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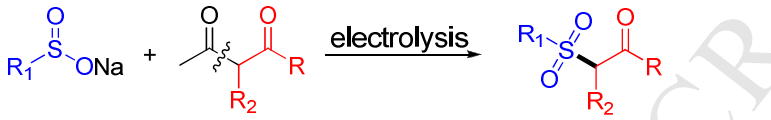

22 examples, 81-95% yields

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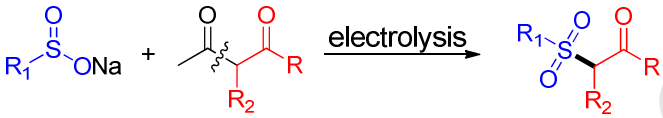

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ABSTRACT

An efficient electrochemical synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds has been developed. The present electrochemical route could afford the target products in high to excellent yields under mild conditions.

1. Introduction

Sulfones are a core functional group in both organic and medicinal chemistry.[1] Among their derivatives, β-keto sulfones are important motifs in pharmaceuticals synthesis.[2-4] For instance, some β-keto sulfones have been confirmed as new antagonists of bacterial quorum sensing in Vibrio harveyi (Fig. 1a),[2] and β-keto sulfones derivatives are found as potent inhibitors of several enzymes, such as LpxC and MMP (Fig. 1b and c).[3] In addition, β-keto sulfones as synthetic intermediates could achieve particular transformations.[4] The routine synthesis of β-keto sulfones is based on acylation of alkyl sulfones.[5] Other attractive approaches include alkylation of metallic arene sulfinates,[6] oxidation of β-oxo-sulfides,[7] and the Roskamp reaction.[8] From the viewpoint of synthetic methodology, it is still needed to develop a new route for the synthesis of β-keto sulfones.

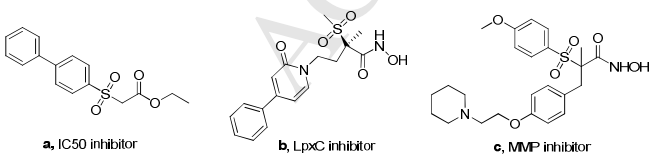

Fig. 1 β-Keto sulfones as inhibitors

An electrochemical method has been widely applied in organic synthesis because it could be used to develop environmentally compatible processes.[9] In recent years, iodine-mediated[10] or iodine-catalyzed[11] reactions have attracted more and more attention in organic synthesis. In our previous investigations, we found that the *in situ* generated I_2 by an electrochemical method could promote some transformations effectively.[12] Based on our interest in organic electrosynthesis, herein we report an efficient and convenient electrochemical synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds by using ammonium iodide as the supporting electrolyte.

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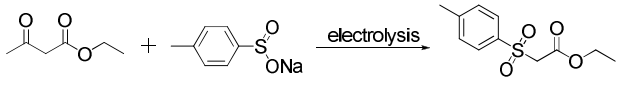
2. Result and Discussion

2.1. Influence of supporting electrolytes

In our initial study, the reaction of ethyl acetoacetate (1a) with sodium p-tolylsulfinate (2a) was selected as a model reaction. According to our previous experience, we would examine three main factors affecting on this reaction, such as supporting electrolytes, solvents and electrode materials. It was found that different supporting electrolytes were involved in this transformation leading to different results, as shown in Table 1. When NH_4I was used as the supporting electrolyte, the desired product could be obtained in 95% yield (Table 1, entry 1). However, no corresponding product could be obtained at all with a similar ammonium salt NH_4Br or NH_4Cl as the supporting electrolyte (Table 1, entries 2 and 3). Moreover, the efficiency of this transformation slightly decreased if the supporting electrolyte NH_4I was replaced by *n*-Bu_4NI (Table 1, entry 4). Similar results were obtained when employing alkali metal iodide salts as the supporting electrolyte instead of NH_4I (Table 1, entries 5–6 and 8–9). Strangely, only 24% yield of the corresponding product was obtained when KI was employed as the supporting electrolyte (Table 1, entry 7). This is mainly due to the formation of side-product 1-tosylpropan-2-one. In addition, it should be noted the raw materials could not be converted into the corresponding product successfully under the same reaction conditions with NH_4OAc as the supporting electrolyte (Table 1, entry 10). This means that iodide salts are necessary for this

transformation.

Table 1
Influence of supporting electrolytes on the electrosynthesis of β-keto sulfones [a]



1a 2a 3aa

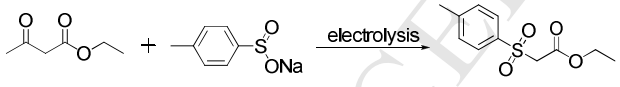
Entry	Anode-Cathode	Supporting electrolyte	Solvent	Yield (%) [b]
1	C—Ni	NH_4I	DMSO	95
2	C—Ni	NH_4Br	DMSO	0
3	C—Ni	NH_4Cl	DMSO	0
4	C—Ni	*n*-Bu_4NI	DMSO	81
5	C—Ni	LiI	DMSO	90
6	C—Ni	NaI	DMSO	88
7	C—Ni	KI	DMSO	24
8	C—Ni	RbI	DMSO	75
9	C—Ni	CsI	DMSO	70
10	C—Ni	NH_4OAc	DMSO	0

[a] Electrolytic conditions: **1a** (1 mmol), **2a** (1.2 mmol), solvent (8 mL), supporting electrolyte (0.5 mol L^{-1}), undivided cell, electrolysis with constant current 50 mA for 2 h and then continuously stirring for 5 h at rt. [b] Isolated yield based on **1a**.

2.2. Influence of solvents

Electrolytic medium (solvent) was an important factor as well. Compared to other solvents, DMSO was the most suitable solvent for this transformation (Table 2, entry 1). In the *N*,*N*-dimethylacetamide (DMA) or formamide and H_2O solvents, the corresponding products were obtained in 75%, 87% and 70% yield, respectively (Table 2, entries 3–5). When *N*,*N*-dimethylformamide (DMF) was employed as the electrolytic medium, only a trace amount of the desired product was detected (Table 2, entry 2). In the DMF solvent, side-product sulfonamide was formed so that the yield of the desired product was greatly decreased.

Table 2
Influence of solvents on the electrosynthesis of β-keto sulfones [a]



1a 2a 3aa

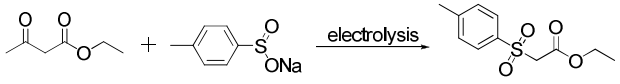
Entry	Anode-Cathode	Supporting electrolyte	Solvent	Yield (%) [b]
1	C—Ni	NH_4I	DMSO	95
2	C—Ni	NH_4I	DMF	trace
3	C—Ni	NH_4I	DMA	75
4	C—Ni	NH_4I	formamide	87
5	C—Ni	NH_4I	H_2O	70

[a] Electrolytic conditions as shown in Table 1. [b] Isolated yield based on **1a**.

2.3. Influence of cathode materials

From the experimental results listed in Table 3, the cathode materials including Ni, Cu, Al and Ag were well appropriate for this reaction, giving desired products in excellent yields (Table 3, entries 1–4).

Table 3
Influence of cathode materials on the electrosynthesis of β-keto sulfones [a]



1a 2a 3aa

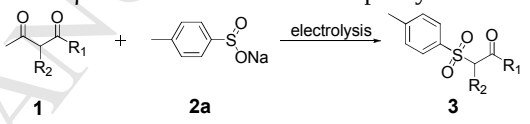
Entry	Anode-Cathode	Supporting electrolyte	Solvent	Yield (%) [b]
1	C—Ni	NH_4I	DMSO	95
2	C—Cu	NH_4I	DMSO	93
3	C—Al	NH_4I	DMSO	90
4	C—Ag	NH_4I	DMSO	91

[a] Electrolytic conditions as shown in Table 1. [b] Isolated yield based on **1a**.

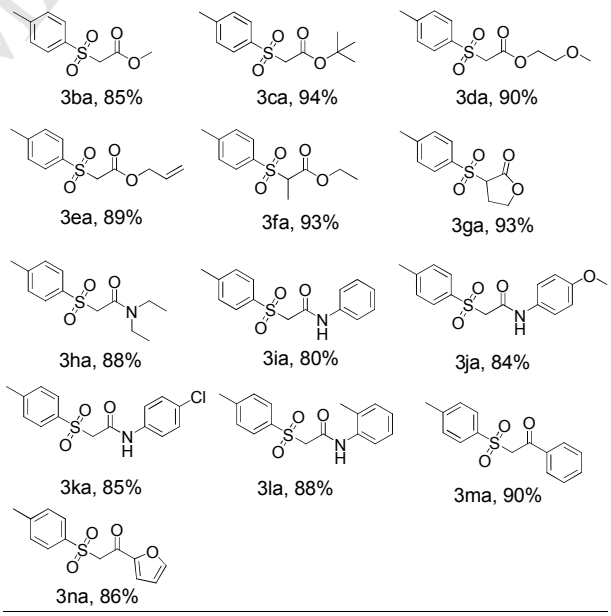
According to the experimental results (Table 1–3), the optimized conditions for this reaction was summarized as follows: **1a** (1 mmol), **2a** (1.2 mmol), supporting electrolyte NH_4I (4 mmol), solvent DMSO (8 mL), Ni cathode and graphite anode, electrolysis with current 50 mA for 2 h and then continuously stirring for 5 h at room temperature.

2.4. Electrosynthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds

Table 4
Reaction of β-diketones **1** with sodium p-tolylsulfinate **2a**[a]



1 2a 3

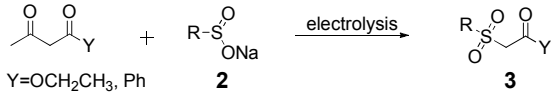


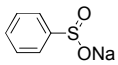
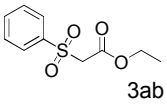
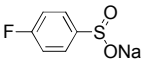
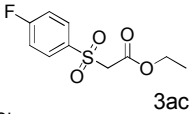
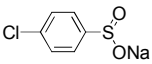
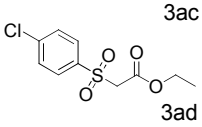
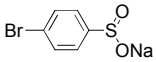
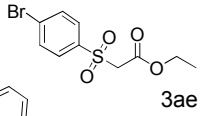
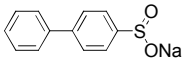
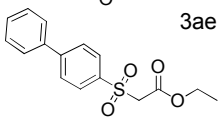
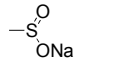
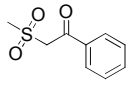
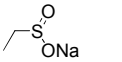
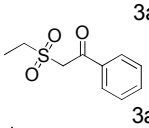
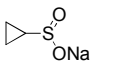
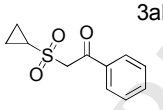
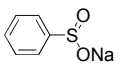
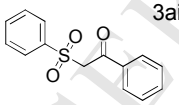
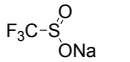
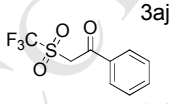
[a] Electrolytic conditions as shown in Table 1. Isolated yield based on **1**.

Under the optimized electrolytic conditions, the scope of 1,3-dicarbonyl compounds was first examined and the results were summarized in Table 4. With the methyl or tert-butyl 3-oxobutanoate as a substrate instead of ethyl 3-oxobutanoate, the desired products **3ba** and **3ca** were isolated in 85% and 94% yield, respectively. Furthermore, 2-methoxyethyl or allyl 3-oxobutanoate and ethyl 2-methyl-3-oxobutanoate were allowed to react with sodium sulfinates smoothly exhibiting the corresponding products in excellent yields (**3da**–**3fa**). 3-acetyldihydrofuran-2(3*H*)-one also provided a good result (**3ga**). In addition, 1,3-dicarbonyl compounds bearing amide groups

could react with **2a** effectively to afford the corresponding sulfonyl acetamides (**3ha**–**3la**). *N*-phenyl-2-tosylacetamide with chloro, methyl and methoxyl (**3ja**–**3la**) on aryl rings gave higher yields than that without substituents (**3ia**). Interestingly, 1,3-butanedione bearing phenyl and furfuryl groups could be also transformed into the desired products under the optimized conditions (**3ma**, **3na**).

Table 5
The scope of various sodium sulfinates [a]



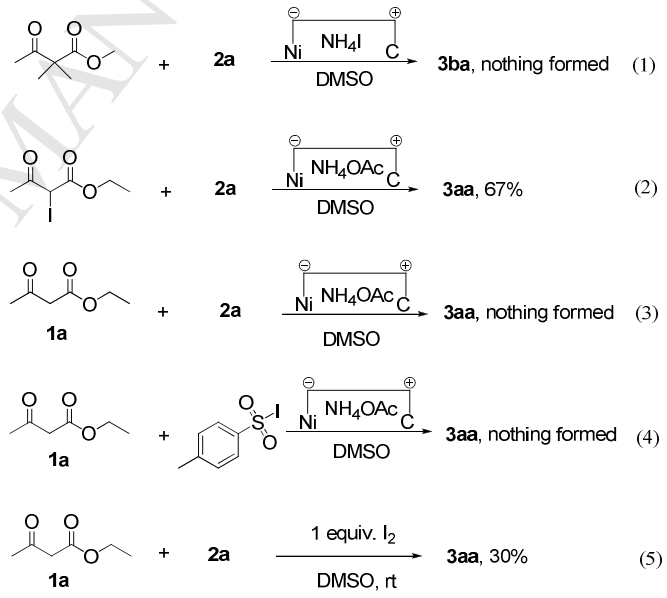
Entry	Sodium sulfinate	Product	Yield (%)
1		 3ab	90
2		 3ac	81
3		 3ad	85
4		 3ae	88
5		 3af	82
6		 3ag	92
7		 3ah	89
8		 3ai	90
9		 3aj	84
10		 3ak	0

[a] Electrolytic conditions as shown in Table 1. Isolated yield based on 1,3-dicarbonyl compounds.

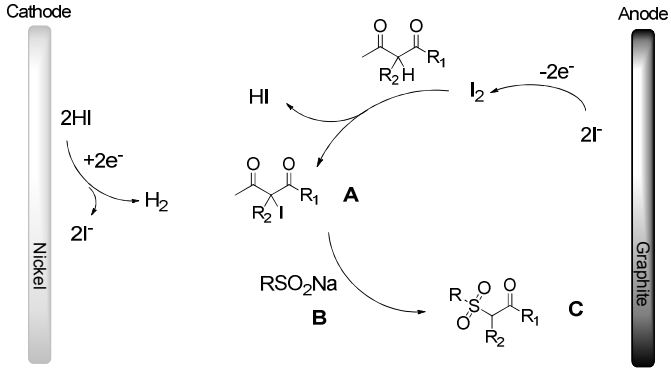
Further, we examined various sodium sulfinates. As shown in Table 5, benzene sulfinic acid sodium salt or its derivatives reacted readily with ethyl 3-oxobutanoate, affording the desired products in 81–90% yields (**3ab–3af)**. When aliphatic or benzene sulfinic acid sodium reacted with 1-phenylbutane-1,3-dione, excellent yields of desired products were observed (**3ag–3aj**). However, no corresponding product could be obtained when trifluoromethane sulfinic acid sodium was subjected to the reaction, indicating that strong electron-withdrawing groups had a great impact on the transformation under the optimized conditions. It is worth mentioning that sodium biphenyl-4-sulfinate with ethyl acetoacetate (**1a**) could be smoothly converted to **3af** (i.e., IC50 inhibitor as shown in Fig. 1) in 82% yield under the standard conditions (Table 5, entry 5). This means that the present electrochemical route has a potential application.

2.5. Reaction mechanism

To obtain a better understanding of the reaction mechanism, several control experiments were carried out (Scheme 1). No desired product **3ba** was formed when methyl 2,2-dimethyl-3-oxobutanoate was employed as the substrate (Eq. 1). The reaction of ethyl 2-iodo-3-oxobutanoate with sodium p-tolylsulfinate (**2a**) was performed to afford the product **3aa** in yield 67% in the presence of CH_3COONH_4 and DMSO (Eq. 2). However, when **1a** was used as a substrate instead of ethyl 2-iodo-3-oxobutanoate, no product was obtained (Eq. 3). Therefore, we deduced that ethyl 2-iodo-3-oxobutanoate may be an intermediate for this transformation. When sodium p-tolylsulfinate (**2a**) was replaced by freshly prepared 4-methylbenzene-1-sulfonyl iodide,[12c] the raw materials could not be converted into the desired product, which indicated that 4-methylbenzene-1-sulfonyl iodide was not an intermediate for this reaction (Eq. 4). In addition, 30% yield of the desired product was obtained even under non-electrochemical conditions in the presence of iodine (Eq. 5). According to this result, we infer that the *in situ* electrogenerated I_2 plays an important role in this transformation.



Scheme 1. Control experiments



Scheme 2. Proposed reaction mechanism

The reaction of sulfinates with α-chloro-β-dicarbonyl compounds to synthesis of β-keto sulfones via C-C bond cleavage has been reported by Kowal *et al.*, who demonstrated that the reaction proceeded via S_N mechanism.[13] In the present case, the formation of β-keto sulfones may undergo the similar reaction mechanism. On the basis of the above results and the reported literatures, a possible mechanism is outlined in Scheme 2. Iodine ions are electro-oxidized to I_2 at the inert graphite anode ($2I^- \rightarrow I_2 + 2e^-$),[14] followed by the reaction with 1,3-dicarbonyl compounds to afford the intermediate product **A**.[15] Then, the reaction of **A** with sulfinate **B** gives β-keto sulfone **C** via S_N mechanism.[13]

3. Conclusion

We have developed an efficient electrochemical synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonylcompounds, which is promoted by the *in situ* electrogenerated I_2. The present work provides a new route for the synthesis of β-keto sulfones. Further mechanistic studies on this transformation are currently underway in our laboratory.

4. Experimental section

4.1. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). The chemical shifts were referenced to signals at 7.26 and 77.0 ppm, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). GC-MS was obtained using electron ionization. HRMS analysis was performed in a MAT95XP high resolution mass spectrometer.

4.2. A typical procedure for the electrosynthesis of β-keto sulfones

In a typical experiment, 1,3-dicarbonyl compounds (1 mmol), sodium sulfinates (1.2 mmol), DMSO (8 mL) and NH_4I (4 mmol) were added to the undivided cell. The electrosynthesis was carried out in the undivided cell fitted with a Ni sheet cathode (2 cm × 2.5 cm × 0.02 cm) and a graphite rod anode at a constant current (50 mA) at room temperature under magnetic stirring for 2 h and then continuously stirring for 5 h. After the reaction was finished, the electrolyte solution was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (10 mL × 3). The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (5:1) as eluent.

4.2.1. Ethyl 2-tosylacetate **(3aa)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.4 Hz, 2H), 7.37 (d, *J*=8.0 Hz, 2H), 4.15 (q, *J*=7.2 Hz, 2H), 4.09 (s, 2H), 2.46 (s, 3H), 1.20 (t, *J*=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 145.4, 135.8, 129.8, 128.5, 62.3, 61.1, 21.6, 13.8 ppm. HRMS (ESI) m/z: calcd for $C_{11}H_{14}NaO_4S$ $[M+Na]^+$, 265.0505; found 265.0516.

