Heterogeneous chitosan@copper catalyzed selective C(sp^3)-H sulfonylation of ketone hydrazones with sodium sulfinates: direct access to β-ketosulfones

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1. General Information

a. Materials

Chitosan powder (MW: 10,000-50,000, deacetylation degree 95%, purchased from Aladdin reagent (Shanghai) Co., Ltd.) was used without further purification. Sodium sulfinates were purchased from Alfa Aesar. Other chemicals were obtained commercially and used without any prior purification. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90 °C) unless otherwise noted. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy, using methods consistent with those reported in the literature[37].

b. Methods

Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard.

IR spectra were recorded using a Nicolet 380 FT-IR spectrophotometer using KBr discs.

Transmission electron microscopy (TEM) images were taken using a Hitachi HT-7700 microscope.

The X-ray diffraction (XRD) analysis was carried out using a Bruker D8 X-ray diffractometer with Cu Ka radiation.

Thermogravimetric analyses were performed with a Netzsch STA409PC analyzer at 10 °C/min in air (10 ml/min). A total of 5 mg of each sample in an alumina pan was analyzed in a temperature range of 30-650 °C.

Analytical thin layer chromatography (TLC) was performed using Merk precoated TLC (silica gel 60 F254) plates.

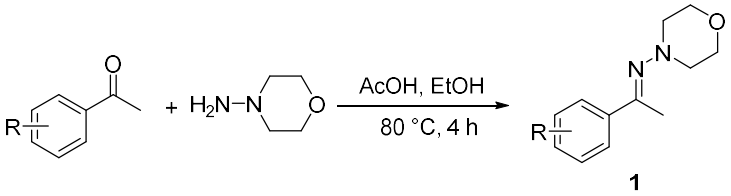
2. Experimental Section

General procedure for the synthesis of biomass-derived copper catalysts[47]:

In a 100 mL round-bottomed flask equipped with a reflux condenser and magnetic stir bar, cupric acetate anhydrous (90.83 mg, 0.500 mmol) was dissolved in H_2O (40 mL). Then Chitosan (690 mg) was added to the solution to obtain a suspension, which was stirred at 50 °C for 3 hours. After the solution cooled to room temperature, H_2O was removed slowly under reduced pressure. The obtained light blue colored solid was dried for 12 hours at 60 °C under vacuum.

The dried sample was transferred to a porcelain boat and placed in an oven. The oven was placed under a vacuum and then rinsed with nitrogen for half an hour. The oven was then heated to an appropriate temperature (e.g., 300, 400, or 500 °C), with a temperature gradient of 2 °C/min, and kept at the same temperature for 2 hours in a nitrogen atmosphere. After that, the oven was cooled to room temperature. During the whole process, nitrogen was continuously purged through the oven. The prepared catalyst was stored in a small bottle with a screw cap without any special air protection at room temperature.

General procedure for preparation of ketone hydrazones [65]:



1

Acetophenone (4 mmol), N-Aminomorpholine (4.4 mmol), 0.5 mL acetic acid, and 10 mL ethanol were added to a 25 mL reaction tube, and the reaction was stirred under reflux for 4 h and detected by TLC. After the reaction was complete, the mixture was cooled with ice water, and the product was precipitated. The precipitate was filtered and washed three times with petroleum ether and ice water to give the target ketone hydrazones product **1**.

General procedure for heterogeneous copper-catalyzed coupling of ketone hydrazones with sodium sulfinates

A mixture of ketone hydrazones **1** (0.2 mmol), sodium sulfinates **2** (0.4mmol), Cu_xO_y@CS-400 (30 mg), Ag_2CO_3 (20 mol%), and $K_2S_2O_8$ (2.0 equiv) in acetone (1.5 mL) in a 25 mL Schlenk tube was stirred at 80 °C for 5 h. After cooling to room temperature, the mixture was filtered through a pad of Celite. The solvent was removed under reduced pressure. The gathered residue was then purified by column chromatography (200-300 mesh silica gel, petroleum ether/EtOAc=10:1).

General procedure for catalyst recycling experiment

To probe whether Cu_xO_y@CS-400 (30 mg) was recyclable, the C-S coupling reaction was repeated five times with the same catalyst sample, which was recovered after each reaction. The initial amount of catalyst was 10 mol% and reactions were performed for 5 h. Upon completion of the reaction, the catalyst was filtered off, washed (2V) with ethyl acetate and water, and then dried for 3 h at 80 °C. It was then stored under ambient conditions overnight and used again.

3. Catalyst Characterization

3.1 Yield (in pyrolysis process):

Cu_xO_y@CS-300: 93.1% (wt)

Cu_xO_y@CS-400: 54.8% (wt)

Cu_xO_y@CS-500: 11.3% (wt)

3.2 Fourier transform infrared (FTIR)

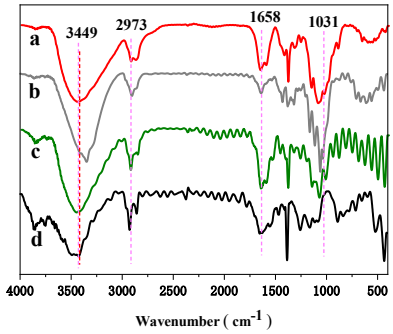


Figure S1. Infrared spectra of (a) Chitosan (CS); (b) $Cu(OAc)_2$@CS; (c) Cu_xO_y@CS-300; (d) Cu_xO_y@CS-400; (e) Cu_xO_y@CS-500.

3.3 Thermogravimetry (TG)

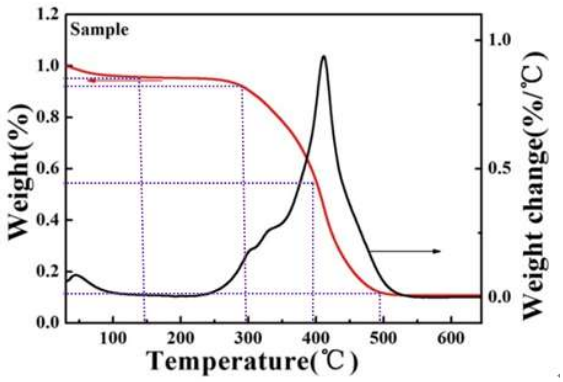
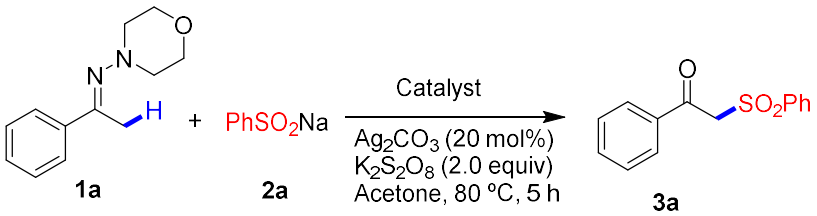


Figure S2. Thermogravimetry (TG) of Cu_xO_y@CS-400

4. Control and mechanism experiments

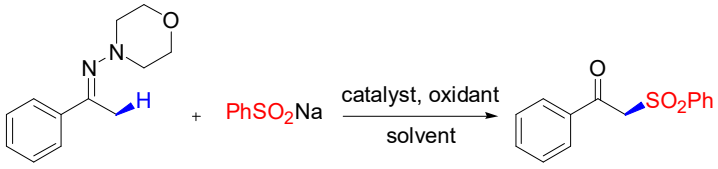
Table S1 Control experiments [a]



Entry	Catalyst	Yield (%)[b]
1	Cu/C@Fe_3O_4	trace
2	Cu@MXene	trace
3	CS@$Cu(OAc)_2$	16
4	GPT-$CuCl_2$	15

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (30 mg), silver carbonate (20 mol%), potassium persulfate (2.0 equiv), acetone (1.5 mL), stirred at 80 °C, under air, 5 h. [b] Isolated yields.

Table S2. Optimization of Cocatalysts [a]

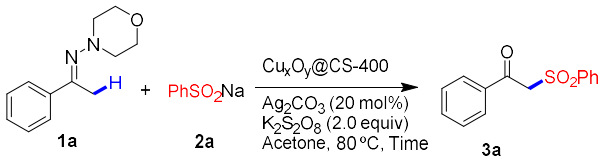


1a **2a** **3a**

entry	catalyst	cocatalyst	oxidant	solvent	yield (%)[b]
1	CuxOy@CS-400	Ag_2CO_3	$Na_2S_2O_8$	acetone	81
2	CuxOy@CS-400	Ag_2O	$Na_2S_2O_8$	acetone	32
3	CuxOy@CS-400	Ag_2SbF_6	$Na_2S_2O_8$	acetone	44
4	CuxOy@CS-400	AgCl	$Na_2S_2O_8$	acetone	20
5	CuxOy@CS-400	Ag_2SO_4	$Na_2S_2O_8$	acetone	34

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), Cu_xO_y@CS-400 (30mg), silver carbonate (20 mol %), potassium persulfate (2.0 equiv), acetone (1.5 mL), 80 °C, 5 h, air. [b] Isolated yields.

Table S3. Optimization of time [a]

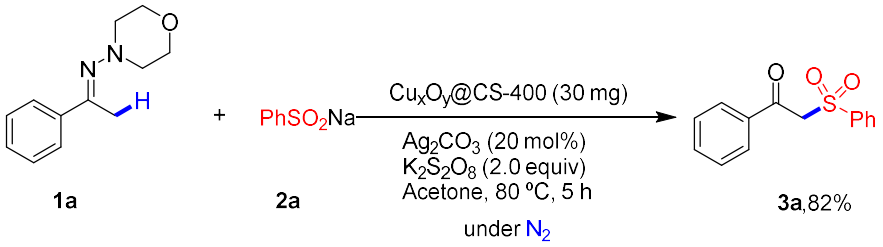


1a 2a 3a

Entry	Time	Yield (%)[b]
1	1	25
2	2	41
3	3	66
4	4	75
5	5	81

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), Cu_xO_y@CS-400 (30mg), silver carbonate

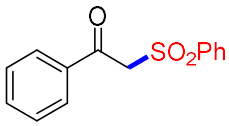
(20 mol %), potassium persulfate (2.0 equiv), acetone (1.5 mL), 80 ºC, 5 h, air. [b] Isolated yields.



Scheme S1 Investigation of Influence of Atmosphere on the Reactions.

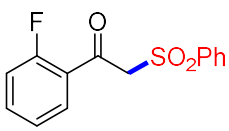
5. Characterization of the Products

1-Phenyl-2-(phenylsulfonyl)ethanone (3a)[37]



Obtained as a light white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.3 Hz, 2H), 7.90 (d, J = 7.3 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.9 Hz, 2H), 7.48 (t, 2H), 4.74 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.99, 138.71, 135.73, 134.35 (d, J = 17.7 Hz), 129.28 (d, J = 9.9 Hz), 128.90, 128.62, 63.46. HRMS (ESI+): Calculated for $C_{14}H_{12}FO_3S$: $[M+H]^+$ 261.0585, Found 261.0581.

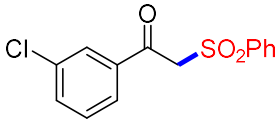
1-(2-Fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (3b)[17]



Obtained as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.81 (td, J = 7.7, 1.7 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.59 – 7.52

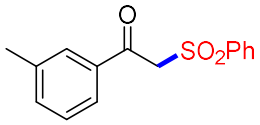
(m, 3H), 7.24 (d, J = 7.7 Hz, 1H), 7.11 (dd, J = 11.4, 8.4 Hz, 1H), 4.81 (s, 2H). 13C NMR (126 MHz, $CDCl_3$) δ 185.97 (d, J = 3.0 Hz), 161.93 (d, J = 255.3 Hz), 139.13, 136.16 (d, J = 9.5 Hz), 134.15, 131.17 (d, J = 1.7 Hz), 129.16, 128.58, 124.87 (d, J = 3.4 Hz), 116.95, 116.76, 67.04 (d, J = 8.9 Hz). HRMS (ESI+): Calculated for $C_{14}H_{11}FO_3S$: $[M+H]^+$ 279.0491, Found 279.0493.

1-(3-Chlorophenyl)-2-(phenylsulfonyl) ethan-1-one (3c)[66]



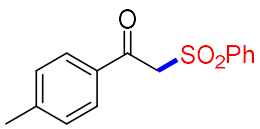
Obtained as a light yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 3H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 7.7 Hz, 3H), 7.44 (t, *J* = 7.9 Hz, 1H), 4.71 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.89, 138.54, 137.20, 135.33, 134.37 (d, *J* = 15.8 Hz), 130.20, 129.32, 129.16, 128.59, 127.55, 63.58. HRMS (ESI^+): Calculated for $C_{14}H_{11}ClO_3S$: $[M+H]^+$ 295.0195, Found 295.0199.

2-(Phenylsulfonyl)-1-(*m*-tolyl) ethan-1-one (3d)[36]



Obtained as a light white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.73 (d, *J* = 10.0 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 4.73 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.13, 138.78 (d, *J* = 5.1 Hz), 135.77, 135.24, 134.23, 129.69, 129.20, 128.77, 128.64, 126.63, 63.45, 21.33. HRMS (ESI+): Calculated for $C_{15}H_{14}O_3S$: $[M+H]^+$ 275.0742, Found 275.0748.

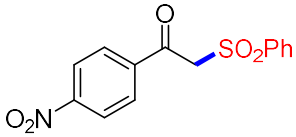
2-(Phenylsulfonyl)-1-(*p*-tolyl) ethan-1-one (3e)[36]



Obtained as a light white solid.^1H NMR (500 MHz, $CDCl_3$) δ 7.89

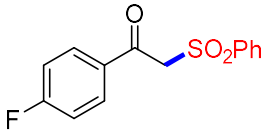
(d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.30 – 7.25 (m, 2H), 4.72 (s, 2H), 2.42 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 187.50, 145.69, 138.72, 134.23, 133.31, 131.53, 129.55 (d, J = 14.0 Hz), 129.21, 128.61, 63.44, 21.83. HRMS (ESI+): Calculated for $C_{15}H_{14}O_3S$: $[M+H]^+$ 275.0742, Found 275.0745.

1-(4-Nitrophenyl)-2-(phenylsulfonyl) ethan-1-one (3f)[43]



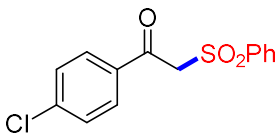
Obtained as a light yellow solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 7.4 Hz, 2H), 7.71 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 2H), 4.77 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.84, 150.92, 139.93, 138.35, 134.65, 130.49, 129.46, 128.52, 124.03, 64.01. HRMS (ESI+): Calculated for $C_{14}H_{11}NO_5S$: $[M+H]^+$ 306.0436, Found 306.0435.

