Supporting Information

Operando X-ray absorption and EPR evidence for a single electron redox process in copper catalysis

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1. Details of the Decarboxylative Sulfonylation/Oxygenation Reactions

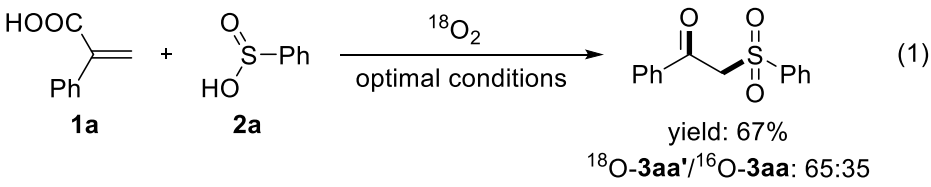
General Information

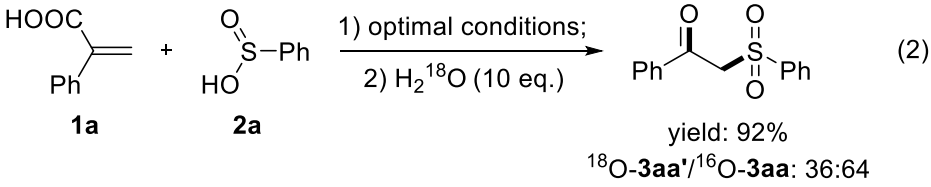
All reactions were carried out under a dry air atmosphere with a dry air balloon fitted on a Schlenk tube. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. N, N-Dimethylformamide was purified by distillation with calcium(II) hydride. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. 2-Arylacrylic acids[1] and sulfinic acids[2] were prepared following literature procedures. 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). EPR spectra were recorded on a Bruker A-200 spectrometer. EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. XANES measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. 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 and ^{19}F NMR. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), DMSO-d_6 (2.50 ppm for ^{1}H), and $CDCl_3$ (77.16 ppm for ^{13}C), respectively. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the pseudo molecular ion ($[M+H]^+$).

General Procedure for the Preparation of β-Keto Sulfones

2-Arylacrylic acid (0.2 mmol), sulfinic acid (0.6 mmol) and $CuBr_2$ (4.5 mg, 0.02 mmol) were placed in an oven-dried Shlenck tube equipped with a stir bar, and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. DMF (2.0 mL) was then injected and the mixture was stirred at room temperature for 2 h. Upon completion, the reaction mixture was quenched by saturated sodium bicarbonate solution and the suspension was extracted with ethyl acetate (4 x 15 mL), the organic layers were combined, and dried over sodium sulfate. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give the desired product **3**.

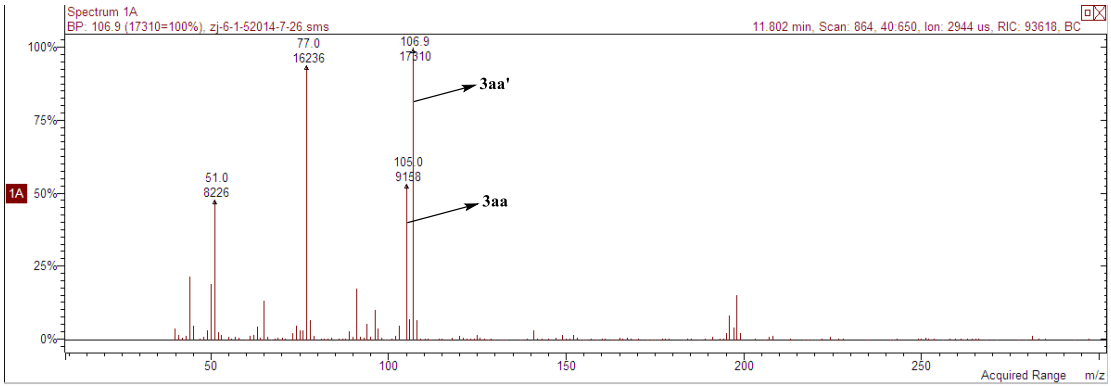
^{18}O labeling experiments

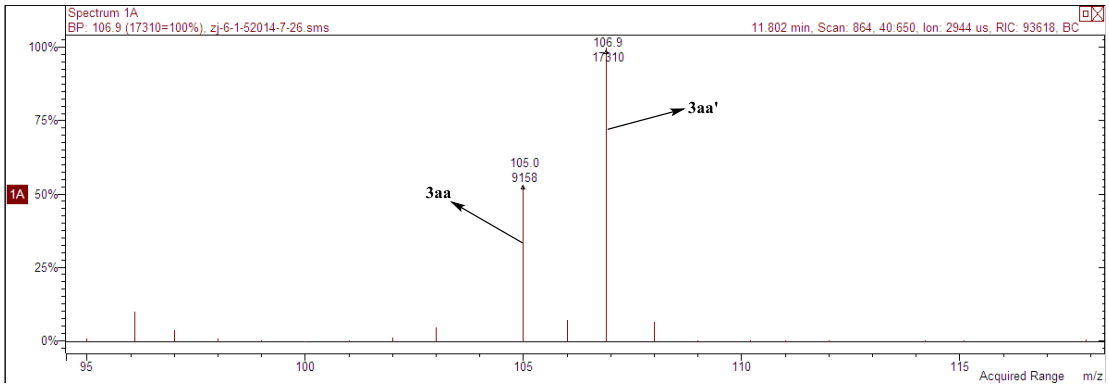




Typical procedure for $^{18}O_2$ labeling experiment (eq 1): An oven-dried Schlenk tube equipped with a stir bar were capped by septa for injections and a three way cock which was connected to a nitrogen line and a balloon filled with $^{18}O_2$ respectively. After evacuation under vacuum and flushing with N_2 for one time, 2-phenylacrylic acid (0.2 mmol), benzenesulfinic acid (0.6 mmol) and $CuBr_2$ (0.02 mmol) was quickly added under N_2, and the reaction mixture was cooled with liquid nitrogen. DMF (2.0 mL) was further injected into the reaction tube, and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 5 times. $^{18}O_2$ was purged one time afterwards, and the reaction mixture was vigorous stirred at room temperature for 2 h. Upon completion, the reaction mixture was analyzed by GC-MS immeditately. Then, the reaction mixture was quenched by saturated sodium bicarbonate solution and the suspension was extracted with ethyl acetate (4 x 15 mL), the organic layers were combined, and dried over sodium sulfate. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the desired products. Isolated yeild: 67%.

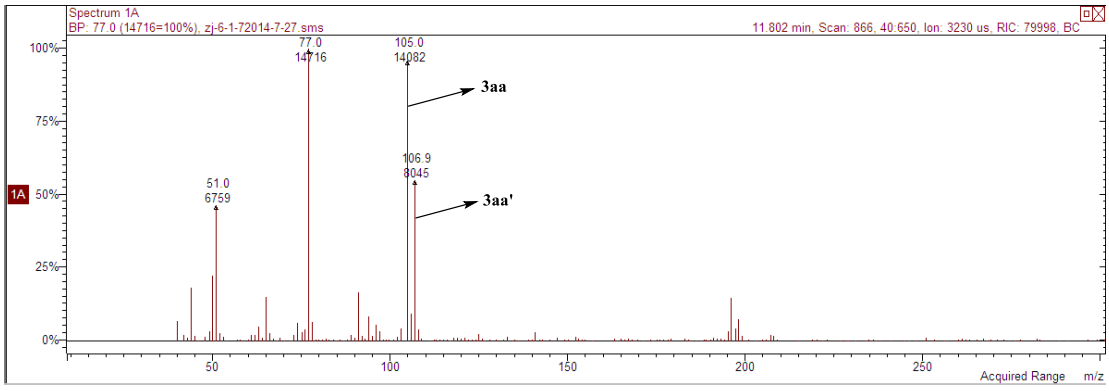
The EI-MS spectra of the products

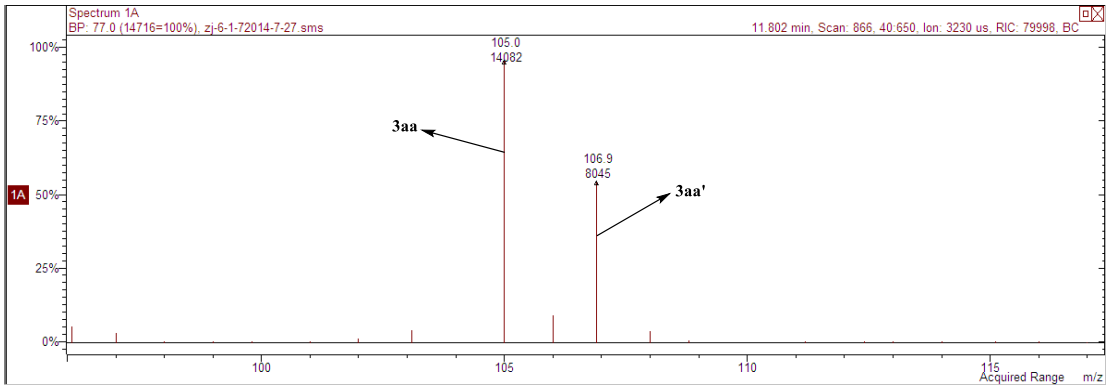




Typical procedure for $H_2{}^{18}O$ labeling experiment (eq 2): 2-Phenylacrylic acid (0.2 mmol), benzenesulfinic acid (0.6 mmol) and $CuBr_2$ (4.5 mg, 0.02 mmol) were placed in an oven-dried Shlenck tube equipped with a stir bar, and a balloon filled with dry air was connected to the Schlenk tube through the side arm and purged one time. DMF (2.0 mL) was then added and the mixture was stirred at room temperature for 2 h. At the end of the reaction, $H_2{}^{18}O$ (2.0 mmol) was injected into the reaction tube and keeping the reaction continuing for 2 h. Then, the reaction mixture was analyzed by GC-MS first, and the reaction mixture was quenched by saturated sodium bicarbonate solution and the suspension was extracted with ethyl acetate (4 x 15 mL), the organic layers were combined, and dried over sodium sulfate. After removal of the solvent in vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to afford the desired products. Isolated yeild: 92%.

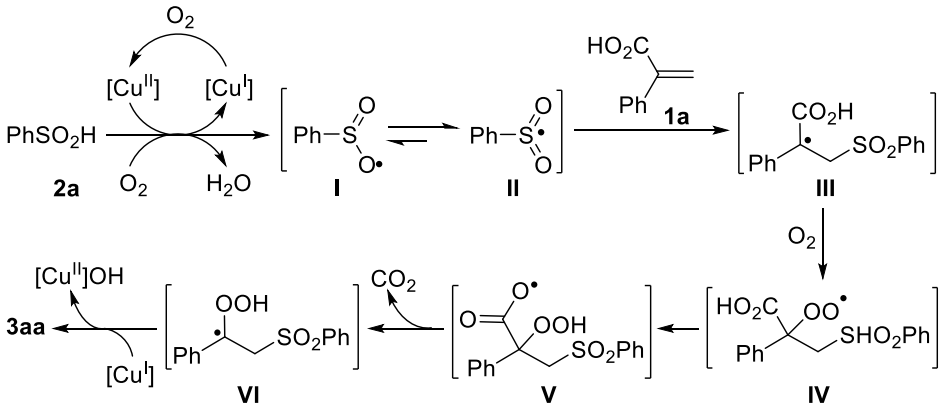
The EI-MS spectra of the products





Proposed Mechanism

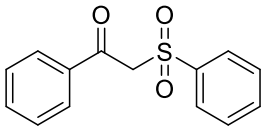
A tentative mechanism for the oxysulfonylation of 2-arylacrylic acids is shown as follow:



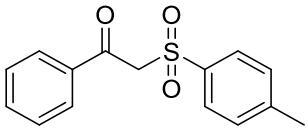
Scheme S1. Tentative mechanism for the oxysulfonylation of 2-arylacrylic acids

Initially, benzenesulfinic acid was activated by copper(II) salt and dioxygen via the single electron transfer (SET) and concomitant proton transfer (PT) to produce an oxygen-centered radical **I,** resonating with sulfonyl radical **II**. Subsequently, the addition of sulfonyl radical to 2-arylacrylic acid (**2a**) generated a carbon-centered radical **III**, which could be further trapped by dioxygen to form the peroxy radical **IV**. Afterwards, an intramolecular hydrogen atom transfer through redox process took place to afford intermediate **V**. Then the generated intermediate **V** experienced a radical decarboxylative process to release CO_2 and the alkyl radical **VI**, followed by fragmentation to give β-keto sulfone **3aa**. The copper salts might also interact with intermediate **IV** and **V** to facilitate the C-C cleavage process.

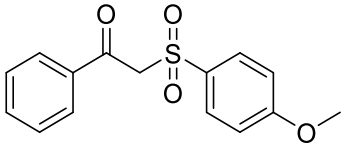
Characterization of Products



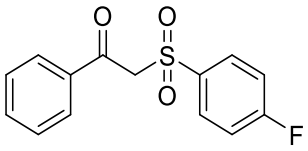
1-Phenyl-2-(phenylsulfonyl)ethan-1-one (3aa).[3] white solid was obtained with 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.66-7.58 (m, 2H), 7.56-7.51 (m, 2H), 7.50-7.41 (m, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 138.8, 135.7, 134.5, 134.3, 129.3, 129.3, 128.9, 128.6, 63.4.



1-Phenyl-2-tosylethan-1-one (3ab).[3] white solid was obtained with 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 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, 134.5, 130.0, 129.5, 129.0, 128.7, 63.7, 21.8.

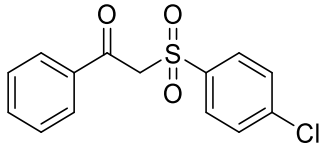


2-((4-Methoxyphenyl)sulfonyl)-1-phenylethan-1-one (3ac).[3] white solid was obtained with 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.82-7.78 (m, 2H), 7.64-7.59 (m, 1H), 7.50-7.46 (m, 2H), 7.00-6.96 (m, 2H), 4.72 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 164.2, 135.9, 134.4, 131.0, 30.3, 129.4, 129.0, 114.5, 63.8, 55.8.

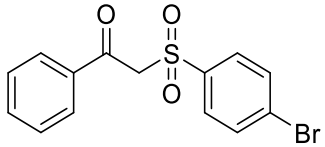


2-((4-Fluorophenyl)sulfonyl)-1-phenylethan-1-one (3ad).[3] white solid was obtained with 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (m, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 8.6 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ188.1, 166.2 (d,

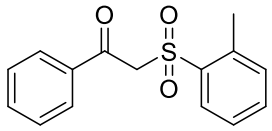
$^{1}J_{C\text{-}F}$ = 258.2 Hz), 135.7, 134.8 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 134.6, 131.8 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 129.3, 129.0, 116.6 (d, $^{2}J_{C\text{-}F}$ = 22.8 Hz), 63.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.36 ppm.



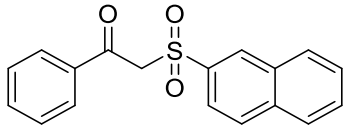
2-((4-Chlorophenyl)sulfonyl)-1-phenylethan-1-one (3ae).[3] white solid was obtained with 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.85-7.82 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53-7.48 (m, 4H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 141.2, 137.2, 135.7, 134.7, 130.3, 129.7, 129.4, 129.1, 63.4.



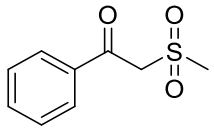
2-((4-Bromophenyl)sulfonyl)-1-phenylethan-1-one (3af).[3] white solid was obtained with 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 4.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.0, 137.7, 135.6, 134.7, 132.6, 130.3, 129.9, 129.4, 129.0, 63.4.



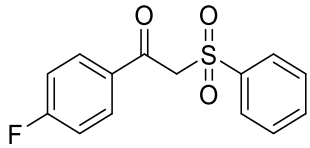
1-Phenyl-2-(o-tolylsulfonyl)ethan-1-one (3ag).[4] white solid was obtained with 64% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98-7.95 (m, 2H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70-7.65 (m, 1H), 7.61 (td, *J* = 7.4, 1.4 Hz, 1H), 7.54-7.50 (m, 2H), 7.46-7.40 (m, 2H), 5.26 (s, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 138.5, 137.0, 135.9, 134.5, 134.4, 132.9, 130.7, 129.5, 129.0, 126.7, 63.0, 20.7.



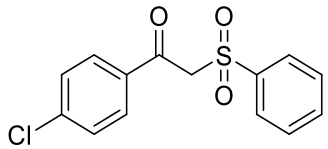
2-(Naphthalen-2-ylsulfonyl)-1-phenylethan-1-one (3ah).[5] white solid was obtained with 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00-7.91 (m, 5H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.69-7.57 (m, 3H), 7.45 (t, *J* = 7.2 Hz, 2H), 4.82 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 135.8, 135.7, 135.6, 134.5, 132.1, 130.8, 129.7, 129.7, 129.6, 129.4, 129.0, 128.1, 127.9, 123.1, 63.6.



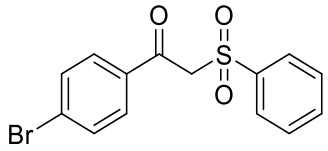
2-(Methylsulfonyl)-1-phenylethan-1-one (3ai).[6] white solid was obtained with 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 4.61 (s, 2H), 3.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 135.7, 134.9, 129.4, 129.2, 61.4, 41.9.



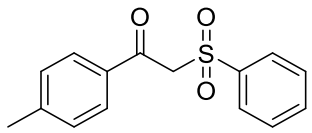
1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (3ba).[3] white solid was obtained with 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 166.6 (d, $^{1}J_{C\text{-}F}$ = 258.7 Hz), 138.6, 134.5, 132.4, 132.3, 129.4, 128.7, 116.3 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 63.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.24 ppm.



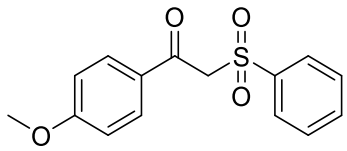
1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one (3ca).[3] white solid was obtained with 84% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.91-7.89 (m, 2H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.65-7.58 (m, 4H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.0, 141.3, 138.6, 134.5, 134.1, 130.9, 129.4(3), 129.3(8), 128.7, 63.7.



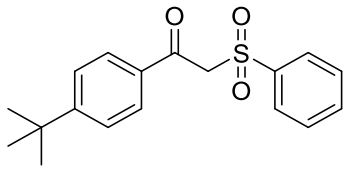
1-(4-Bromophenyl)-2-(phenylsulfonyl)ethan-1-one (3da).[3] white solid was obtained with 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 138.6, 134.5, 132.3, 130.9, 130.1, 129.4, 128.6, 63.6.



