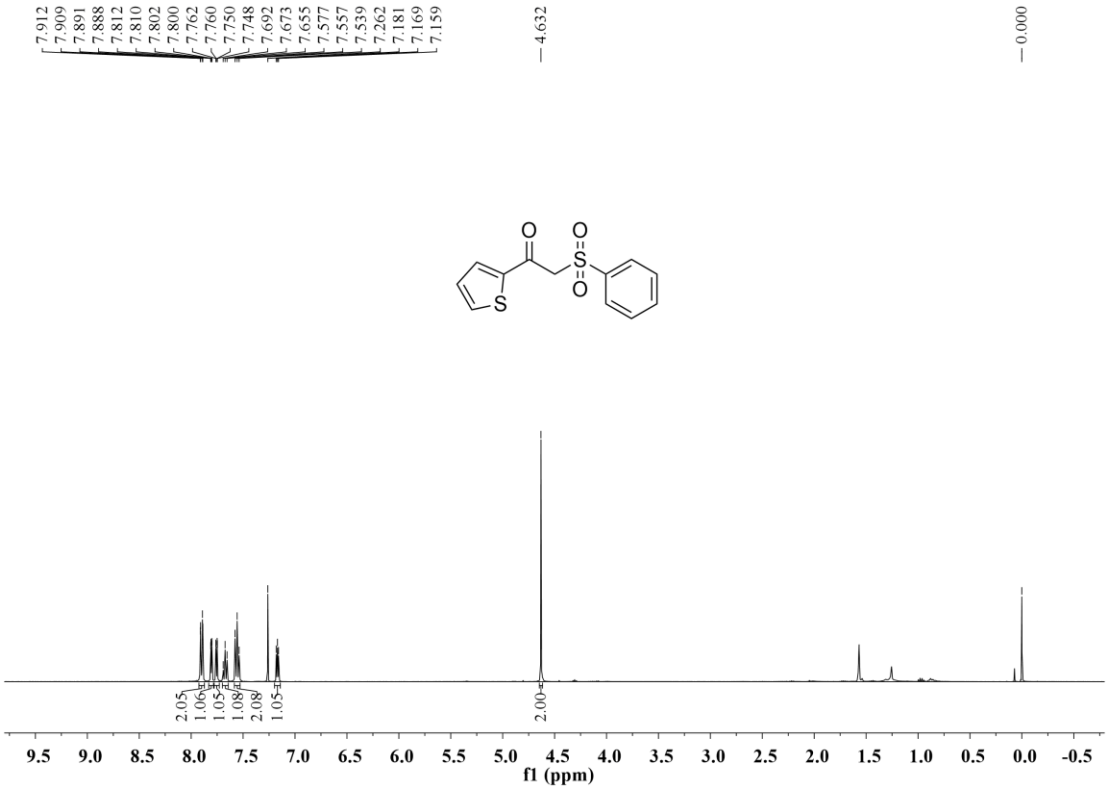

187.111
138.493
134.418
132.255
130.804
130.050
129.321
128.546
77.390
77.072
76.754
63.538
O
O
S
O
Br
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

