中央大学理工学研究所論文集　第27号　2021年
Journal of the Institute of Science and Engineering. CHUO UNIVERSITY

# Trifluoroacetic Acid-Mediated Desulfurilative Sulfonylation of Activated Olefins Using Potassium *p*-Toluenethiosulfonate

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## Abstract

A trifluoroacetic acid (TFA)-mediated desulfurilative sulfonylation of activated olefins using potassium *p*-toluenethiosulfonate is described. A control experiment suggested that the reaction proceeds through the desulfurilation of potassium *p*-toluenethiosulfonate, followed by the sulfonylation of olefins via a Michael addition-type reaction. The reaction was compatible with a variety of activated olefins, including α,β-unsaturated aldehydes/ketones, and a nitroolefin, to afford the corresponding sulfones. Although α-sulfonylated aldehydes are easily decomposed into the original olefins, subsequent acetalization of the formyl group is effective to handle.

Keywords: Sulfonylation, Sulfone, Potassium *p*-toluenethiosulfonate

## Introduction

Organosulfur compounds find widespread applications in medicinal chemistry, materials science, and agrochemistry, [1, 2] because they have five oxidation states, and can exist as various functional groups. [1-3] One of the most characteristic features of organosulfur compounds is the facile construction of polysulfide structures via S–S bond formation. [2]

Given the increasing utilization of sulfide and polysulfide derivatives, it is imperative to control the number of sulfur atoms for obtaining organosulfur compounds with the desired structure. [2, 4-8] Effective control of sulfur elimination is the most challenging task in this regard. For example, some disulfides are converted into sulfides [4] by desulfurization via a thiosulfoxide intermediate (Figure 1A). [4e-4h] We also reported the trifluoroacetic acid (TFA)-mediated desulfurilative sulfonylthiolation of arenes, which proceeds via electrophilic aromatic substitution, followed by sulfur extrusion (Figure 1C). [7] Thus, it is of great importance to investigate the conditions under which desulfurization can occur. Recent studies have also revealed that desulfurization reactions are beneficial for the preparation of functional molecules, such as electronic materials [4j-4l] and the functionalized peptides (Figure 1B). [4m, 4n, 5] However, the desulfurization of thiosulfonates or thiosulfonic salts has not been reported yet. Herein, we report the TFA-mediated sulfonylation of

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activated olefins through an unexpected desulfurization, using potassium *p*-toluenethiosulfonate (Figure 1D).

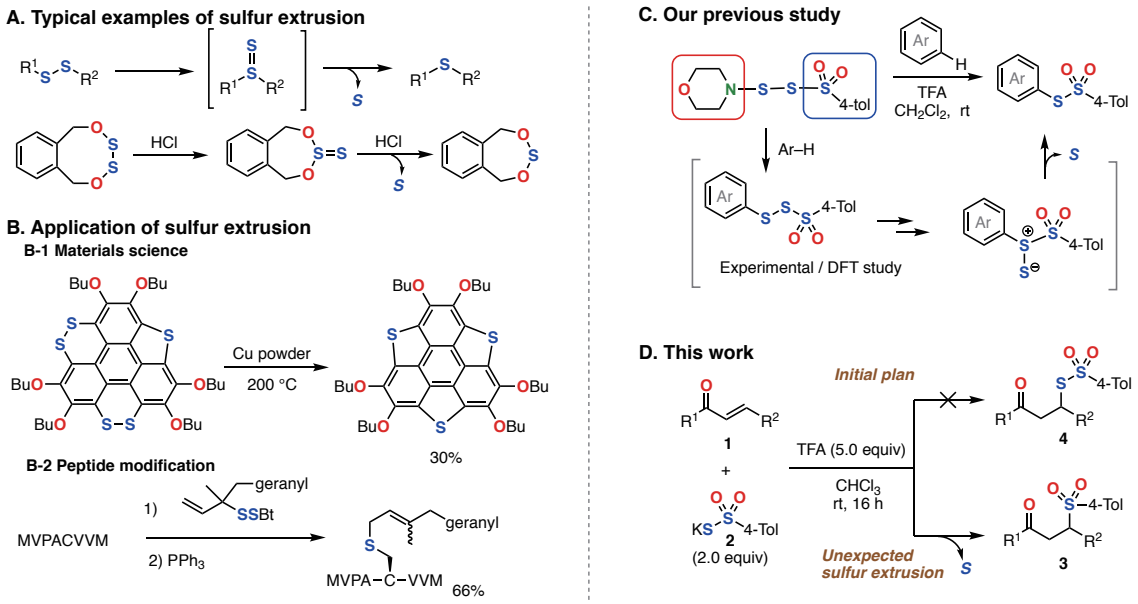
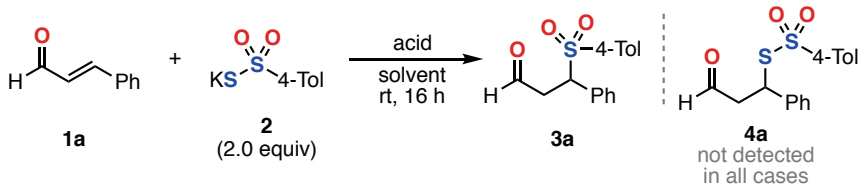