1-(4-Fluorophenyl)-2-(phenylsulfonyl) ethan-1-one (3g)[36]



Obtained as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 - 7.97 (m, 2H), 7.89 (d, J = 7.3 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 8.6 Hz, 2H), 4.72 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.42, 166.51 (d, J = 257.8 Hz), 134.39, 132.26 (d, J = 9.6 Hz), 128.93 (d, J = 93.6 Hz), 116.17 (d, J = 22.2 Hz), 63.60.HRMS (ESI+): Calculated for $C_{14}H_{11}FO_3S$: $[M+H]^+$ 279.0491, Found 279.0494.

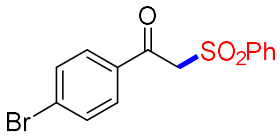
1-(4-Chlorophenyl)-2-(phenylsulfonyl) ethan-1-one (3h)[36]



Obtained as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 4H), 7.69 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 4.70 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.85, 141.21, 138.53, 134.41,

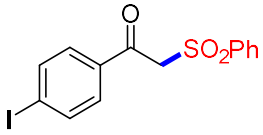
134.04, 130.78, 129.30 (d, J = 5.5 Hz), 128.57, 63.62. HRMS (ESI$^+$): Calculated for $C_{14}H_{11}ClO_3S$: $[M+H]^+$ 295.0195, Found 295.0196.

1-(4-Bromophenyl)-2-(phenylsulfonyl) ethan-1-one (3i)[36]



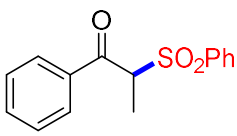
Obtained as a light yellow solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (t, J = 7.7 Hz, 4H), 7.68 (t, J = 7.5 Hz, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 4.71 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.88, 141.18, 138.53, 134.42, 130.78, 129.32, 129.26, 128.56, 63.57. HRMS (ESI$^+$): Calculated for $C_{14}H_{11}BrO_3S$: $[M+H]^+$ 338.9690, Found 338.9691.

1-(4-Iodophenyl)-2-(phenylsulfonyl) ethan-1-one (3j)[17]



Obtained as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 - 7.82 (m, 4H), 7.68 - 7.62 (m, 3H), 7.55 (t, J = 7.8 Hz, 2H), 4.69 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.45, 138.56, 138.26, 134.98, 134.40, 131.50, 130.57, 129.74, 129.31, 128.55, 103.11, 63.50. HRMS (ESI+): Calculated for $C_{14}H_{11}IO_3S$: $[M+H]^+$ 386.9552, Found 386.9551.

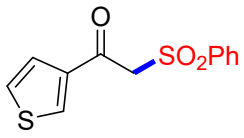
1-Phenyl-2-(phenylsulfonyl)propan-1-one (3j)[36]



Obtained as a light yellow solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.3 Hz, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.63 (dt, J = 20.0, 7.4 Hz, 2H), 7.50 (dt, J = 22.0, 7.8 Hz, 4H), 5.17 (q, J = 6.9 Hz, 1H), 1.58 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.49, 136.21, 136.10, 134.24, 134.11, 129.82, 129.16, 128.91, 128.79,

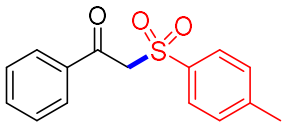
64.98, 13.20. HRMS (ESI+): Calculated for $C_{15}H_{14}O_3S$: $[M+H]^+$ 275.0742, Found 275.0742.

2-(Phenylsulfonyl)-1-(thiophen-3-yl)ethan-1-one (3l)[67]



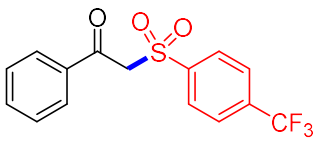
Obtained as a light white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.72 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.18, 145.40, 135.78, 134.35, 129.86, 129.56, 129.35, 128.86, 128.70, 128.62, 63.58, 21.73. HRMS (ESI+): Calculated for C15H14O3S: [M+H] + 275.0742, Found 275.0745.

1-Phenyl-2-(toluene-4-sulfonyl)-ethan-1-one (3m)[37]



Obtained as a light white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.72 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.18, 145.40, 135.78, 134.35, 129.86, 129.56, 129.35, 128.86, 128.70, 128.62, 63.58, 21.73. HRMS (ESI+): Calculated for $C_{15}H_{14}O_3S$: $[M+H]^+$ 275.0742, Found 275.0745.

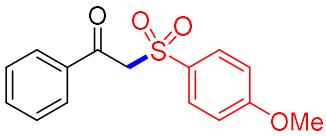
1-Phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl) ethan-1-one (3n)



Obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.95 – 7.91 (m, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 4.78 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.73,

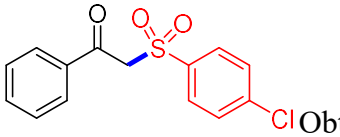
142.08, 135.48, 134.71, 129.43, 129.22, 129.03, 126.36 (q, J = 3.7 Hz), 121.97, 63.10. HRMS (ESI+): Calculated for $C_{15}H_{11}F_3O_3S$: $[M+H]^+$ 329.0459, Found 329.0458.

2-((4-methoxyphenyl) sulfonyl)-1-phenylethan-1-one (3o)[37]



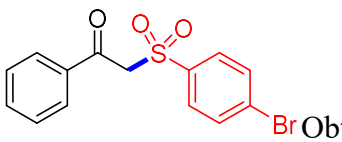
Obtained as a light white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.62 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 4.72 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.34, 164.17, 135.78, 134.35, 130.90, 130.15, 129.36, 128.87, 114.39, 63.76, 55.73. HRMS (ESI+): Calculated for $C_{15}H_{14}O_4S$: $[M+H]^+$ 291.0691, Found 291.0692.

2-((4-chlorophenyl) sulfonyl)-1-phenylethan-1-one (3p)[37]



Obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.56 – 7.47 (m, 4H), 4.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.93, 141.16, 137.04, 135.57, 134.60, 130.21, 129.57, 129.28, 128.99, 63.34. HRMS (ESI+): Calculated for $C_{14}H_{11}ClO_3S$: $[M+H]^+$ 295.0195, Found 295.0195.

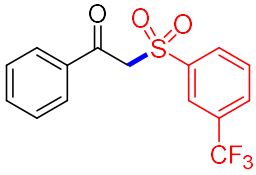
2-((4-bromophenyl) sulfonyl)-1-phenylethan-1-one (3q)[37]



Obtained as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.79 – 7.73 (m, 2H), 7.73 – 7.67 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 4.74 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.90, 137.60, 135.57, 134.60, 132.55, 130.24, 129.82, 129.28, 128.98, 63.32. HRMS (ESI+): Calculated for

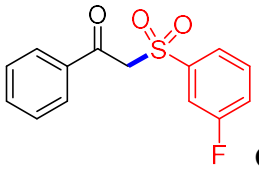
$C_{14}H_{11}BrO_3S$: $[M+H]^+$ 338.9690, Found 338.9697.

1-Phenyl-2-((3-(trifluoromethyl) phenyl)sulfonyl)ethan-1-one (3r)



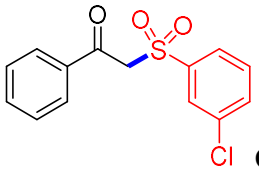
Obtained as a light brown solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.56 – 7.47 (m, 4H), 4.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.93, 141.16, 137.04, 135.57, 134.60, 130.21, 129.57, 129.28, 128.99, 63.34. HRMS (ESI+): Calculated for $C_{15}H_{11}F_3O_3S$: $[M+H]^+$ 329.0459, Found 329.0458.

2-((3-fluorophenyl) sulfonyl)-1-phenylethan-1-one (3s)[68]



Obtained as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 2H), 7.71 (d, J = 7.8 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.57 – 7.54 (m, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.39 – 7.35 (m, 1H), 4.75 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.72, 162.34 (d, J = 252.8 Hz), 140.60 (d, J = 6.7 Hz), 135.58, 134.60, 131.08 (d, J = 7.7 Hz), 129.27, 128.98, 124.53 (d, J = 3.4 Hz), 121.61 (d, J = 21.2 Hz), 116.08 (d, J = 24.5 Hz), 63.24. HRMS (ESI+): Calculated for $C_{14}H_{11}FO_3S$: $[M+H]^+$ 279.0491, Found 279.0492.

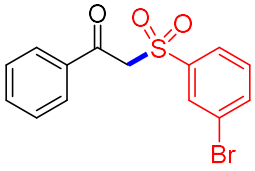
2-((3-chlorophenyl)sulfonyl)-1-phenylethanone (3t)[69]



Obtained as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.3 Hz, 2H), 7.89 (d, J = 1.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.1 Hz,

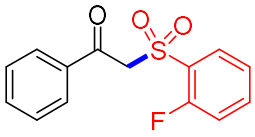
2H), 7.50 (t, J = 7.9 Hz, 3H), 4.76 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.73, 140.30, 135.54 (d, J = 5.1 Hz), 134.53 (d, J = 22.3 HAz), 130.50, 129.26, 128.99, 128.72, 126.88, 63.25. HRMS (ESI+): Calculated for $C_{14}H_{11}ClO_3S$: $[M+H]^+$

2-((3-bromophenyl) sulfonyl)-1-phenylethanone (3u)[70]



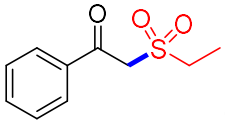
Obtained as a yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.84 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.43 (t, J = 7.9 Hz, 1H), 4.75 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.71, 140.49, 137.33, 134.59, 131.10 (d, J = 105.5 Hz), 129.25, 128.98, 127.32, 123.21, 63.29. HRMS (ESI^+): Calculated for $C_{14}H_{11}BrO_3S$: $[M+H]^+$ 338.9690, Found 338.9699.

2-((2-fluorophenyl) sulfonyl)-1-phenylethan-1-one (3v)[71]



Obtained as a light brown solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.92 - 7.85 (m, 1H), 7.72 - 7.60 (m, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.27 (t, 1H), 4.93 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.76, 159.66 (d, J = 256.0 Hz), 136.70 (d, J = 8.6 Hz), 135.67, 134.55, 130.81, 129.22, 128.96, 124.82 (d, J = 3.7 Hz), 117.14 (d, J = 21.1 Hz), 62.19. HRMS (ESI+): Calculated for $C_{14}H_{11}FO_3S$: $[M+H]^+$ 279.0491, Found 279.0497.

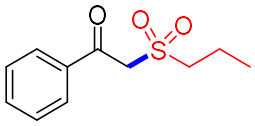
2-(ethylsulfonyl)-1-phenylethanone (3w)[37]



Obtained as a white solid (81% yield); M.p. 150-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 - 7.99 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 4.57 (s, 2H), 3.29 (q, J = 7.4 Hz, 2H), 1.47 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126

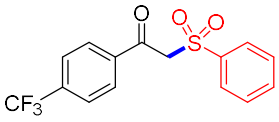
MHz, $CDCl_3$) δ 189.26, 135.77, 134.67, 129.34, 129.02, 58.80, 48.22, 6.70. HRMS (ESI^+): Calculated for $C_{10}H_{12}O_3S$: $[M+H]^+$ 213.0585, Found 213.0584.

1-phenyl-2-(propylsulfonyl) ethanone (3x)[72]



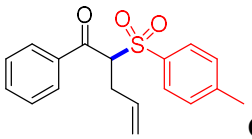
Obtained as a white solid; M.p. 150-151 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 - 7.94 (m, 2H), 7.66 (s, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 4.56 (s, 2H), 3.29 - 3.19 (m, 2H), 2.00 - 1.89 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.30, 135.77, 134.66, 129.34, 129.02, 59.64, 55.36, 15.82, 13.05. HRMS (ESI^+): Calculated for $C_{11}H_{14}O_3S$: $[M+H]^+$ 227.0742, Found 227.0745.

2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one(3y) [16]



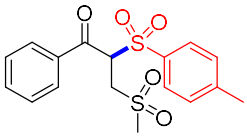
Obtained as a white solid. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, 2H, J = 8.2 Hz), 7.97−7.90 (m,2H), 7.83 (d, 2H, J = 8.3 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.51 (t, 2H, J= 7.8 Hz), 4.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 187.7,142.0, 135.9 (q, JC−F = 32.8 Hz), 135.5, 134.7, 129.4, 129.2, 129.0,126.4 (q, JC−F = 3.8 Hz), 123.0 (q, JC−F = 273.4 Hz), 63.1. ^{19}F NMR ($CDCl_3$, 471 MHz) δ −63.2.

5-Methyl-1-phenyl-2-tosylhex-4-en-1-one (4a)[73]



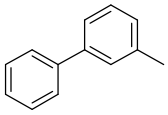
Obtained as a white solid. ^1H NMR ($CDCl_3$, 500MHz) δ 7.90 (dd, 2H, J = 8.3, 1.1 Hz), 7.66 (d, 2H, J = 8.3 Hz),7.61−7.56 (m, 1H), 7.46 (t, 2H, J = 7.8 Hz), 7.30 (d, 2H, J = 8.0 Hz),5.02 (dd, 1H, J = 10.2, 4.4 Hz), 4.87 (t, 1H, J = 7.4 Hz), 2.82−2.69(m, 2H), 2.43 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H); ^{13}C NMR($CDCl_3$, 126 MHz) δ 192.6, 145.3, 137.4, 136.5, 133.8, 133.6, 129.8,129.5, 129.0, 128.7, 117.5, 69.7, 27.3, 25.6, 21.7, 17.8.

3-(Methylsulfonyl)-1-phenyl-2-tosylpropan-1-one (4b)[7]



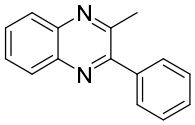
Obtained as a white solid. ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.93−7.89 (m, 2H), 7.58 (dd, 3H, J = 10.1, 7.9 Hz), 7.44 (t,2H, J = 7.9 Hz), 7.28 (s, 2H), 5.61 (dd, 1H, J = 11.2, 2.0 Hz), 4.11(dd, 1H, J = 13.9, 11.2 Hz), 3.76 (dd, 1H, J = 14.0, 1.3 Hz), 2.87 (s,3H), 2.42 (s, 3H); ^{13}CNMR ($CDCl_3$, 126 MHz) δ 190.1, 146.5,

3-Methyl-1,1′-biphenyl (5a)[64]



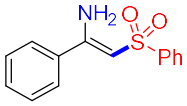
Obtained as a colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (dd, 2H, J = 8.0, 0.9 Hz), 7.37 (dd, 4H, J = 14.0, 6.2 Hz), 7.28 (t, 2H, J =7.5 Hz), 7.12 (d, 1H, J = 7.5 Hz), 2.37 (s, 3H); ^{13}CNMR($CDCl_3$, 126 MHz) δ 141.6, 141.4, 138.5, 128.9, 128.8, 128.2, 128.1,127.4, 127.3, 124.5, 21.7.