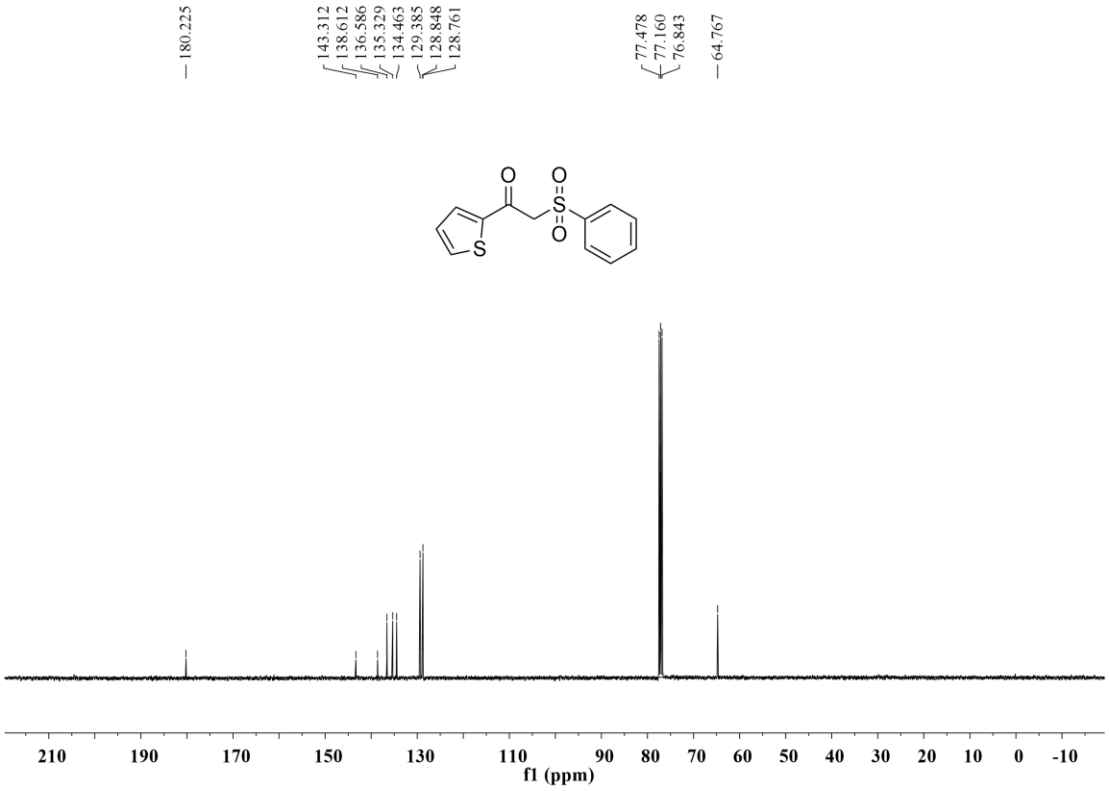

7.911
7.890
7.873
7.705
7.686
7.668
7.583
7.564
7.545
7.475
7.454
7.264
4.706
-0.000
O
O
S
O
Cl
3.97
1.00
2.00
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