**Figure 1.** Background of this work.

## Results and Disucussion

Recently, thiosulfonates have attracted increasing attention because they are transformable into various organosulfur compounds without any unpleasant odor or catalyst poisoning. [9] Although potassium *p*-toluenethiosulfonate (**2**) is frequently used as a nucleophilic sulfonylthiolating reagent in $S_N2$ reactions, [9a] its application to other types of reaction is limited. With this background, we initially attempted to achieve a simple sulfonylthiolation of cinnamaldehyde (**1a**), which is an α,β-unsaturated aldehyde, using potassium *p*-toluenethiosulfonate (**2**) as a nucleophile via the Michael addition (Figure 1D). However, the reaction of **1a** with **2** in the presence of TFA (5.0 equiv) in $CH_2Cl_2$ afforded the sulfonylation product **3a** in 73% yield, instead of the sulfonylthiolation product **4a** (Table 1, entry 1). [10] Other acids such as AcOH, $HBF_4$, TfOH, and 10-camphorsulfonic acid (CSA) proved ineffective (entries 2 to 5). The optimal concentration of TFA for this reaction was 5.0 equiv (entries 1, 6, and 7). The reaction proceeded smoothly in other low-polarity solvents, such as $CHCl_3$, toluene, and chlorobenzene (entries 8 to 10), affording the highest yield of the product in $CHCl_3$ (entry 8). The sulfonylation gave moderate product yields in ether solvents (entries 11 to 13) and was unsuccessful in polar and alcoholic solvents (entries 14 to 16).

**Table 1.** Optimization of the reaction conditions




**1a** + **2** (2.0 equiv) → **3a** + **4a** (not detected in all cases)

| Entry | Acid (equiv) | Solvent | Yield of **3a**/%[a] |
|---|---|---|---|
| 1 | TFA (5.0) | $CH_2Cl_2$ | 73 |
| 2 | AcOH (5.0) | $CH_2Cl_2$ | 5 |
| 3 | $HBF_4$ (5.0) | $CH_2Cl_2$ | trace |
| 4 | TfOH (5.0) | $CH_2Cl_2$ | ND |
| 5 | CSA (5.0) | $CH_2Cl_2$ | 15 |
| 6 | TFA (3.0) | $CH_2Cl_2$ | 37 |
| 7 | TFA (10) | $CH_2Cl_2$ | 56 |
| 8 | TFA (5.0) | $CHCl_3$ | 89 (65)[b] |
| 9 | TFA (5.0) | toluene | 81 |
| 10 | TFA (5.0) | chlorobenzene | 81 |
| 11 | TFA (5.0) | THF | 73 |
| 12 | TFA (5.0) | $Et_2O$ | 44 |
| 13 | TFA (5.0) | 1,4-dioxane | 50 |
| 14 | TFA (5.0) | MeOH | 9 |
| 15 | TFA (5.0) | DMF | ND |
| 16 | TFA (5.0) | DMAc | ND |

[a]Yields based on $^1$H NMR analysis, unless otherwise noted. [b]Isolated yield.