2-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one(3y) [7]



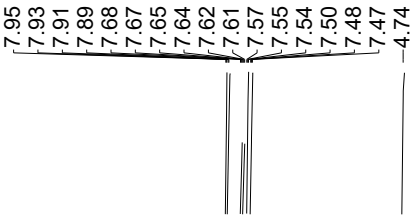
Obtained as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ8.13−8.08 (m, 1H), 8.05 (dd, 1H, J = 8.2, 1.5 Hz), 7.70 (pd, 2H, J =7.0, 1.7 Hz), 7.65 (dd, 2H, J = 8.1, 1.3 Hz), 7.49 (ddd, 3H, J = 8.5,7.8, 6.3 Hz), 2.77 (s, 3H); ^{13}CNMR ($CDCl_3$, 126 MHz) δ154.9, 152.5, 141.2, 141.0, 139.1, 129.7, 129.2, 129.2, 129.0, 128.9,128.5, 128.3, 24.4.

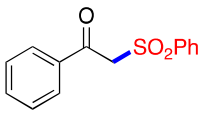
(Z)-1-Phenyl-2-(phenylsulfonyl)ethen-1-amine(D)[74]



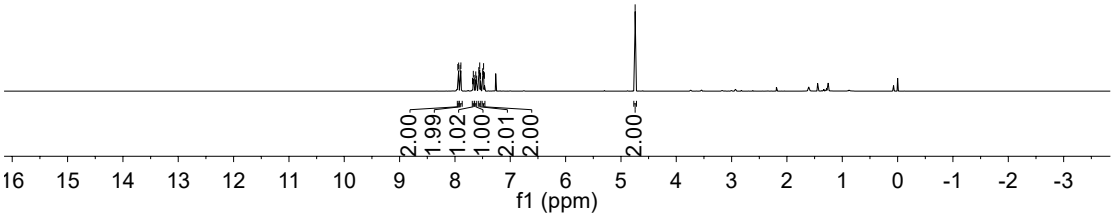
Obtained as a yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.94 (d, 2H, J = 7.4 Hz), 7.53 (t, 1H, J = 7.3 Hz), 7.48 (t, 2H, J = 7.6 Hz), 7.45 (d, 2H, J = 7.2 Hz), 7.41 (d, 1H, J = 7.1 Hz), 7.36 (t, 2H, J= 7.4 Hz), 5.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 156.7,144.5, 136.8, 132.4, 130.9, 129.0, 128.9, 126.4, 125.9, 91.4.

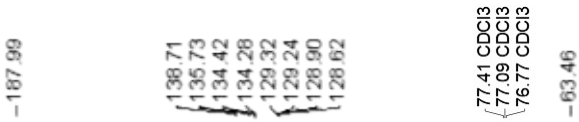
6. NMR spectra

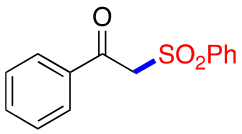

7.95
7.93
7.91
7.89
7.68
7.67
7.65
7.64
7.62
7.61
7.57
7.55
7.54
7.50
7.48
7.47
4.74


O
SO2Ph

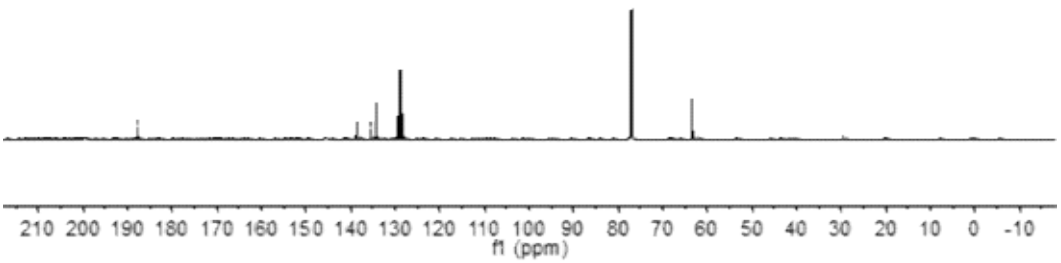
3a

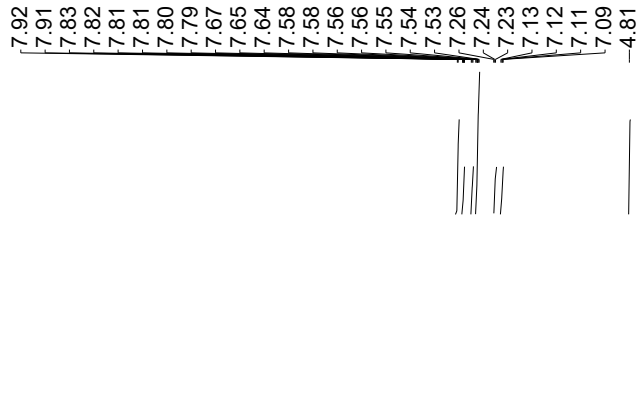

2.00
1.99
1.02
1.00
2.01
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.99
138.71
135.73
134.42
134.28
129.32
129.24
128.90
128.62
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
63.46


O
SO2Ph

3a


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.92
7.91
7.83
7.82
7.81
7.81
7.80
7.79
7.67
7.65
7.64
7.58
7.58
7.56
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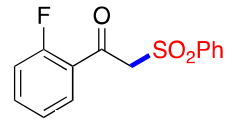
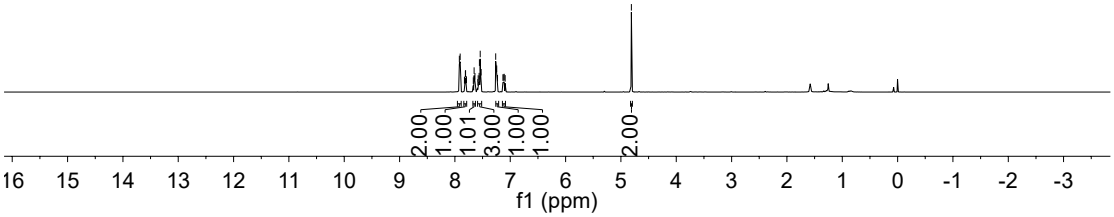
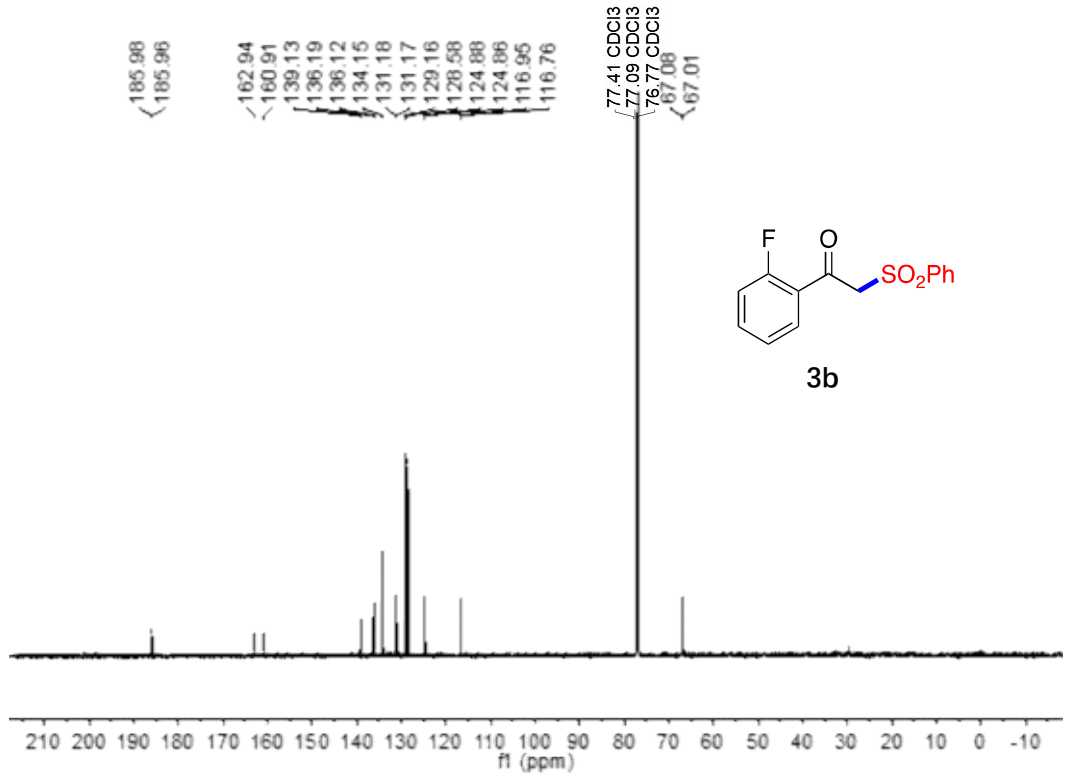
7.24
7.23
7.13
7.12
7.11
7.09
4.81


F
O
SO2Ph

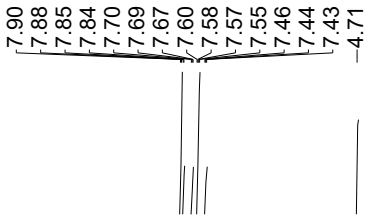
3b

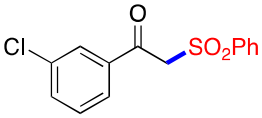

2.00
1.00
1.01
3.00
1.00
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


185.98
185.96
162.94
160.91
139.13
136.19
136.12
134.15
131.18
131.17
129.16
128.58
124.88
124.86
116.95
116.76
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
67.08
67.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

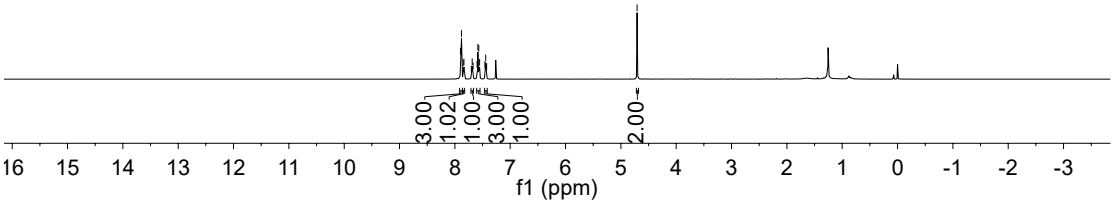
F
O
SO2Ph

3b

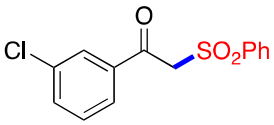

7.90
7.88
7.85
7.84
7.70
7.69
7.67
7.60
7.58
7.57
7.55
7.46
7.44
7.43
4.71


O
Cl
SO2Ph

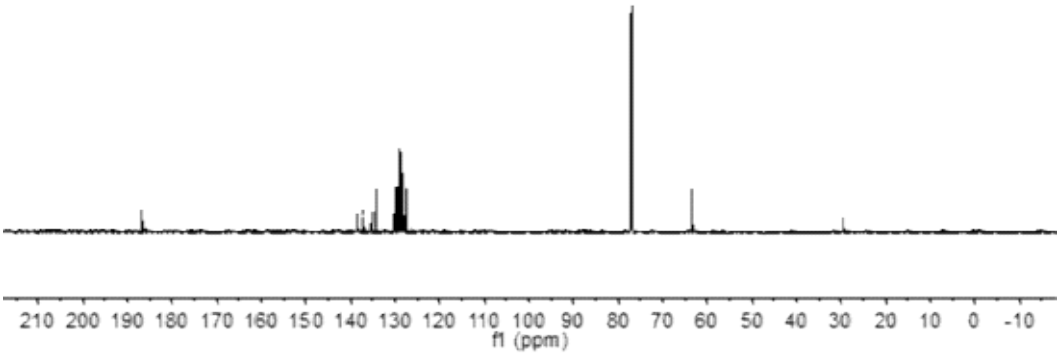
3c

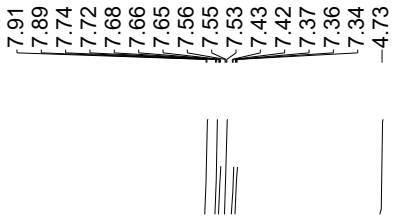

3.00
1.02
1.00
3.00
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

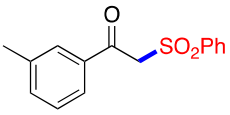

186.89
136.54
137.20
135.33
134.44
134.31
130.20
129.32
129.16
128.59
127.55
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
63.58


O
Cl
SO2Ph

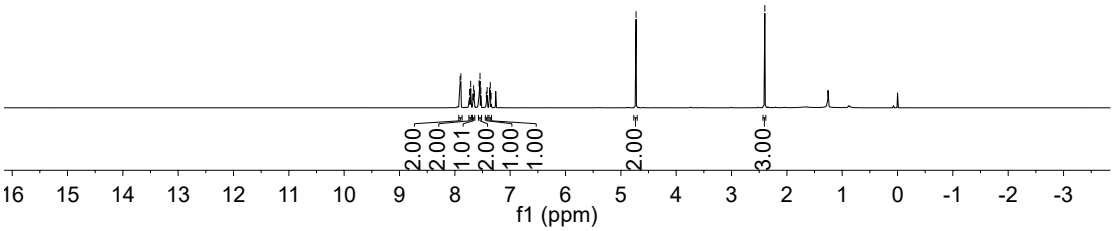
3c


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

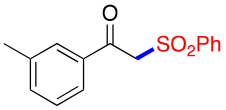

7.91
7.89
7.74
7.72
7.68
7.66
7.65
7.56
7.55
7.53
7.43
7.42
7.37
7.36
7.34
4.73
2.40