2-(Phenylsulfonyl)-1-(p-tolyl)ethan-1-one (3ea).[3] white solid was obtained with 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 7.28-7.26 (m, 2H), 4.72 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 145.8, 138.8, 134.3, 133.4, 129.7, 129.6, 129.3, 128.7, 63.5, 21.9.

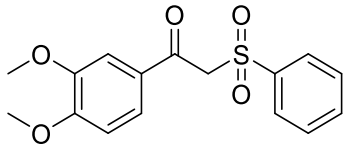


1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethan-1-one (3fa).[3] white solid was obtained with 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 4H), 7.65-7.63 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.93 (dd, *J* = 8.8, 1.2 Hz, 2H), 4.69 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3, 164.7, 138.9, 134.2, 132.0, 129.3, 128.9, 128.6, 114.2, 63.5, 55.7.

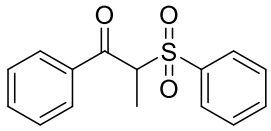


1-(4-(tert-Butyl)phenyl)-2-(phenylsulfonyl)ethan-1-one (3ga). pale yellow liquid was obtained with 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 4H), 7.65 (t, *J* = 6.8 Hz, 1H), 7.56-

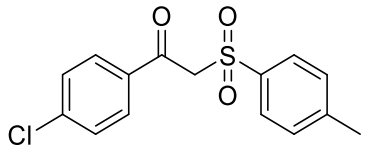
7.52 (m, 2H), 7.49-7.47 (m, 2H), 4.73 (s, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 158.5, 138.8, 134.3, 133.3, 129.4, 129.2, 128.7, 126.0, 63.4, 35.4, 31.1. HRMS (ESI) calcd for $[C_{18}H_{20}O_3S+H]^+$: 317.1167; found: 317.1213.



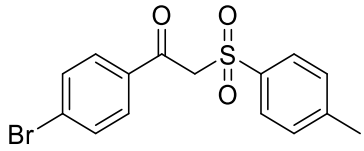
1-(3,4-Dimethoxyphenyl)-2-(phenylsulfonyl)ethan-1-one (3ha). colorless liquid was obtained with 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.89 (m, 2H), 7.69-7.65 (m, 1H), 7.61 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.58-7.54 (m, 2H), 7.47 (d, *J* = 2.0 Hz , 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.72 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.3, 154.6, 149.3, 138.8, 134.3, 129.3, 129.0, 128.7, 125.2, 110.7, 110.2, 63.4, 56.3, 56.1. HRMS (ESI) calcd for $[C_{16}H_{16}O_5S+H]^+$: 321.0752; found: 321.0786.



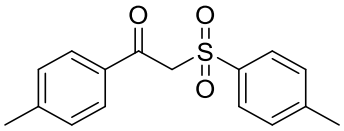
1-Phenyl-2-(phenylsulfonyl)propan-1-one (3ia).[3] white solid was obtained with 38% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03-8.01 (m, 2H), 7.80-7.78 (m, 2H), 7.77-7.73 (m, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 5.79 (q, *J* = 6.7 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.1, 137.2, 136.5, 134.8, 134.5, 129.7, 129.6, 129.5, 129.1, 64.0, 12.9.



1-(4-Chlorophenyl)-2-tosylethan-1-one (3cb).[6] white solid was obtained with 88% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.30 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 145.7, 141.2, 135.6, 134.2, 130.9, 130.0, 129.3, 128.7, 63.9, 21.9.



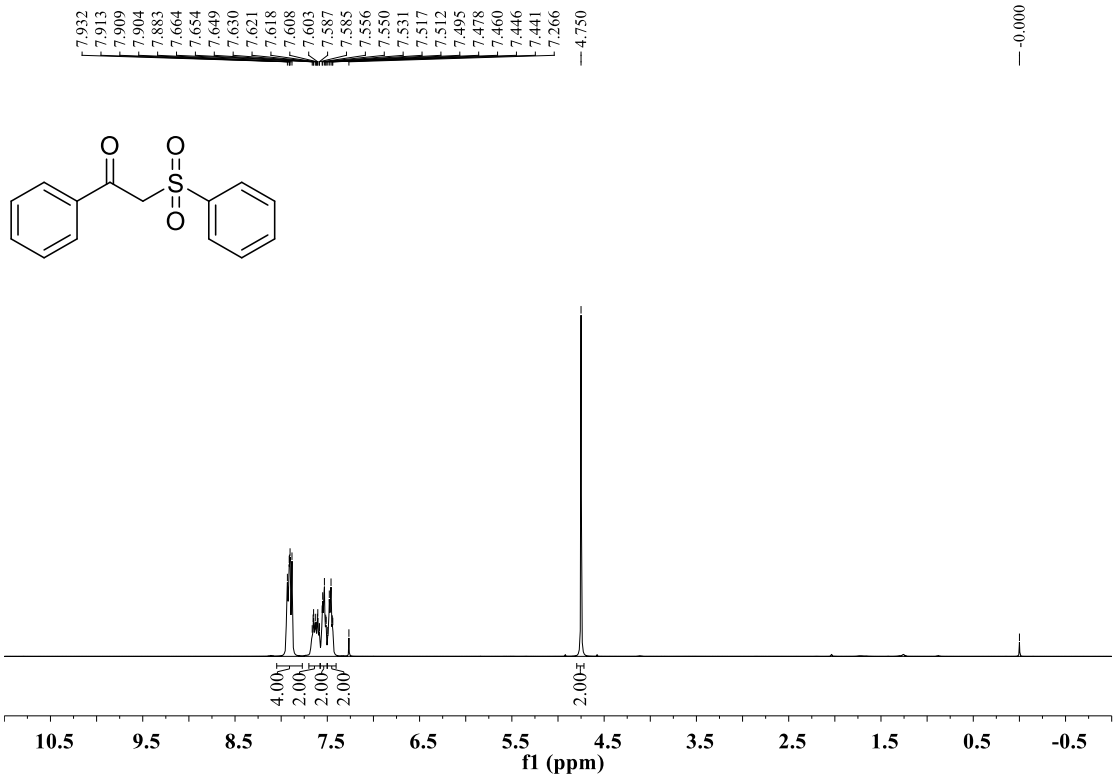
1-(4-Bromophenyl)-2-tosylethan-1-one (3db).[3] white solid was obtained with 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 145.7, 135.6, 134.6, 132.3, 130.9, 130.0, 128.7, 63.8, 21.9.



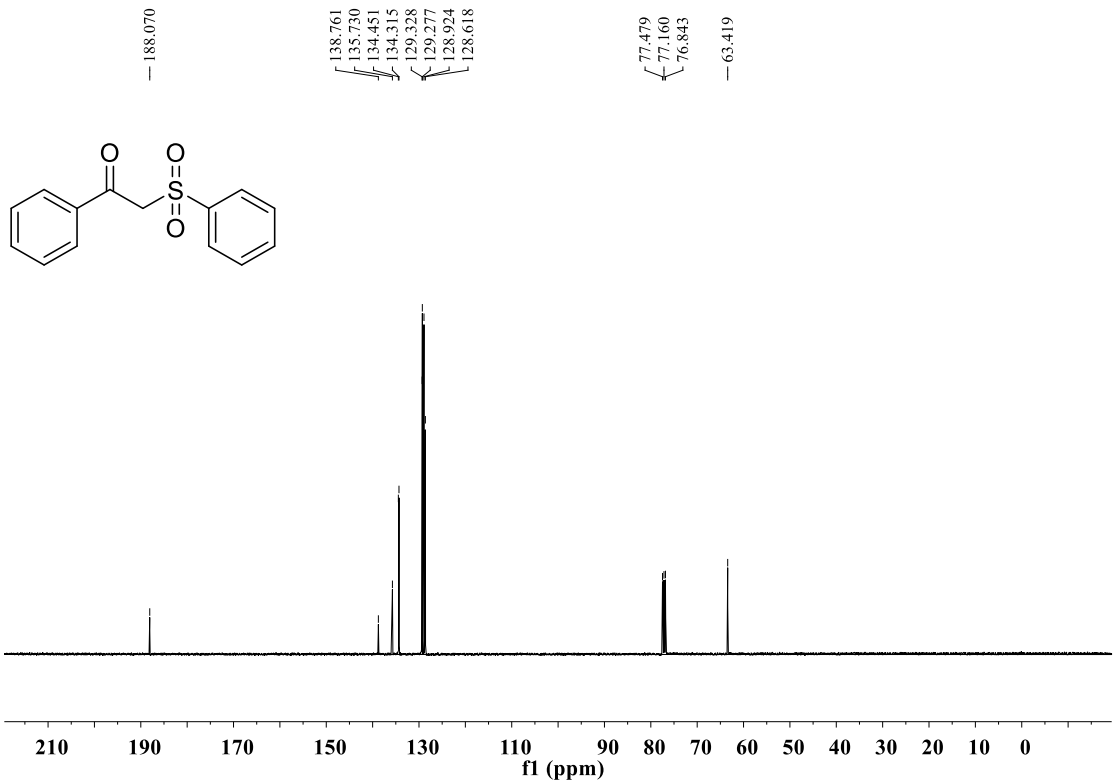
1-(p-Tolyl)-2-tosylethan-1-one (3eb).[7] white solid was obtained with 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 4.69 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 145.7, 145.4, 135.9, 133.5, 129.9, 129.7, 129.6, 128.7, 63.7, 22.0, 21.9.

NMR Spectra of Products

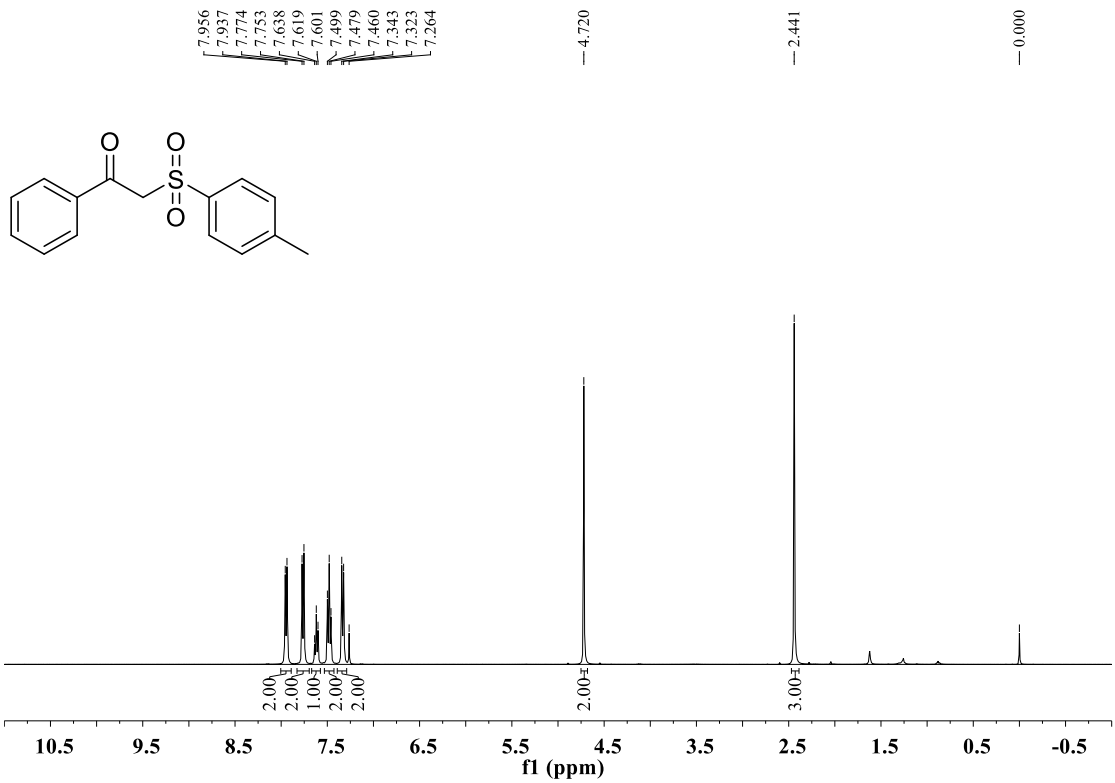
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



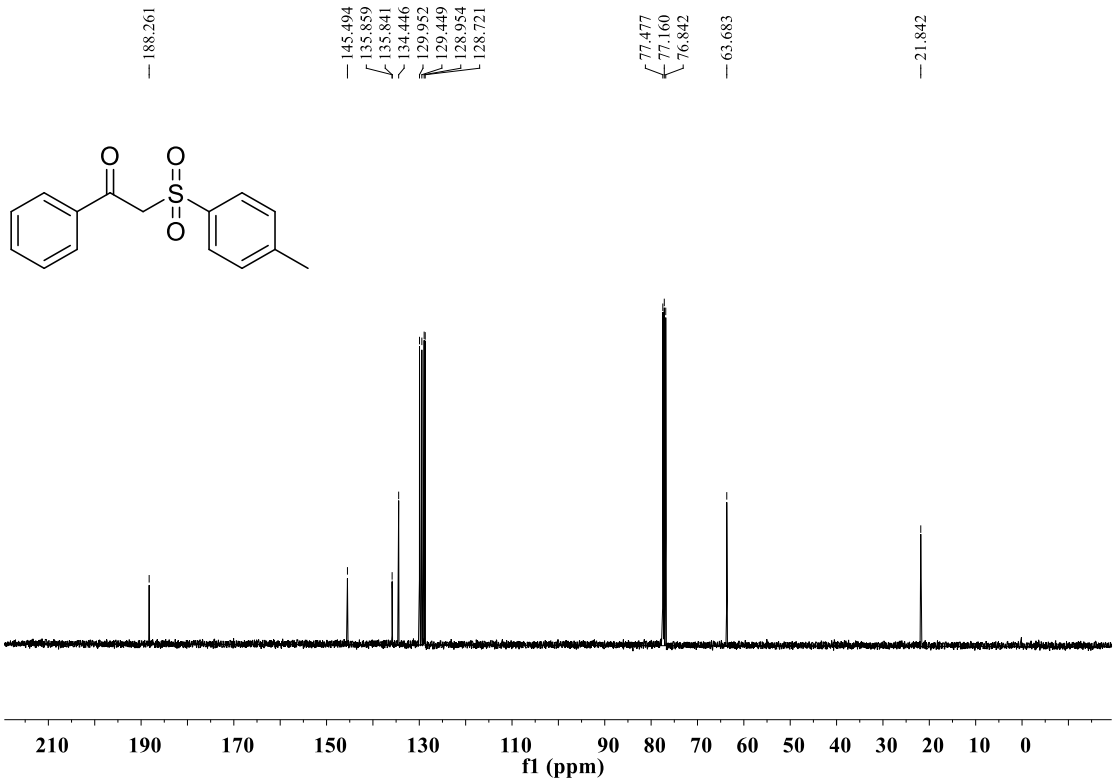
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3aa**



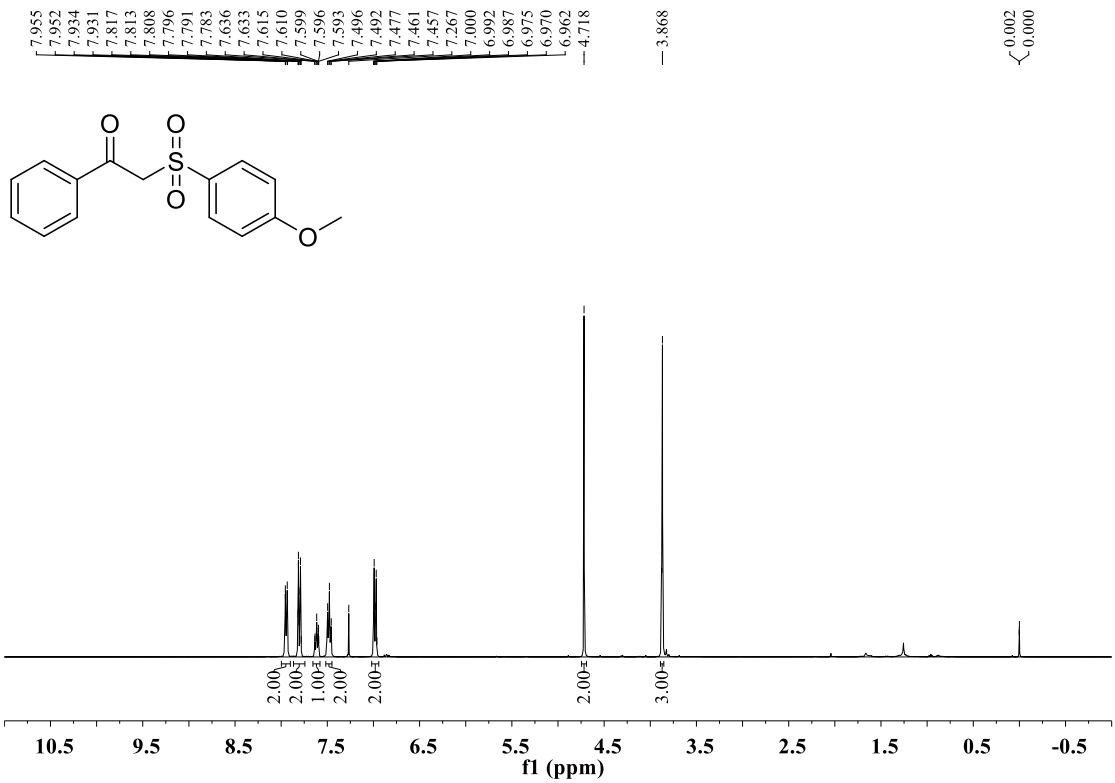
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