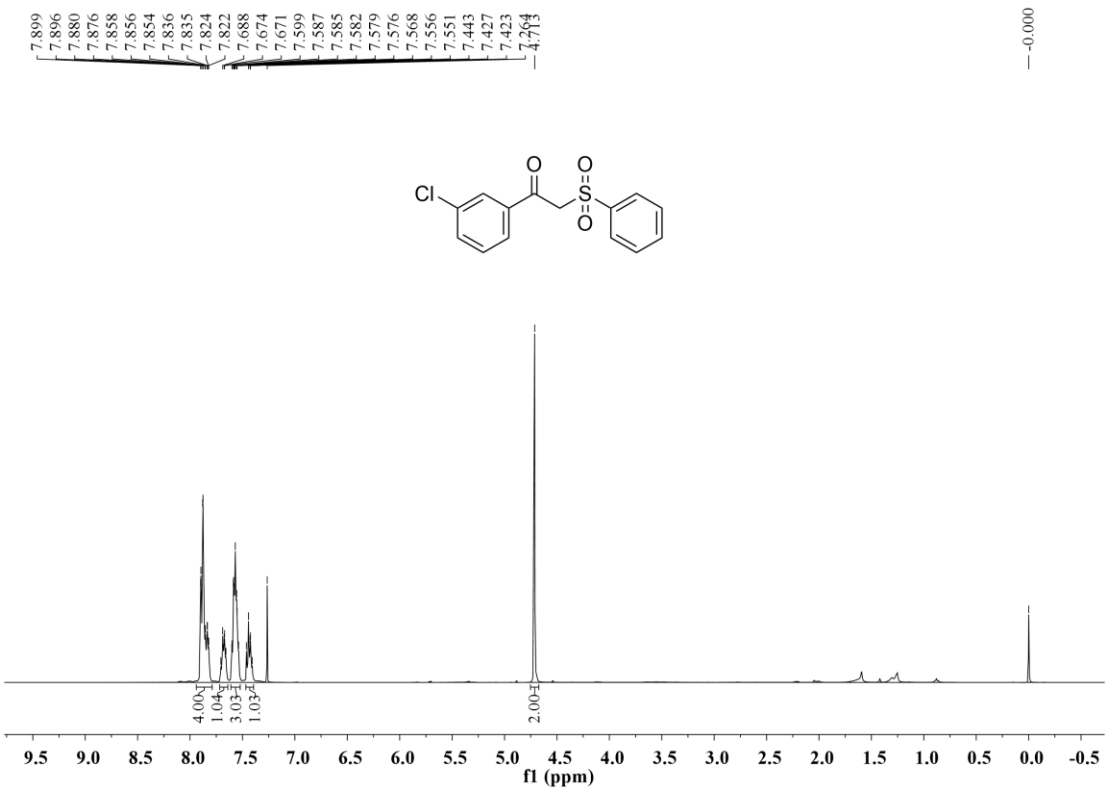

186.961
141.307
138.624
134.525
134.144
130.884
129.427
129.379
128.670
77.477
77.160
76.842
63.713
O
O
S
O
Cl
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

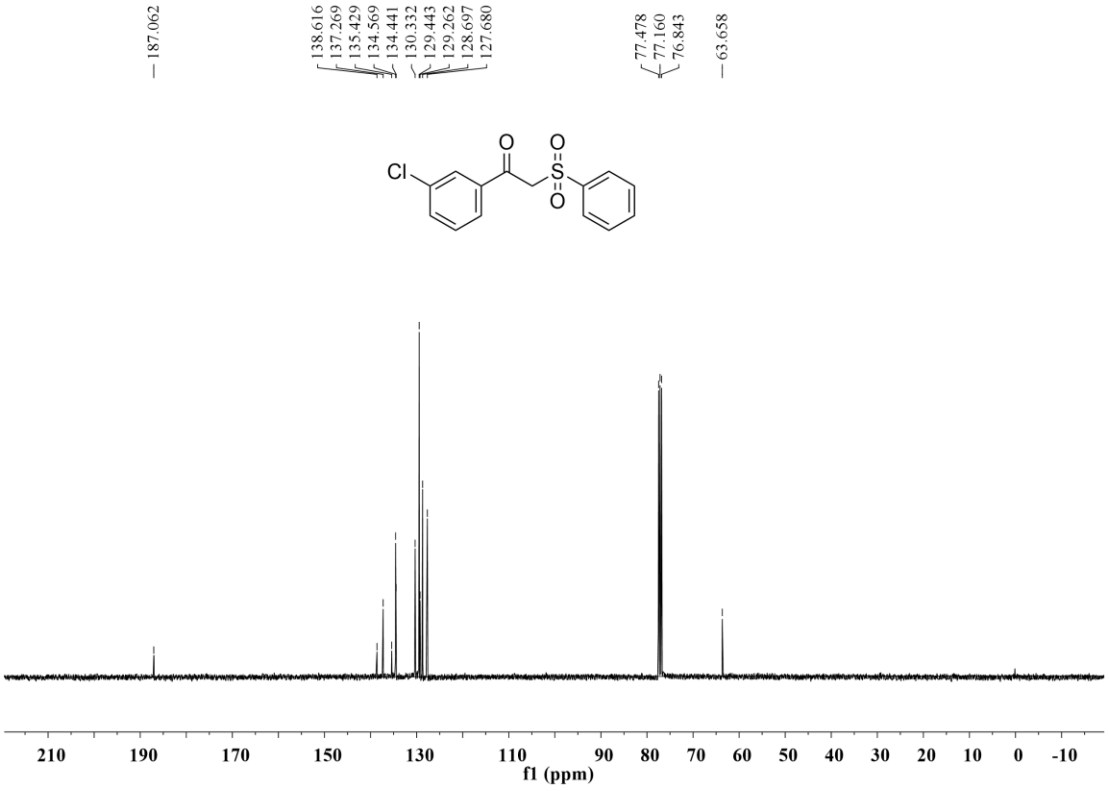

8.077
8.057
7.896
7.893
7.880
7.875
7.872
7.750
7.729
7.706
7.703
7.700
7.689
7.684
7.680
7.668
7.665
7.662
7.580
7.576
7.560
7.545
7.541
7.269
4.785
-0.000
O
O
S
O
F3C
2.00
2.00
2.00
1.02
2.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