O
SO2Ph

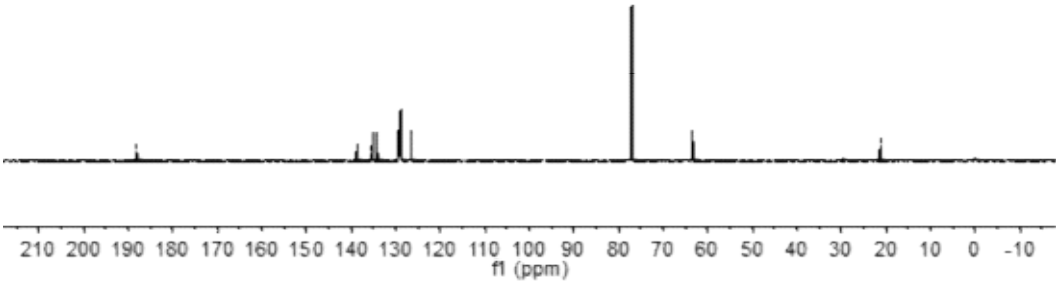
3d

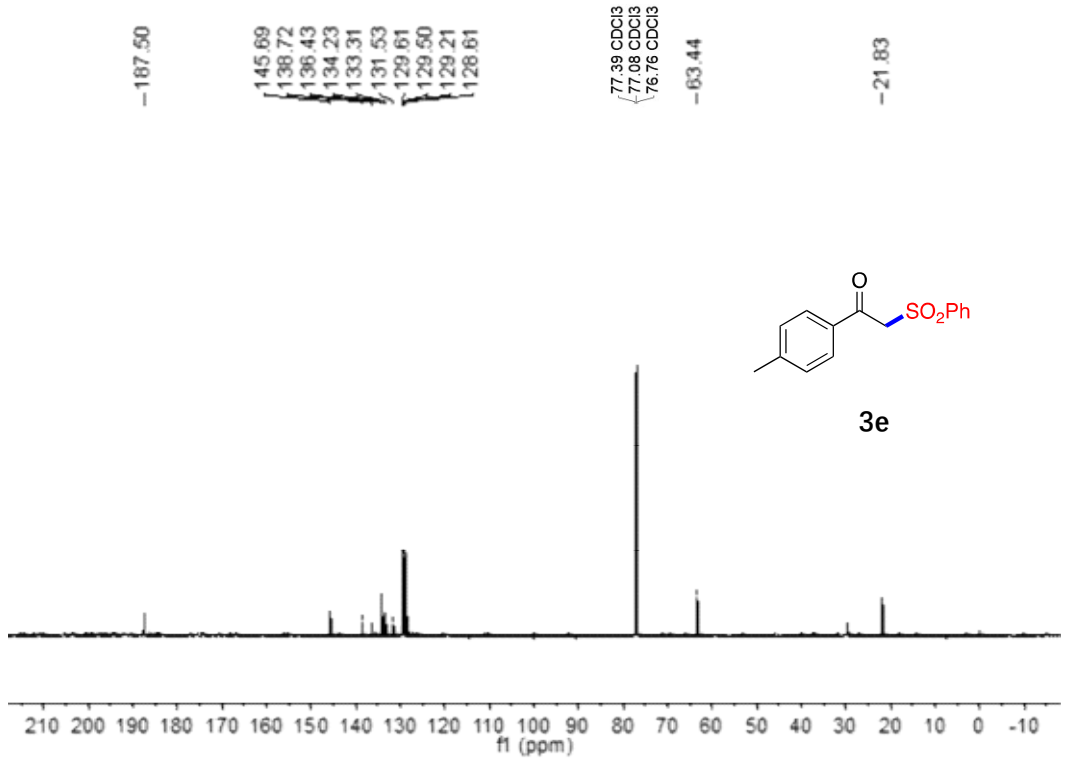

2.00
2.00
1.01
2.00
1.00
1.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

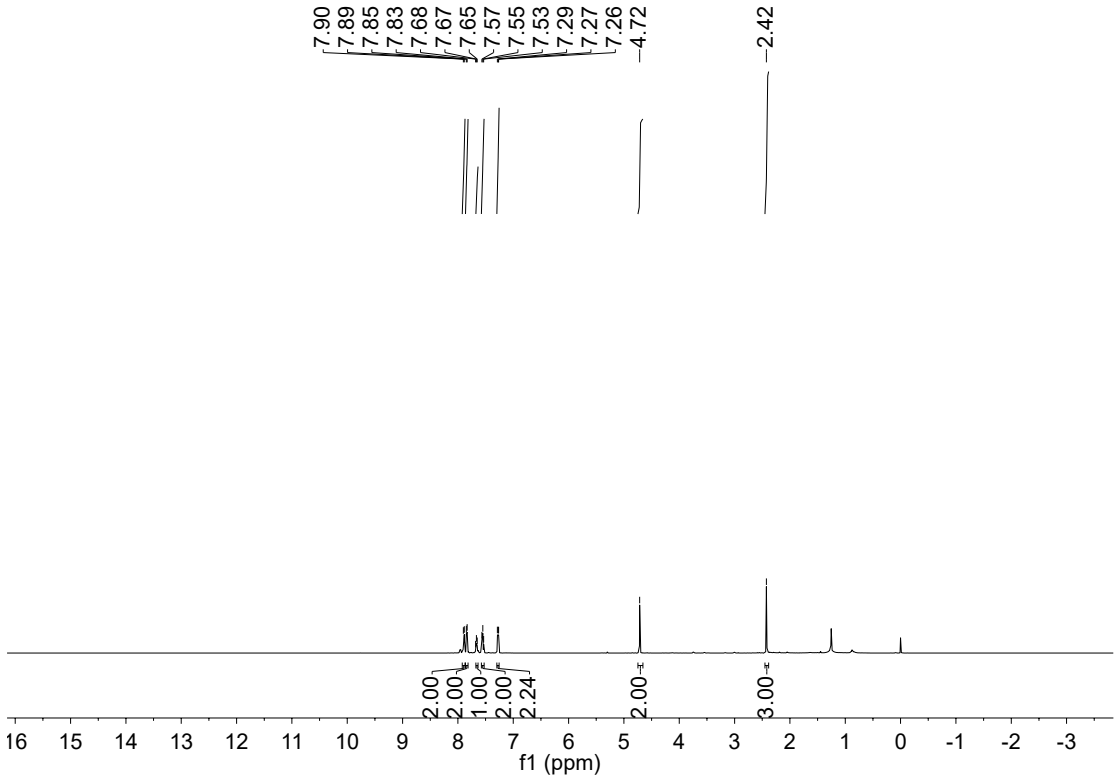

188.13
138.80
138.76
135.77
135.24
134.23
129.69
129.20
128.77
128.64
126.63
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
63.45
21.33

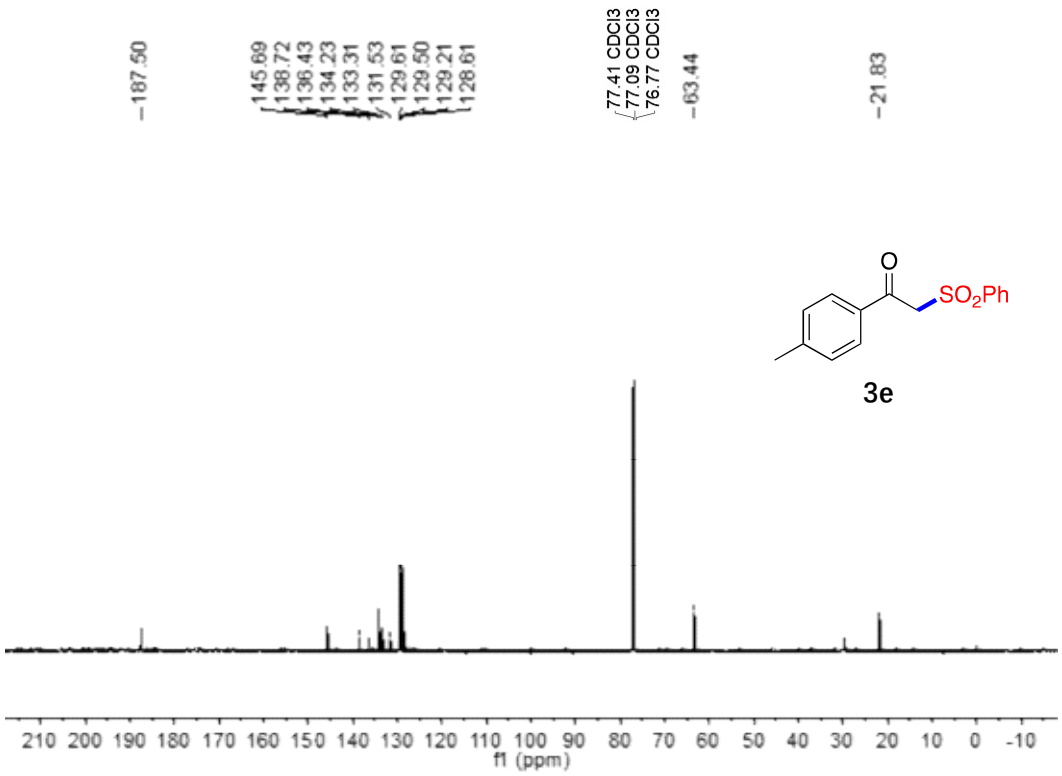

O
SO2Ph

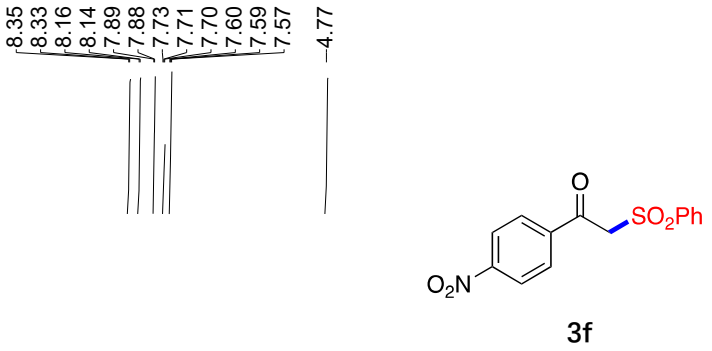
3d

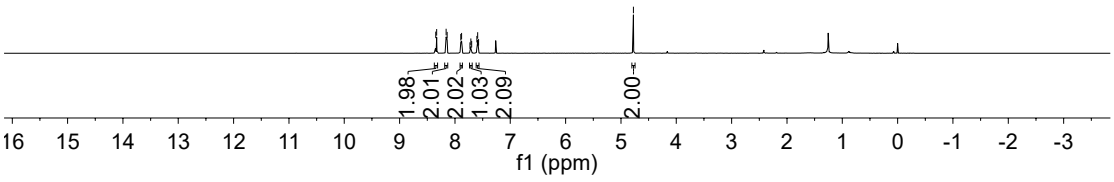

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

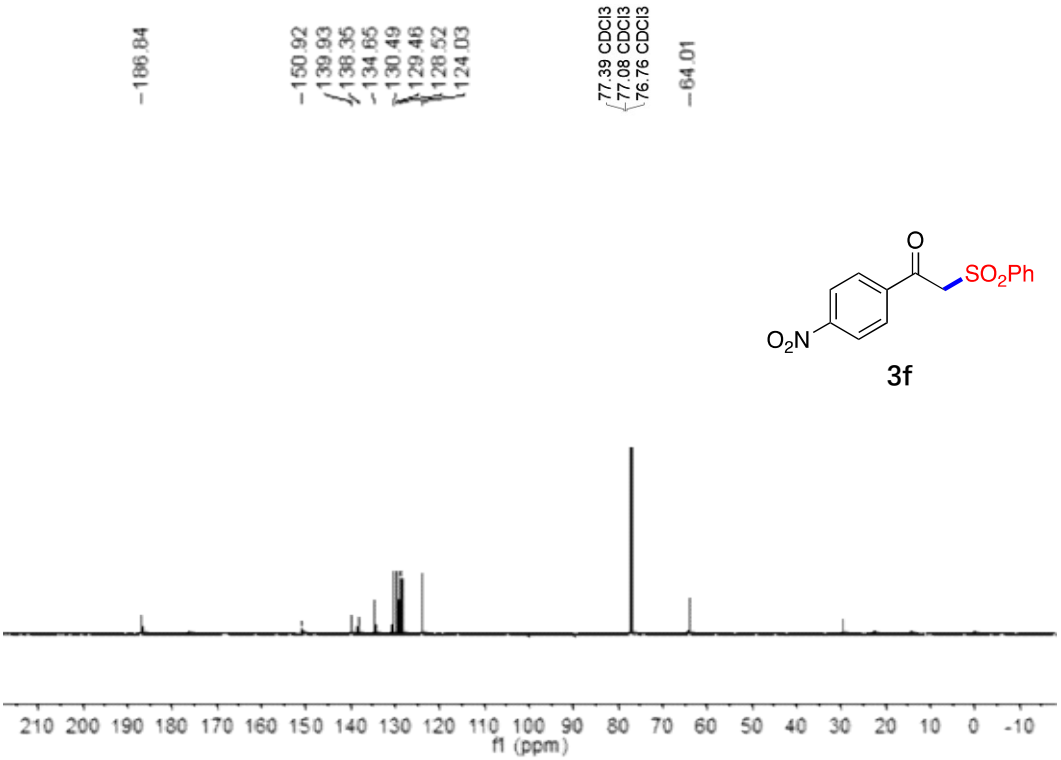

187.50
145.69
138.72
136.43
134.23
133.31
131.53
129.61
129.50
129.21
128.61
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.44
21.83
O
SO2Ph
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.90
7.89
7.85
7.83
7.68
7.67
7.65
7.57
7.55
7.53
7.29
7.27
7.26
4.72
2.42
2.00
2.00
1.00
2.00
2.24
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.50
145.69
138.72
136.43
134.23
133.31
131.53
129.61
129.50
129.21
128.61
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
63.44
21.83
O
SO2Ph
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