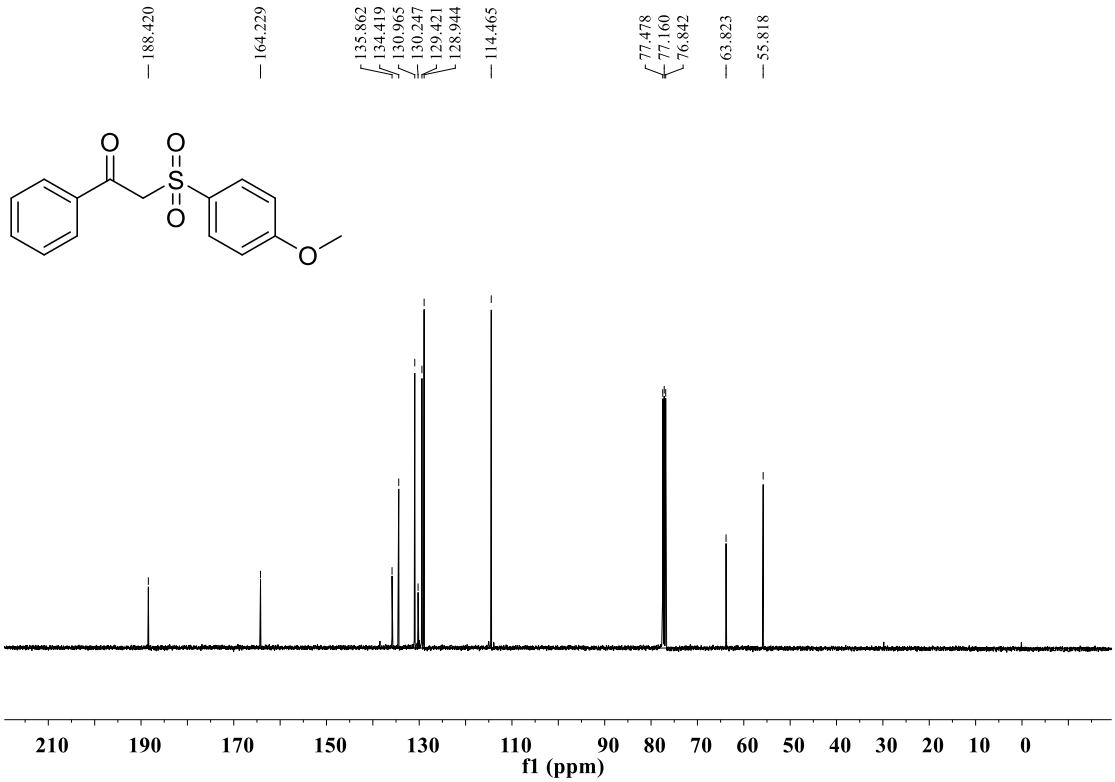
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ab**



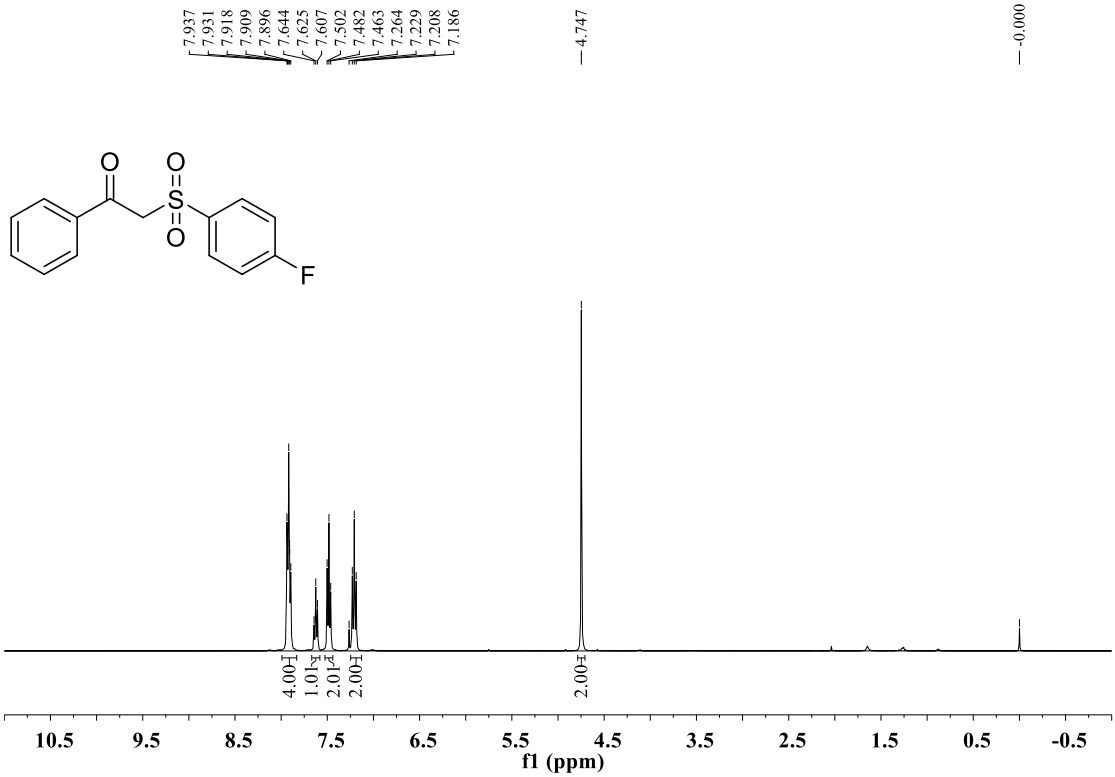
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



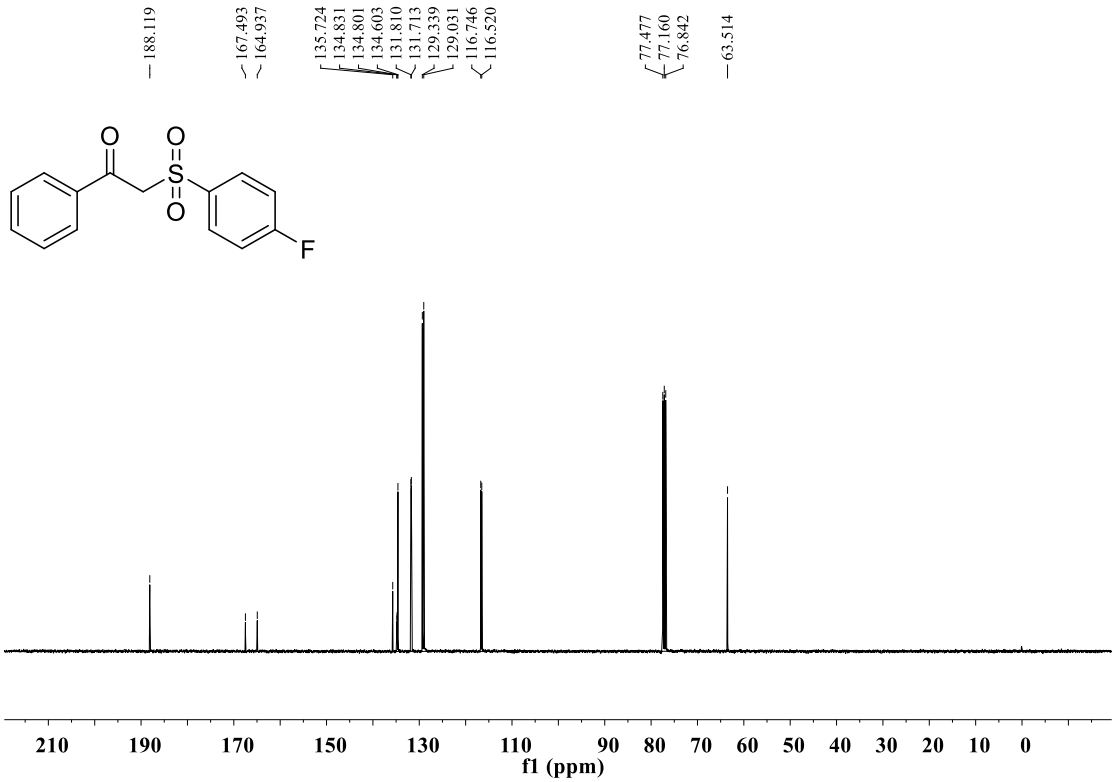
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



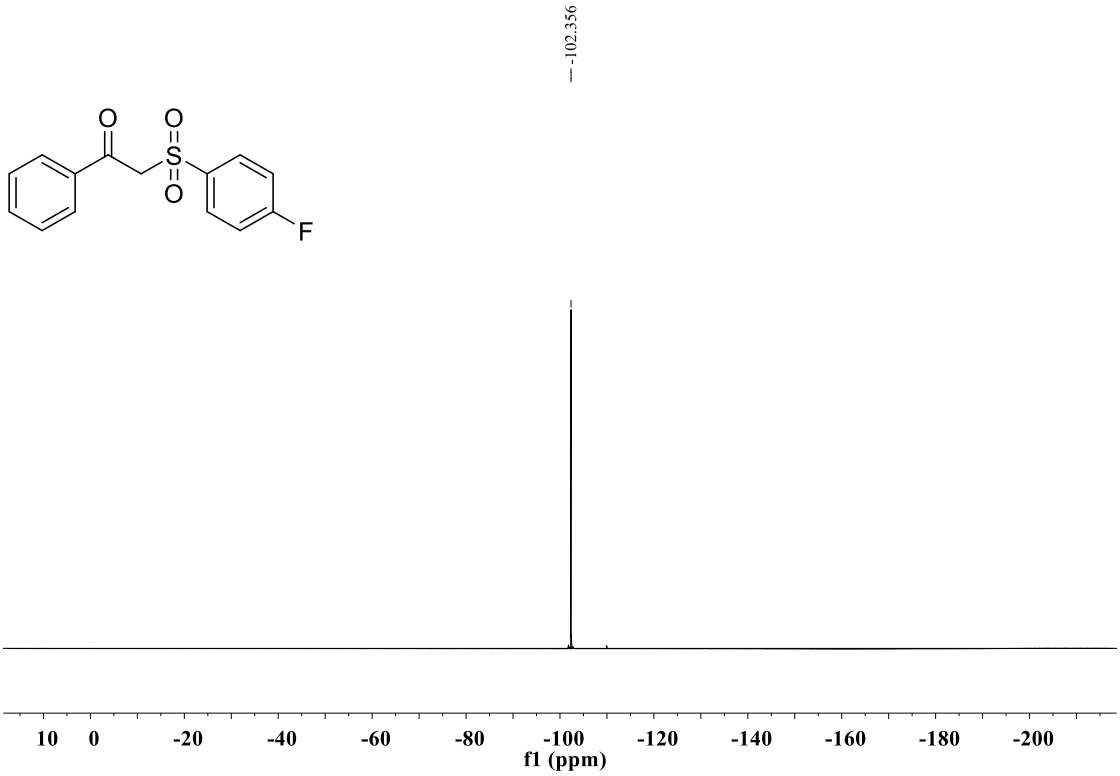
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



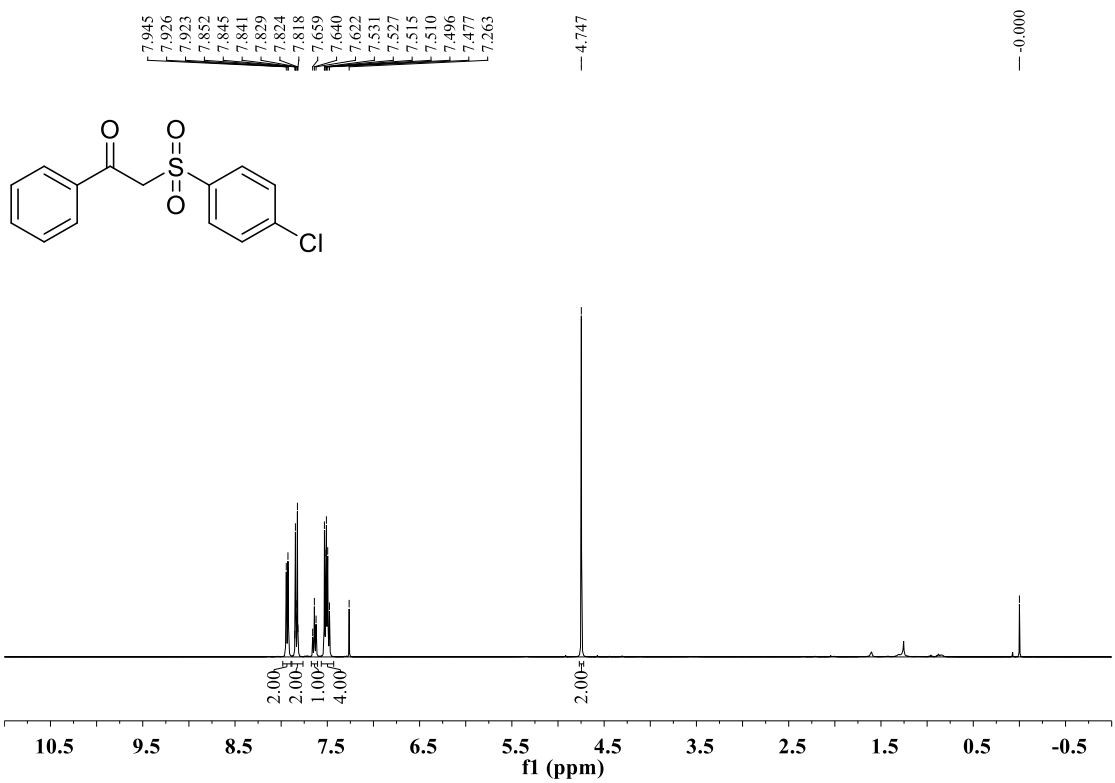
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ad**



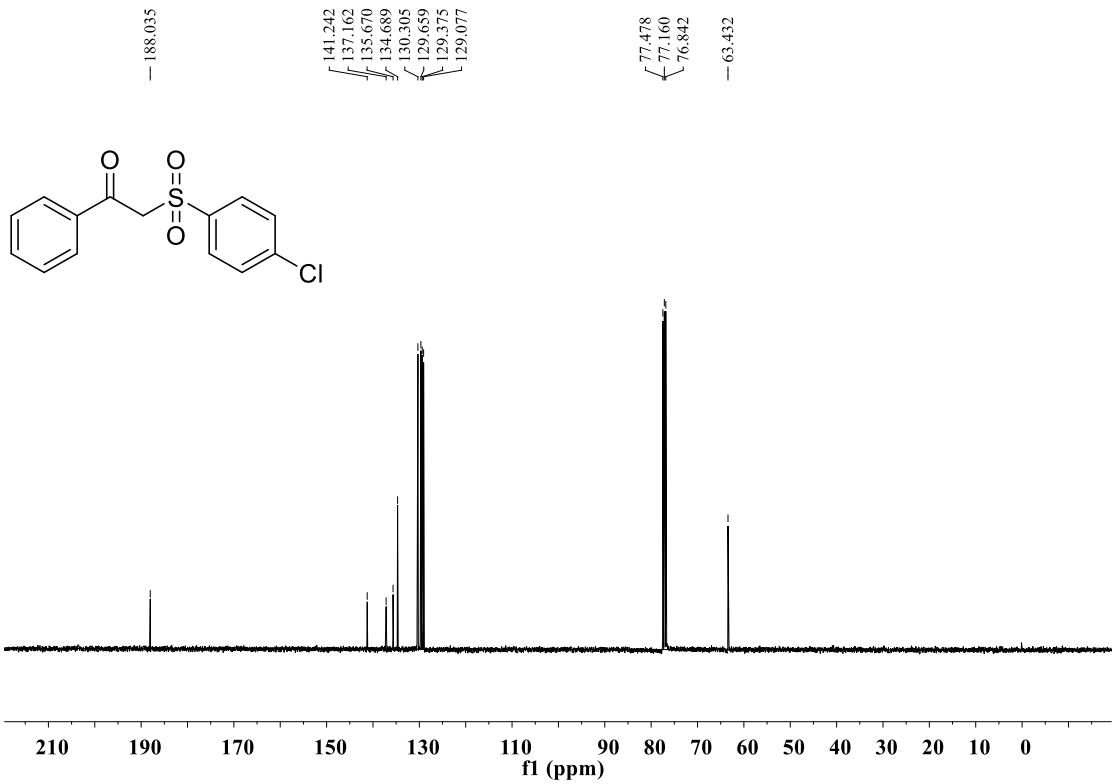
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3ad**



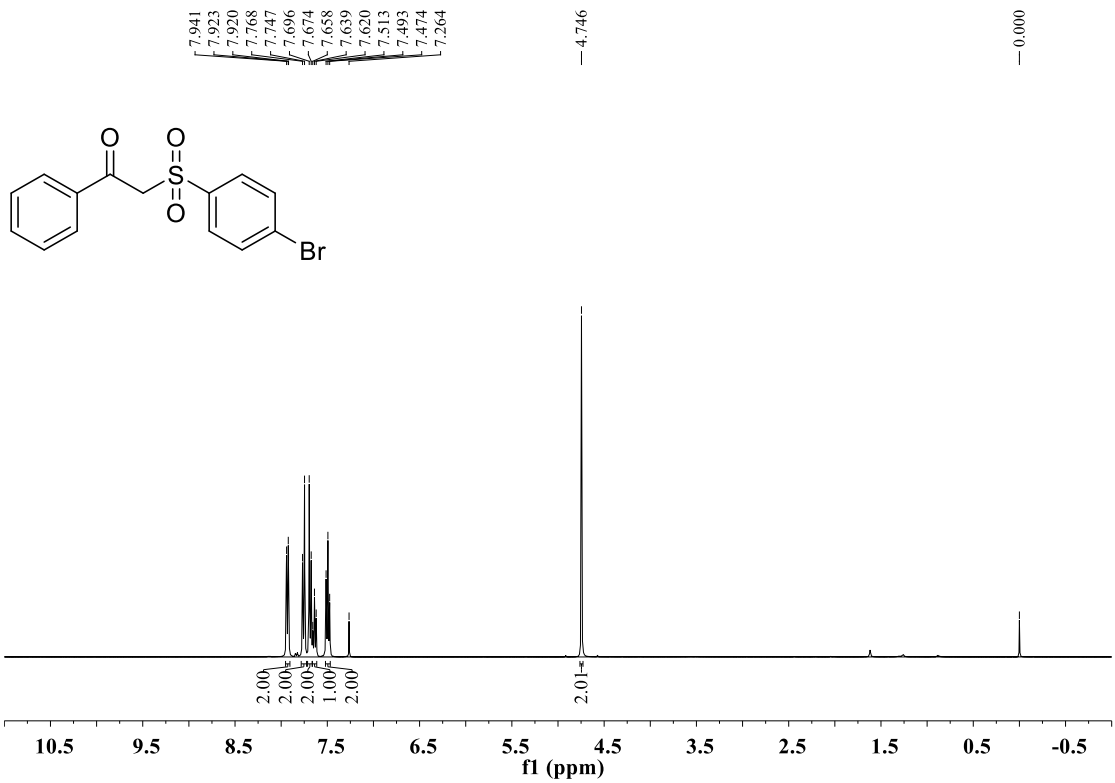
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