A wide range of electron-deficient alkenes were successfully sulfonylated (Figure 2) under the optimized conditions (Table 1, entry 8). The reaction with α,β-unsaturated aldehyde proceeded smoothly to afford a sulfone **3b** in high yield. Sulfonylated aldehydes are unstable for the silica gel column chromatography or toward treatment with a base to afford the original olefin **1**. However, the use of *n*-hexane/$CHCl_3$ instead of *n*-hexane/EtOAc as the mobile phase improved the isolated yield. The reaction with α,β-unsaturated ketones also proceeded efficiently to afford the sulfonylated ketones **3c**–**3k** in high yields. For example, aliphatic enones such as *trans*-ethylideneacetone (**1c**) and cyclopentenone (**1d**) furnished the desired sulfones in high yields. Benzylideneacetone derivatives bearing methyl and chloro groups on the benzene ring also participated in the reaction to give the corresponding products **3e**–**3h** in good yields. The reaction of chalcone derivatives proceeded smoothly to afford **3i**–**3k** in high yields. The nitro-substituted sulfone **3l** was also synthesized in good yield by the sulfonylation of nitroolefin **1l**.

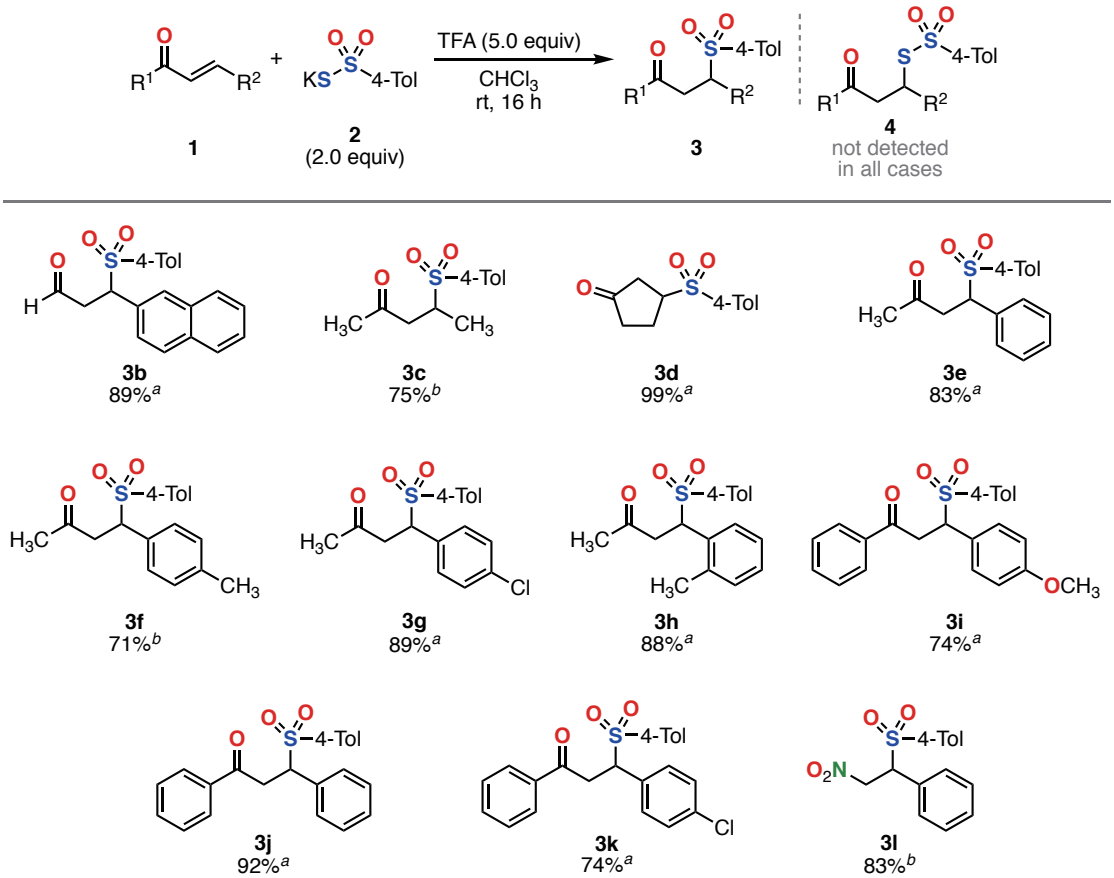
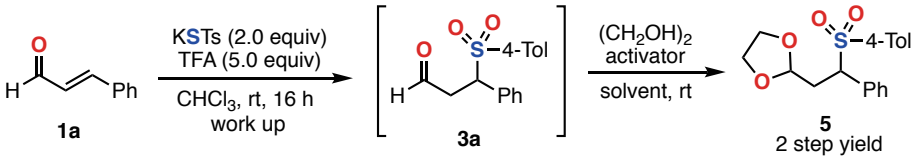