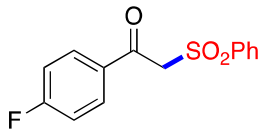

8.35
8.33
8.16
8.14
7.89
7.88
7.73
7.71
7.70
7.60
7.59
7.57
4.77
O
SO2Ph
O2N
3f

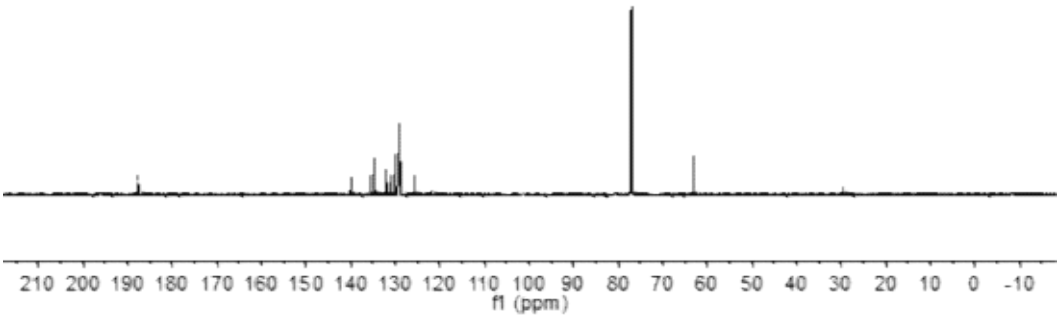

1.98
2.01
2.02
1.03
2.09
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

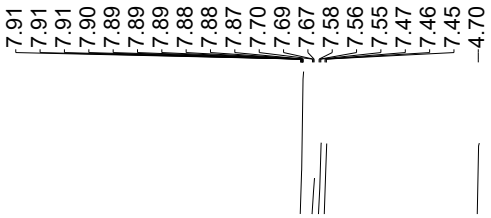

186.84
150.92
139.93
138.35
134.65
130.49
129.46
128.52
124.03
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
64.01
O
SO2Ph
O2N
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
8.17
8.13
8.11
7.93
7.91
7.73
7.72
7.66
7.64
7.63
7.51
7.50
7.48
4.79
O
SO2Ph
F
3g
0.98
1.00
3.02
1.04
1.04
2.02
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

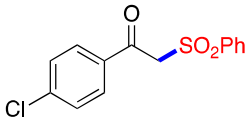
3g


187.71
139.87
135.50
134.67
132.17
131.83
130.93
130.90
130.00
129.20
129.01
125.90
125.87
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.19

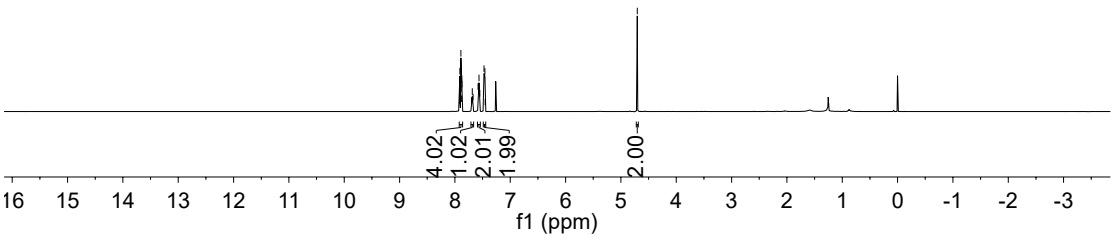

O
SO2Ph
F

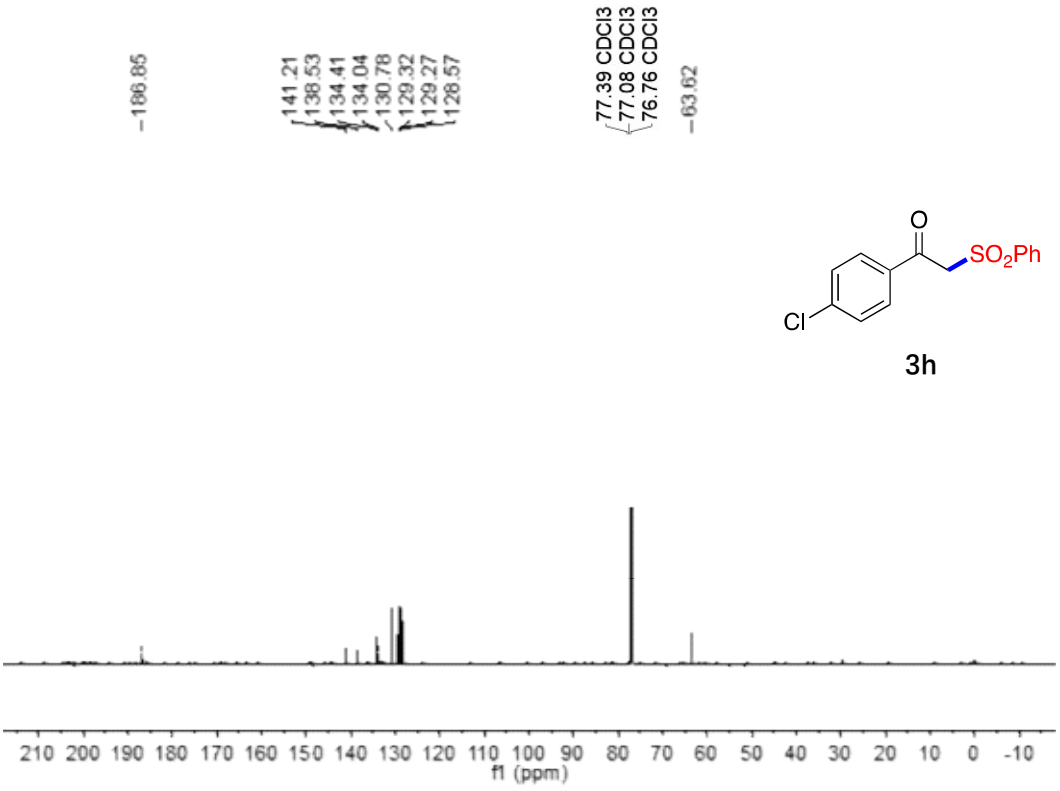

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.91
7.91
7.91
7.90
7.89
7.89
7.89
7.88
7.88
7.87
7.70
7.69
7.67
7.58
7.56
7.55
7.47
7.46
7.45
4.70


O
SO2Ph
Cl

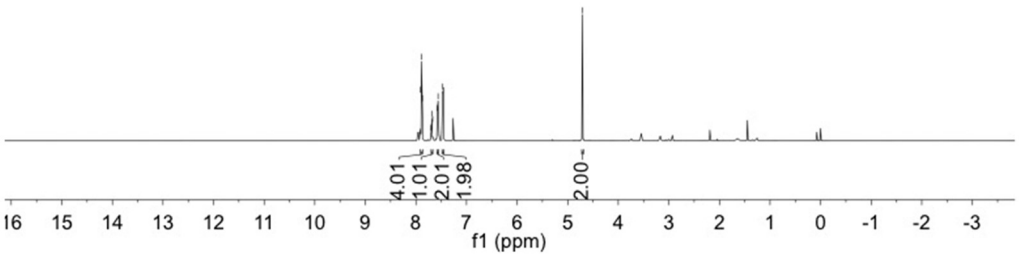
3h


4.02
1.02
2.01
1.99
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

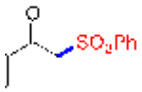

186.85
141.21
138.53
134.41
134.04
130.78
129.32
129.27
128.57
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.62
O
SO2Ph
Cl
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.91
7.89
7.87
7.70
7.68
7.67
7.58
7.56
7.47
7.45
4.71
O
SO2Ph
Br

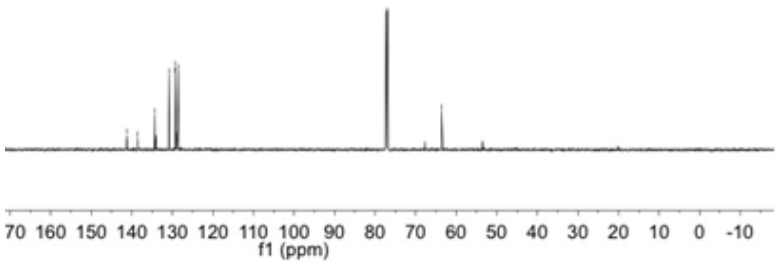
3i

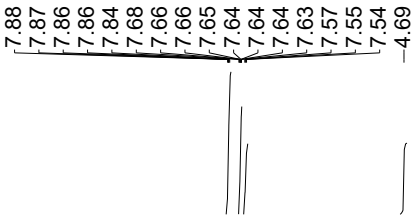

4.01
1.01
2.01
1.98
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

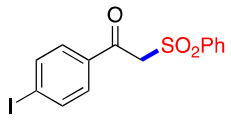

77.39 CDCl3
77.08 CDCl3
76.76 CDCl3


O
SO2Ph

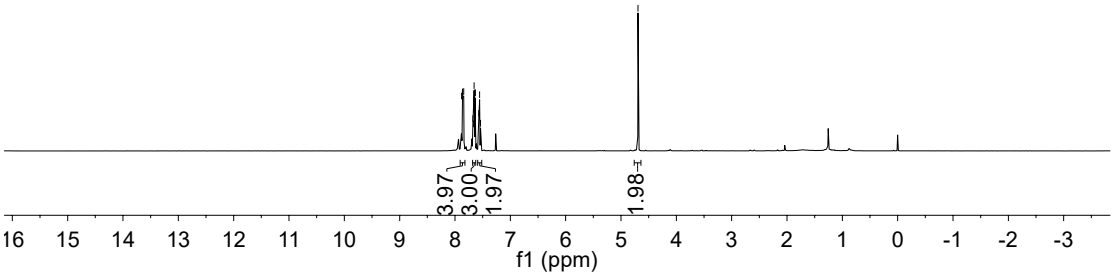
3i


70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

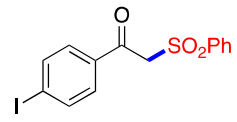

7.88
7.87
7.86
7.86
7.84
7.68
7.66
7.66
7.65
7.64
7.64
7.64
7.63
7.57
7.55
7.54
4.69


O
SO2Ph
I

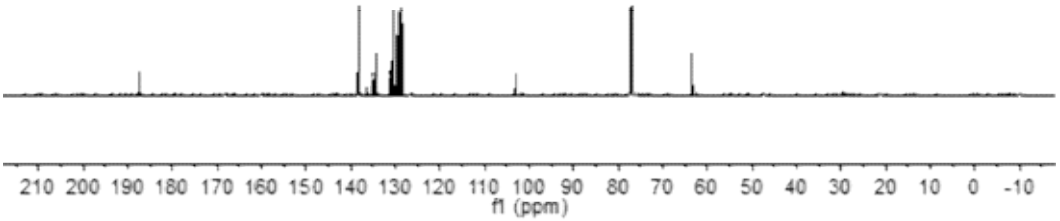
3j

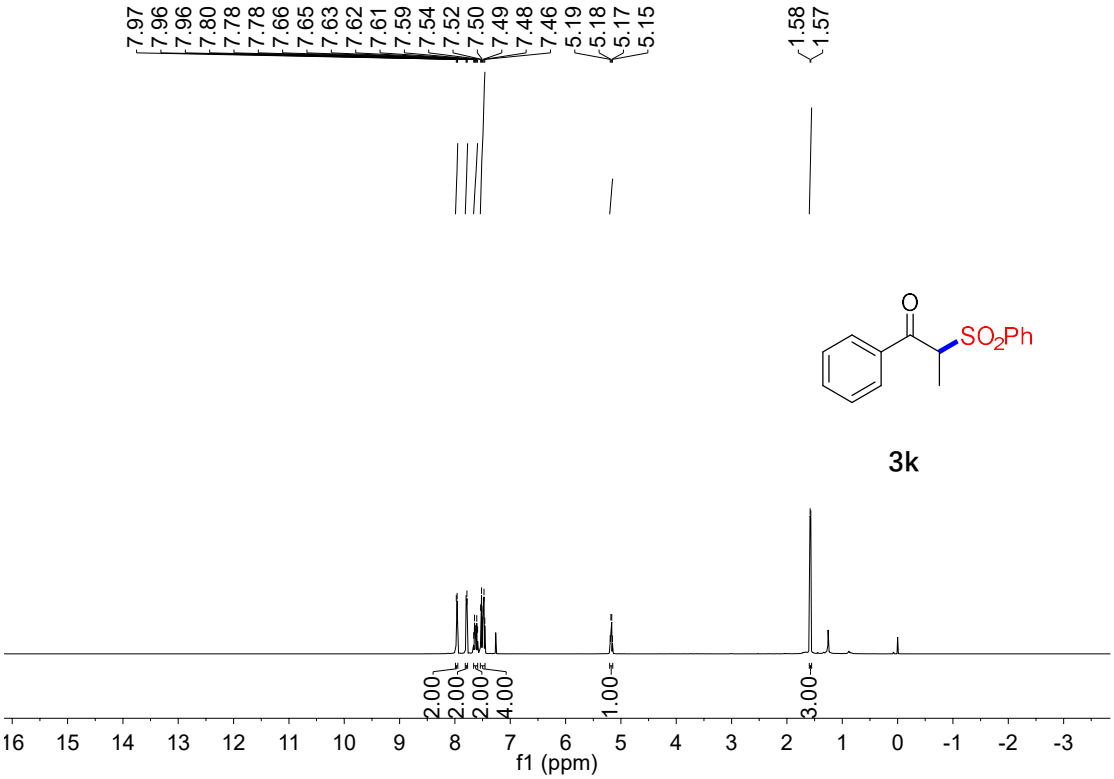

3.97
3.00
1.97
1.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.45
138.56
138.26
134.96
134.40
131.50
130.57
129.74
129.31
128.55
103.11
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.50