4.2.2. Methyl 2-tosylacetate **(3ba)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.0 Hz, 2H), 7.38 (d, *J*=8.0 Hz, 2H), 4.13 (s, 2H), 3.71 (s, 3H), 2.46 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 145.4, 135.6, 129.8, 128.4, 60.8, 53.0, 21.6 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{12}NaO_4S$ $[M+Na]^+$, 251.0349; found 251.0345.

4.2.3. tert-Butyl 2-tosylacetate **(3ca)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J*=8.4 Hz, 2H), 7.38 (d, *J*=8 Hz, 2H), 5.39 (s, 2H), 2.48 (s, 3H), 1.39 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 146.1, 131.8, 130.4, 129.6, 84.9, 36.0, 27.4, 21.8 ppm. HRMS (ESI) m/z: calcd for $C_{13}H_{18}NaO_4S$ $[M+Na]^+$, 293.0818; found 293.0811.

4.2.4. 2-Methoxyethyl 2-tosylacetate **(3da)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*=6.4 Hz, 2H), 7.36 (d, *J* = 6.4 Hz, 2H), 4.21 (d, *J*=4.4 Hz, 2H), 4.17 (s, 2H), 3.50 (d, *J*=4.8 Hz, 2H), 3.35–3.29 (m, 3H), 2.45 (d, *J*=4.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 145.1, 135.5, 129.5, 128.2, 69.4, 64.7, 60.5, 58.5, 21.3 ppm. HRMS (ESI) m/z: calcd for $C_{12}H_{16}NaO_5S$ $[M+Na]^+$, 295.0611; found 295.0618.

4.2.5. Allyl 2-tosylacetate **(3ea)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J*=8.4 Hz, 2H), 7.36 (d, *J*=8.0 Hz, 2H), 5.84–5.75 (m, 1H), 5.32–5.20 (m, 2H), 4.57 (dd, *J* =4.4, 1.2 Hz, 2H), 4.14 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 145.2, 135.6, 130.7, 129.7, 128.3, 119.4, 66.5, 60.8, 21.5 ppm. HRMS (ESI) m/z: calcd for $C_{12}H_{14}NaO_4S$ $[M+Na]^+$, 277.0505; found 277.0514.

4.2.6. Ethyl 2-tosylpropanoate **(3fa)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J*=6.4 Hz, 2H), 7.35 (d, *J*=7.6 Hz, 2H), 4.25–4.21 (m, 3H), 2.47 (s, 3H), 2.39 (t, *J*=1.6 Hz, 3H), 1.30–1.25 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 145.9, 131.6, 130.5, 129.2, 63.5, 51.7, 27.5, 21.7, 13.5 ppm. HRMS (ESI) m/z: calcd for $C_{12}H_{16}NaO_4S$ $[M+Na]^+$, 279.0662; found 279.0670.

4.2.7. 3-Tosyldihydrofuran-2(3H)-one **(3ga)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J*=8.4 Hz, 2H), 7.37 (d, *J*=8.0 Hz, 2H), 4.39–4.29 (m, 2H), 4.16 (q, *J*=5.1 Hz, 1H), 2.88–2.63 (m, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 145.7, 133.4, 129.7, 128.9, 66.8, 63.1, 23.8, 21.4 ppm. HRMS (ESI) m/z: calcd for $C_{11}H_{12}NaO_4S$ $[M+Na]^+$, 263.0349; found 263.0358.

4.2.8. N,N-Diethyl-2-tosylacetamide **(3ha)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J*=8.0 Hz, 2H), 7.36 (d, *J*=8.4 Hz, 2H), 5.81 (s, 2H), 3.39–3.24 (m, 4H), 2.46 (s, 3H), 1.23 (t, *J*=7.2 Hz, 3H), 1.06 (t, *J*=6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.5, 145.9, 131.9, 131.4, 129.1, 43.5, 42.0, 33.7, 21.8, 14.3, 12.2 ppm. HRMS (ESI) m/z: calcd for $C_{13}H_{19}NNaO_3S$ $[M+Na]^+$, 292.0978; found 292.0984.

4.2.9. N-Phenyl-2-tosylacetamide **(3ia)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.80 (d, *J*=8.4 Hz, 2H), 7.49 (d, *J*=7.6 Hz, 2H), 7.38–7.30 (m, 4H), 7.16 (t, *J*=7.6 Hz, 1H), 4.15 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 145.8, 137.1, 135.0, 130.1, 129.0, 128.1, 125.1, 120.2, 63.1, 21.6 ppm. HRMS (ESI) m/z: calcd for $C_{15}H_{15}NNaO_3S$ $[M+Na]^+$, 312.0665; found 312.0674.

4.2.10. N-(4-Methoxyphenyl)-2-tosylacetamide **(3ja)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.79 (d, *J*=8.0 Hz, 2H), 7.39–7.32 (m, 4H), 6.83 (d, *J*=8.8 Hz, 2H), 4.15 (s, 2H), 3.78 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 156.9, 145.7, 135.1, 130.1, 128.2, 126.4, 122.0, 114.2, 62.9, 55.4, 21.7 ppm. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_4S$ $[M+Na]^+$, 342.0770; found 342.0780.

4.2.11. N-(4-Chlorophenyl)-2-tosylacetamide **(3ka)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.78 (d, *J*=8.4 Hz, 2H), 7.44 (d, *J*=8.8 Hz, 2H), 7.36 (d, *J*=8.0 Hz, 2H), 7.30–7.22 (m, 2H), 4.18 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 146.0, 135.6, 134.8, 130.2, 129.7, 129.1, 128.1, 121.4, 63.0, 21.7 ppm. HRMS (ESI) m/z: calcd for $C_{15}H_{14}ClNNaO_3S$ $[M+Na]^+$, 346.0275; found 346.0283.

4.2.12. N-(o-Tolyl)-2-tosylacetamide **(3la)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.81 (d, *J*=8.0 Hz, 2H), 7.72 (t, *J*=6.8 Hz, 1H), 7.35 (d, *J*=7.6 Hz, 2H), 7.22–7.15 (m, 2H), 7.09 (t, *J*=7.2 Hz, 1H), 4.19 (s, 2H), 2.43 (s, 3H), 2.32 (d, *J*=2.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 145.8, 135.1, 135.0, 130.6, 130.2, 128.0, 126.6, 125.7, 122.8, 122.7, 62.5, 21.6, 17.7 ppm. HRMS (ESI) m/z: calcd for $C_{16}H_{17}NNaO_3S$ $[M+Na]^+$, 326.0821; found 326.0830.

4.2.13. 1-Phenyl-2-tosylethanone **(3ma)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J*=7.2 Hz, 2H), 7.76 (d, *J*=8.0 Hz, 2H), 7.62 (t, *J*=7.2 Hz, 1H), 7.48 (t, *J*=8.0 Hz, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 4.72 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.1, 145.3, 135.8, 134.3, 129.8, 129.3, 128.8, 128.6, 127.4, 63.6, 21.7 ppm. HRMS (ESI) m/z: calcd for $C_{15}H_{14}NaO_3S$ $[M+Na]^+$, 297.0556; found 297.0560.

4.2.14. 1-(Furan-2-yl)-2-tosylethanone **(3na)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.0 Hz, 2H), 7.61 (s, 1H), 7.35–7.31 (m, 3H), 6.58 (s, 1H), 4.57 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 151.8, 148.0, 145.3, 135.7, 129.8, 128.5, 120.4, 113.1, 63.6, 21.6 ppm. HRMS (ESI) m/z: calcd for $C_{13}H_{12}NaO_4S$ $[M+Na]^+$, 287.0349; found 287.0357.

4.2.15. Ethyl 2-(phenylsulfonyl)acetate **(3ab)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J*=7.6 Hz, 2H), 7.69 (t, *J*=7.4 Hz, 1H), 7.58 (t, *J*=7.2 Hz, 2H), 4.16–4.09 (m, 4H), 1.18 (t, *J*=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 138.7, 134.2, 129.1, 128.4, 62.2, 60.9, 13.7 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{12}NaO_4S$ $[M+Na]^+$, 251.0349; found 251.0354.

4.2.16. Ethyl 2-((4-fluorophenyl)sulfonyl)acetate **(3ac)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.95 (m, 2H), 7.27 (t, *J*=8.4 Hz, 2H), 4.19–4.12 (m, 4H), 1.21 (t, *J*=7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 163.5 (d, J_{C-F} = 250.0 Hz), 134.6, 134.6, 131.5, 131.4, 116.5, 116.3, 62.3, 60.8, 13.7 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{11}FNaO_4S$ $[M+Na]^+$, 269.0254; found 269.0259.

4.2.17. Ethyl 2-((4-chlorophenyl)sulfonyl)acetate **(3ad)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J*=8.8 Hz, 2H), 7.56 (d, *J*=8.8 Hz, 2H), 4.16 (q, *J*=7.2 Hz, 2H), 4.12 (s, 2H), 1.22 (t, *J*=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 141.1, 137.1, 130.1, 129.5, 62.5, 60.9, 13.8 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{11}ClNaO_4S$ $[M+Na]^+$, 284.9959; found 284.9965.

4.2.18. Ethyl 2-((4-bromophenyl)sulfonyl)acetateethyl **(3ae)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J*=8.0 Hz, 2H), 7.73 (d, *J*=7.6 Hz, 2H), 4.16 (q, *J*=6.8 Hz, 2H), 4.11 (s, 2H), 1.22 (t, *J*=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 137.7, 132.5, 130.2, 129.8, 62.5, 60.9, 13.9 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{11}BrNaO_4S$ $[M+Na]^+$, 328.9454; found 328.9452.

4.2.19. Ethyl 2-([1,1'-biphenyl]-4-ylsulfonyl)acetate **(3af)** [16]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J*=7.8 Hz, 2H), 7.78 (d, *J*=7.8 Hz, 2H), 7.62 (d, *J*=7.4 Hz, 2H), 7.51–7.42 (m, 3H), 4.20–4.15 (m, 4H), 1.21 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 147.2, 139.0, 137.2, 129.1, 128.8, 127.8, 127.4, 62.4, 61.1, 13.8.

4.2.20. 2-(Methylsulfonyl)-1-phenylethanone **(3ag)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J*=7.2 Hz, 2H), 7.66 (t, *J*=7.4 Hz, 1H), 7.53 (t, *J*=7.8 Hz, 2H), 4.61 (s, 2H), 3.15 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2, 41.8 ppm. HRMS (ESI) m/z: calcd for $C_9H_{10}NaO_3S$ [M+Na]+, 221.0243; found 221.0249.

4.2.21. 2-(Ethylsulfonyl)-1-phenylethanone **(3ah)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J*=7.6 Hz, 2H), 7.64 (t, *J*=7.2 Hz, 1H), 7.51 (t, *J*=7.6 Hz, 2H), 4.57 (s, 2H), 3.27 (q, *J*=7.2 Hz, 2H), 1.44 (t, *J*=7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 135.7, 134.6, 129.2, 128.9, 58.7, 48.2, 6.5 ppm. HRMS (ESI) m/z: calcd for $C_{10}H_{12}NaO_3S$ $[M+Na]^+$, 235.0399; found 235.0404.

4.2.22. 2-(Cyclopropylsulfonyl)-1-phenylethanone **(3ai)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J*=8.4, 1.2 Hz, 2H), 7.68 (t, *J*=7.4 Hz, 1H), 7.54 (t, *J*=7.8 Hz, 2H), 4.67 (s, 2H), 2.81–2.75 (m, 1H), 1.31–1.28 (m, 2H), 1.14–1.09 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.9, 135.8, 134.5, 129.3, 129.0, 61.0, 30.8, 5.5 ppm. HRMS (ESI) m/z: calcd for $C_{11}H_{12}NaO_3S$ $[M+Na]^+$, 247.0399; found 247.0406.

4.2.23. 1-Phenyl-2-(phenylsulfonyl)ethanone **(3aj)**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.91 (m, 4H), 7.71–7.61(m , 2H), 7.57 (t, *J*=7.6 Hz, 2H), 7.50 (t, *J*=7.4 Hz, 2H), 4.74 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 138.7, 135.7, 134.4, 129.3, 129.2, 128.8, 128.6, 63.4 ppm. HRMS (ESI) m/z: calcd for $C_{14}H_{12}NaO_3S$ $[M+Na]^+$, 283.0399; found 283.0404.

Acknowledgments

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Supporting Information

An efficient electrochemical synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds

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NMR spectra

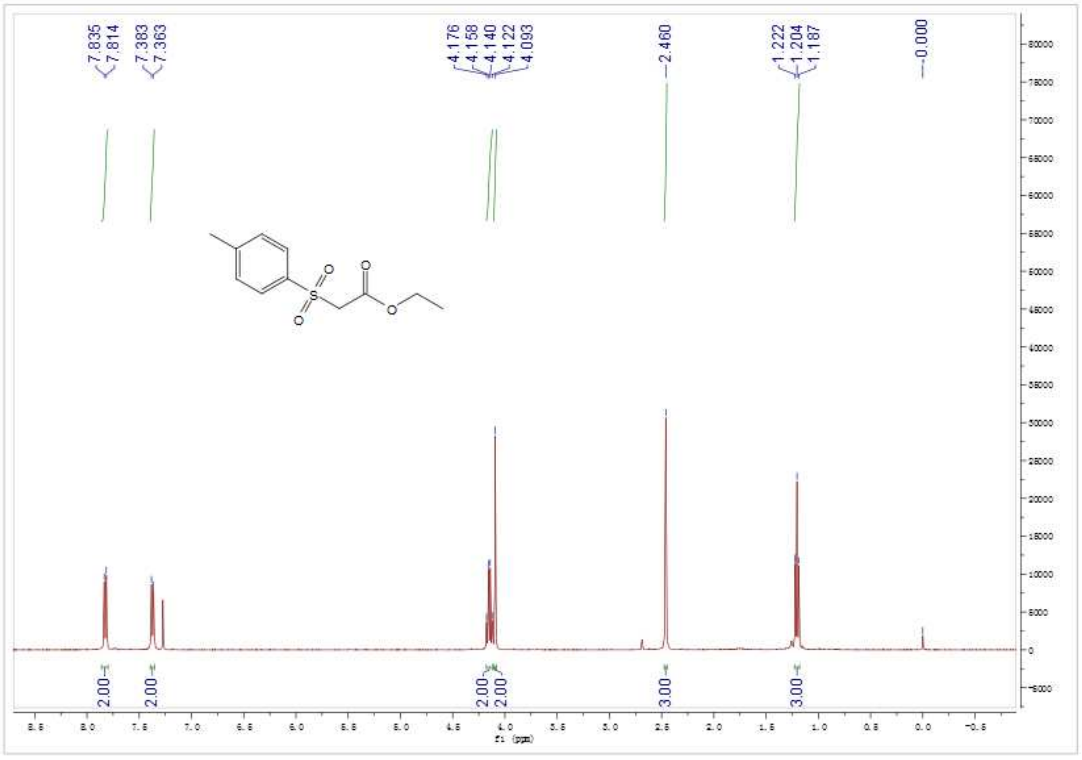

Fig. S-1. ^{1}H-NMR spectrum of (**3aa**).

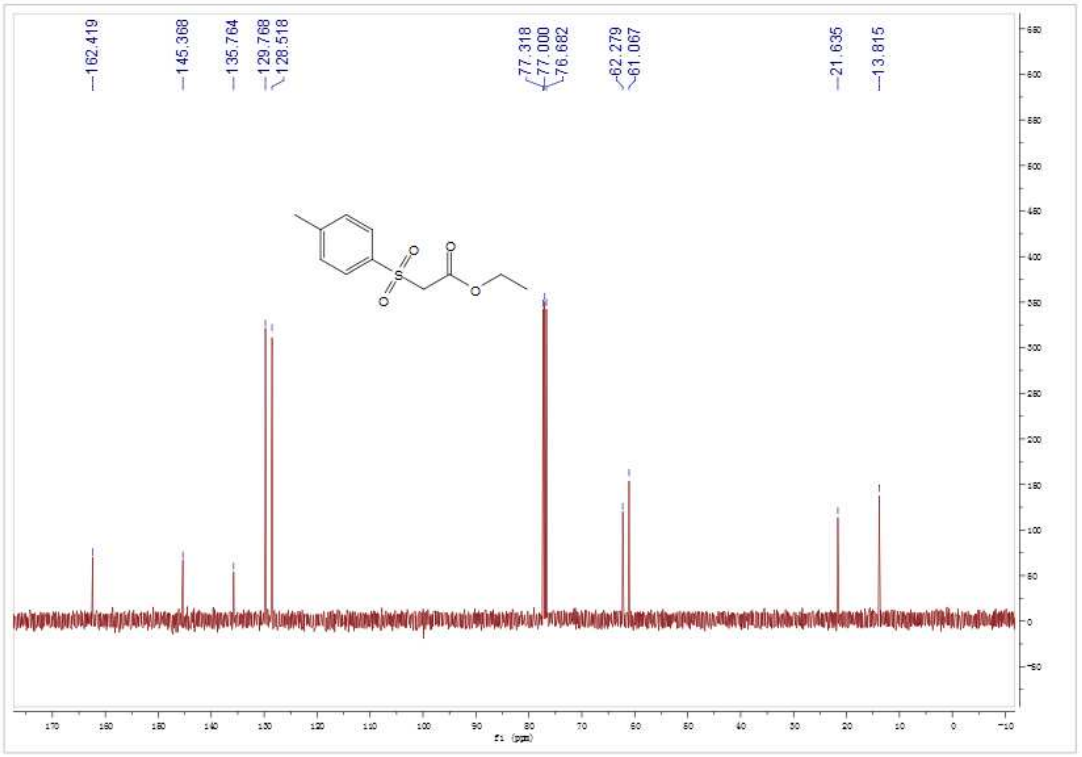

Fig. S-2. ^{13}C-NMR spectrum of (**3aa**).

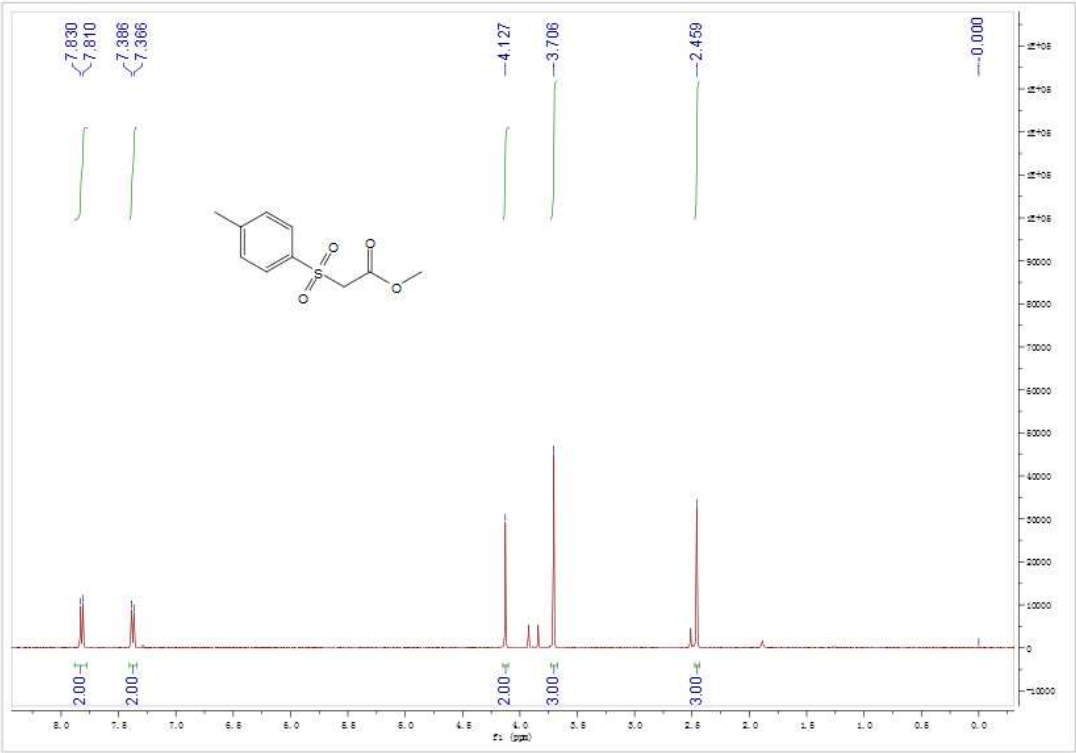

Fig. S-3. ^{1}H-NMR spectrum of (**3ba**).