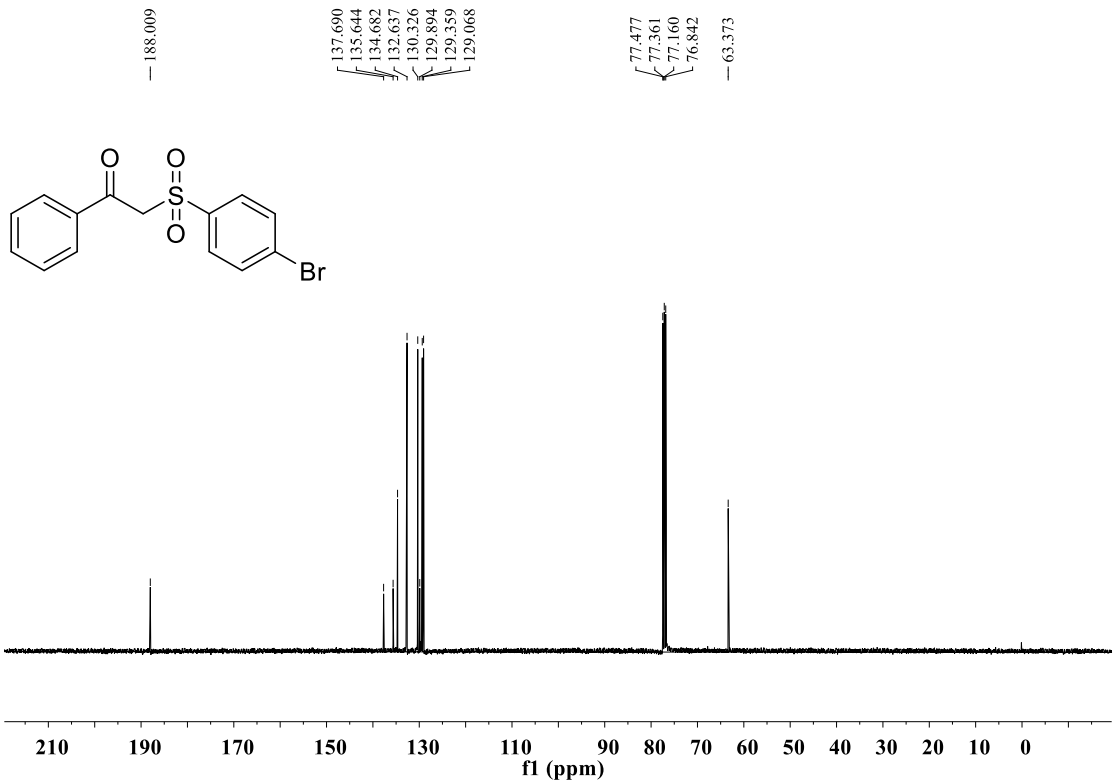
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ae**



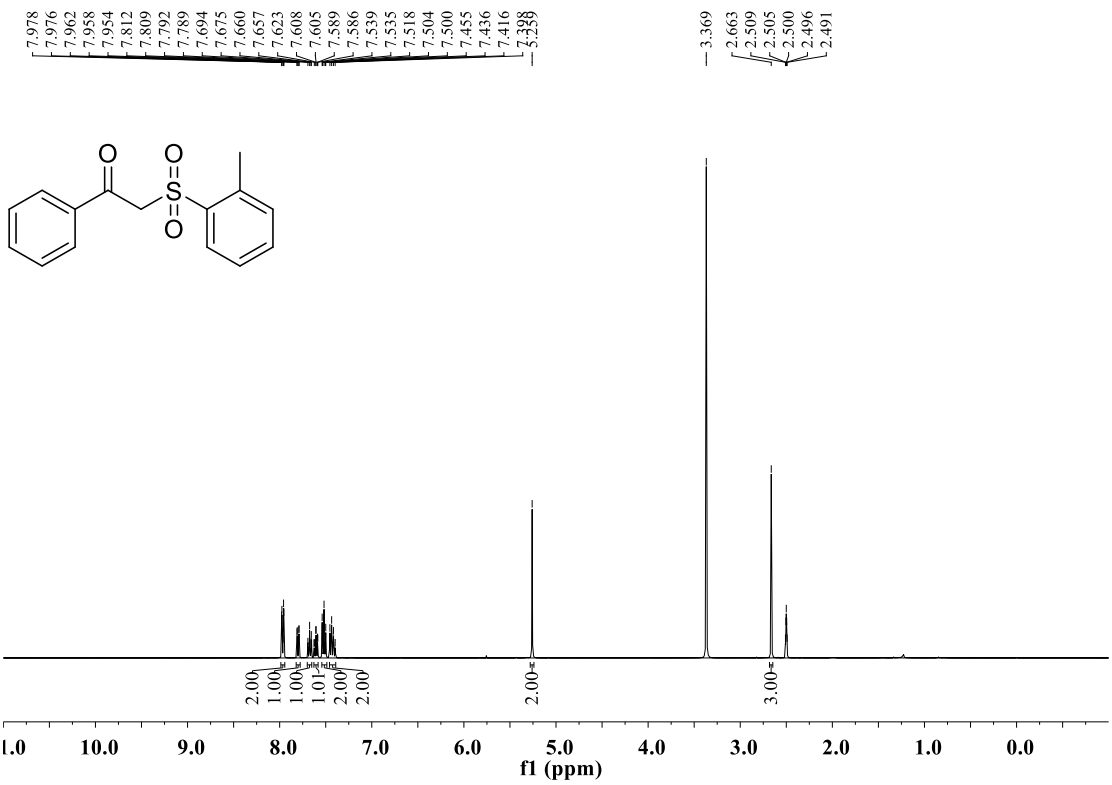
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



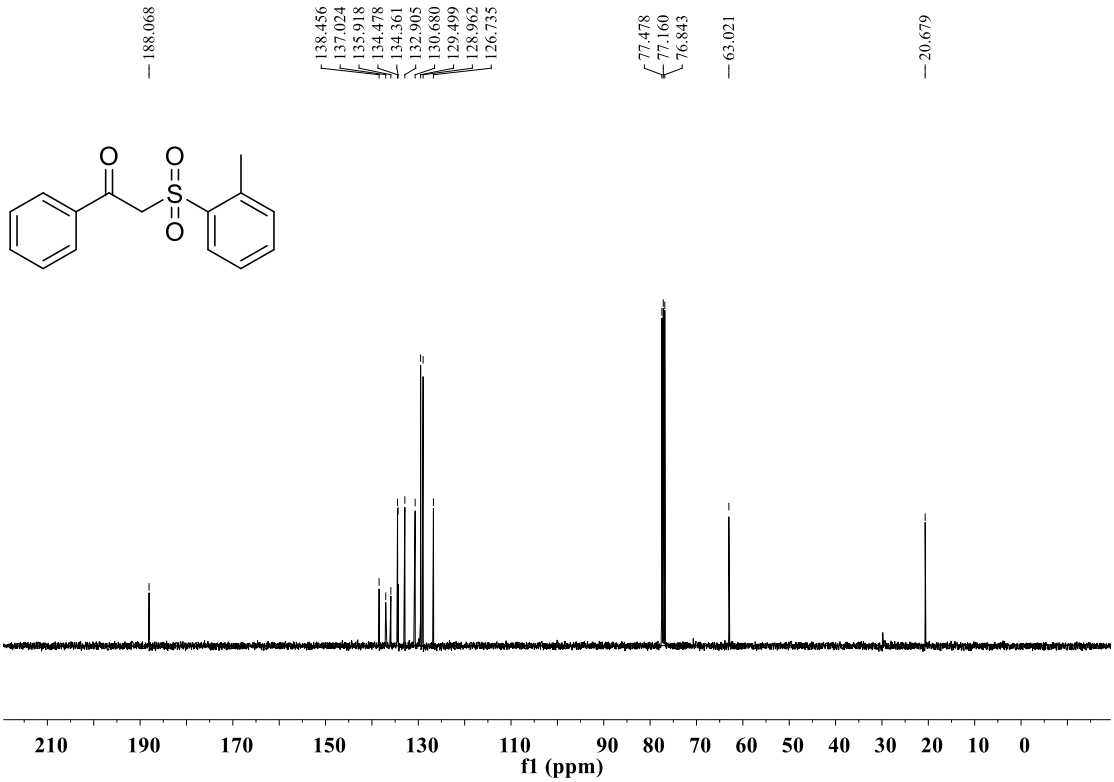
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3af**



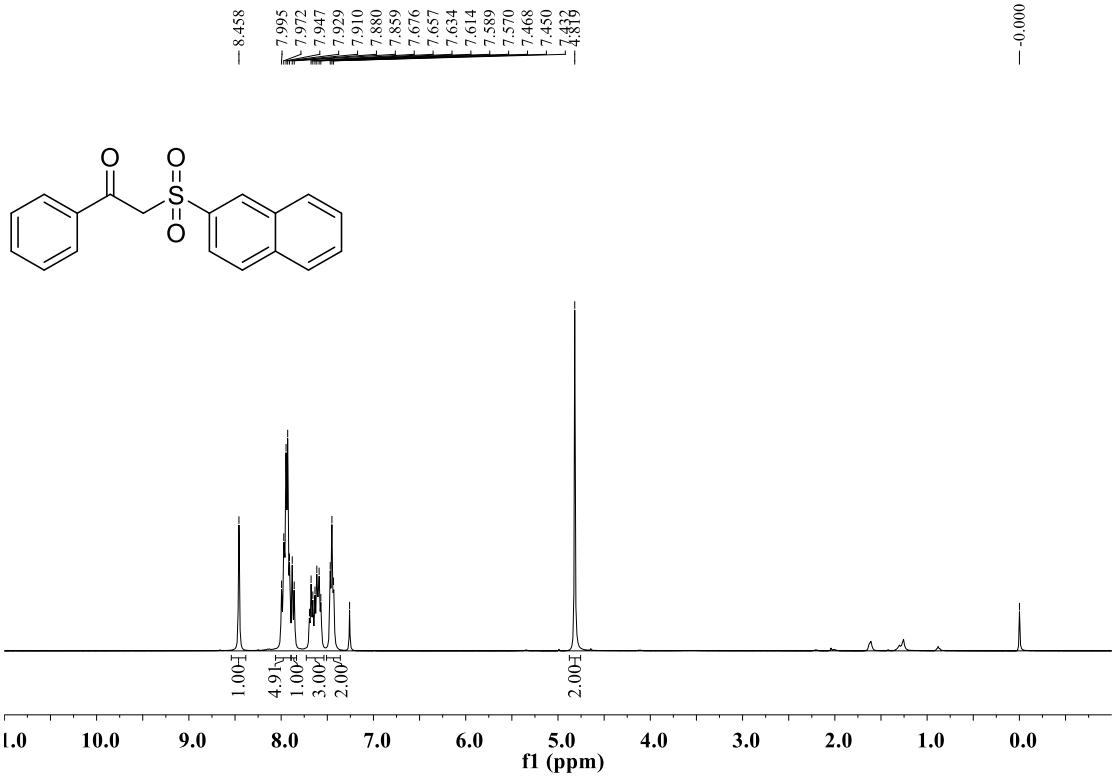
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3ag**



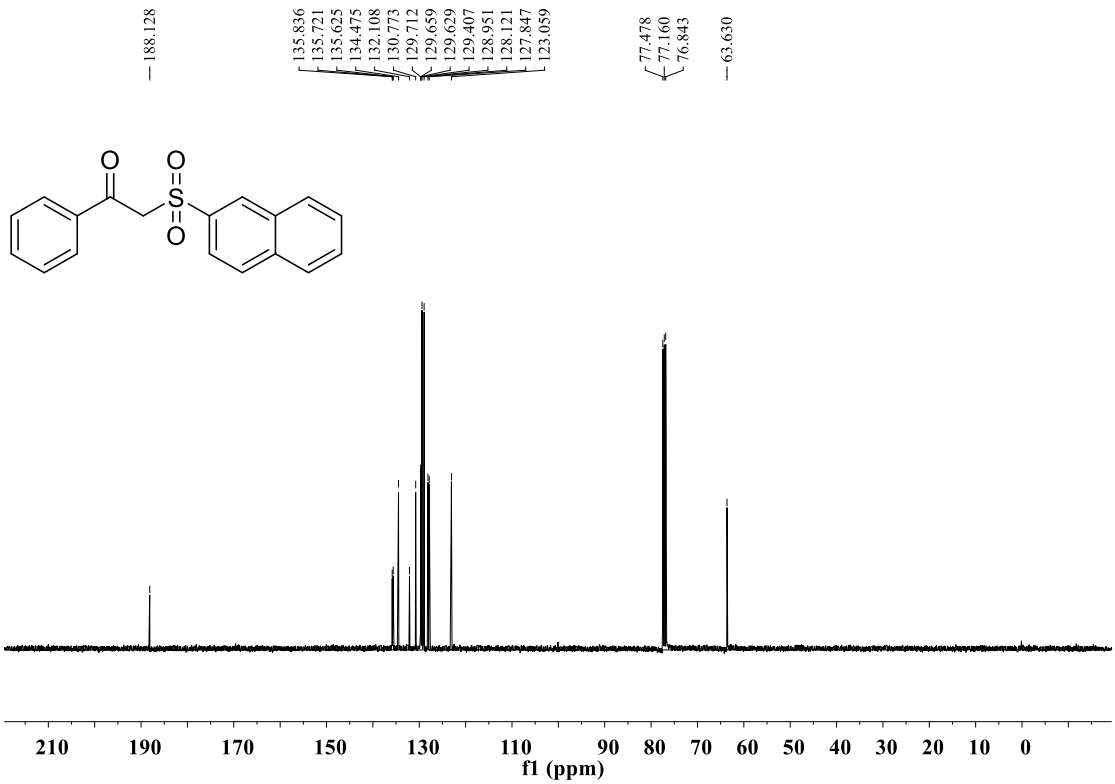
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ag**



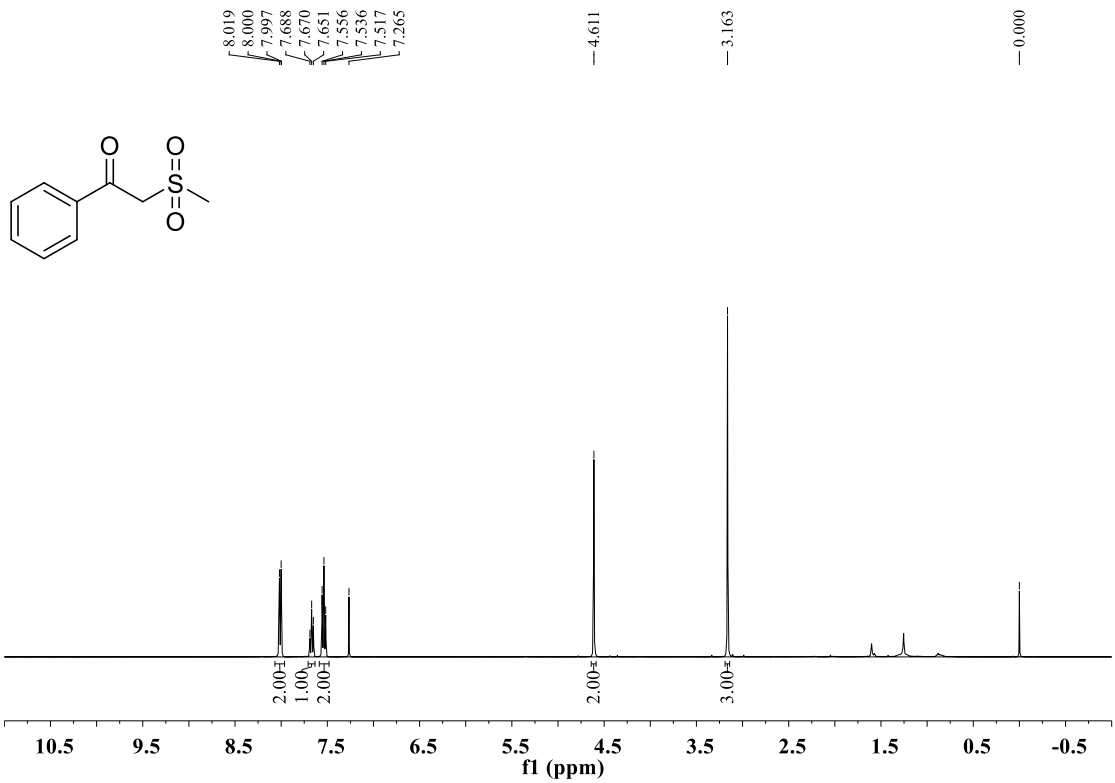
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



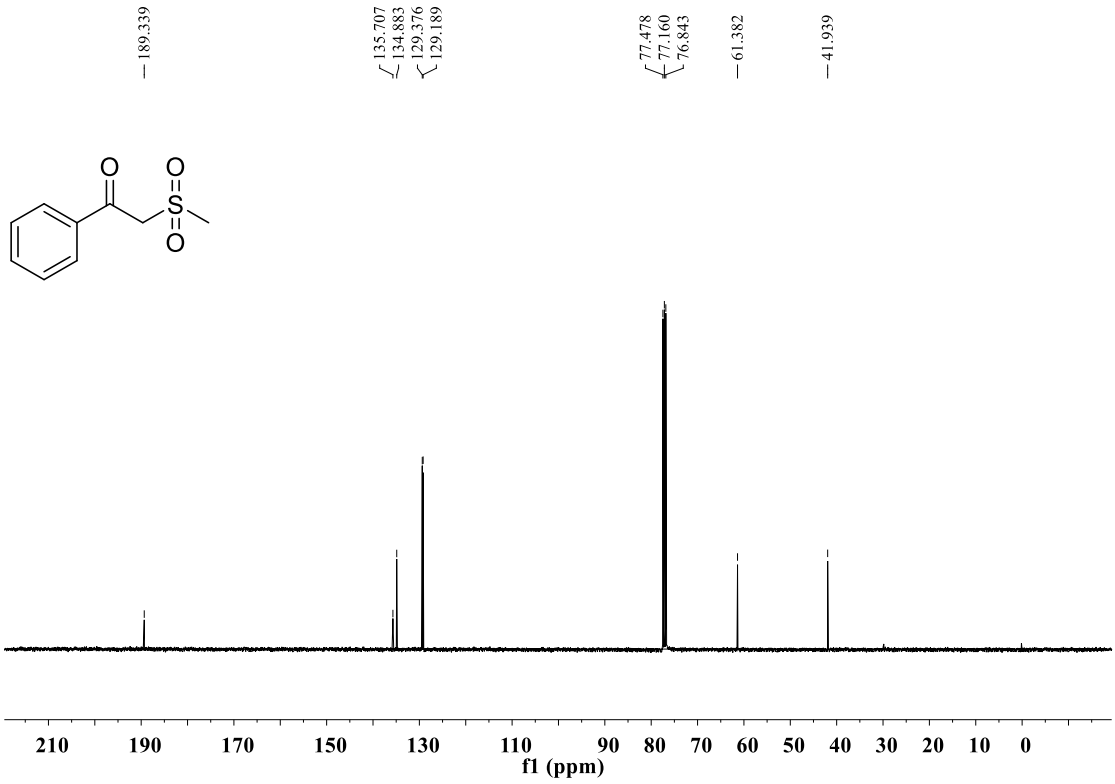
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ah**