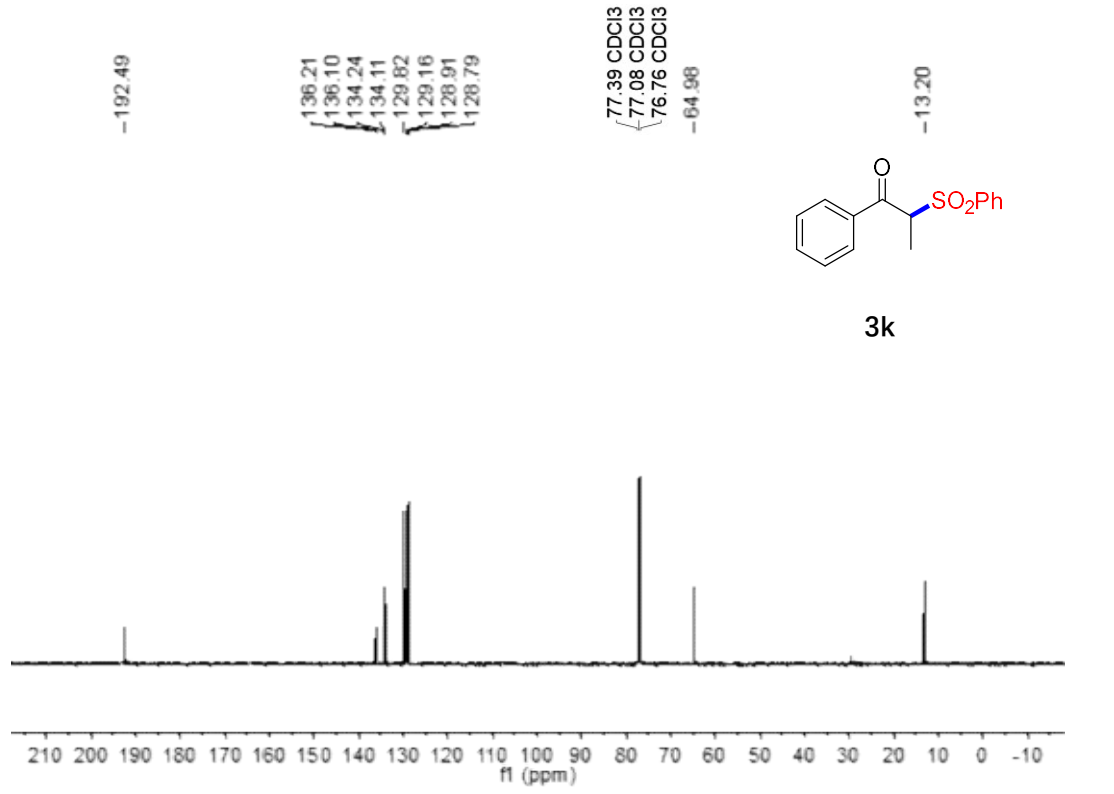

O
SO2Ph
I

3j

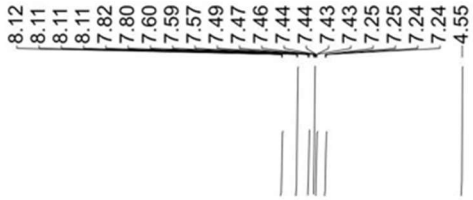

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

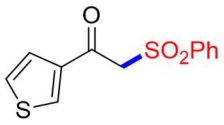

7.97
7.96
7.96
7.80
7.78
7.78
7.66
7.65
7.63
7.62
7.61
7.59
7.54
7.52
7.50
7.49
7.48
7.46
5.19
5.18
5.17
5.15
1.58
1.57
SO2Ph
2.00
2.00
2.00
4.00
1.00
3.00
f1 (ppm)

3k

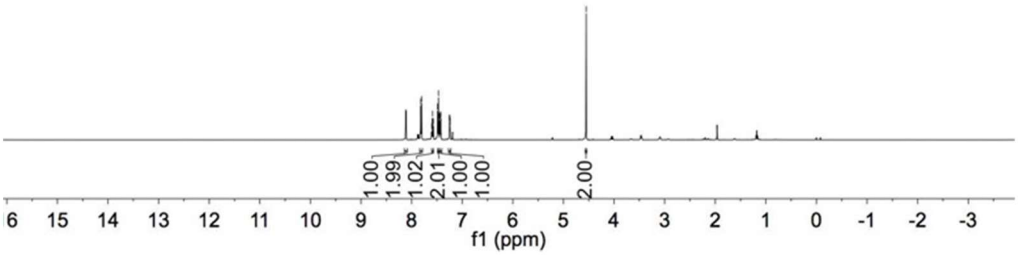

192.49
136.21
136.10
134.24
134.11
129.82
129.16
128.91
128.79
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
64.98
13.20
SO2Ph
f1 (ppm)

3k

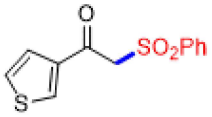

8.12
8.11
8.11
8.11
7.82
7.80
7.60
7.59
7.57
7.49
7.47
7.46
7.44
7.44
7.43
7.43
7.25
7.25
7.24
7.24
4.55


O
SO2Ph
S

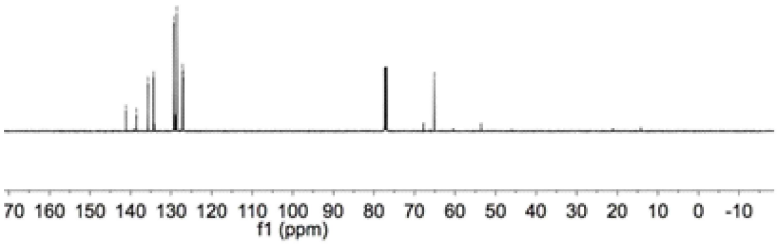
3l

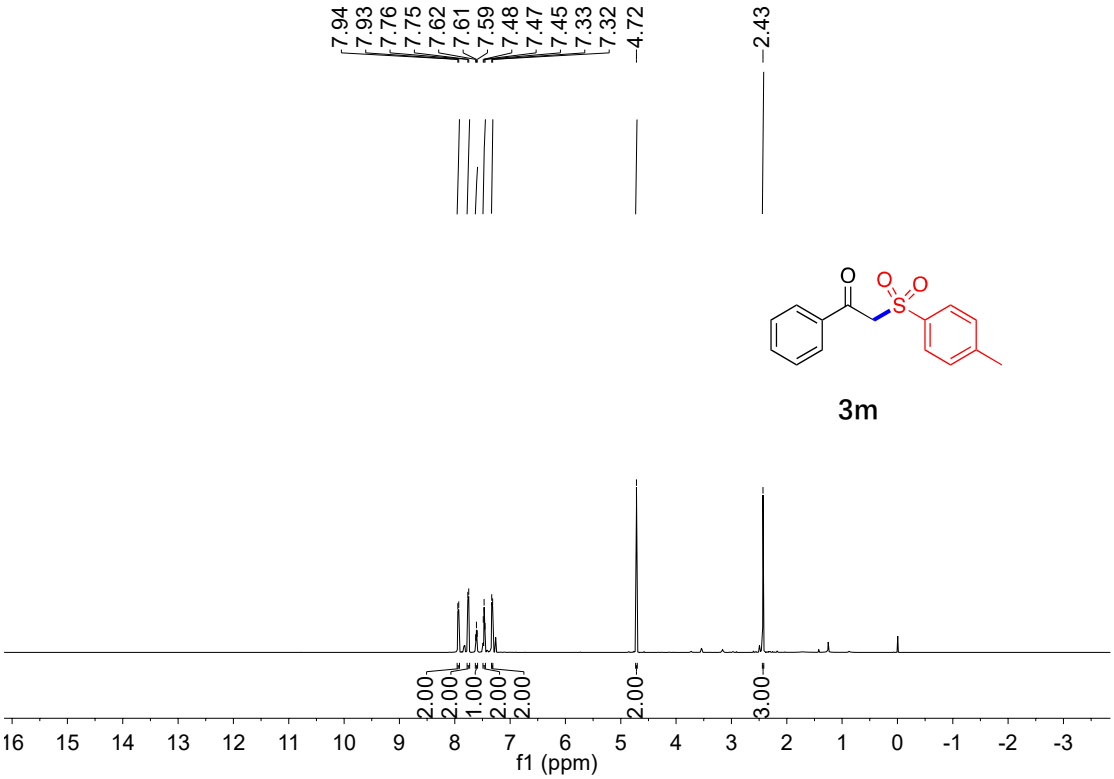

1.00
1.99
1.02
2.01
1.00
1.00
2.00
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

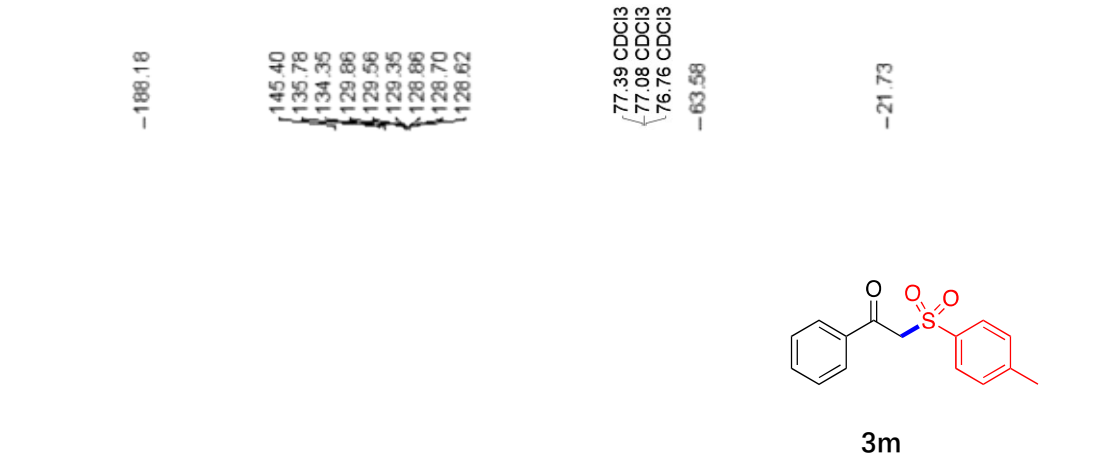

77.39 CDCl3
77.08 CDCl3
76.76 CDCl3

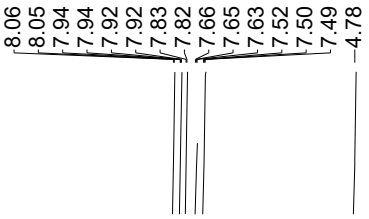

O
SO2Ph
S

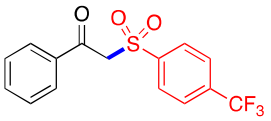
3l


70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

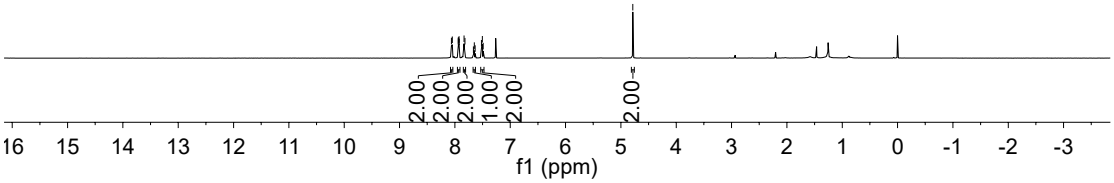

7.94
7.93
7.76
7.75
7.62
7.61
7.59
7.48
7.47
7.45
7.33
7.32
4.72
2.43
O
O
S
O
3m
2.00
2.00
1.00
2.00
2.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


188.18
145.40
135.78
134.35
129.86
129.56
129.35
128.86
128.70
128.62
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.58
21.73
O
O
S
O
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

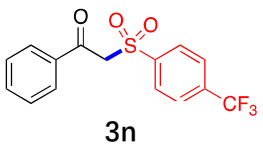

8.06
8.05
7.94
7.94
7.92
7.92
7.83
7.82
7.66
7.65
7.63
7.52
7.50
7.49
4.78


O
O
O
S
CF3

3n

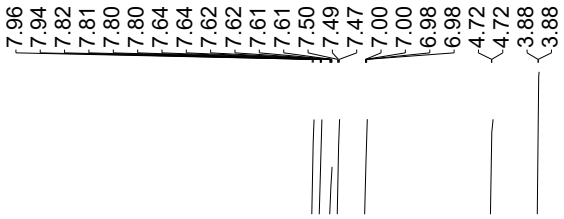

2.00
2.00
2.00
1.00
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

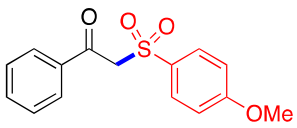

187.73
142.08
136.00
135.46
134.71
131.38
129.43
129.22
129.03
126.40
126.37
126.34
126.31
121.97
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.10


O
O
O
S
CF3

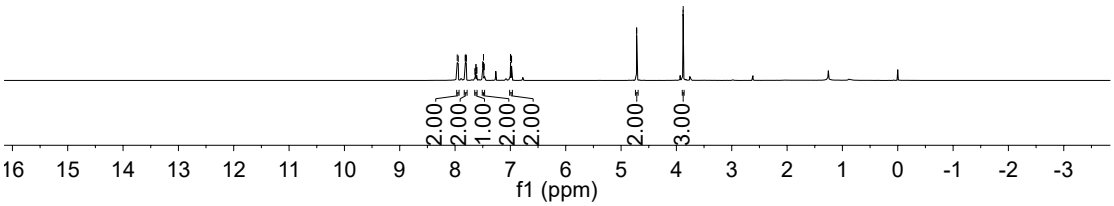
3n

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

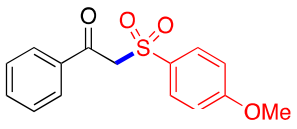

7.96
7.94
7.82
7.81
7.80
7.80
7.64
7.64
7.62
7.62
7.61
7.61
7.50
7.49
7.47
7.00
7.00
6.98
6.98
4.72
4.72
3.88
3.88


O
O
O
S
OMe

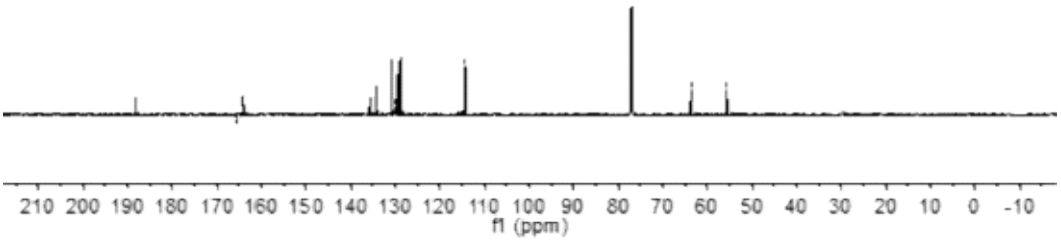
3o

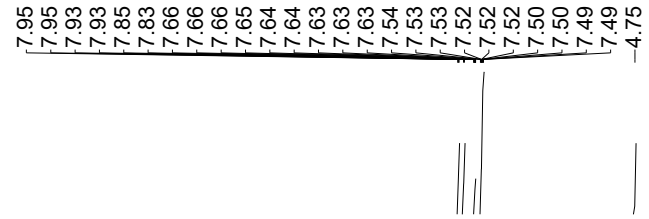

2.00
2.00
1.00
2.00
2.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

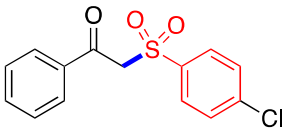

188.34
165.78
164.17
135.78
134.35
130.90
130.15
129.36
128.87
114.39
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.76
55.73