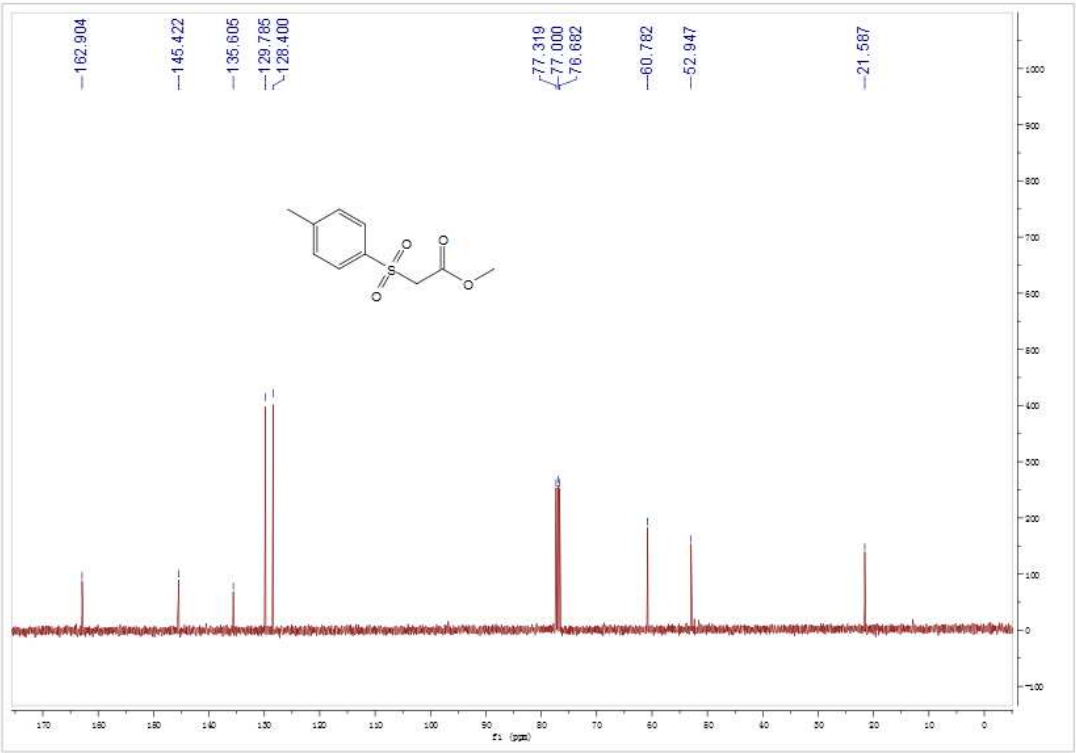

Fig. S-4. ^{13}C-NMR spectrum of (**3ba**).

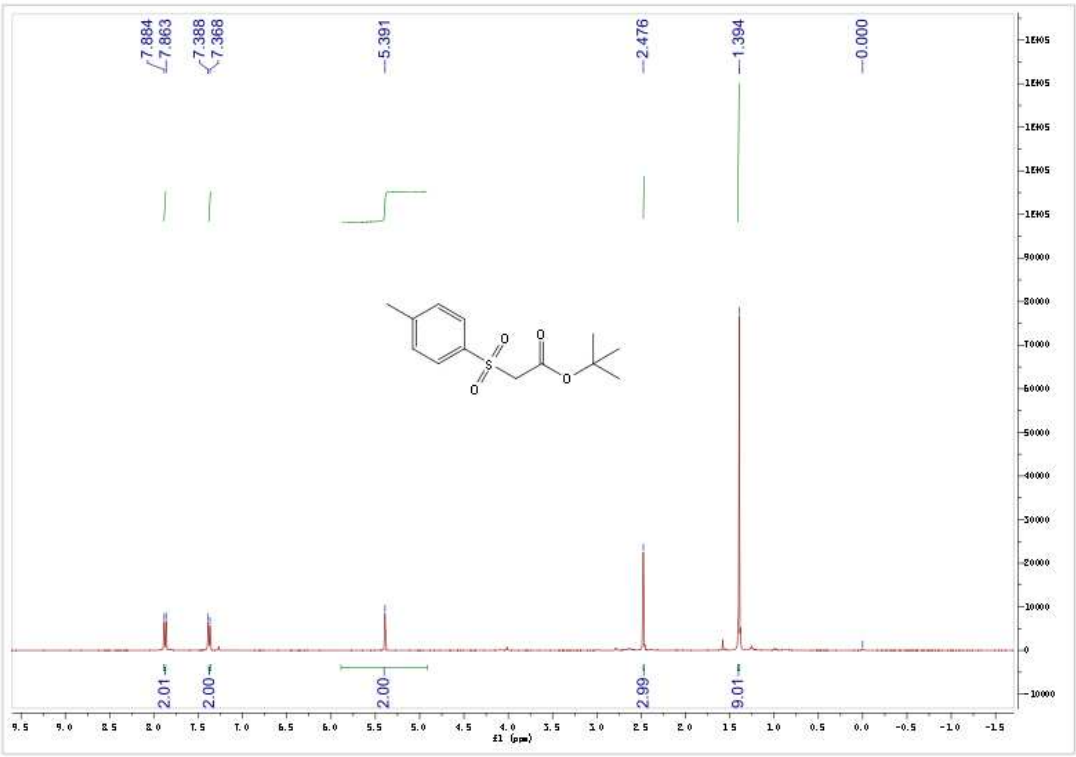

Fig. S-5. ^{1}H-NMR spectrum of (**3ca**).

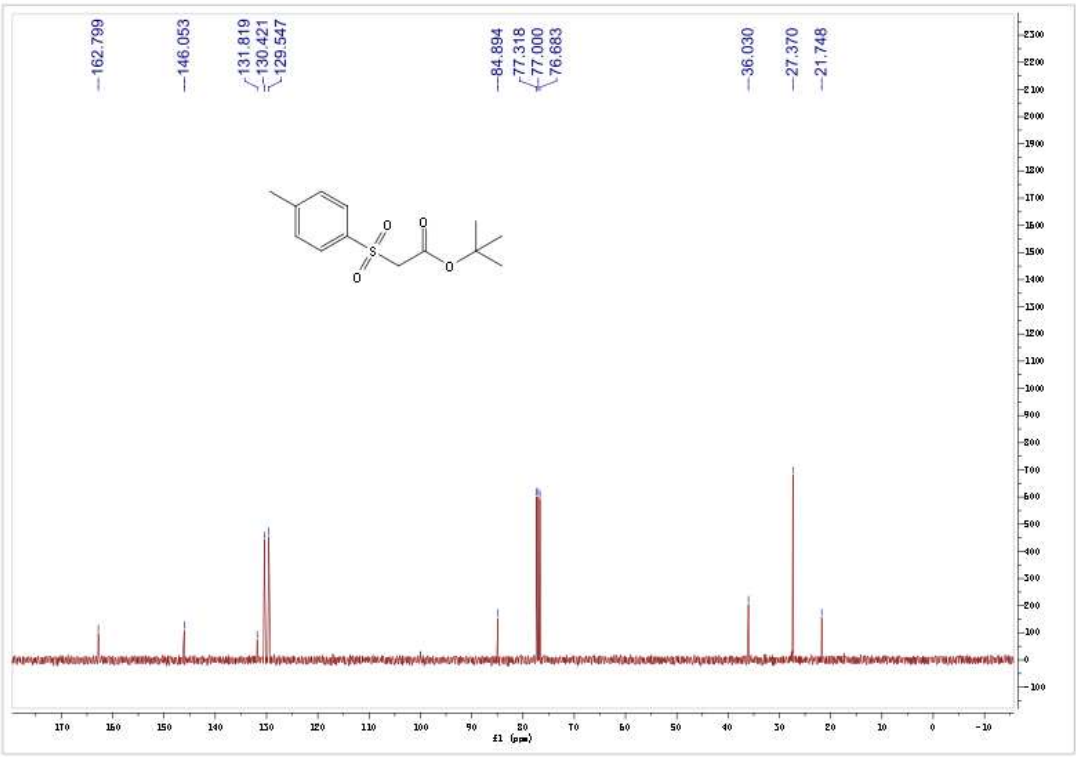

Fig. S-6. ^{13}C-NMR spectrum of (**3ca**).

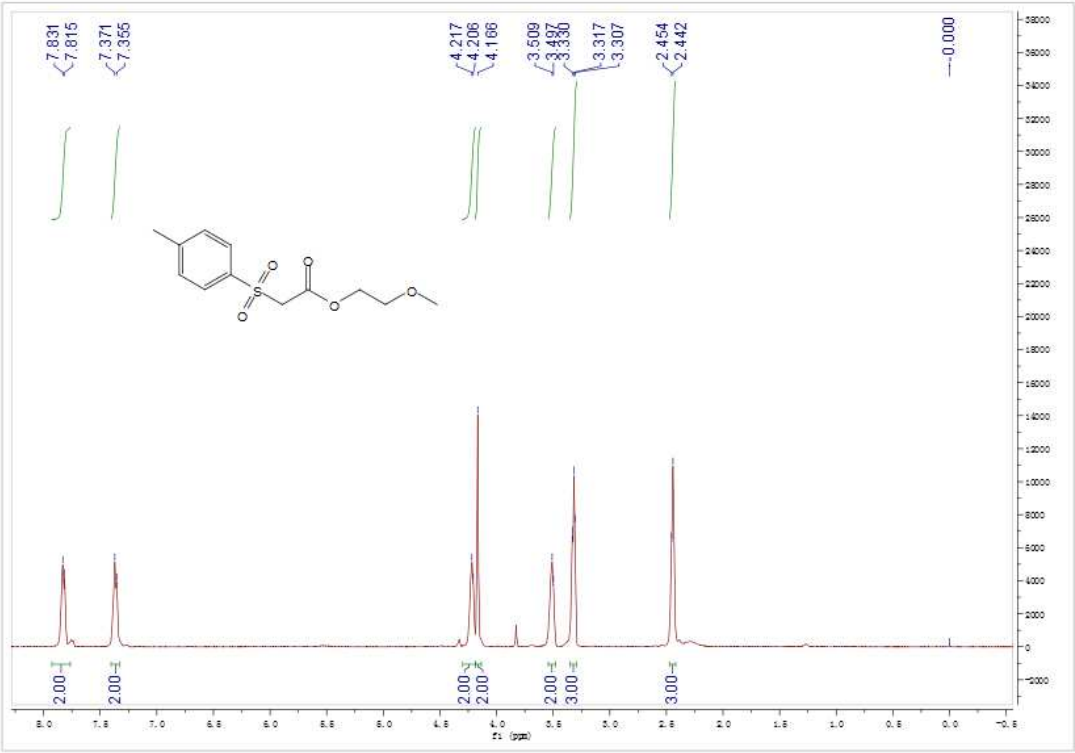

Fig. S-7. ^{1}H-NMR spectrum of (**3da**).

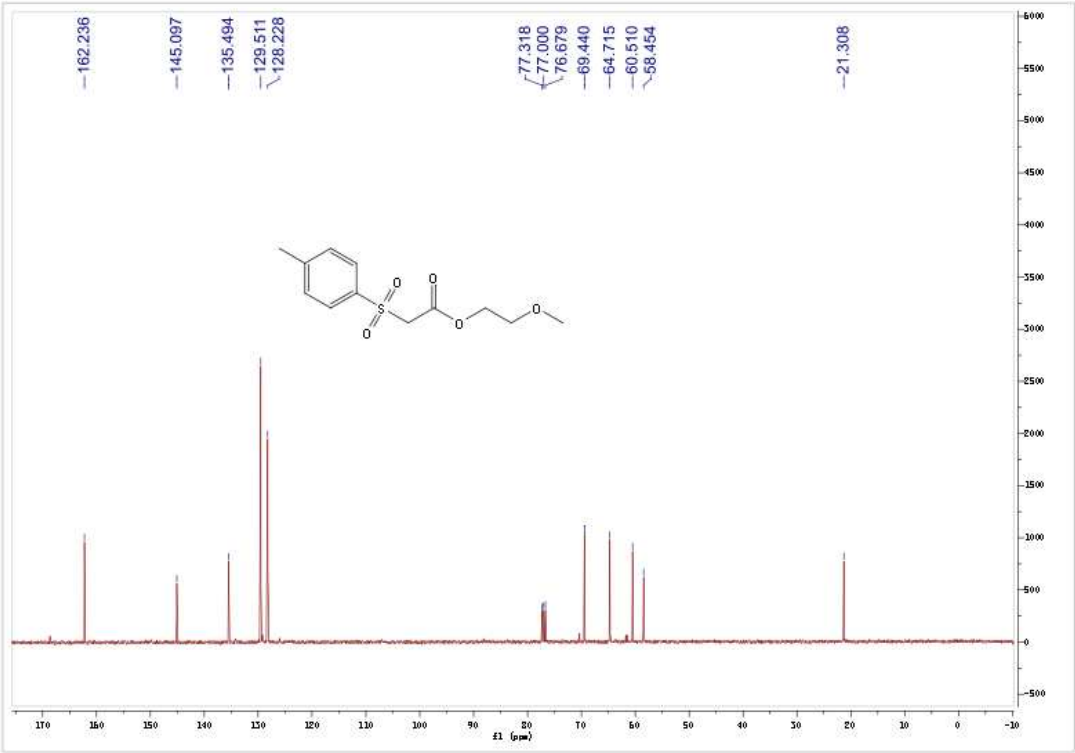

Fig. S-8. ^{13}C-NMR spectrum of (**3da**).

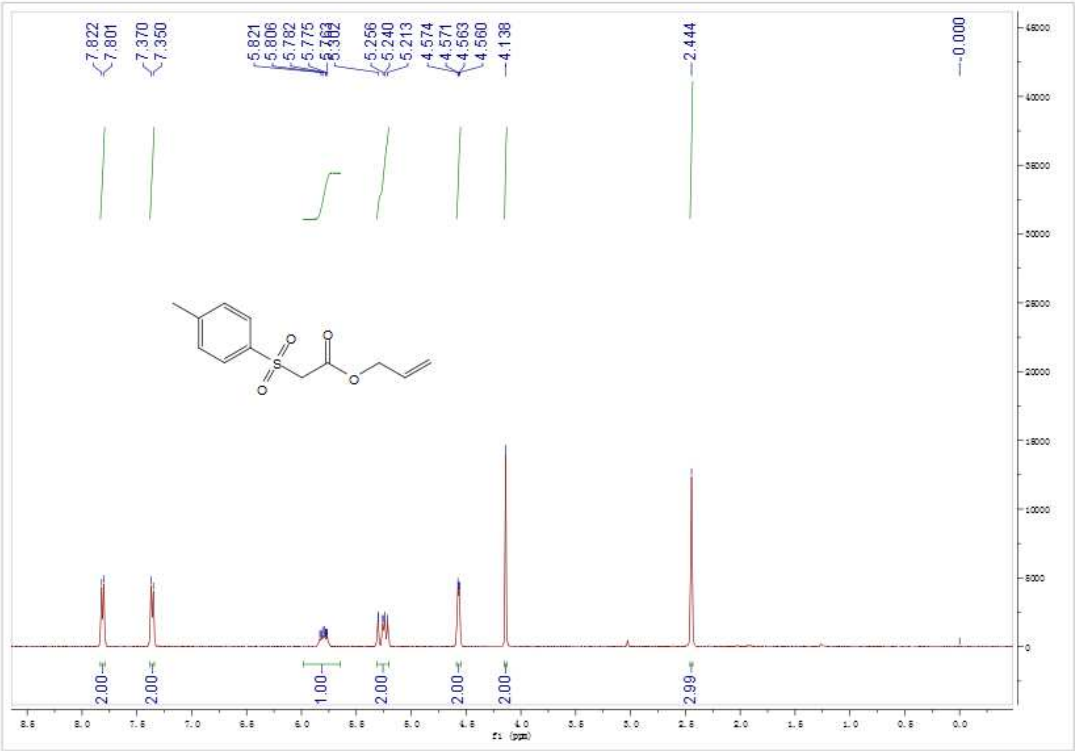

Fig. S-9. ^{1}H-NMR spectrum of (**3ea**).

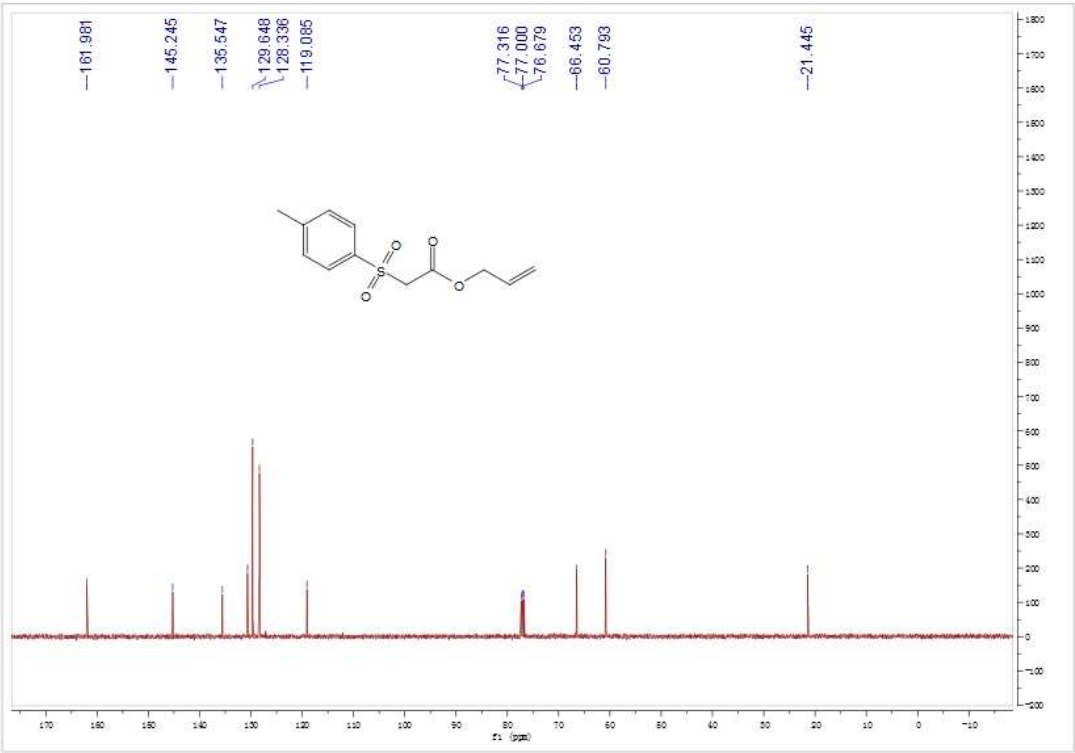

Fig. S-10. ^{13}C-NMR spectrum of (**3ea**).