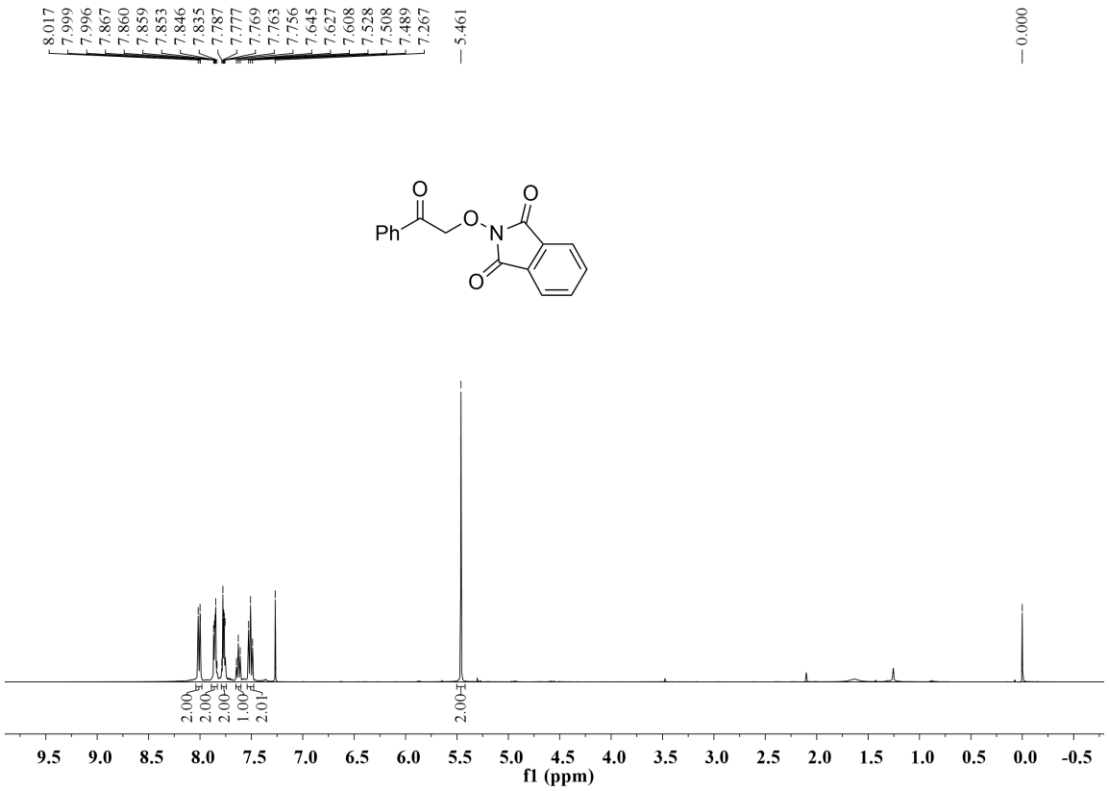

187.403
138.475
138.325
136.079
135.753
135.425
135.102
134.654
129.850
129.499
128.663
127.518
126.130
126.093
126.057
126.020
124.805
122.091
119.363
77.478
77.160
76.843
63.855
O
O
S
O
F3C
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