O
O
O
S
OMe

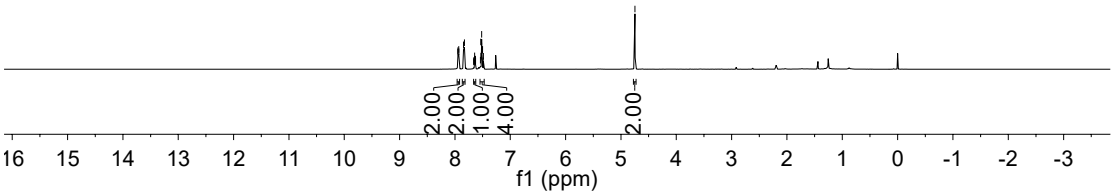
3o


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

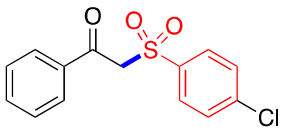

7.95
7.95
7.93
7.93
7.85
7.83
7.66
7.66
7.65
7.64
7.64
7.63
7.63
7.63
7.54
7.53
7.53
7.52
7.52
7.52
7.50
7.50
7.49
7.49
4.75


O
O
O
S
Cl

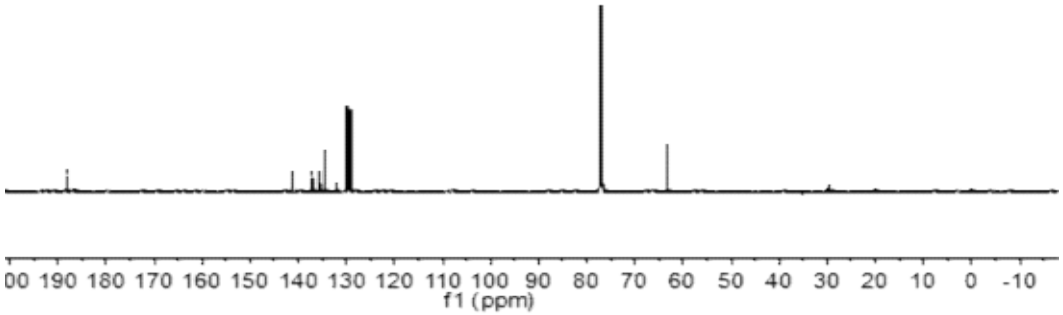
3p

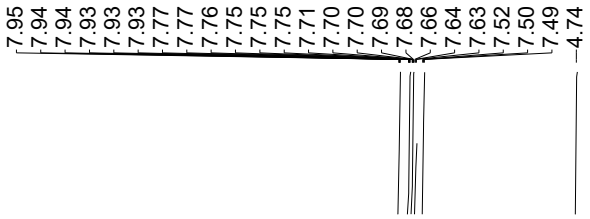

2.00
2.00
1.00
4.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

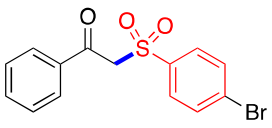

187.93
141.16
137.04
135.57
134.60
132.13
130.21
129.57
129.28
128.99
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.34


O
O
O
S
Cl

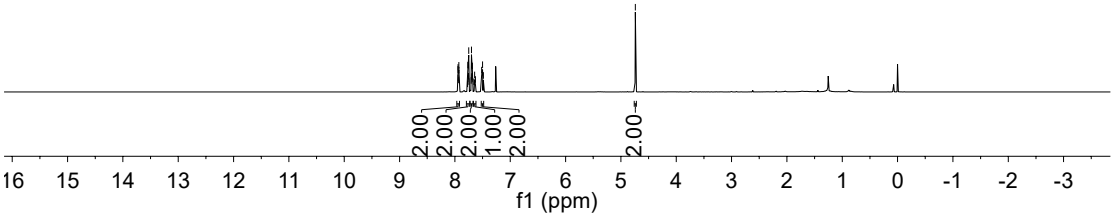
3p


00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

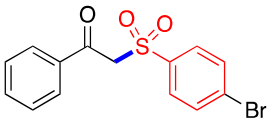

7.95
7.94
7.94
7.93
7.93
7.93
7.77
7.76
7.75
7.75
7.75
7.71
7.70
7.70
7.69
7.68
7.66
7.64
7.63
7.52
7.50
7.49
4.74


O
O
O
S
Br

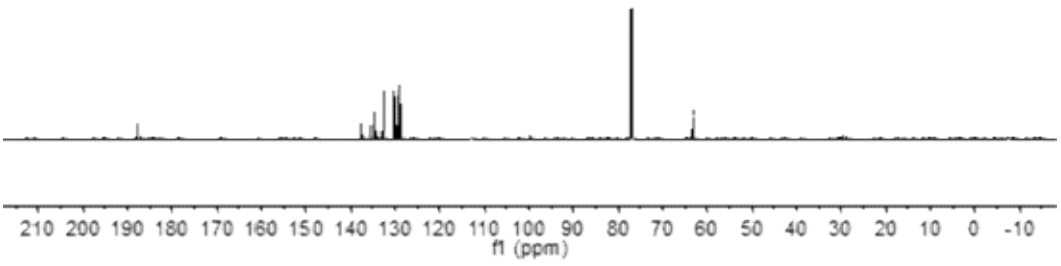
3q

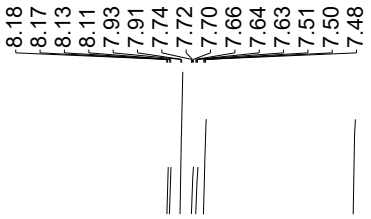

2.00
2.00
2.00
1.00
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

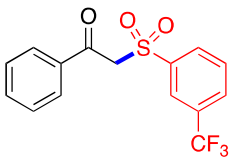

187.90
137.60
135.57
134.60
132.55
130.24
129.82
129.26
128.96
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.32


O
O
O
S
Br

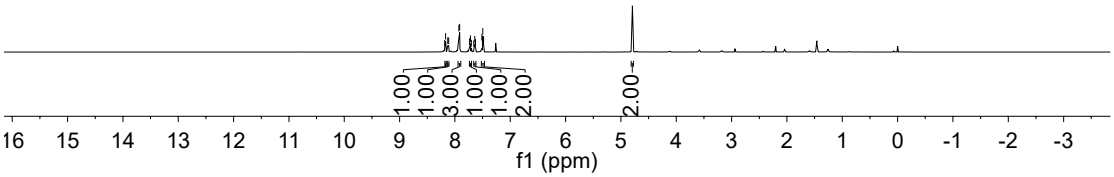
3q

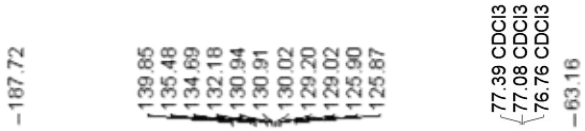

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

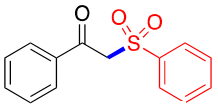

8.18
8.17
8.13
8.11
7.93
7.91
7.74
7.72
7.70
7.66
7.64
7.63
7.51
7.50
7.48


O
O
O
S
CF3

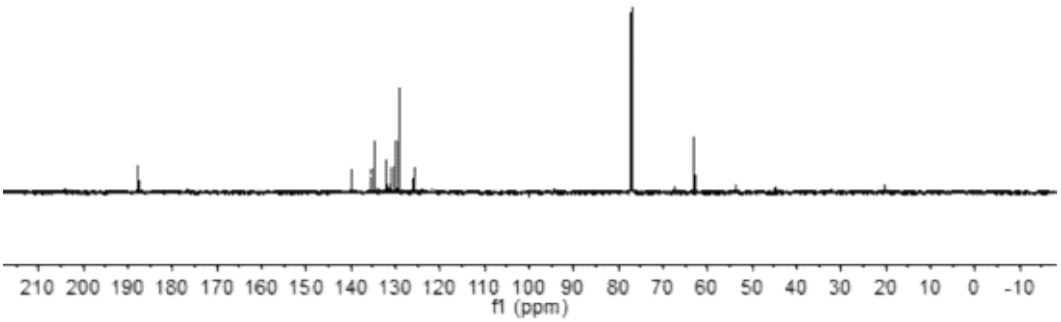
3r

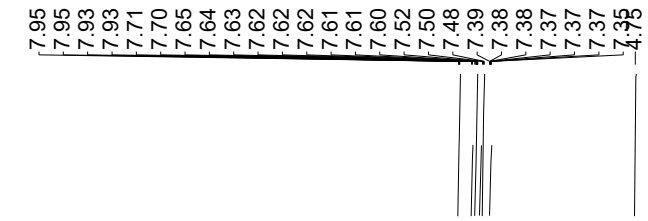

1.00
1.00
3.00
1.00
1.00
2.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.72
139.85
135.48
134.69
132.18
130.94
130.91
130.02
129.20
129.02
125.90
125.87
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.16


O
O
O
S

3r


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.95
7.95
7.93
7.93
7.71
7.70
7.65
7.64
7.63
7.62
7.62
7.62
7.61
7.61
7.60
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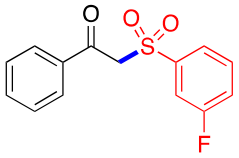
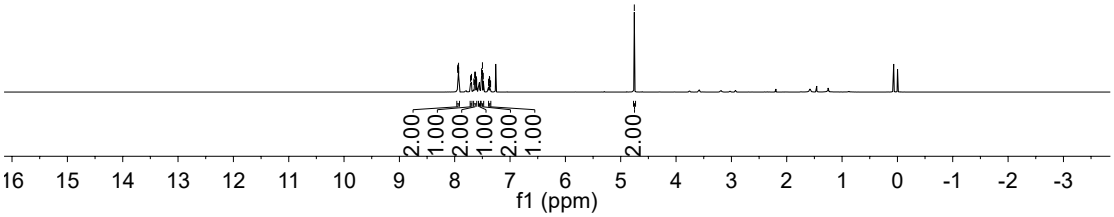
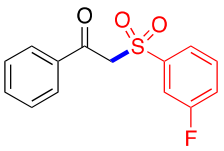
7.48
7.39
7.38
7.38
7.37
7.37
7.37
7.35
4.75


O
O
O
S
F

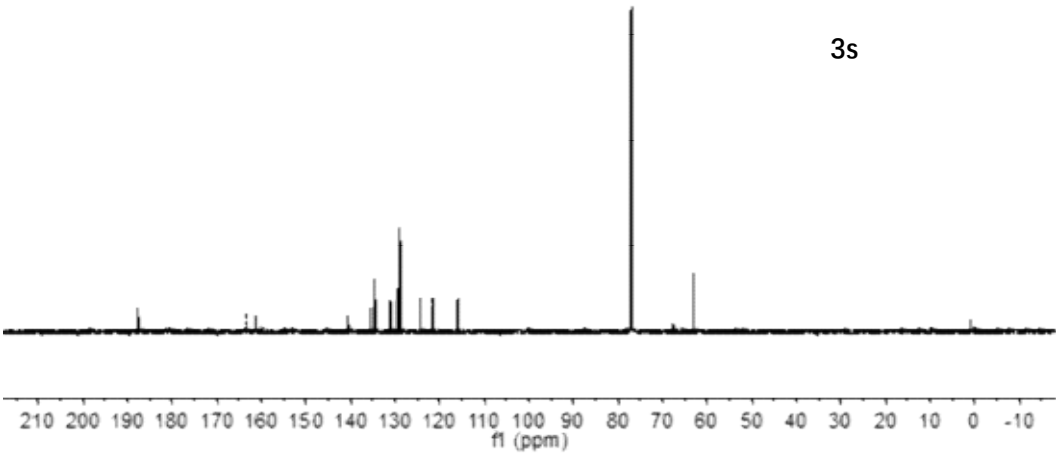
3s

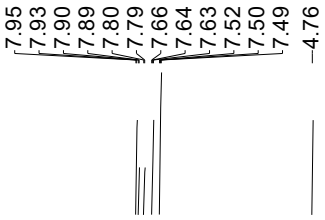

2.00
1.00
2.00
1.00
2.00
1.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

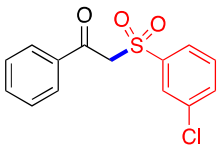

187.72
163.35
161.34
140.57
135.58
134.60
131.11
131.05
129.27
128.98
124.55
124.52
121.70
121.53
116.17
115.98
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.24


O
O
O
S
F

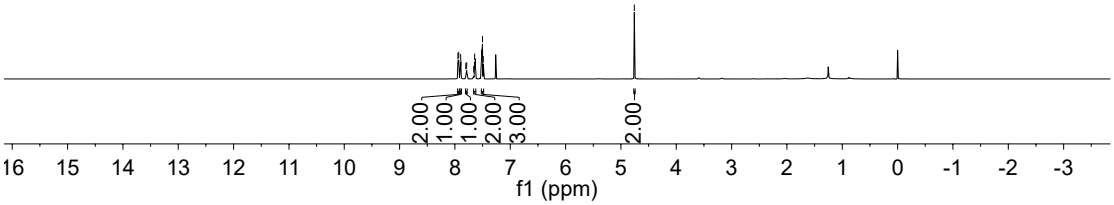
3s


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

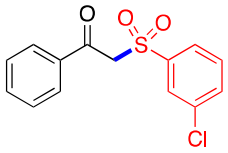

7.95
7.93
7.90
7.89
7.80
7.79
7.66
7.64
7.63
7.52
7.50
7.49
4.76


O
O
S
O
Cl

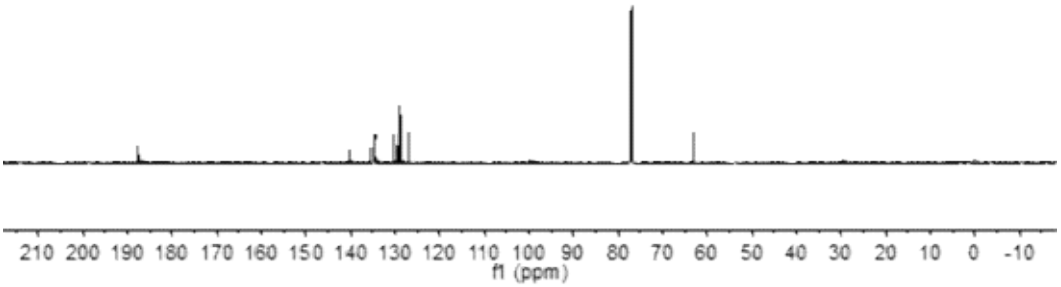
3t

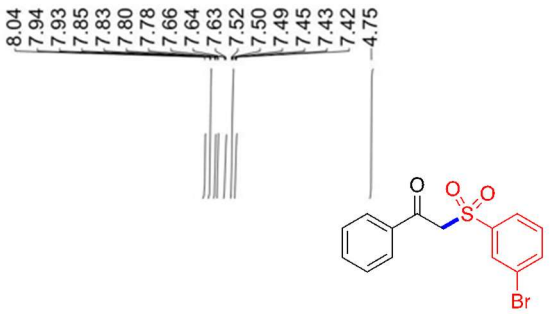

2.00
1.00
1.00
2.00
3.00
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


187.73
140.30
135.56
135.52
134.62
134.44
130.50
129.26
128.99
128.72
126.88
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
63.25