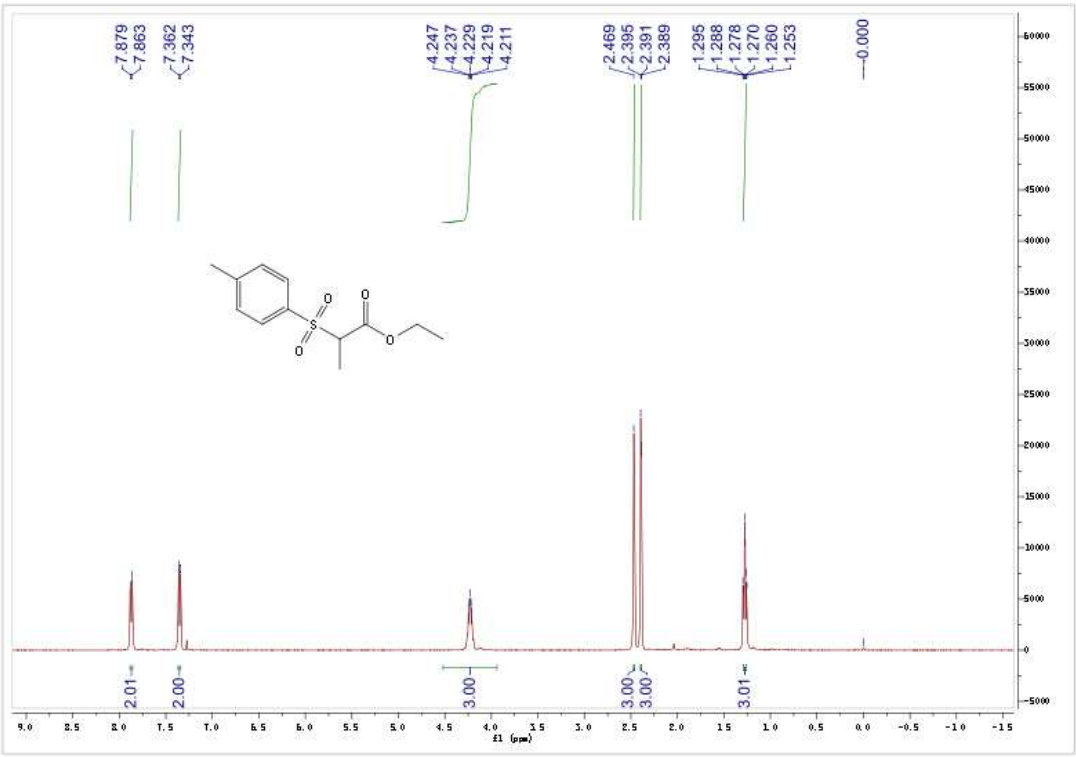

Fig. S-11. ^{1}H-NMR spectrum of (**3fa**).

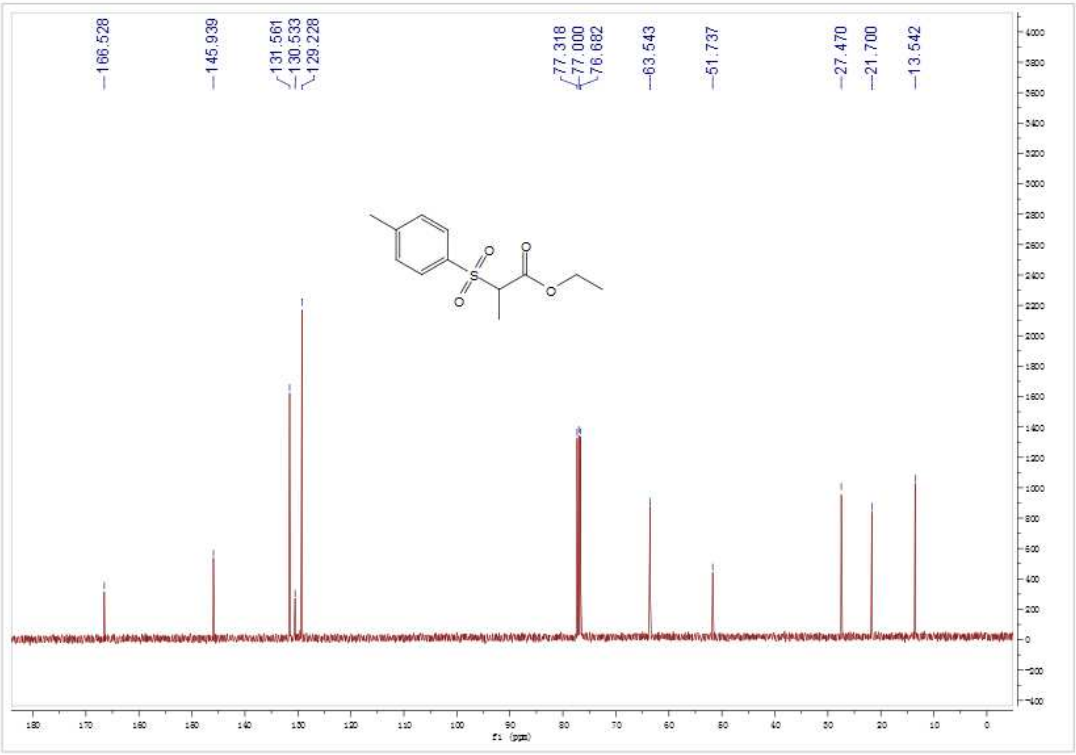

Fig. S-12. ^{13}C-NMR spectrum of (**3fa**).

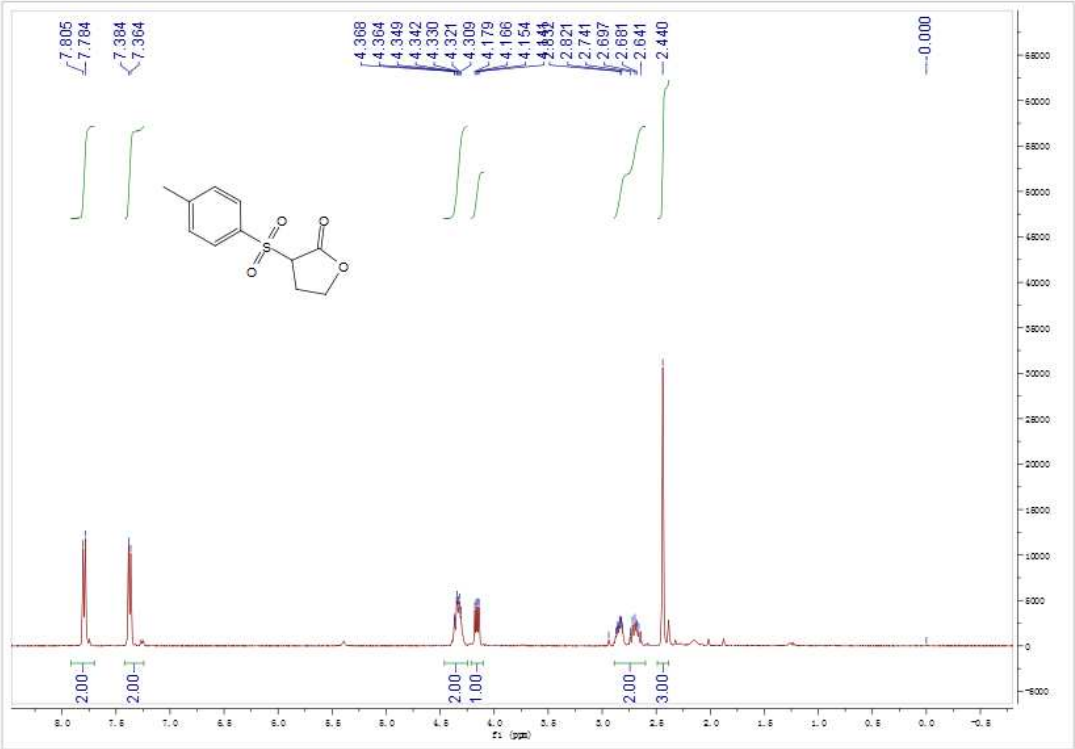

Fig. S-13. ^{1}H-NMR spectrum of (**3ga**).

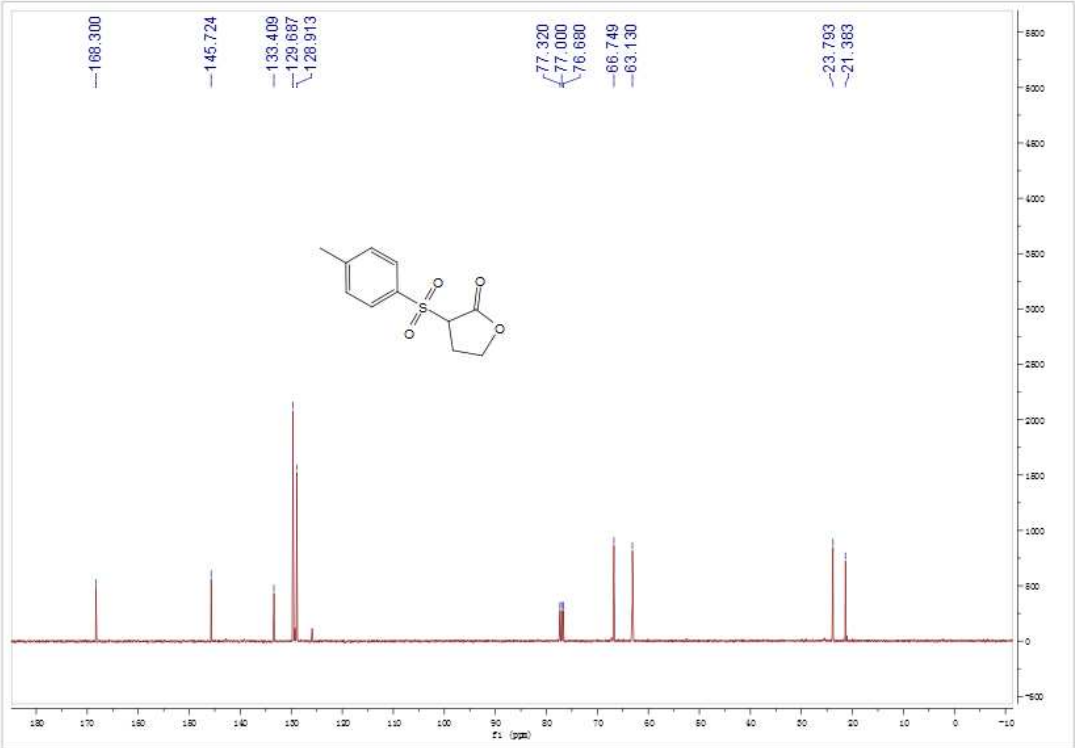

Fig. S-14. ^{13}C-NMR spectrum of (**3ga**).

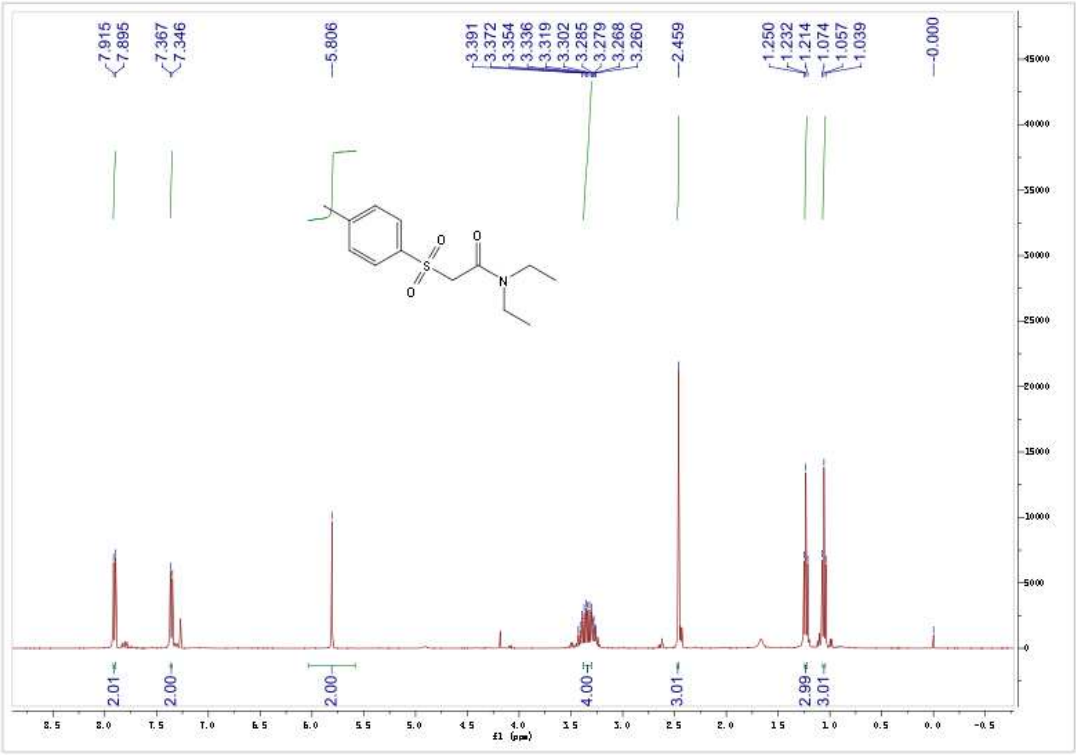

Fig. S-15. ^{1}H-NMR spectrum of (**3ha**).

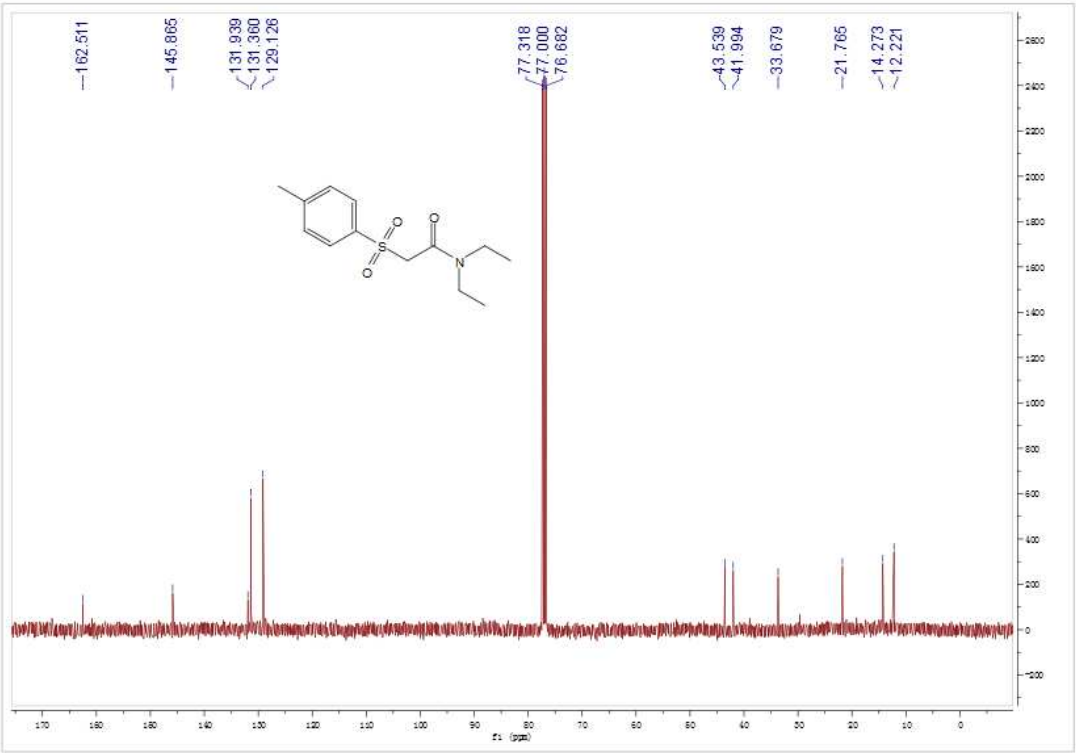

Fig. S-16. ^{13}C-NMR spectrum of (**3ha**).

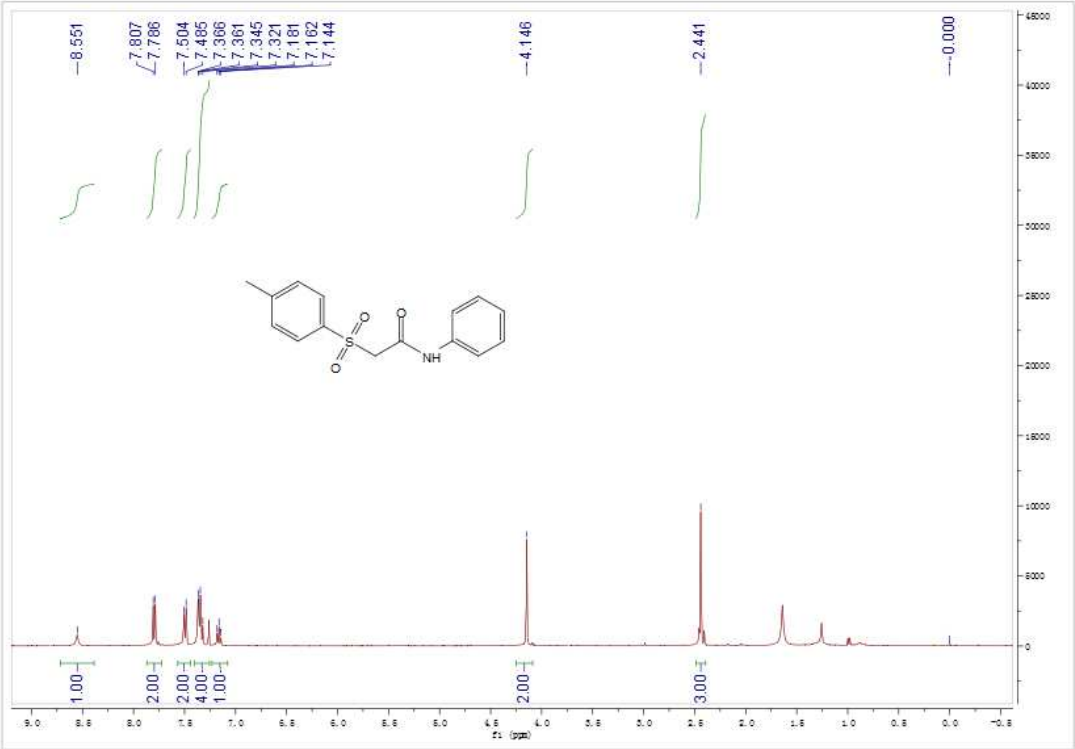

Fig. S-17. ^{1}H-NMR spectrum of (**3ia**).