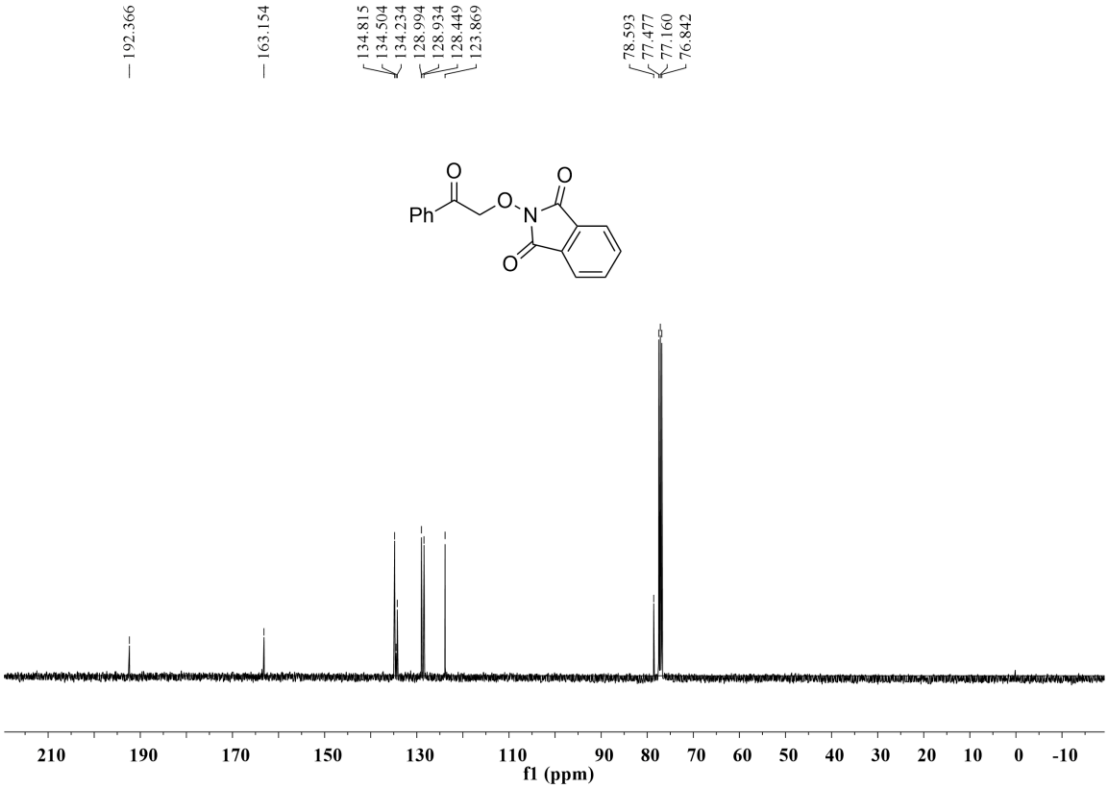

7.912
7.909
7.891
7.888
7.812
7.810
7.802
7.800
7.762
7.760
7.750
7.748
7.692
7.673
7.655
7.577
7.557
7.539
7.262
7.181
7.169
7.159
4.632
0.000
O
O
S
O
S
2.05
1.06
1.05
1.08
2.08
1.05
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


180.225
143.312
138.612
136.586
135.329
134.463
129.385
128.848
128.761
77.478
77.160
76.843
64.767
O
O
S
O
S
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.899
7.896
7.880
7.876
7.858
7.856
7.854
7.836
7.835
7.824
7.822
7.688
7.674
7.671
7.599
7.587
7.585
7.582
7.579
7.576
7.568
7.556
7.551
7.443
7.427
7.423
7.264
4.713
-0.000
Cl
O
O
S
O
4.00
1.04
3.03
1.03
2.00
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)


187.062
138.616
137.269
135.429
134.569
134.441
130.332
129.443
129.262
128.697
127.680
77.478
77.160
76.843
63.658
Cl
O
O
S
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.017
7.999
7.996
7.867
7.860
7.859
7.853
7.846
7.835
7.787
7.777
7.769
7.763
7.756
7.645
7.627
7.608
7.528
7.508
7.489
7.267
5.461
0.000
Ph
O
N
2.00
2.00
2.00
1.00
2.01
2.00
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)


192.366
163.154
134.815
134.504
134.234
128.994
128.934
128.449
123.869
78.593
77.477
77.160
76.842
Ph
O
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)