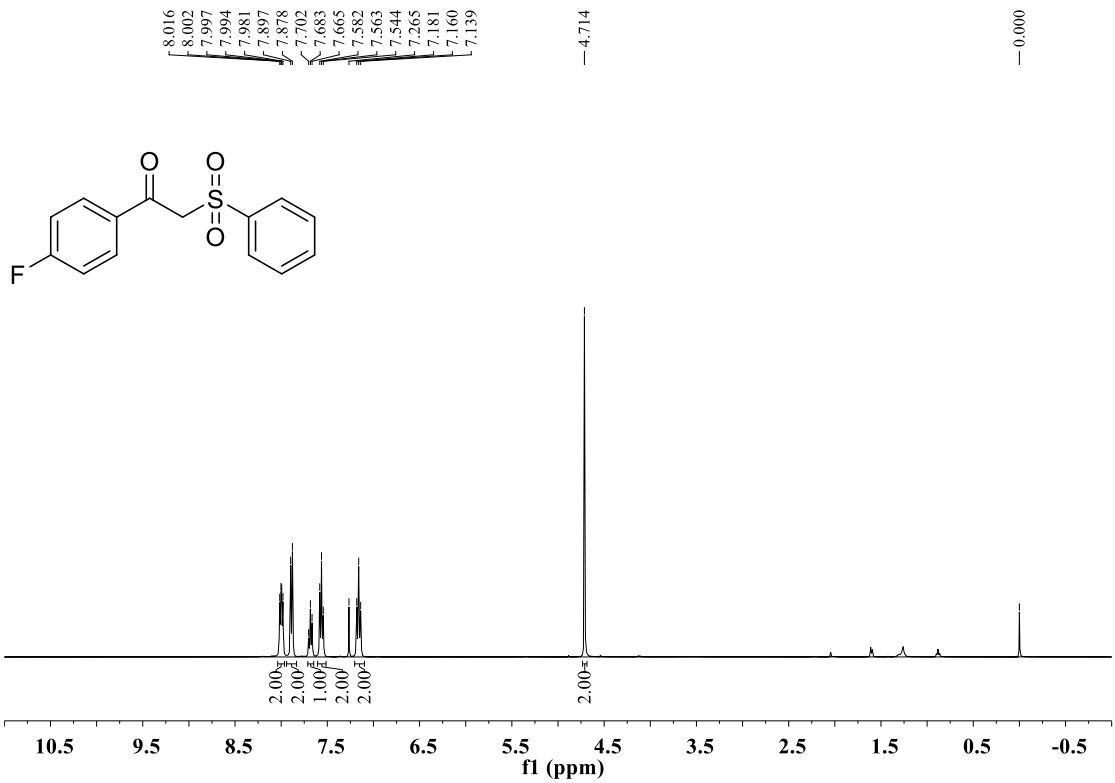
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



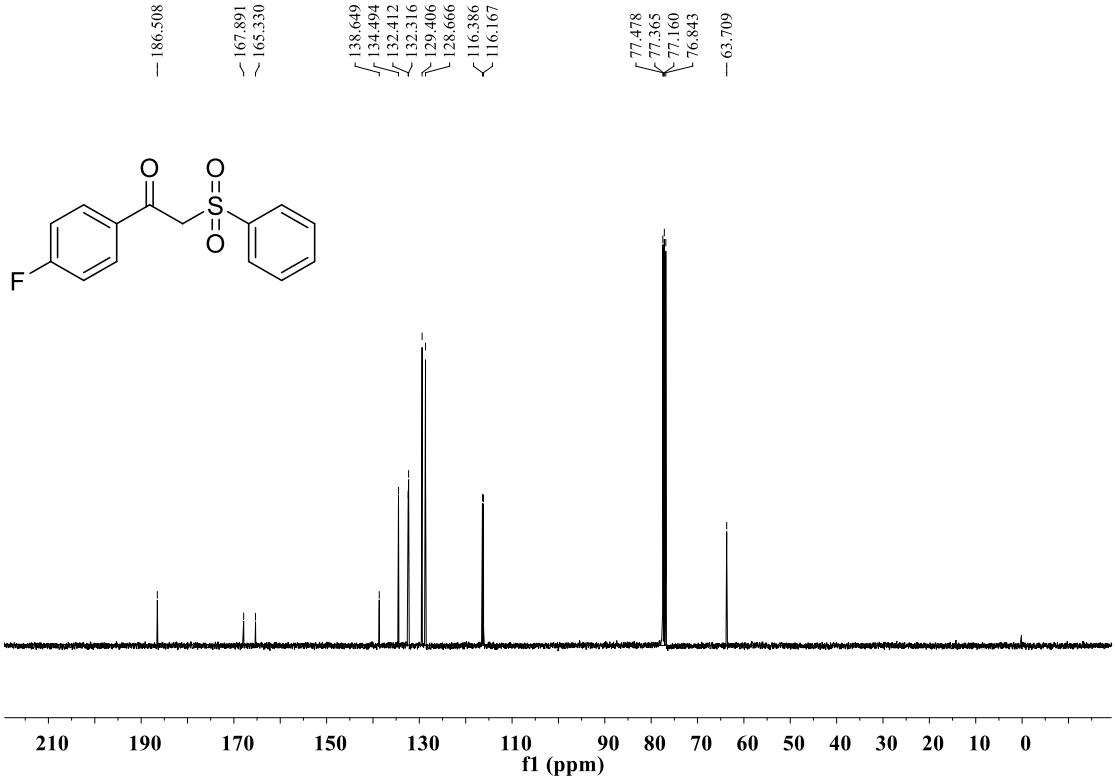
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ai**



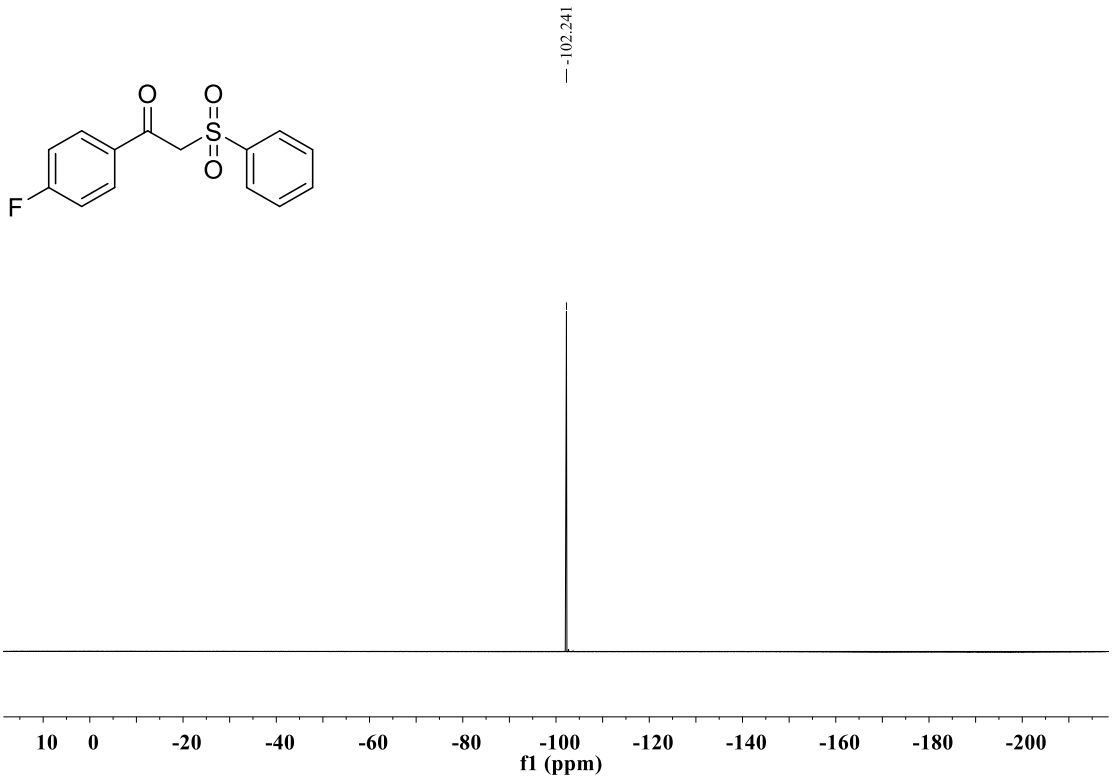
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



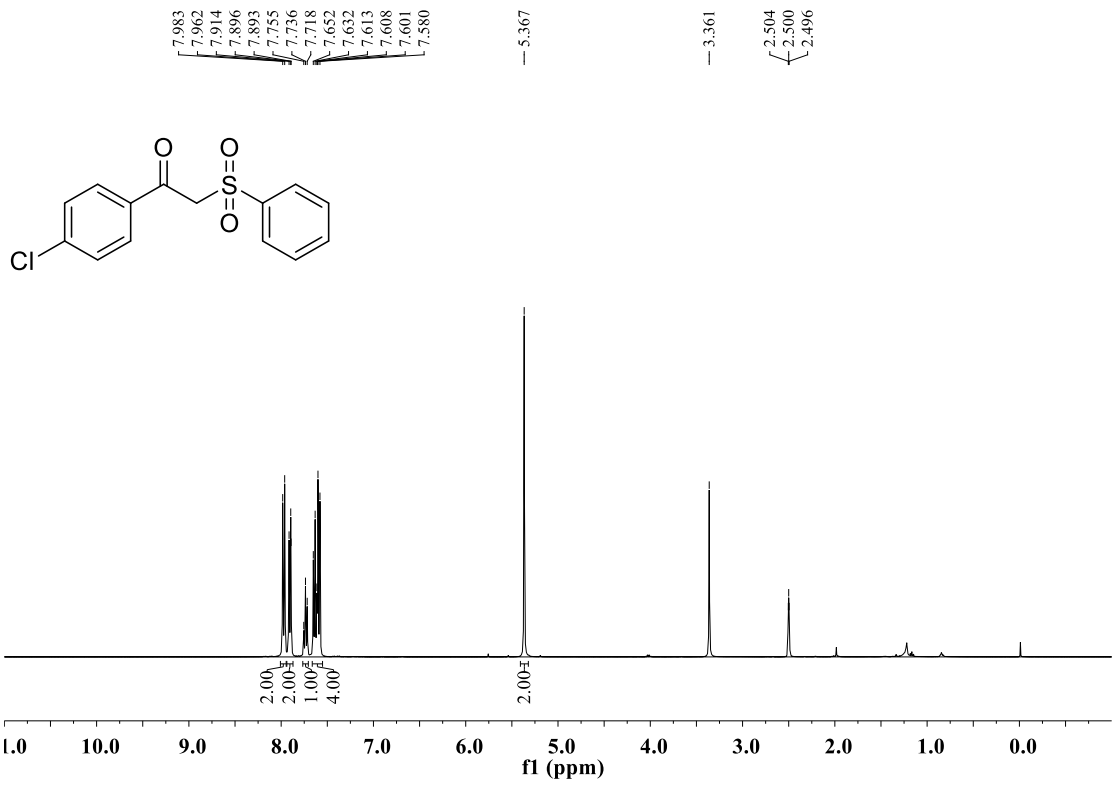
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



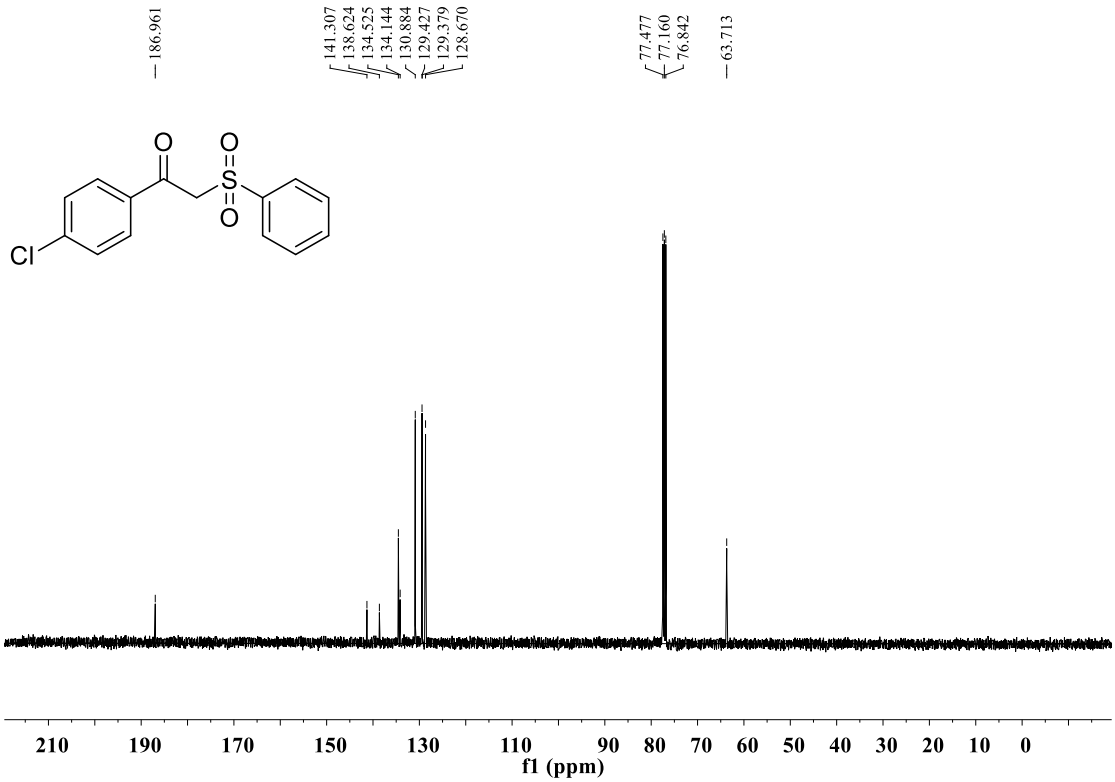
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3ba**



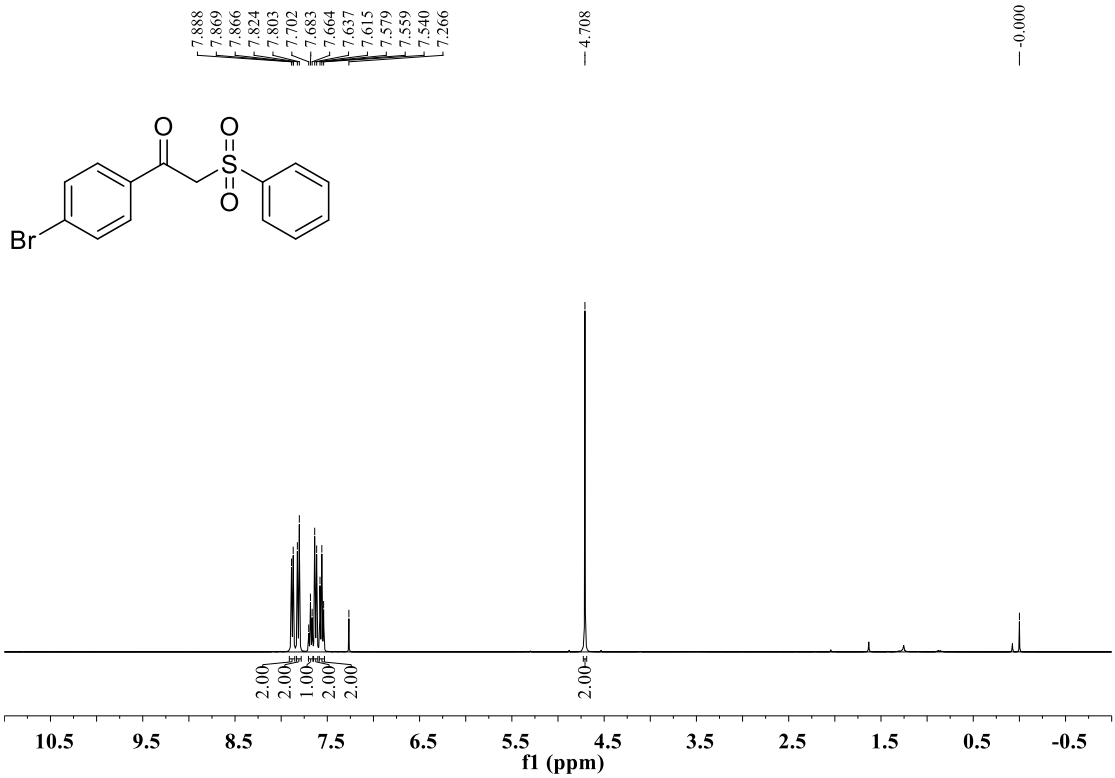
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3ca**



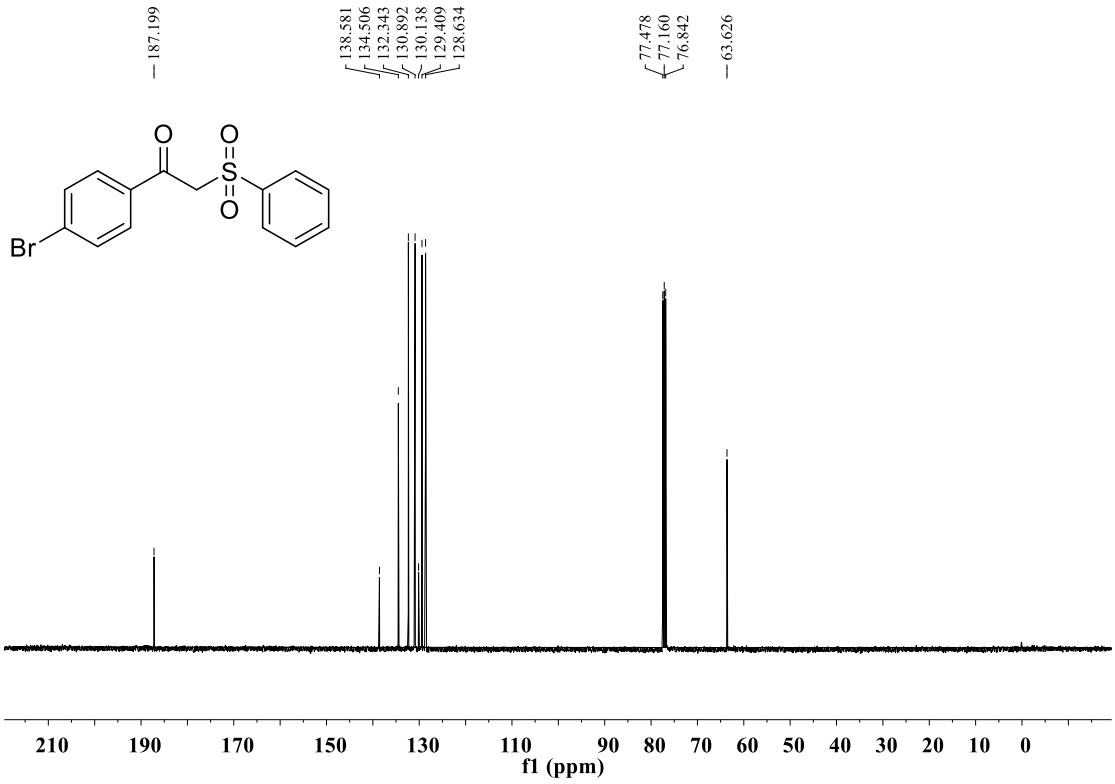
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ca**