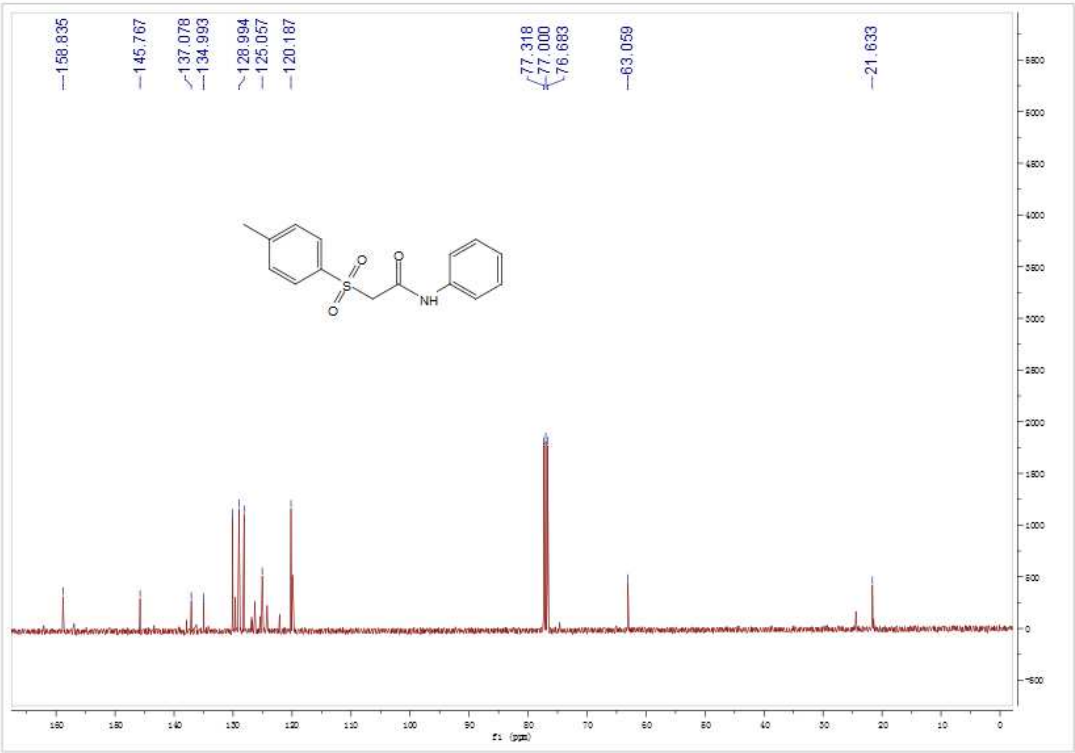

Fig. S-18. ^{13}C-NMR spectrum of (**3ia**).

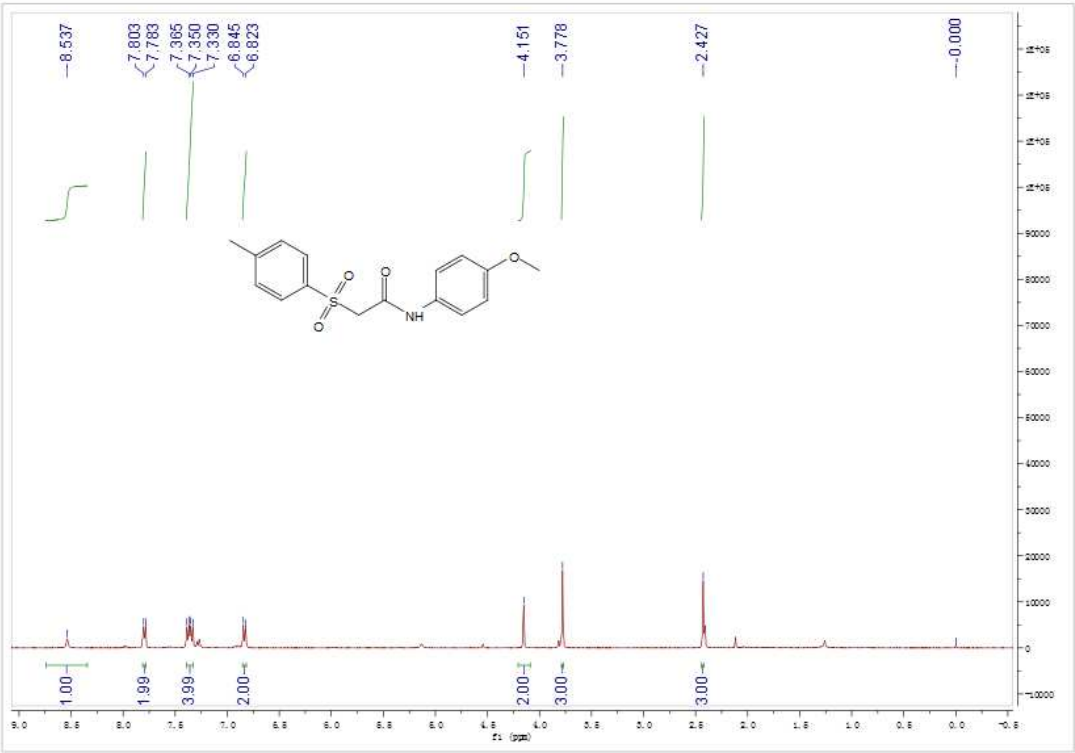

Fig. S-19. ^{1}H-NMR spectrum of (**3ja**).

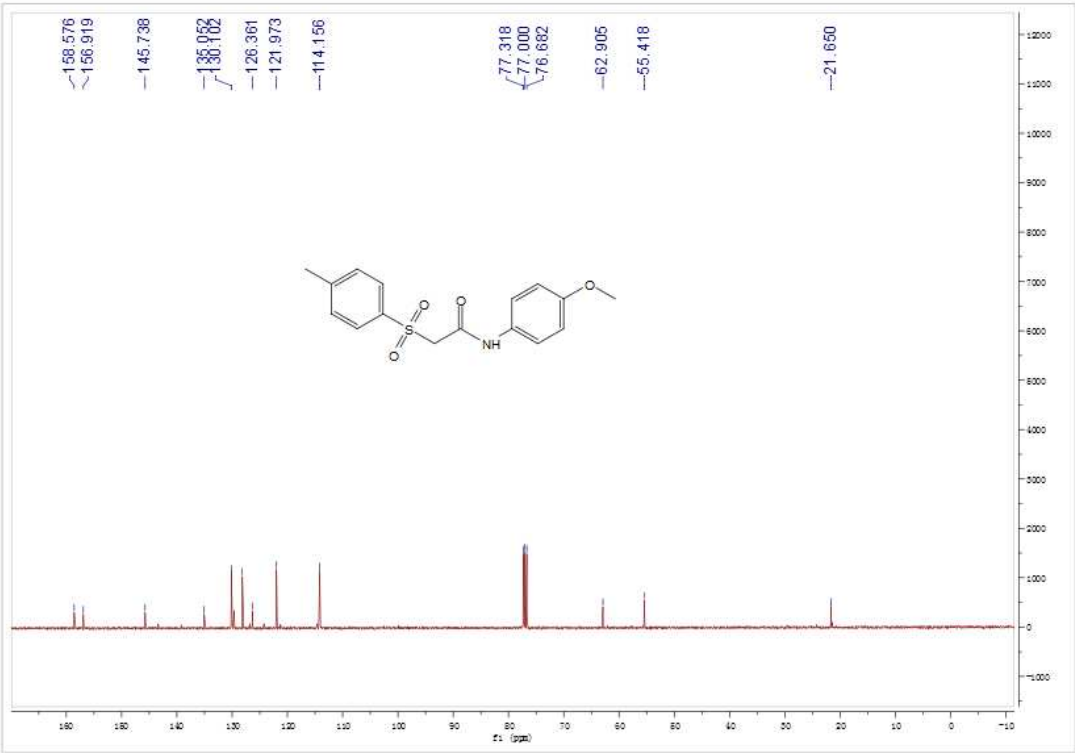

Fig. S-20. ^{13}C-NMR spectrum of (**3ja**).

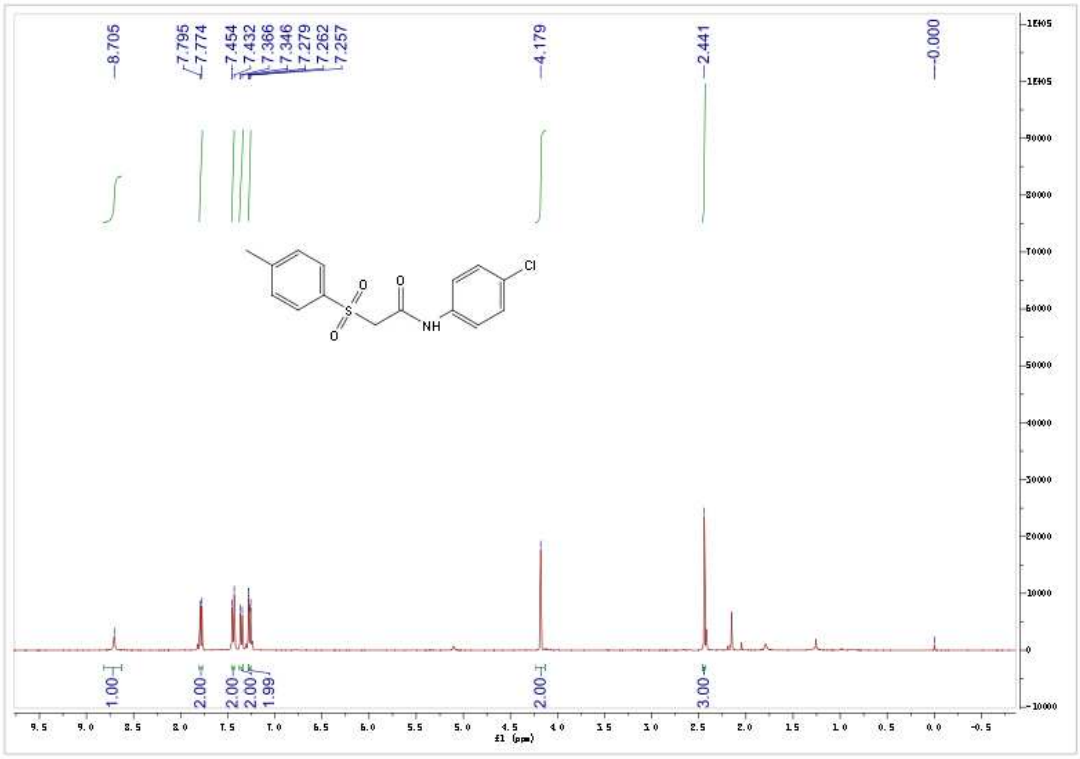

Fig. S-21. ^{1}H-NMR spectrum of (**3ka**).

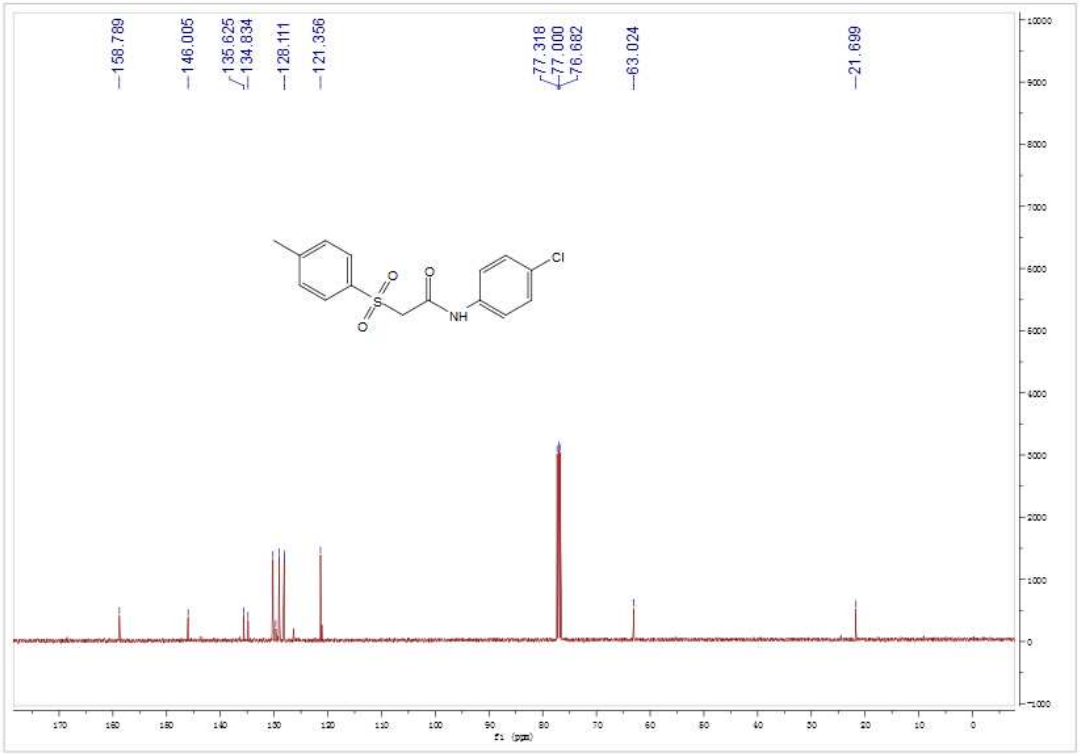

Fig. S-22. ^{13}C-NMR spectrum of (**3ka**).

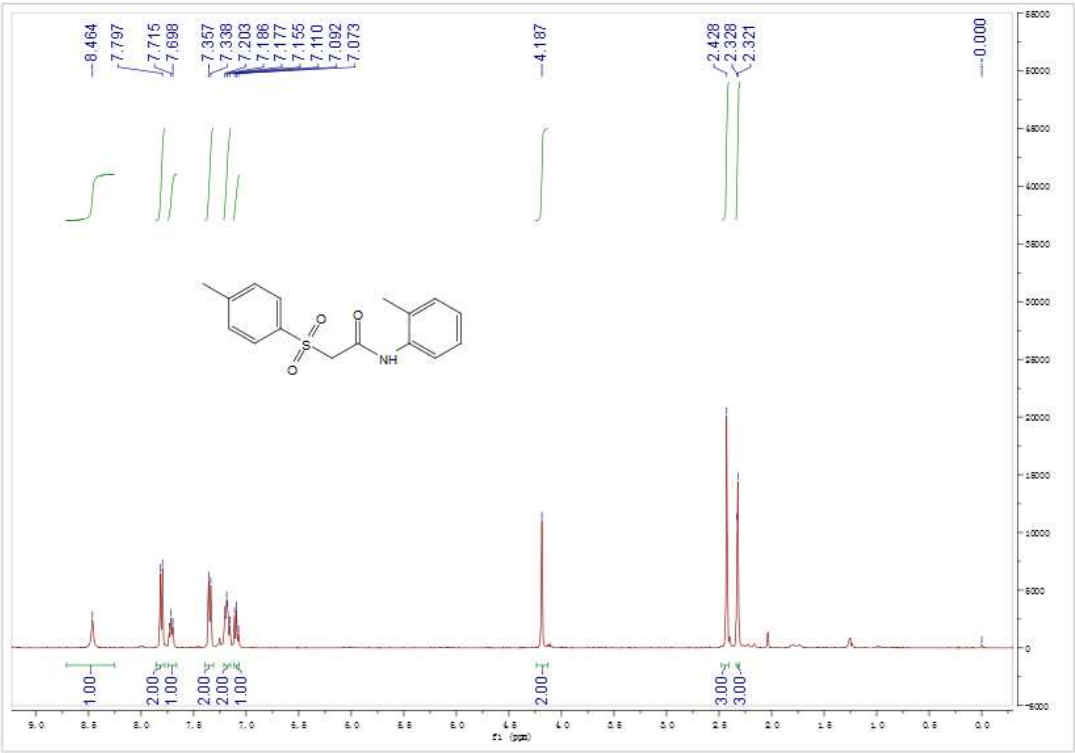

Fig. S-23. ^{1}H-NMR spectrum of (**3la**).

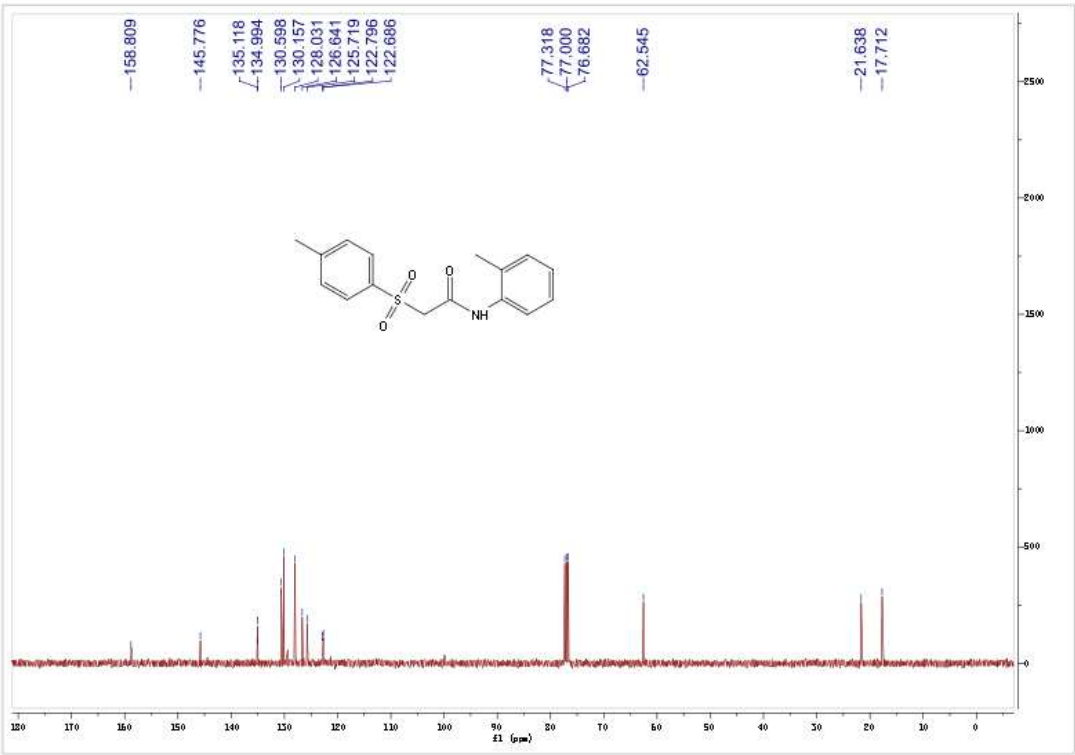

Fig. S-24. ^{13}C-NMR spectrum of (**3la**).