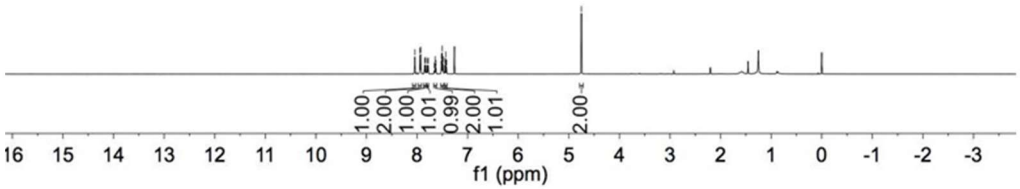

O
O
S
O
Cl

3t

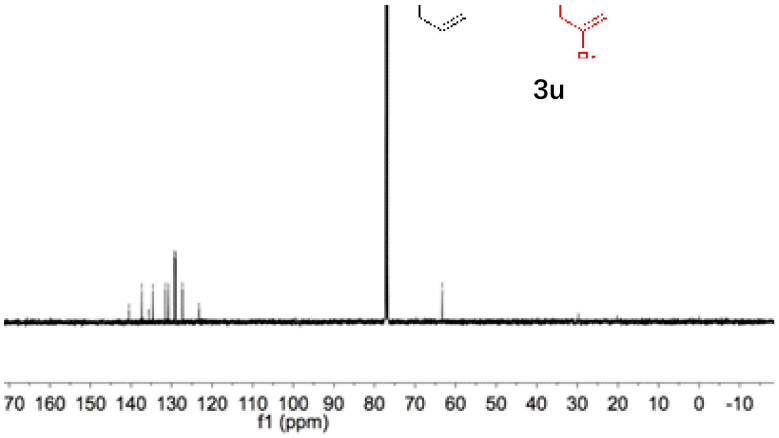

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.04
7.94
7.93
7.85
7.83
7.80
7.78
7.66
7.64
7.63
7.52
7.50
7.49
7.45
7.43
7.42
4.75
O
O
S
O
Br

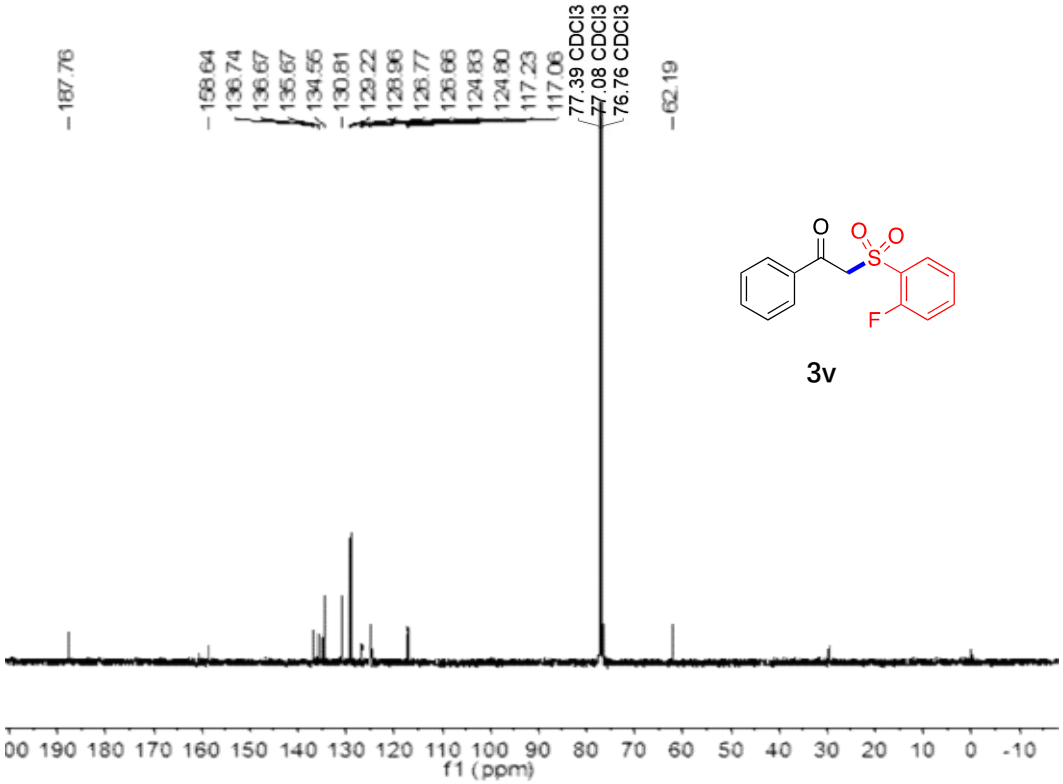
3u


1.00
2.00
1.00
1.01
0.99
2.00
1.01
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

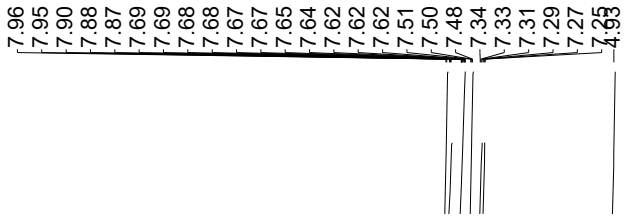

77.39 CDCl3
77.08 CDCl3
76.76 CDCl3

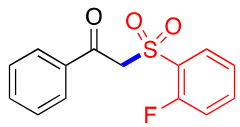

70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3u

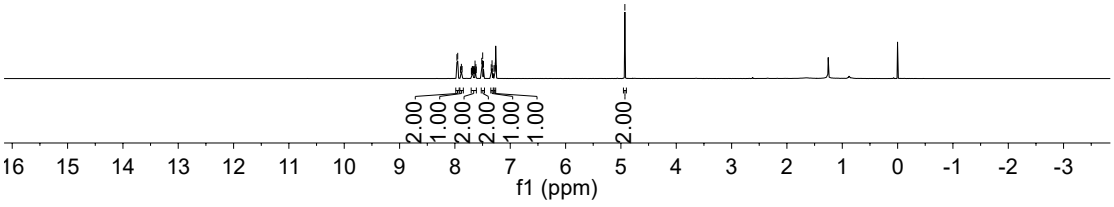

187.76
158.64
136.74
136.67
135.67
134.55
130.81
129.22
128.96
126.77
125.66
124.83
124.60
117.23
117.06
77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
62.19
f1 (ppm)

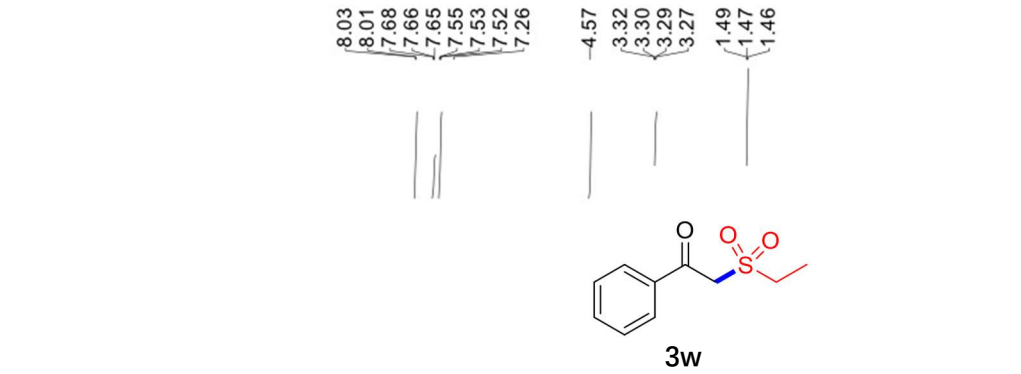
3v

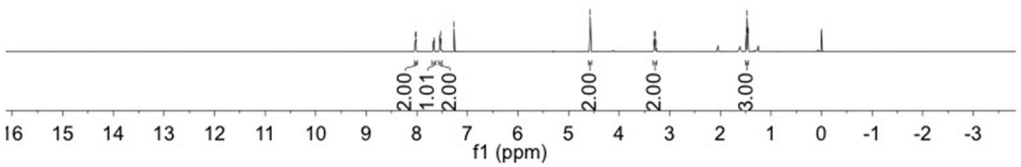

7.96
7.95
7.90
7.88
7.87
7.69
7.69
7.68
7.68
7.67
7.67
7.65
7.64
7.62
7.62
7.62
7.51
7.50
7.48
7.34
7.33
7.31
7.29
7.27
7.25
4.93

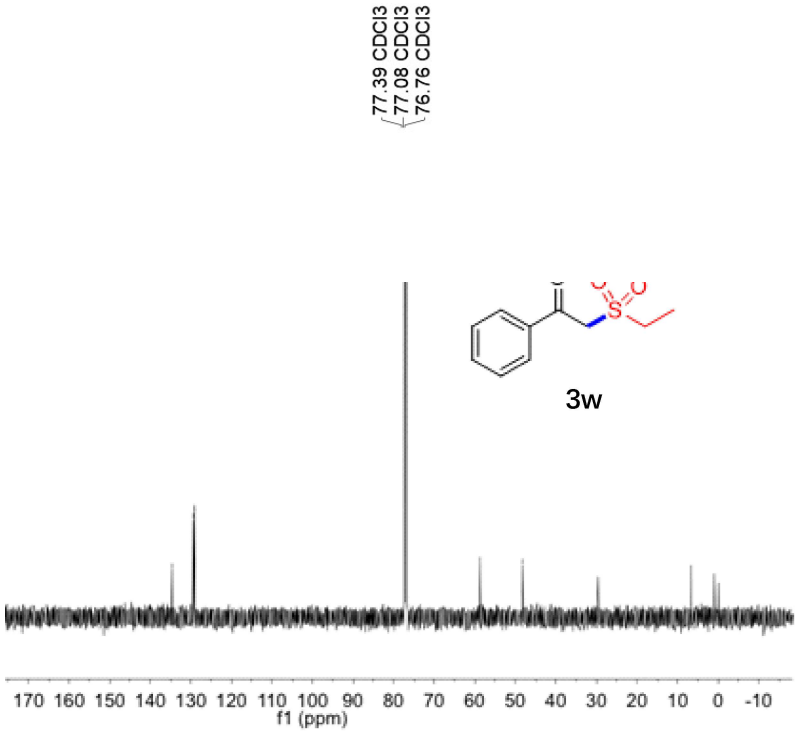


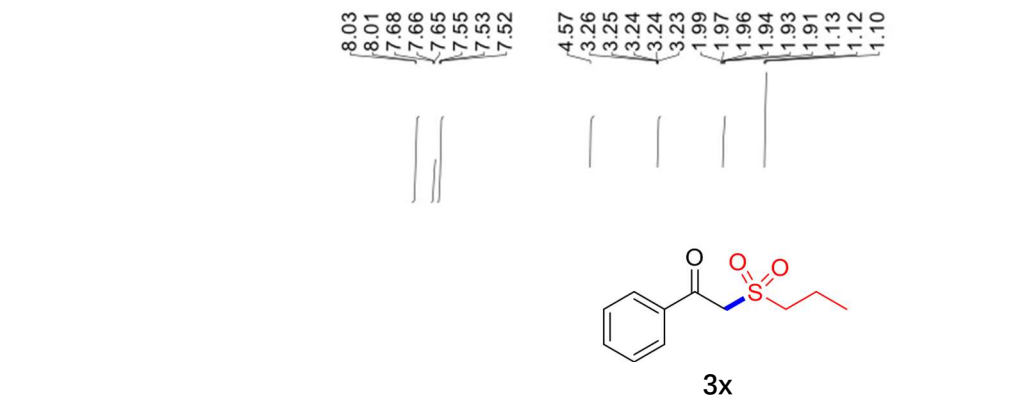
3v


2.00
1.00
2.00
2.00
1.00
1.00
2.00
f1 (ppm)

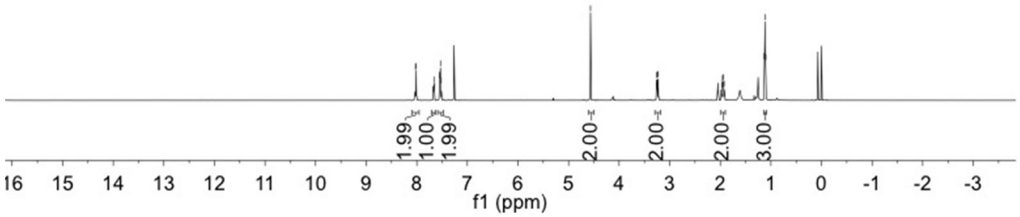

8.03
8.01
7.68
7.66
7.65
7.55
7.53
7.52
7.26
4.57
3.32
3.30
3.29
3.27
1.49
1.47
1.46
O
O
O
S
3w


2.00
1.01
2.00
2.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

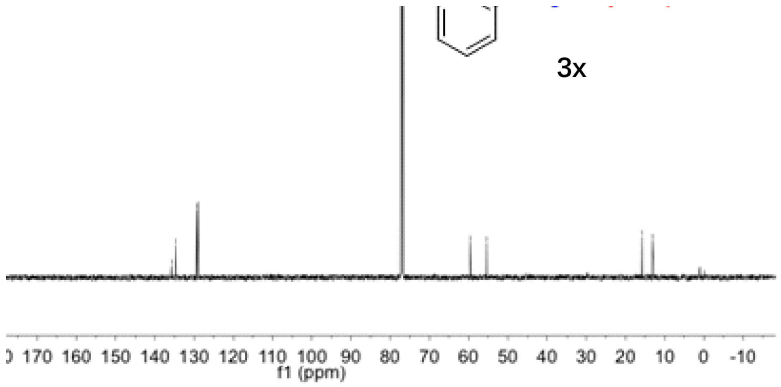

77.39 CDCl3
77.08 CDCl3
76.76 CDCl3
3w
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.03
8.01
7.68
7.66
7.65
7.55
7.53
7.52
4.57
3.26
3.25
3.24
3.24
3.23
1.99
1.97
1.96
1.94
1.93
1.91
1.13
1.12
1.10
O
O
O
S

3x


1.99
1.00
1.99
2.00
2.00
2.00
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


77.39 CDCl3
77.08 CDCl3
76.76 CDCl3


3x
0 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)