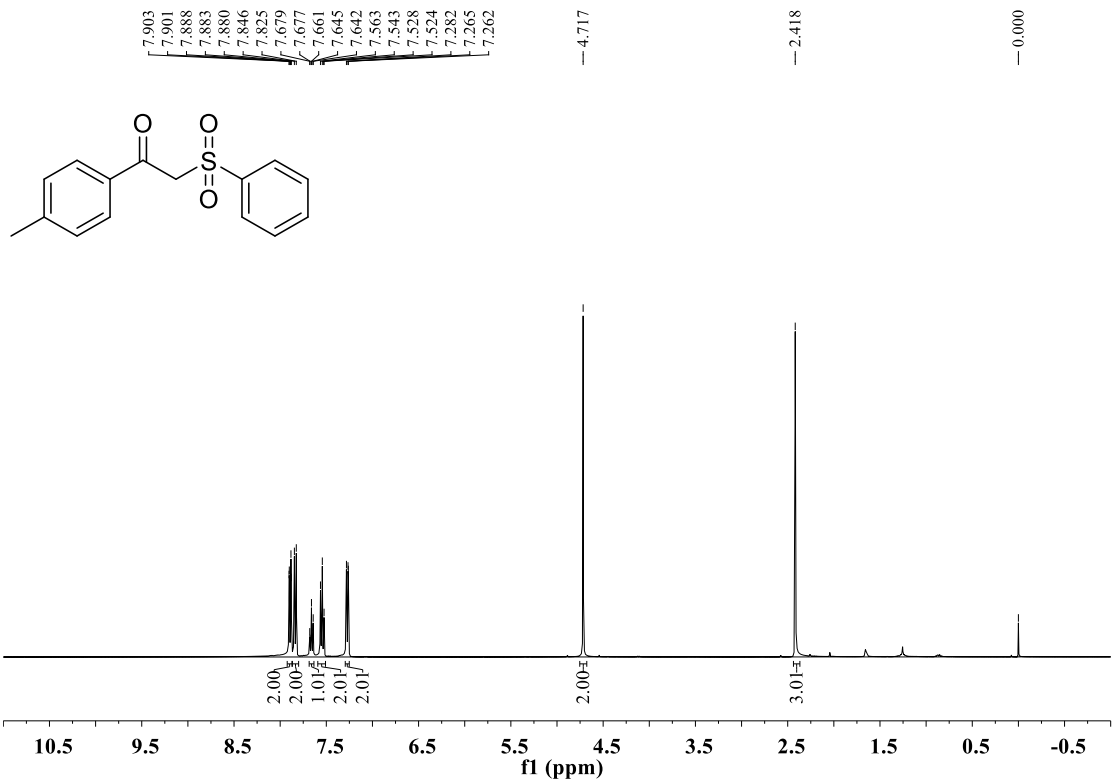
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



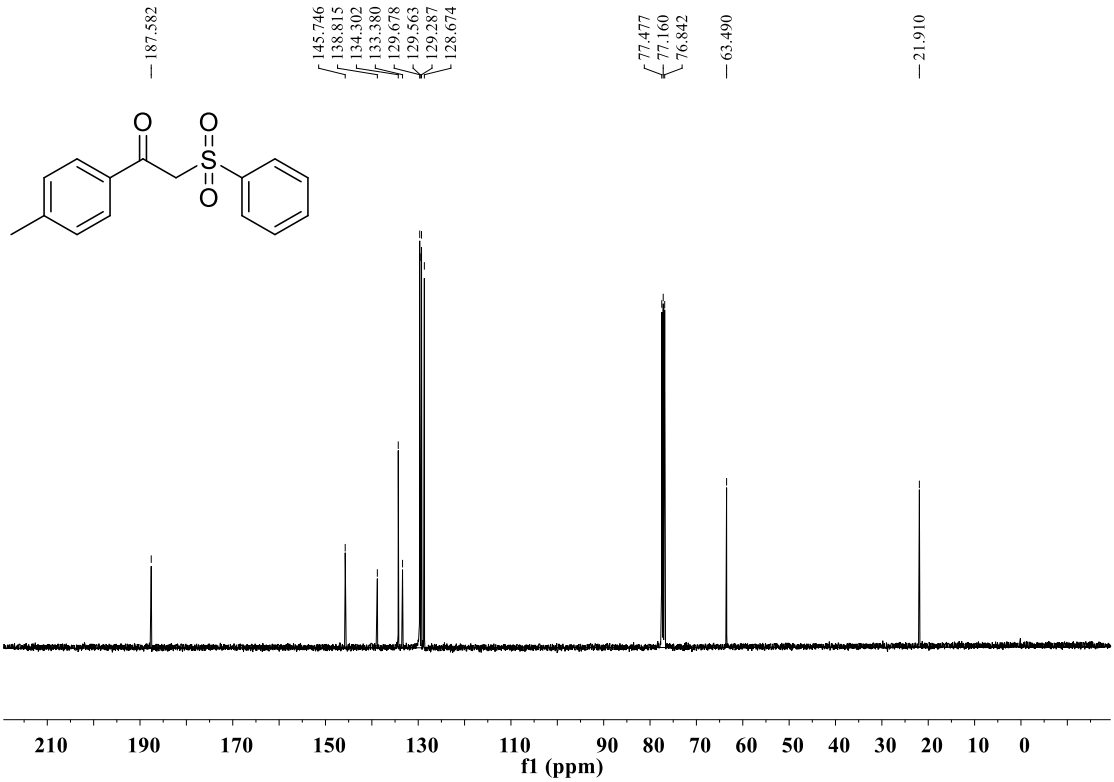
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3da**



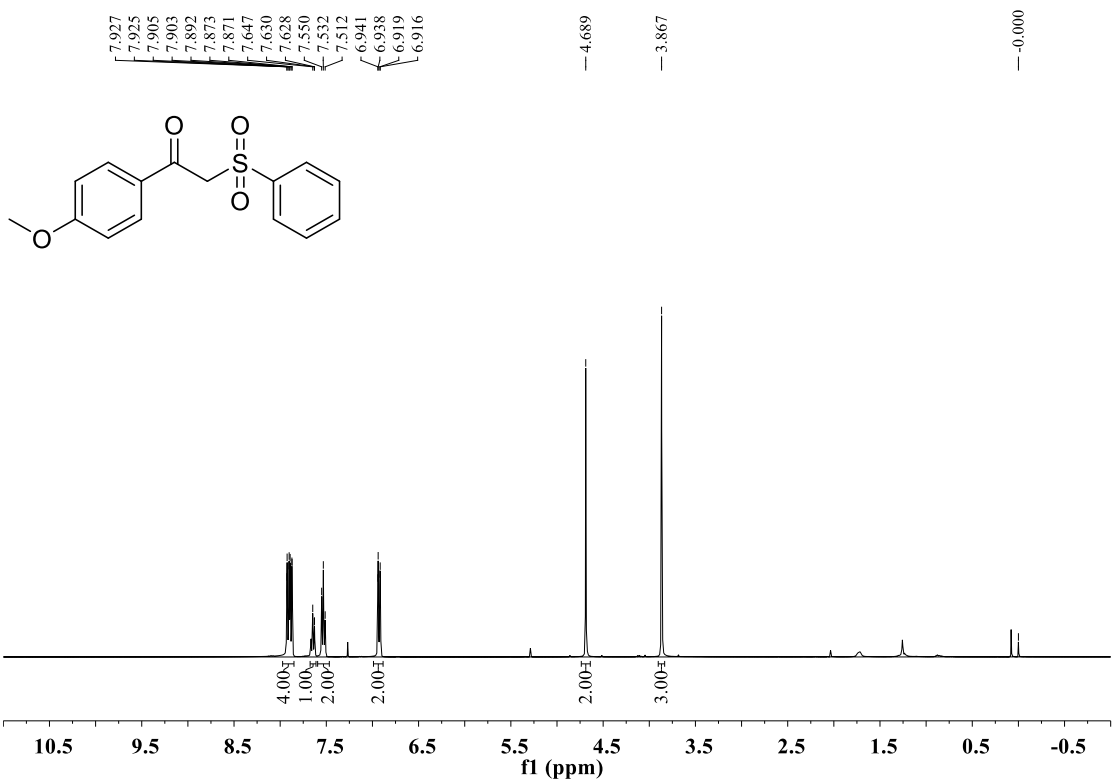
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



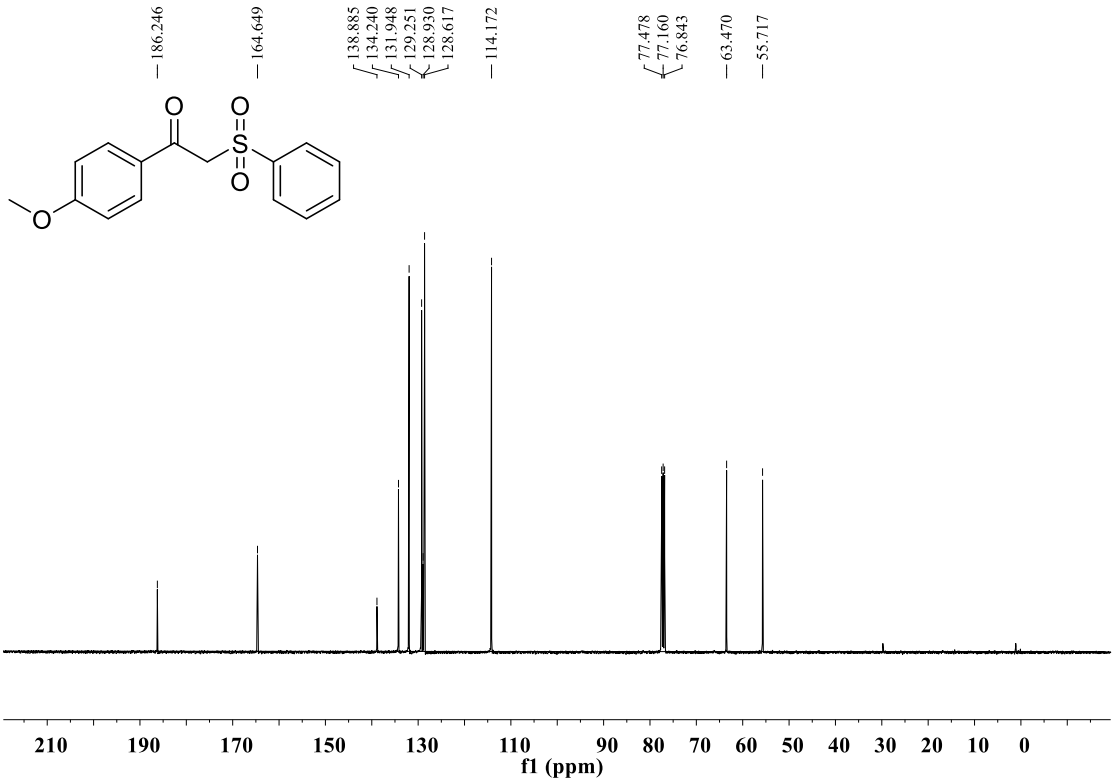
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



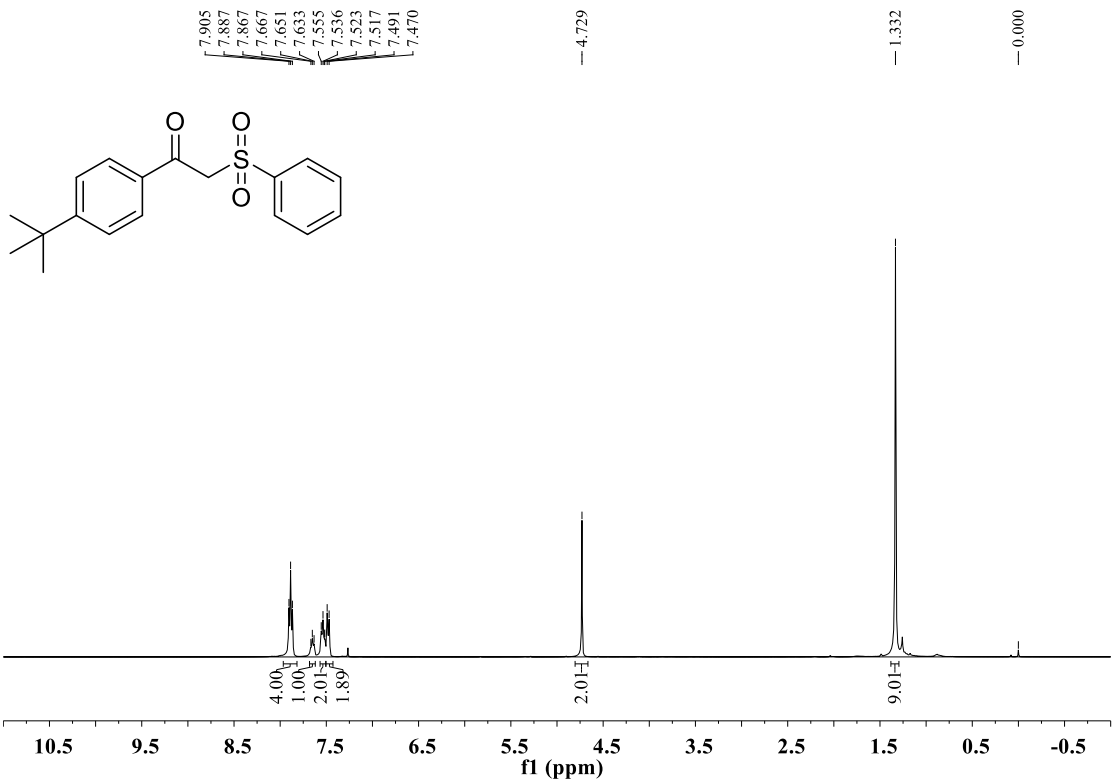
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



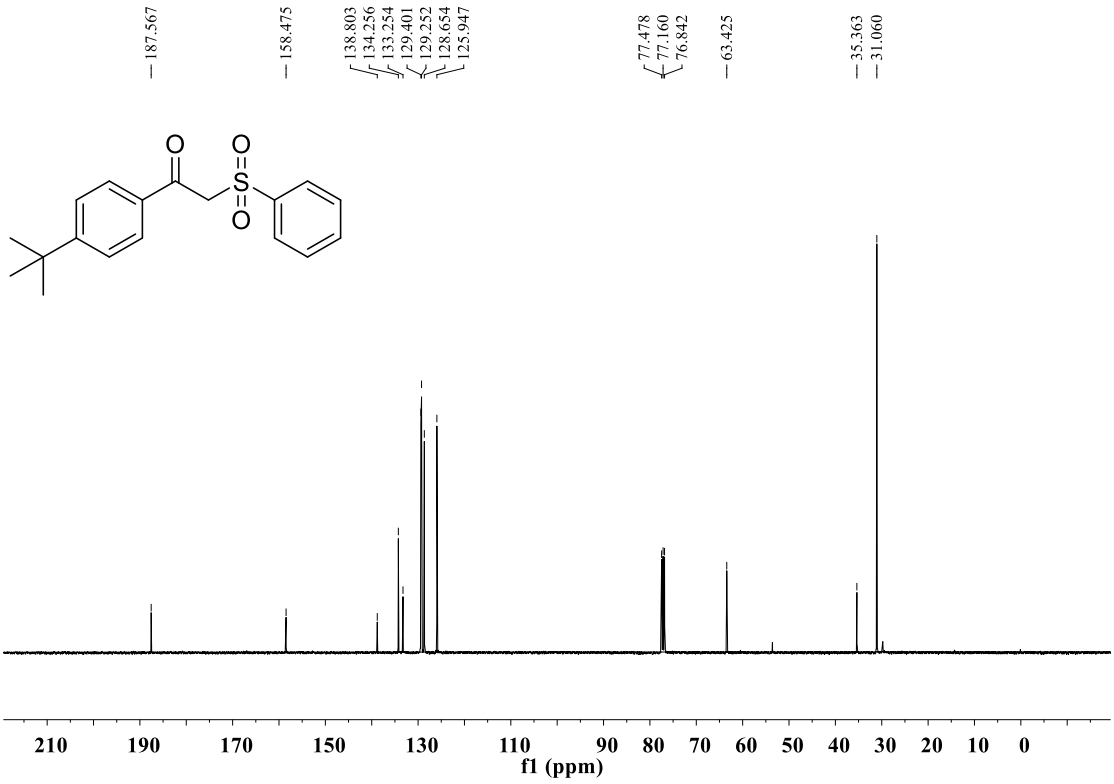
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