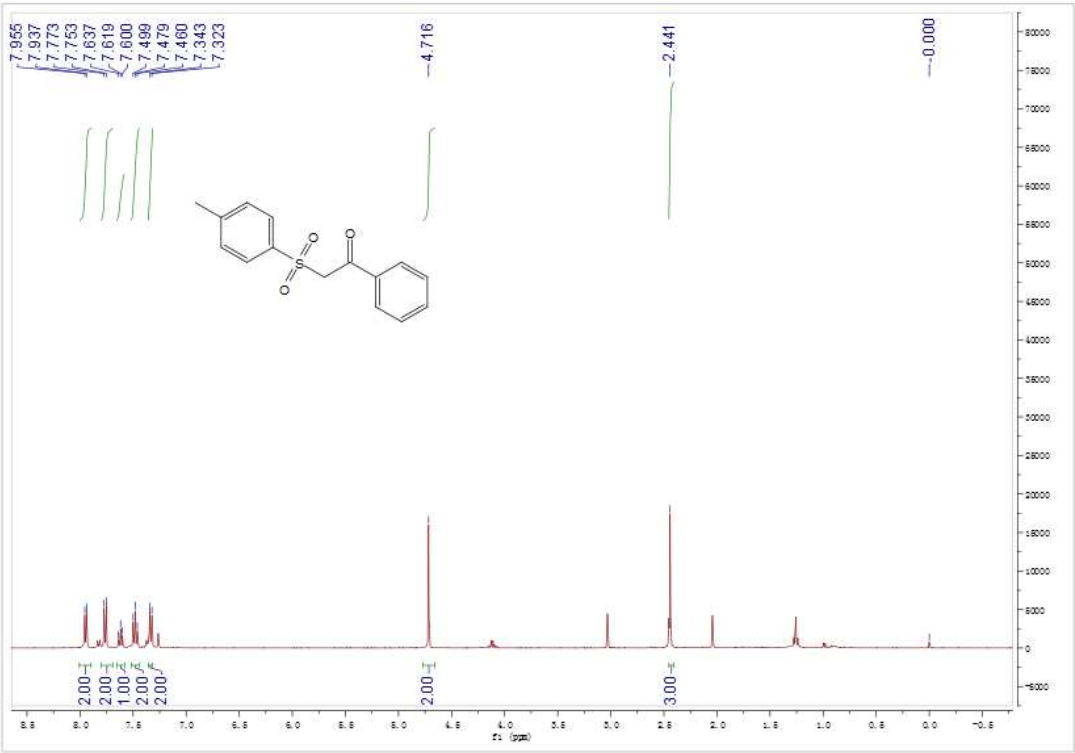

Fig. S-25. ^{1}H-NMR spectrum of (**3ma**).

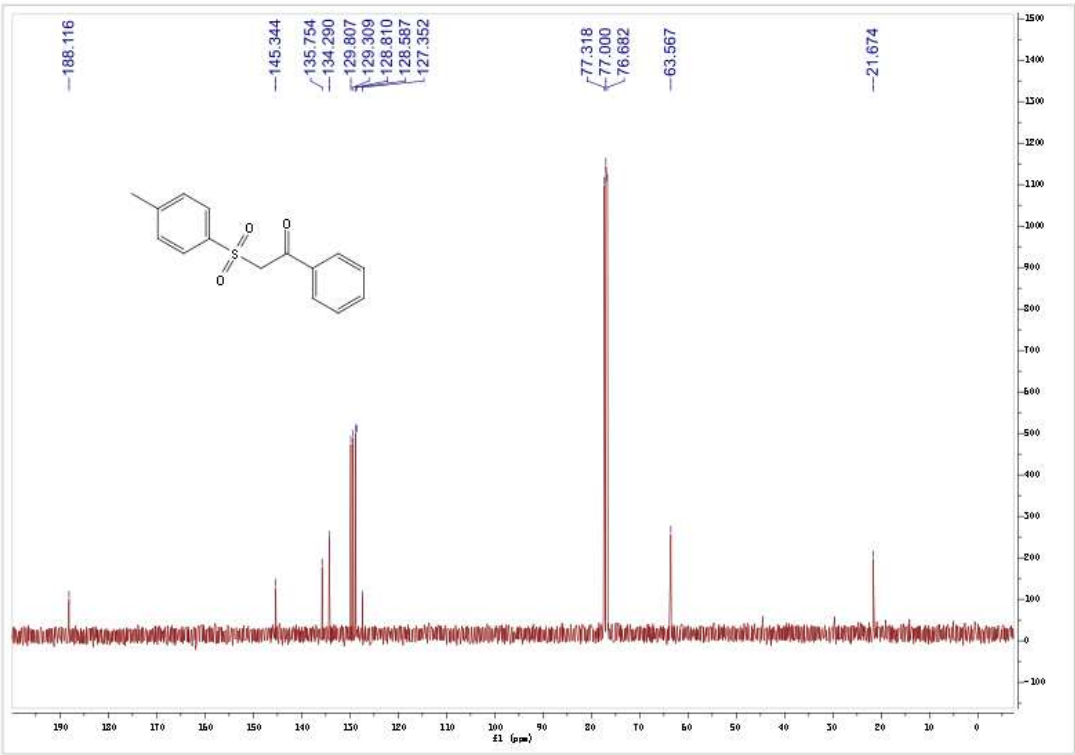

Fig. S-26. ^{13}C-NMR spectrum of (**3ma**).

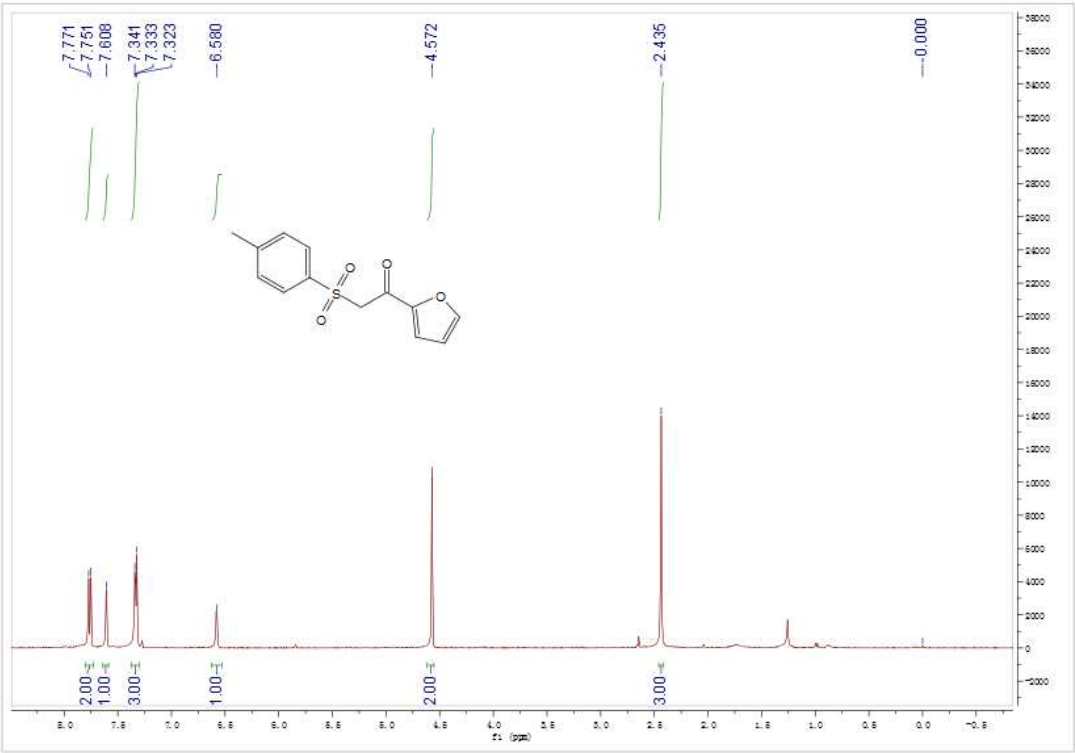

Fig. S-27. ^{1}H-NMR spectrum of (**3na**).

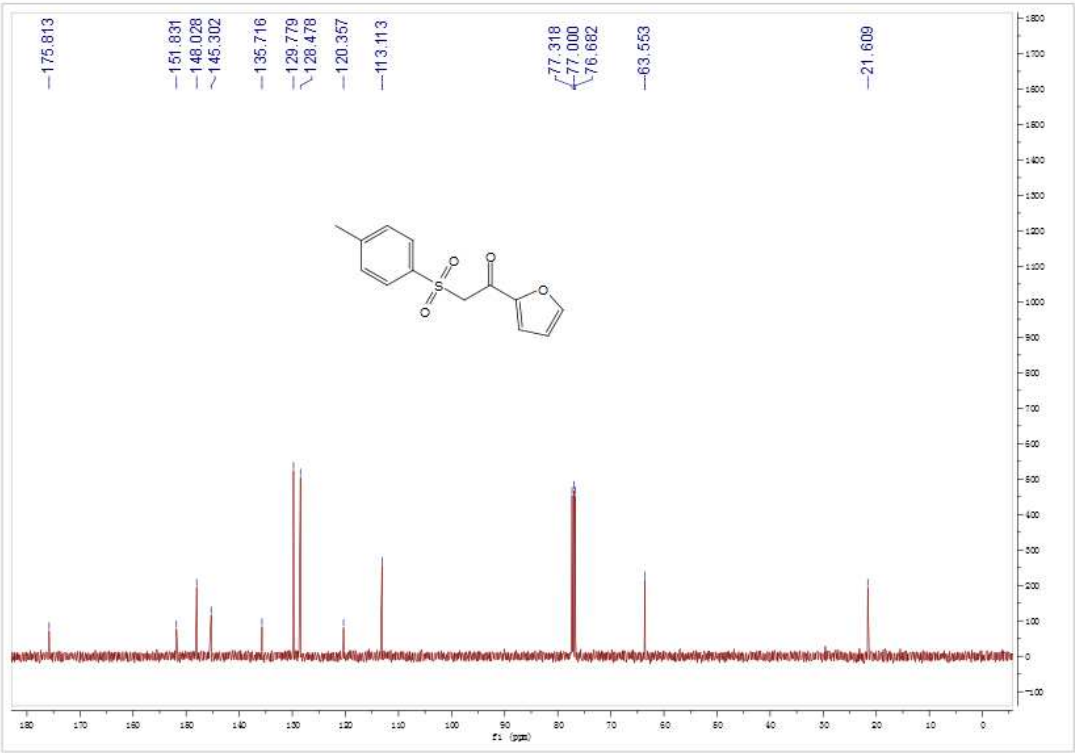

Fig. S-28. ^{13}C-NMR spectrum of (**3na**).

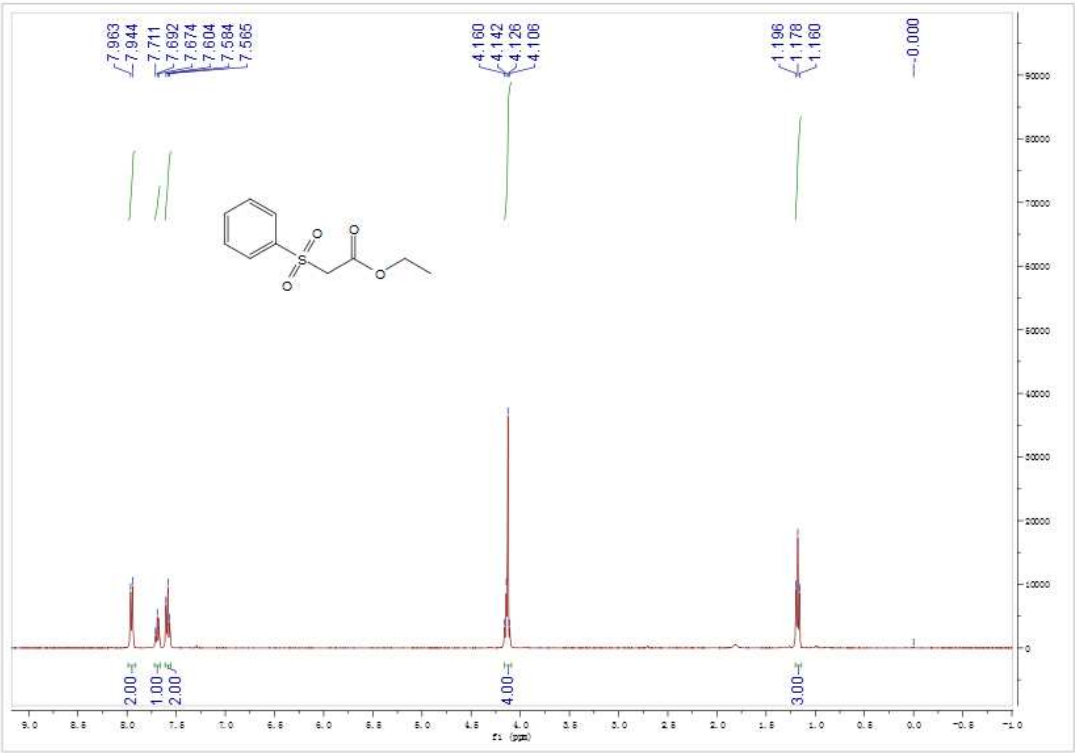

Fig. S-29. ^{1}H-NMR spectrum of (**3ab**).

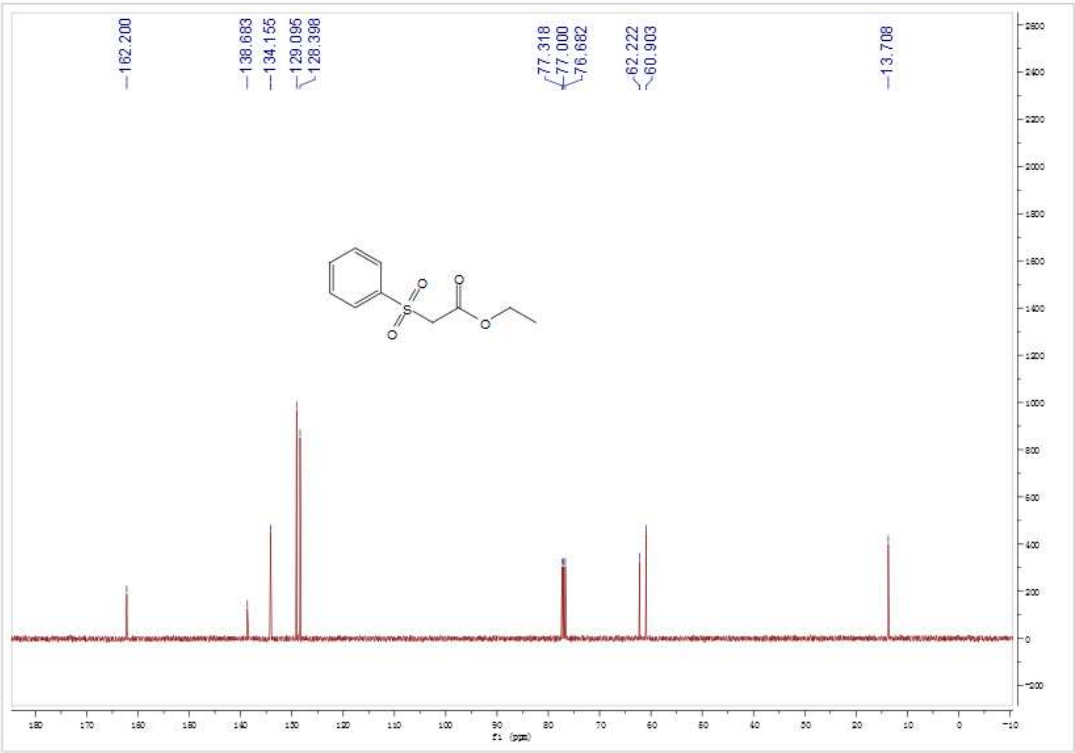

Fig. S-30. ^{13}C-NMR spectrum of (**3ab**).

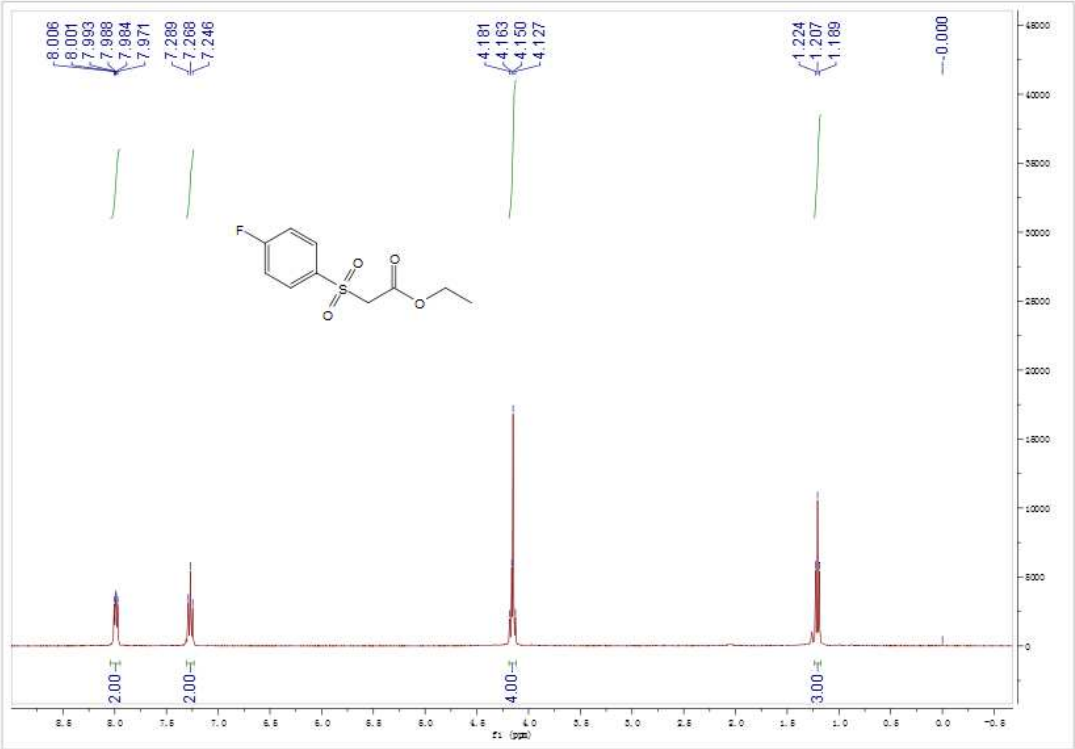

Fig. S-31. ^{1}H-NMR spectrum of (**3ac**).

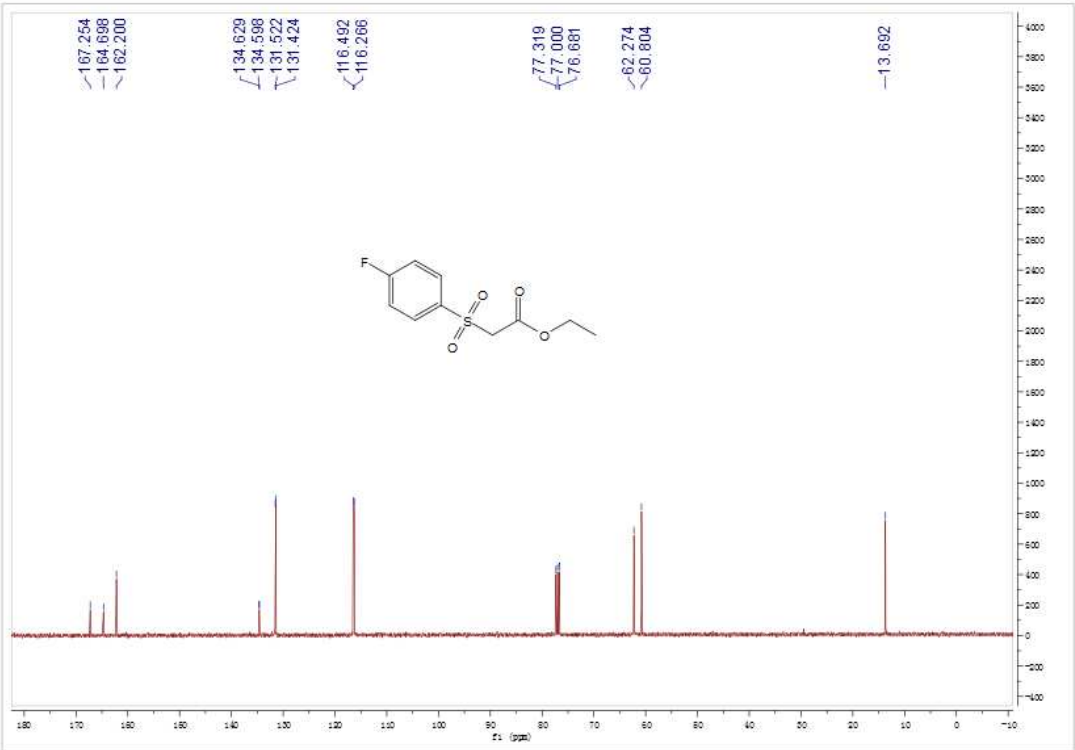

Fig. S-32. ^{13}C-NMR spectrum of (**3ac**).