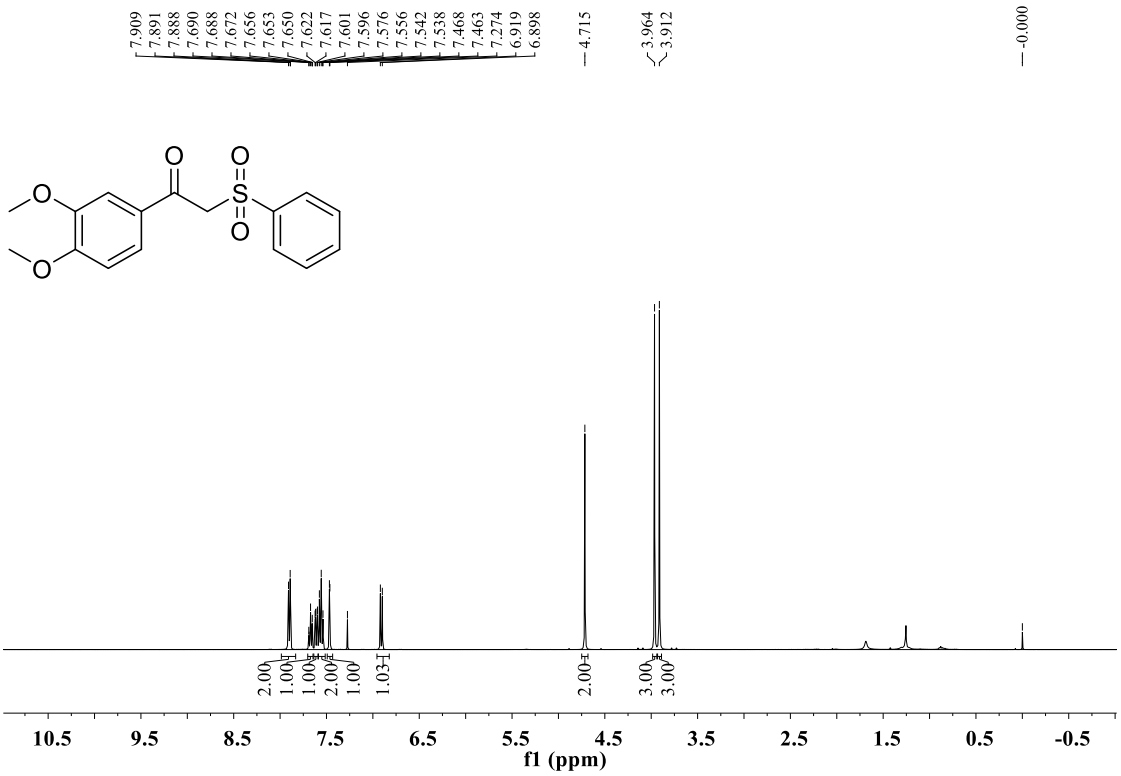
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



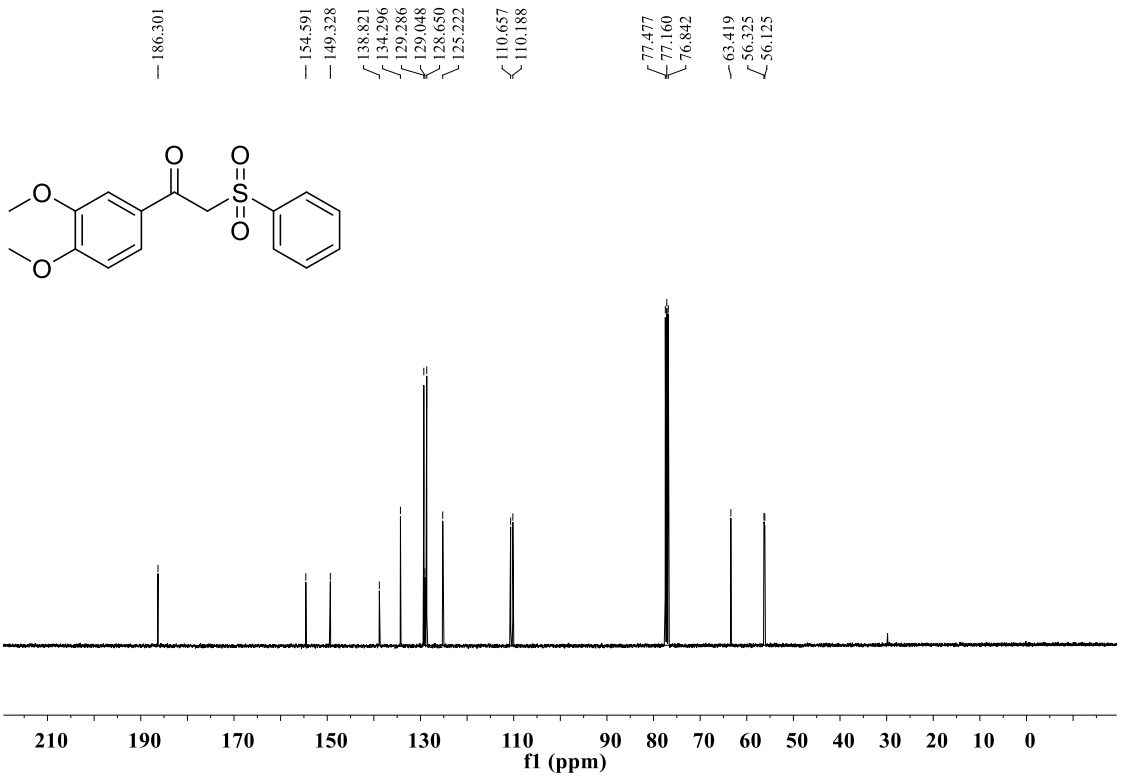
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ga**



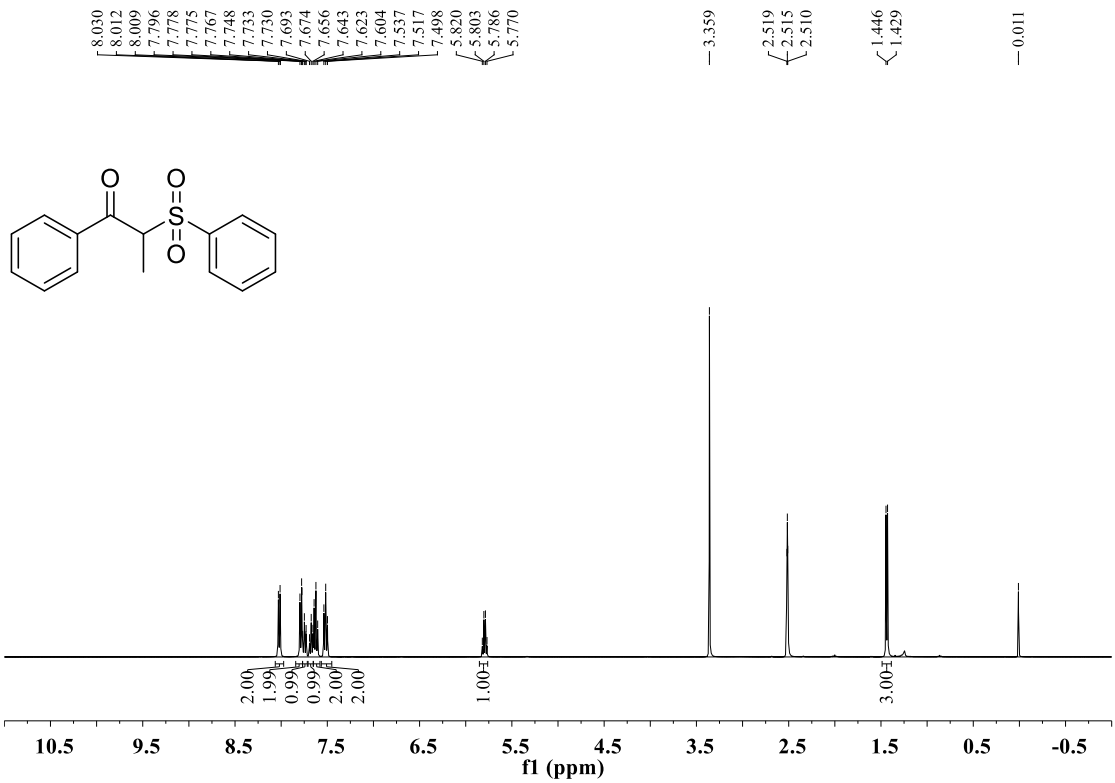
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



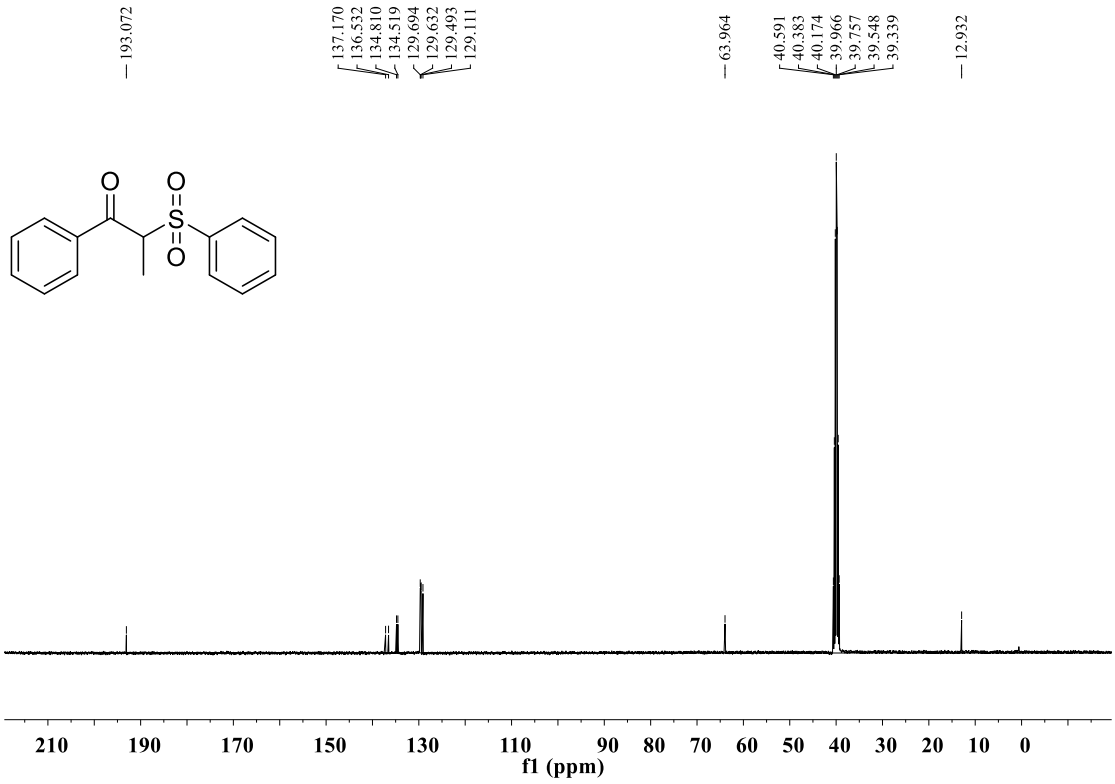
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



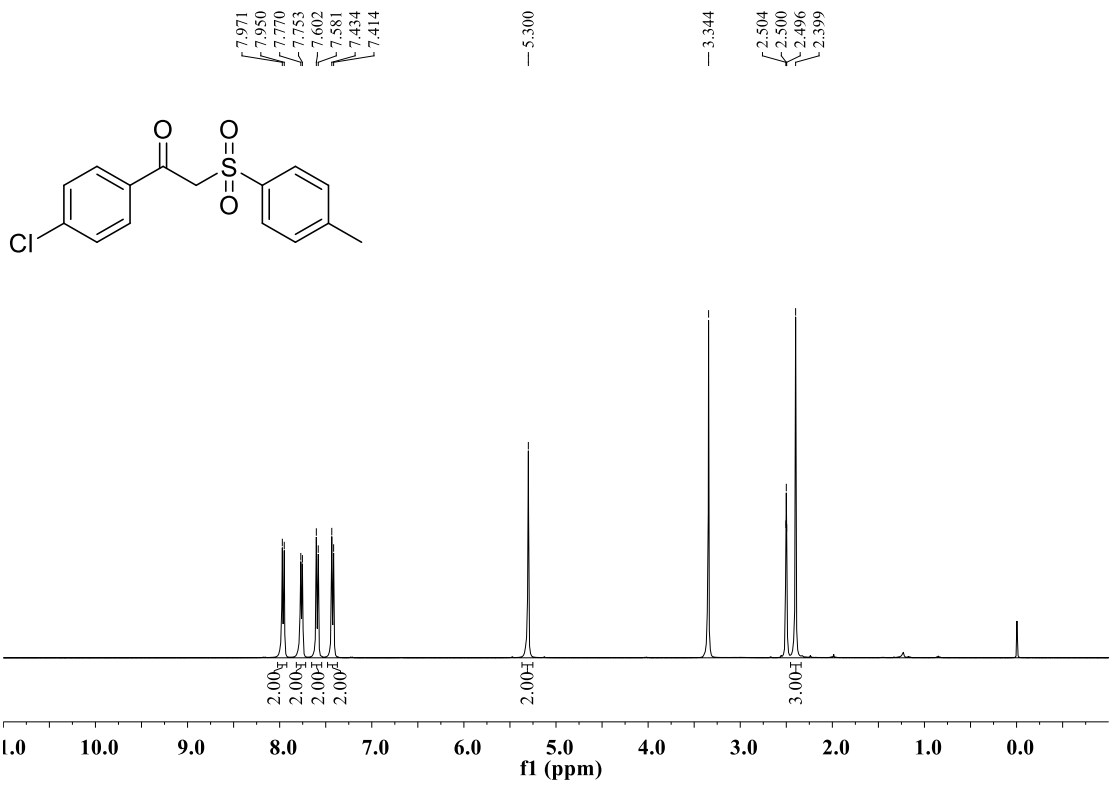
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3ia**



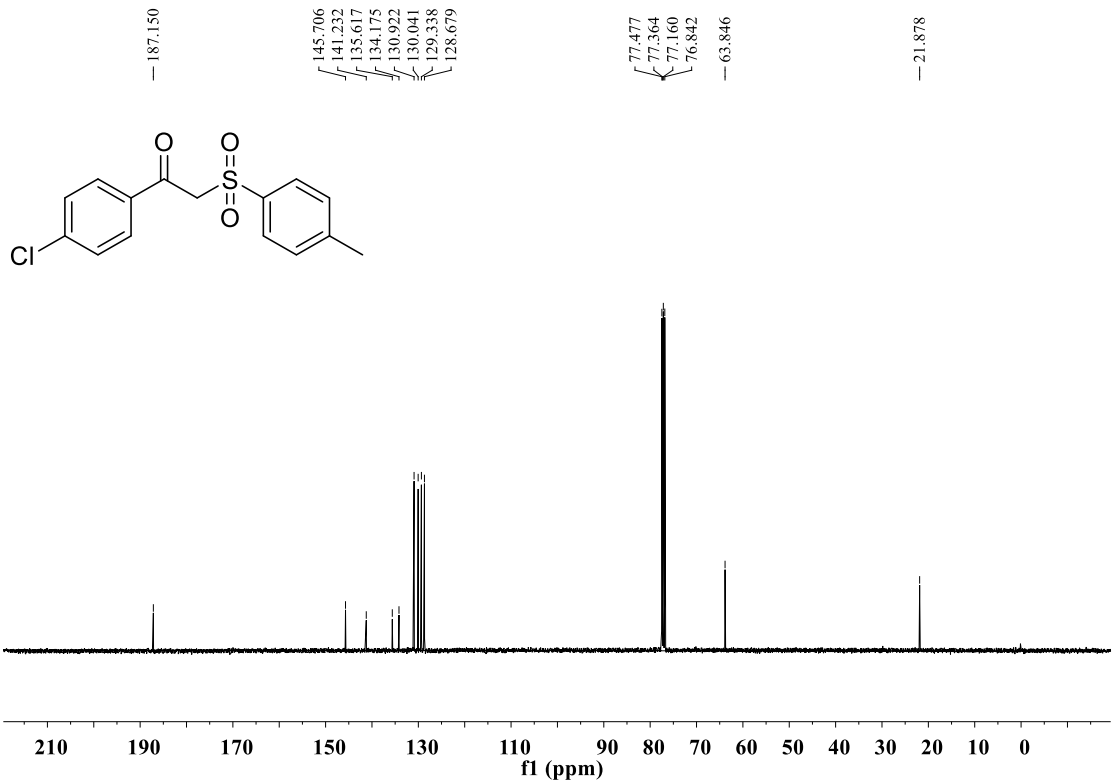
^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **3ia**



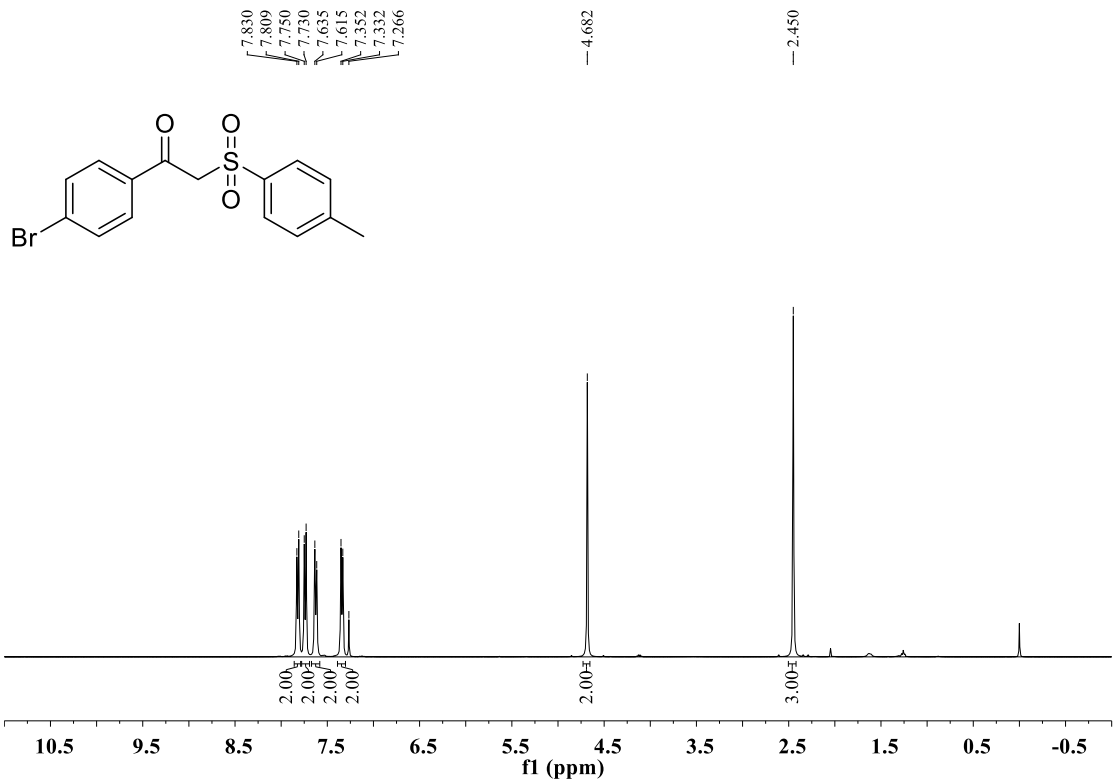
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **3cb**



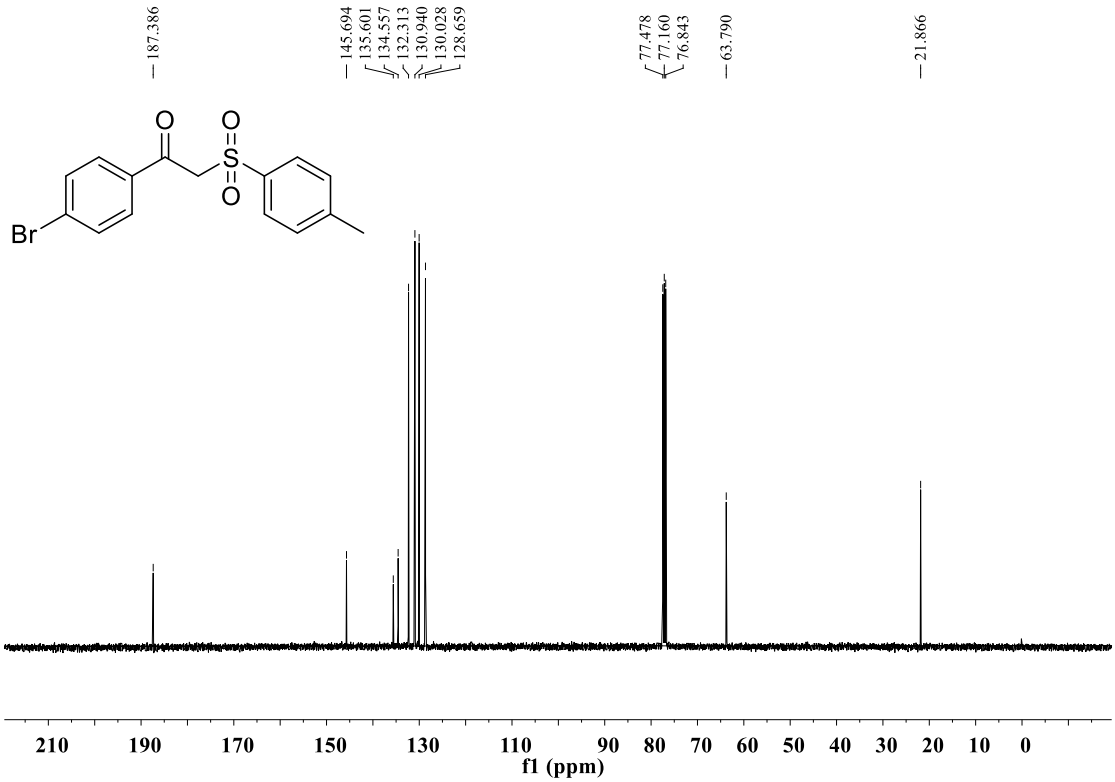
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3cb**



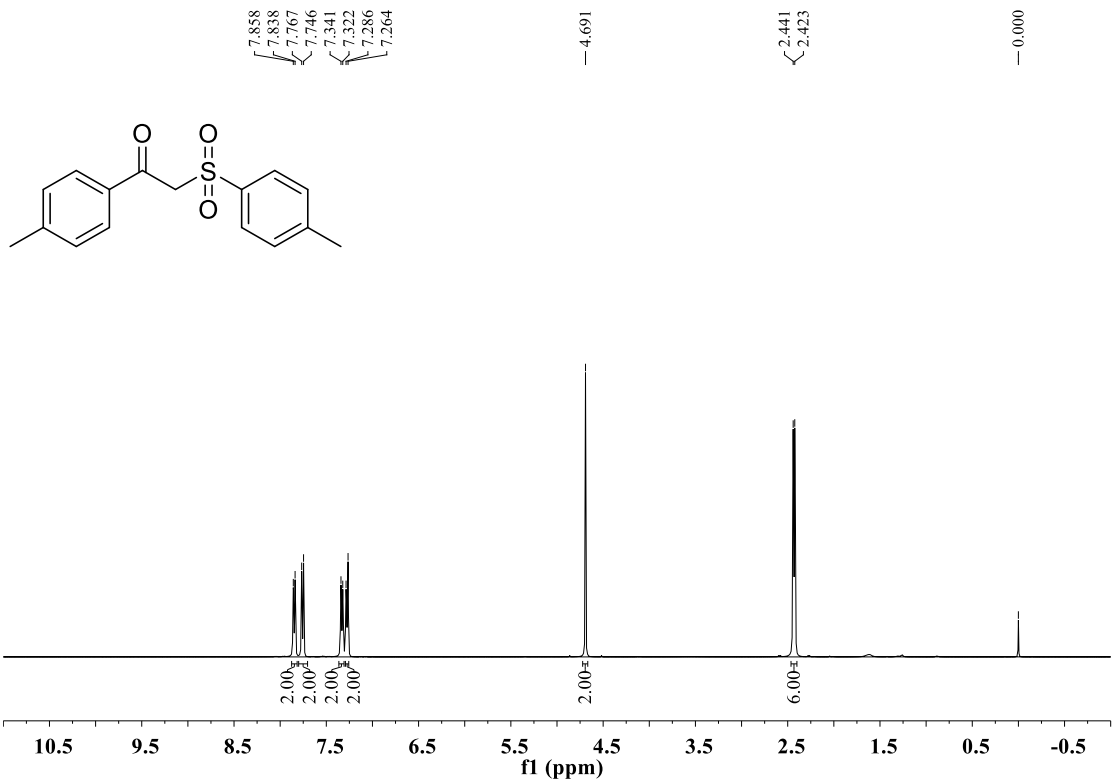
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3db**



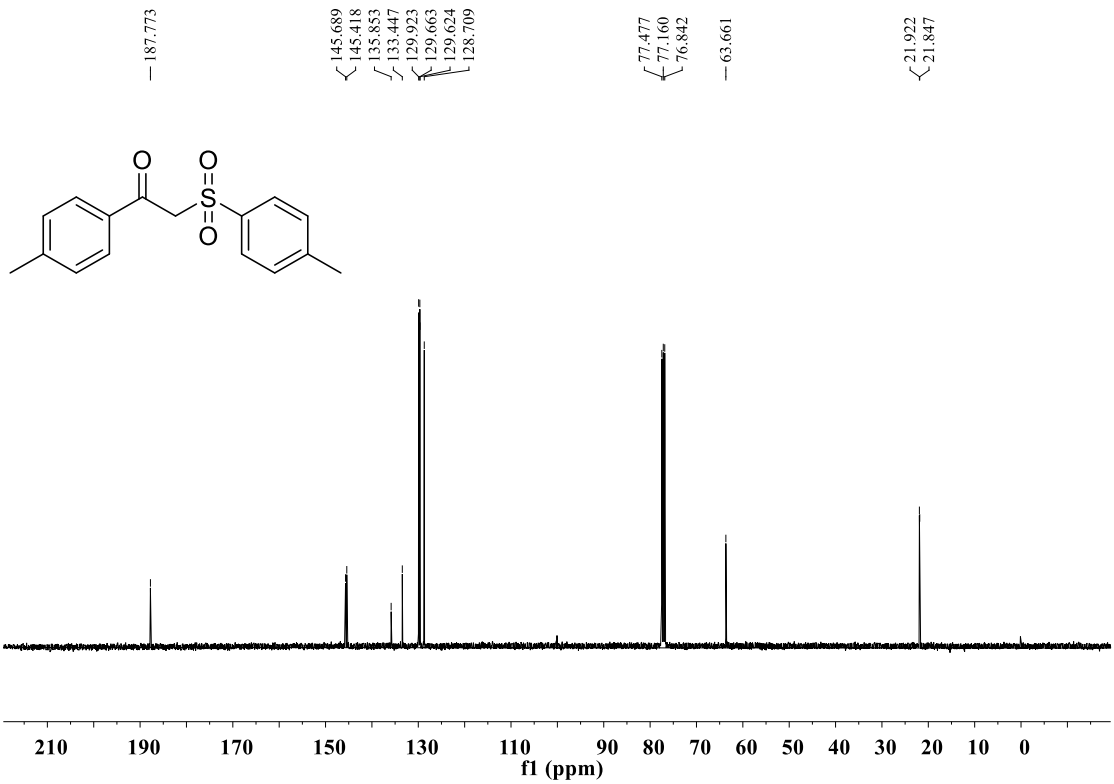
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3db**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3eb**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3eb**



2. EPR Data Collection and Analysis

General Information

EPR spectra were recorded on a Bruker X-band A200 spectrometer. The samples were taken out into a small tube, and then recorded by EPR spectrometer at indicated temperature and parameters.

Experimental Details

2.1 The interaction between $PhSO_2H$ and $CuBr_2$

To an oven-dried Schlenk tube equipped with a stir bar was added $CuBr_2$ (0.4 mmol) and DMF (4.0 mL), and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 5 times. Then, 20 uL of the mixture was taken out into a small tube and analyzed by EPR at room temperature (Figure 1, blue line). EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×105; microwave power: 19.05 mW.

The remaining mixture was degassed the air by the method of freeze-pump-thaw cycle for 2 times, and benzenesulfinic acid (0.8 mmol) was added under N_2. After degassing the air by the method of freeze-pump-thaw cycle for 3 times again, the reaction mixture was stirred under N_2 at room temperature for 5 minutes. After DMPO (10 μL) was added, 20 uL of the mixture was taken out into a small tube and analyzed by EPR at room temperature (Figure 1, red line). EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×105; microwave power: 19.05 mW.

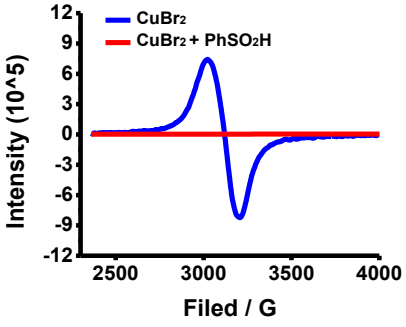


Figure S1. EPR spectra of the interaction between $PhSO_2H$ and $CuBr_2$.

2.2 The interaction between $Cu(OAc)_2$ and LiBr

To an oven-dried Schlenk tube equipped with a stir bar was added $Cu(OAc)_2$ (0.4 mmol) and DMF (4.0 mL), and the reaction mixture was degassed the air by the method of freeze-pump-thaw cycle for 5 times. Then, 20 uL of the mixture was taken out into a small tube and analyzed by EPR at room temperature (Figure 4, black line). EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 2.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×105; microwave power: 19.05 mW.

The remaining mixture was degassed the air by the method of freeze-pump-thaw cycle for 2 times, and LiBr (0.4 mmol) was added under N_2. After degassing the air by the method of freeze-pump-thaw cycle for 3 times again, the reaction mixture was stirred under N_2 at room temperature for 10 minutes, and 20 uL of the mixture was taken out into a small tube and analyzed by EPR at room temperature (Figure 4, red line). EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 2.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×105; microwave power: 19.05 mW.

According to the operating steps above, another 2×0.4 mmol of LiBr and 0.8 mmol of $PhSO_2H$ were added to the remaining mixture successively and the corresponding EPR spectra could be collected (Figure 4, blue line, green line and pink line).

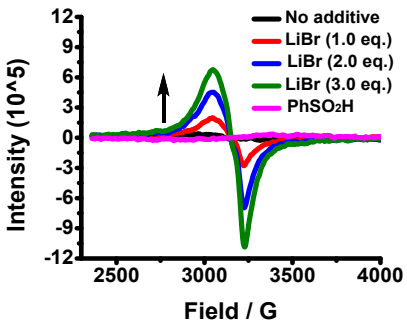


Figure S2. EPR spectra of the interaction between $Cu(OAc)_2$ and LiBr.

3. XANES and EXAFS Data Collection and Analysis

General Information

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response (~10^{10} photons detected/sec) with 10% absorption (N_2) in the incident ion chamber and 70% absorption (60% N_2 and 40% Ar) in the transmission detector. A Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration. Multiple scans were taken to reduce the noise.

All solution samples were placed in a sample holder (the XAS solution cell) made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water.[8] For solution samples, the Cu concentration was adjusted to be 0.05 - 0.1 M with a path length of 3.5 mm. The sample holder was placed in a quartz tube (1–in. OD, 10–in. length) sealed with Kapton windows by two Ultra-Torr fittings and then used for transmission mode measurement.

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak.

Background removal and normalization procedures were carried out using the Athena software package using standard methods.[9] Standard procedures based on Artemis software (Demeter 0.9.20) were used to extract the extended X-ray absorption fine structure (EXAFS) data. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor, k^3-weighted Fourier transform data.

Experimental Details

3.1 $CuBr_2$ / DMF solution: $CuBr_2$ (0.4 mmol, 88.3 mg) was added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of DMF was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature

(Figure S3, blue line).

3.2 $CuBr_2$ / 2 $PhSO_2H$ / DMF solution: $CuBr_2$ (0.4 mmol, 88.3 mg) and $PhSO_2H$ (0.8 mmol, 113.6 mg) were added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of DMF was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature (Figure S3, red line).

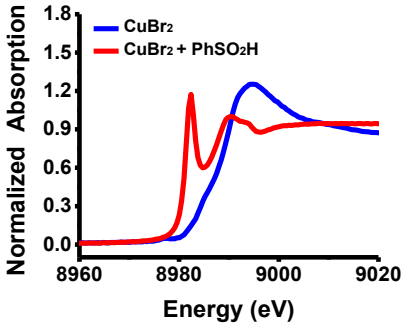


Figure S3. XANES spectra of $CuBr_2$ / DMF solution and $CuBr_2$ / $PhSO_2H$ / DMF solution.

3.3 $CuBr_2$ / 2 $PhSO_2H$ / MeCN solution: $CuBr_2$ (0.4 mmol, 88.3 mg) and $PhSO_2H$ (0.8 mmol, 113.6 mg) were added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of MeCN was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature (Figure S4, green line).

3.4 $CuBr_2$ / 2 $PhSO_2H$ / THF solution: $CuBr_2$ (0.4 mmol, 88.3 mg) and $PhSO_2H$ (0.8 mmol, 113.6 mg) were added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of THF was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature (Figure S4, red line).

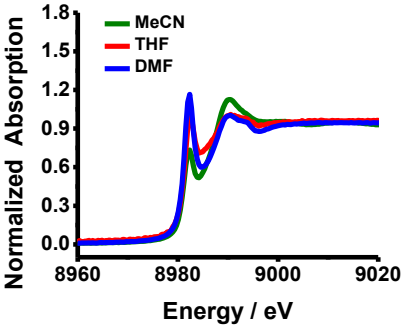


Figure S4. XANES spectra of $CuBr_2$ / $PhSO_2H$ / DMF solution, $CuBr_2$ / $PhSO_2H$ / MeCN solution and $CuBr_2$ / $PhSO_2H$ / THF solution.

3.5 $Cu(OAc)_2$ / 2 $PhSO_2H$ / DMF solution: $Cu(OAc)_2$ (0.4 mmol, 72.6 mg) and $PhSO_2H$ (0.8 mmol,

113.6 mg) were added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of DMF was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature (Figure S5, red line). Next, heated the cell to 80 °C and stirred for 5 minutes. XANES spectrum was measured at 80 °C (Figure S5, green line).

3.6 $Cu(OAc)_2$ / 2 $PhSO_2H$ / 3 LiBr / DMF solution: $Cu(OAc)_2$ (0.4 mmol, 72.6 mg), $PhSO_2H$ (0.8 mmol, 113.6 mg) and LiBr (1.2 mmol, 104.2 mg) were added to the XAS solution cell in a glovebox beforehand. Then, 4.0 mL of DMF was injected into the cell and the solution was stirred under N_2 at room temperature for 5 minutes. XANES spectrum was measured at room temperature (Figure S5, blue line).

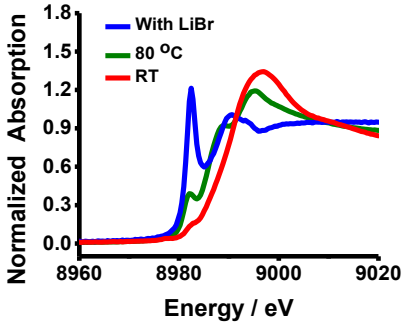


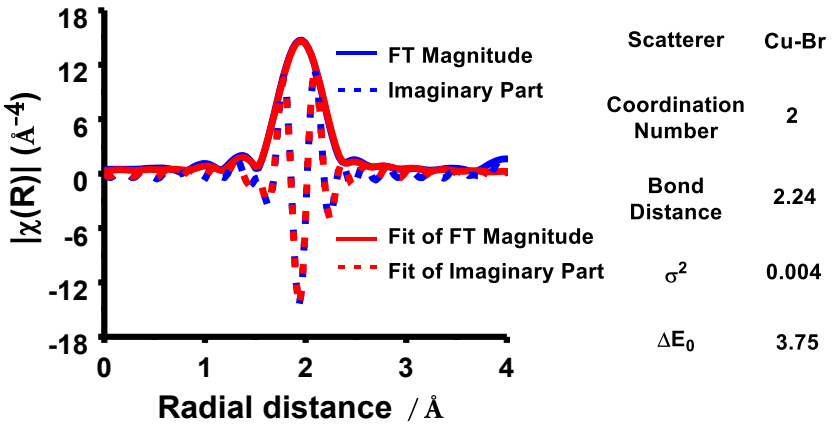
Figure S5. XANES spectra of $Cu(OAc)_2$ / 2 $PhSO_2H$ / DMF solution and $Cu(OAc)_2$ / 2 $PhSO_2H$ / 3 LiBr / DMF solution.

Table S1 Edge Energy and Oxidation States

Sample	Pre-edge Energy (eV)	Edge Energy (eV)	Oxidation State
Cu foil	N.A.	8979.0	0
$CuBr_2$ (DMF solution)	8977.3	8984.2	+2
$CuBr_2$ + 2 $PhSO_2H$ in DMF	N.A.	8981.3	+1
$CuBr_2$ + 2 $PhSO_2H$ in MeCN	N.A.	8981.2	+1
$CuBr_2$ + 2 $PhSO_2H$ in THF	N.A.	8981.6	+1
$Cu(OAc)_2$ + 2 $PhSO_2H$ in DMF	-	-	+1/+2
$Cu(OAc)_2$ + 2 $PhSO_2H$ in DMF (80 °C)	-	-	+1/+2
$Cu(OAc)_2$ + 2 $PhSO_2H$ + 3 LiBr in DMF	N.A.	8981.6	+1

Figure S6. Fitting results of the EXAFS spectra of $CuBr_2$ / 2 $PhSO_2H$ / DMF solution

FT range: 2.93 Å-1 – 13.67 $Å^{-1}$; fitting range: 1.40 Å – 2.50 Å



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