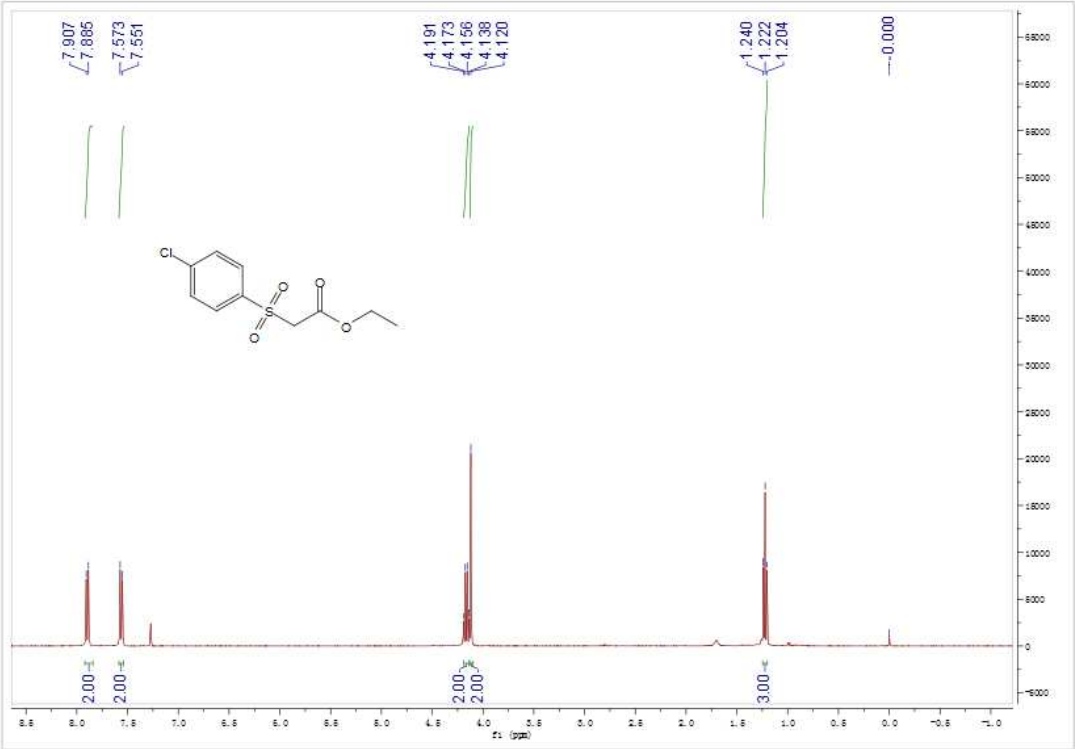

Fig. S-33. ^{1}H-NMR spectrum of (**3ad**).

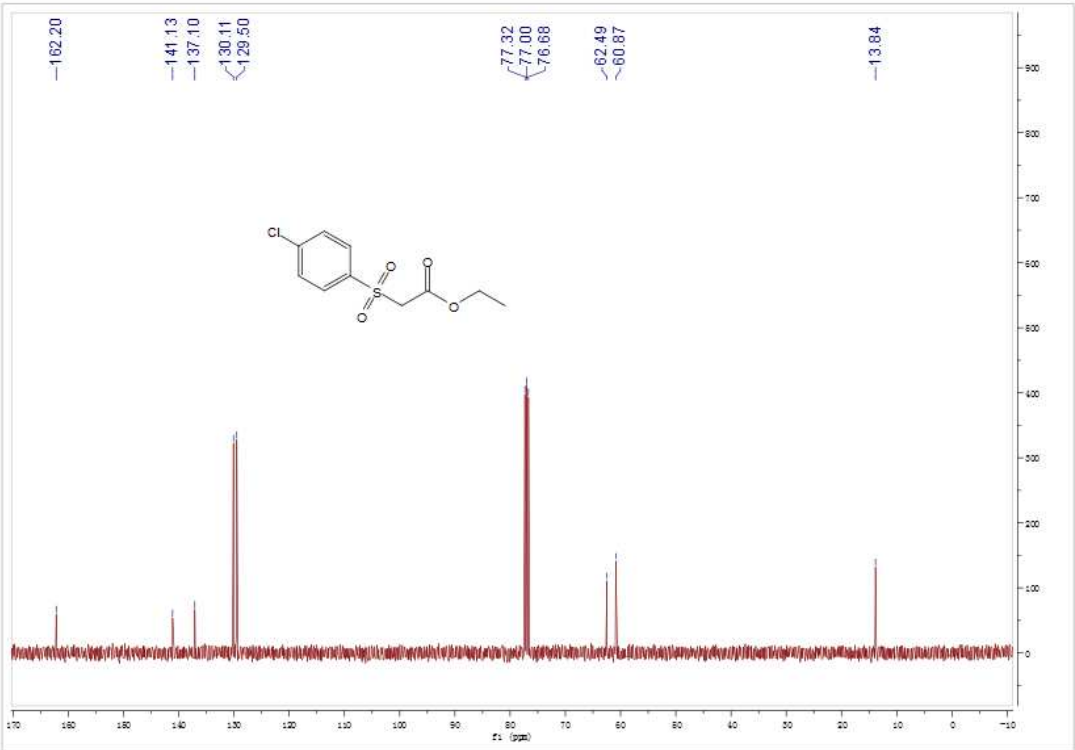

Fig. S-34. ^{13}C-NMR spectrum of (**3ad**).

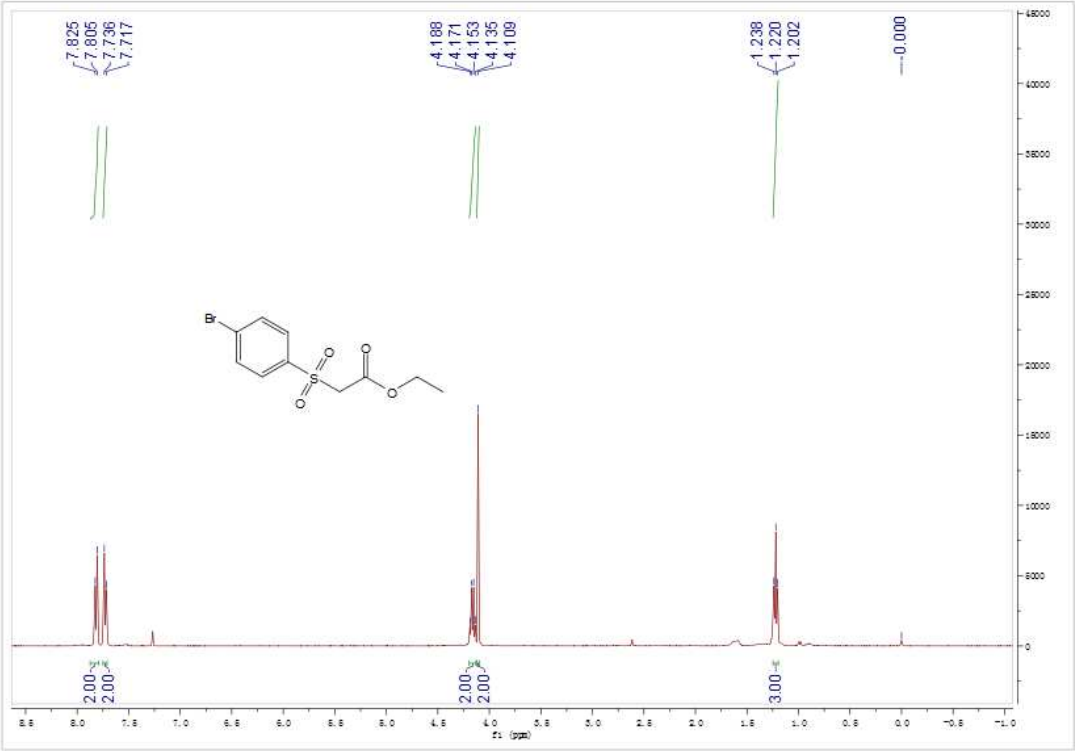

Fig. S-35. ^{1}H-NMR spectrum of (**3ae**).

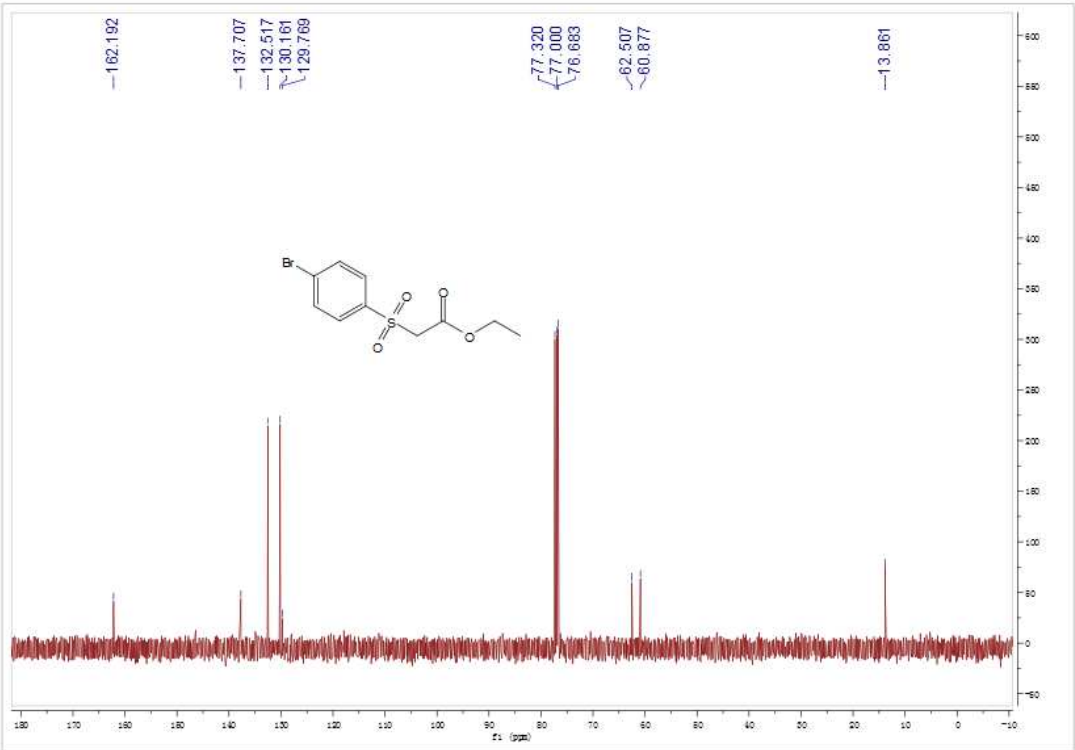

Fig. S-36. ^{13}C-NMR spectrum of (**3ae**).

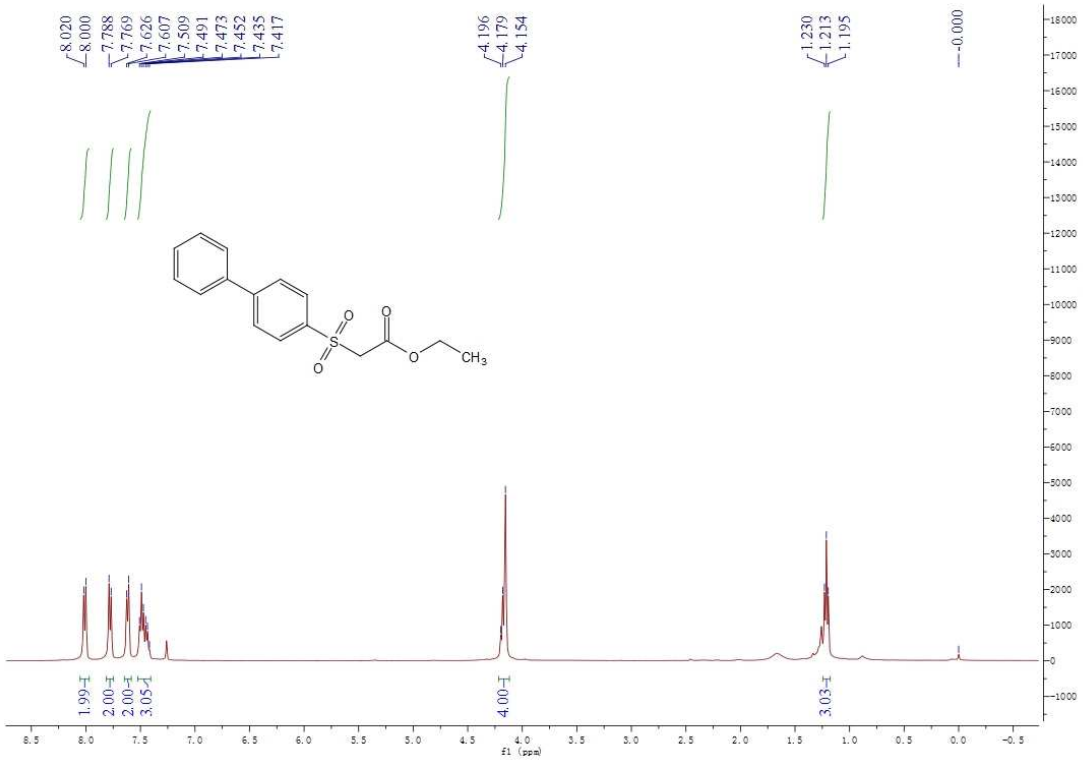

Fig. S-37. ^{1}H-NMR spectrum of (**3af**).

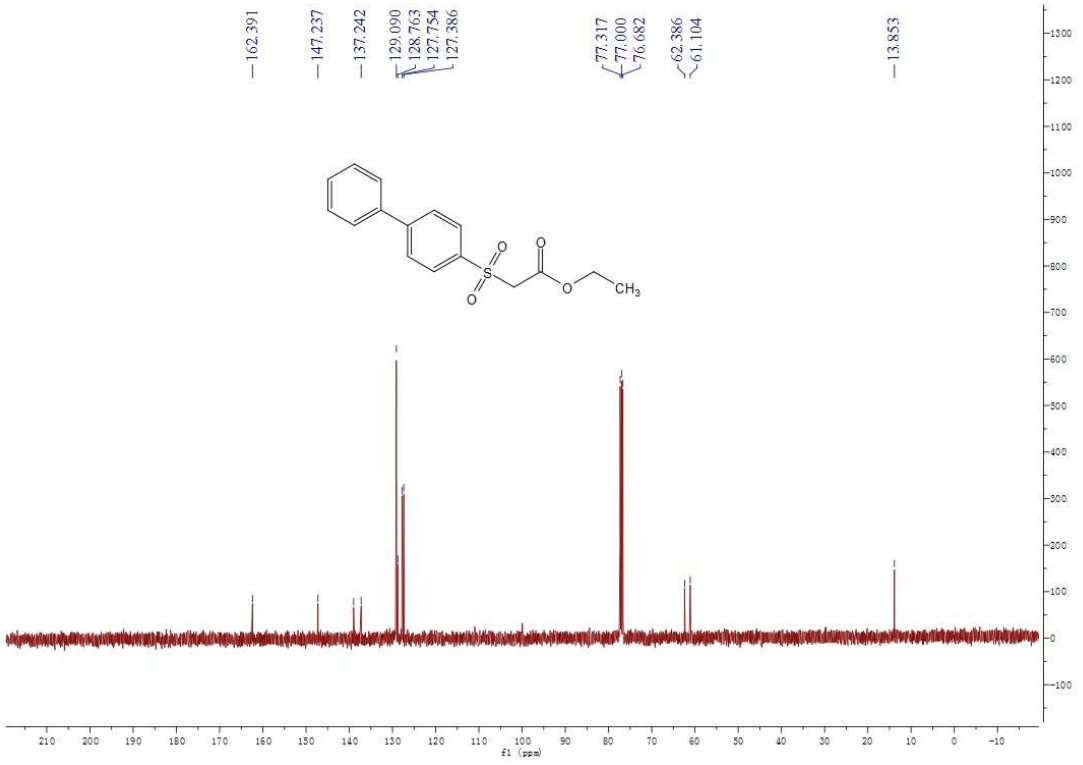

Fig. S-38. ^{13}C-NMR spectrum of (**3af**).

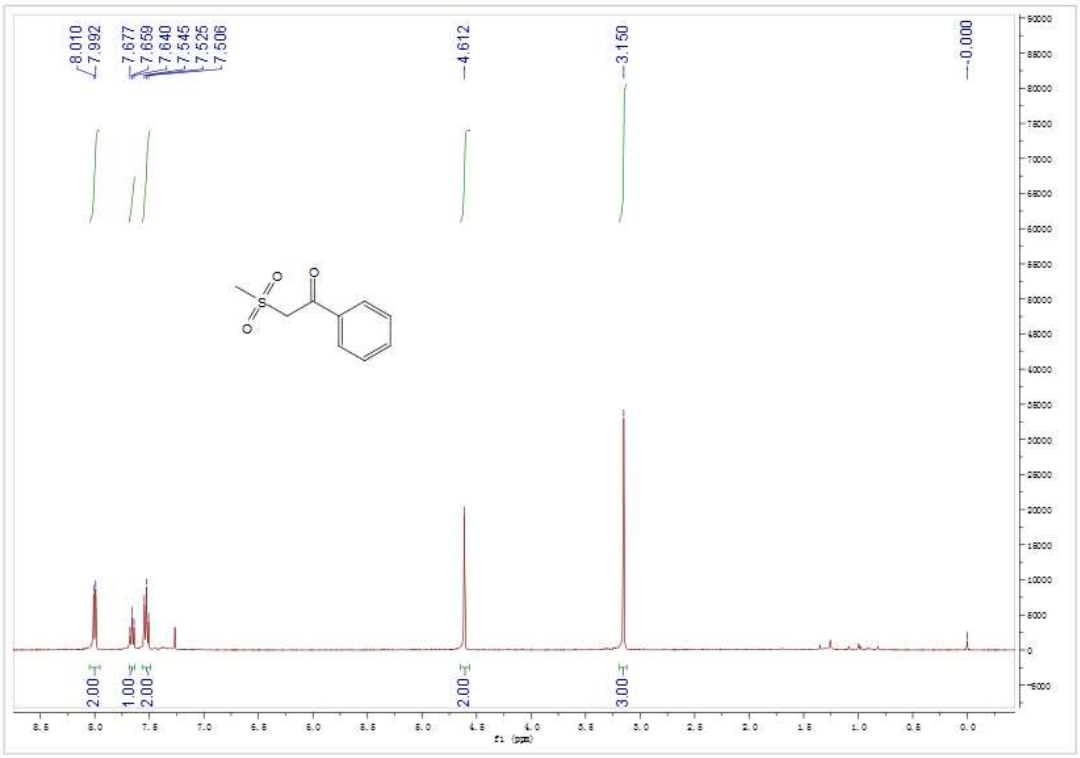

Fig. S-39. ^{1}H-NMR spectrum of (**3ag**).

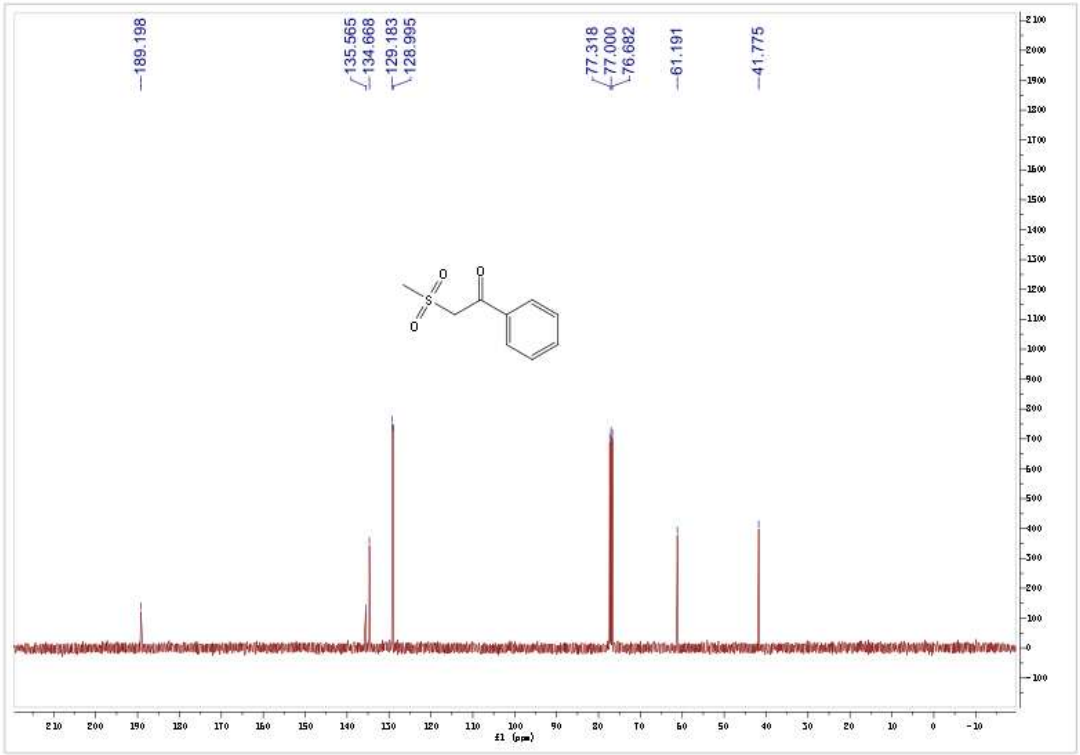

Fig. S-40. ^{13}C-NMR spectrum of (**3ag**).

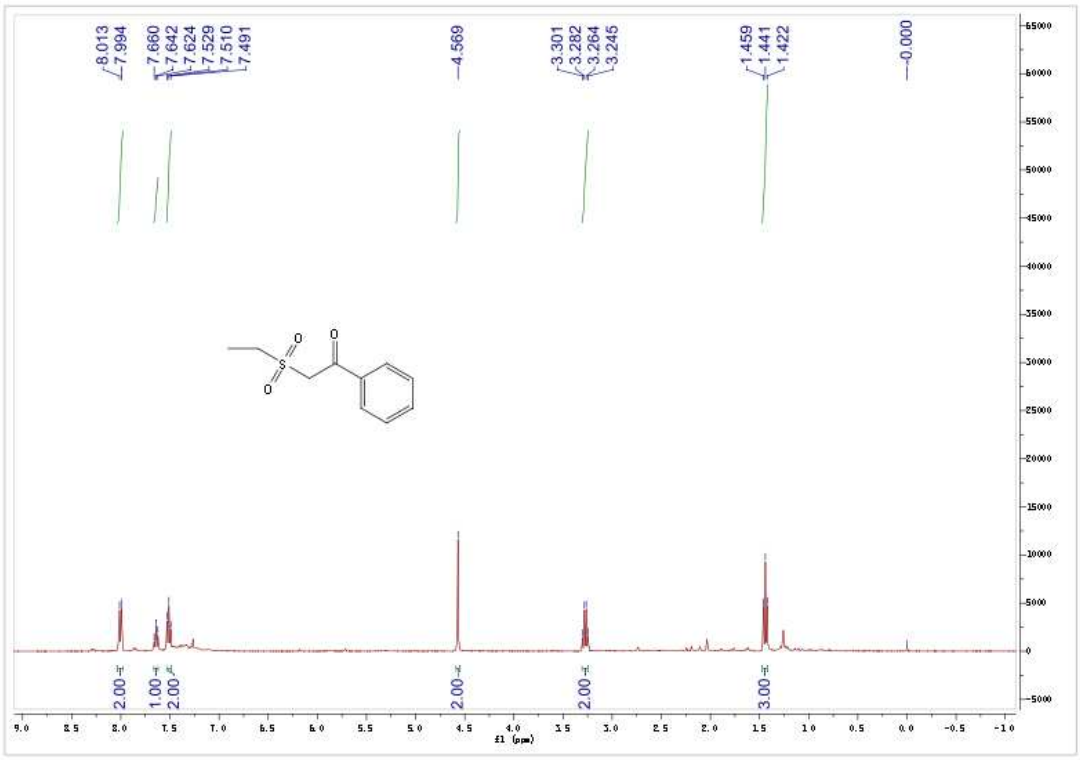

Fig. S-41. ^{1}H-NMR spectrum of (**3ah**).

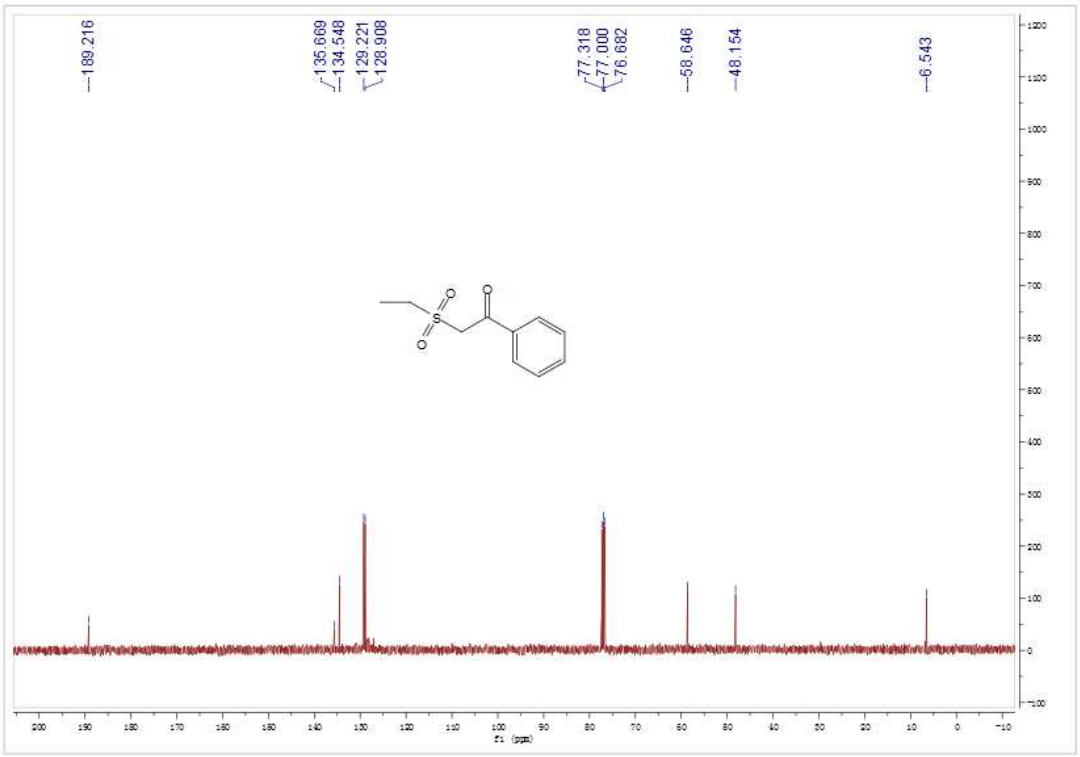

Fig. S-42. ^{13}C-NMR spectrum of (**3ah**).

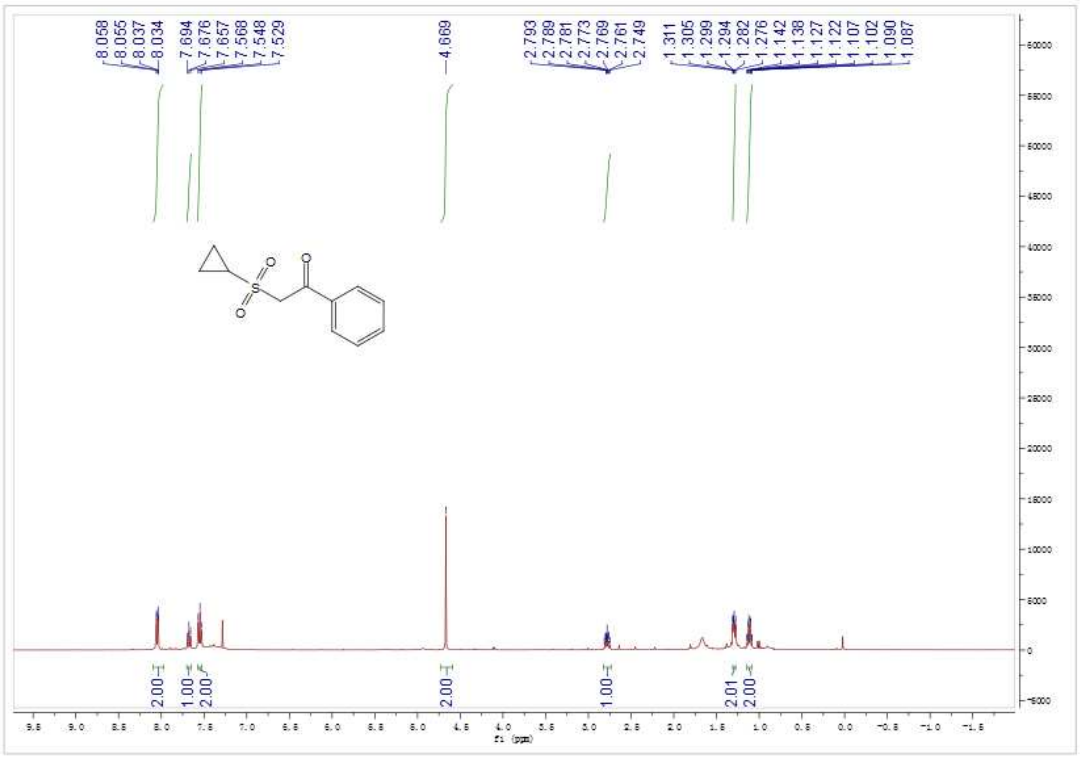

Fig. S-43. ^{1}H-NMR spectrum of (**3ai**).

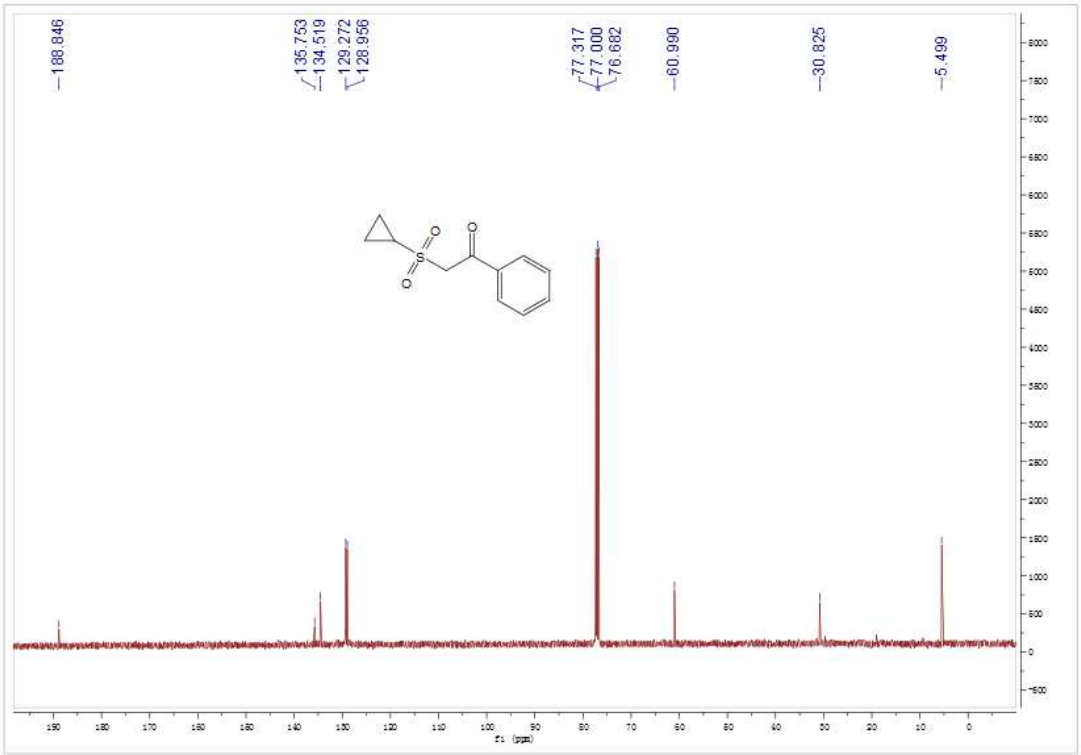

Fig. S-44. ^{13}C-NMR spectrum of (**3ai**).

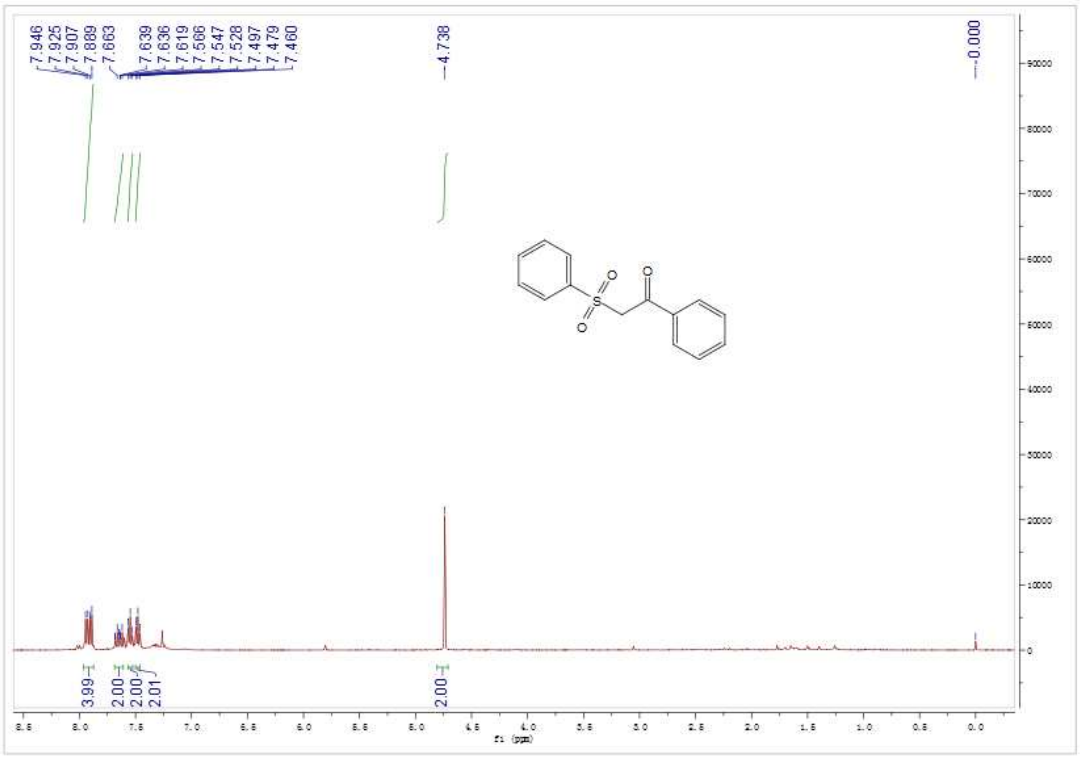

Fig. S-45. ^{1}H-NMR spectrum of (**3aj**).

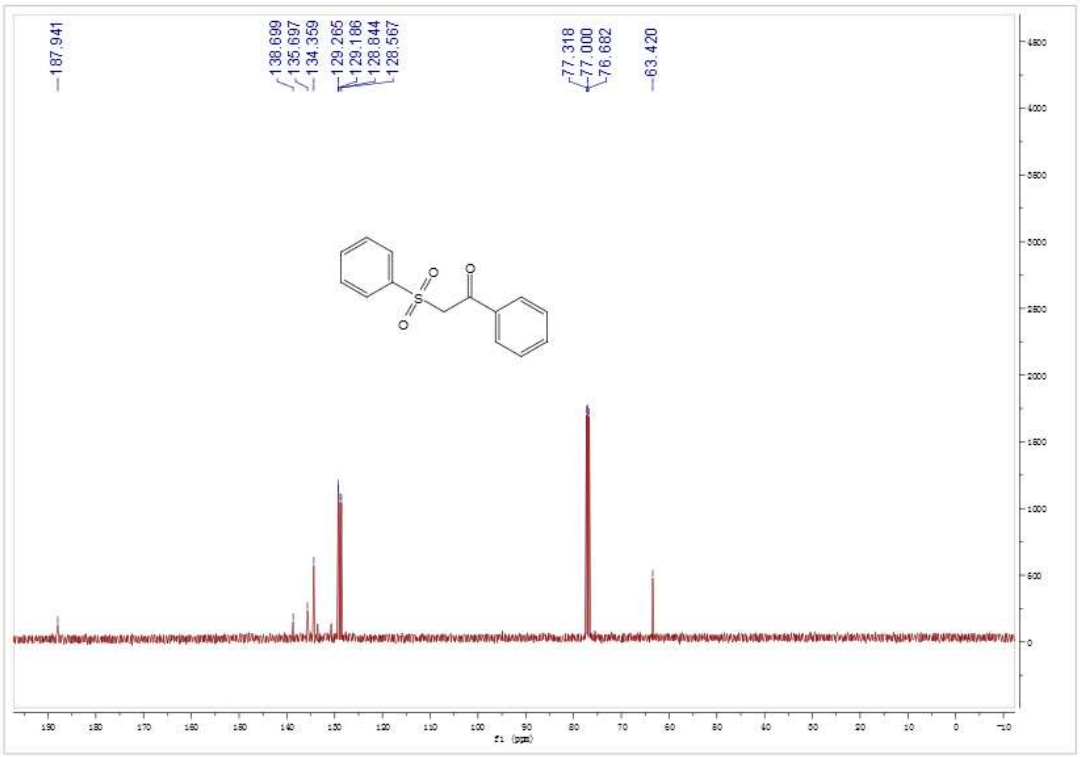

Fig. S-46. ^{13}C-NMR spectrum of (**3aj**).