**Figure 2.** Scope of the reaction. [a]Isolated yield. [b]Yields based on $^1$H NMR analysis.

As described above, the sulfonylated products of α,β -unsaturated aldehydes are unstable, and easily desulfonylated to afford the original olefin when loaded on a chromatographic column or treated with a base. Hence, we sought an easy method to treat sulfonylated aldehydes. After extensive examination, we found that the sequential transformation of **3a** to the corresponding acetal **5** suited our purpose (Table 2). [11] Treatment of the crude reaction mixture containing **3a** with ethylene glycol in the presence of a catalytic amount of $Sc(OTf)_3$ efficiently afforded **5** as a stable solid that could be easily isolated by silica gel column chromatography (Table 2, entry 4). [11e]

To obtain insights into the reaction pathway, we conducted a control experiment (Figure 3). *S*-(3-Oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**), which is the initial intended product, was successfully prepared by the iodination and subsequent $S_N2$-type sulfonylthiolation of chalcone (**1j**) using **2** (Figure 3A). [9a, 12] The treatment of **4b** under standard conditions for 16 h did not produce the desulfurizated product **3j**, and the starting material was recovered in high yield (Figure 3B). Although the detailed mechanism is unclear, based on the control experiment and previous reports, [4e-4h, 7, 8, 10] we speculate that the reaction proceeds via the acid mediated desulfurization of **2** and a subsequent Michael addition-type reaction (Figure 3C).

**Table 2.** Optimization of the acetalization conditions




| Entry | Acetalization conditions | Yield/%[a] |
|---|---|---|
| 1 | $(CH_2OH)_2$ (10 equiv), TFA (5.0 equiv), $CHCl_3$, rt, 16 h | trace |
| 2 | $(CH_2OH)_2$ (neat), $TsOH·H_2O$ (10 mol %), $HC(OEt)_3$ (2.0 equiv), rt, 16 h | trace |
| 3 | $(CH_2OH)_2$ (neat), TMSCl (2.2 equiv), rt, 24 h | 58 |
| 4 | $(CH_2OH)_2$ (1.3 equiv), $Sc(OTf)_3$ (10 mol %), THF, rt, 48 h | 74[b] |

[a]Yields based on $^1$H NMR analysis, unless otherwise noted. [b]Isolated yield.

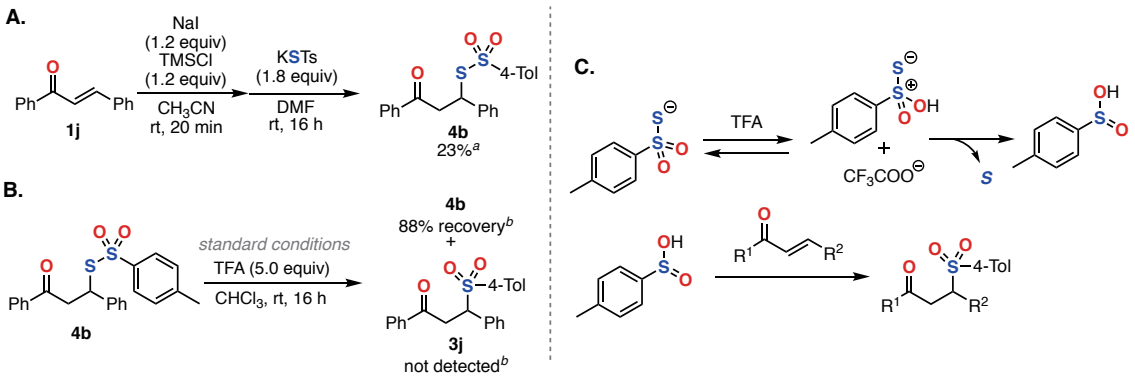



**Figure 3.** Control experiments (A) Thiosulfonate synthesis from α,β-unsaturated ketone. (B) Conversion of β-acylthiosulfonate in the presence of TFA. (C) Proposed mechanism. [a]Isolated yield. [b]Yield based on $^1$H NMR analysis.

## Summary

In summary, we developed a TFA-mediated desulfurilative sulfonylation of electron-deficient olefins using potassium *p*-toluenethiosulfonate. The reaction was applicable to a wide variety of activated olefins, including α,β-unsaturated aldehydes/ketones, and nitroolefins, affording the corresponding sulfones in good yields. A control experiment suggested that the reaction proceeds via the acid-mediated desulfurization of **2** followed by the sulfonylation of olefins via a Michael addition-type reaction.

## Experimental Section

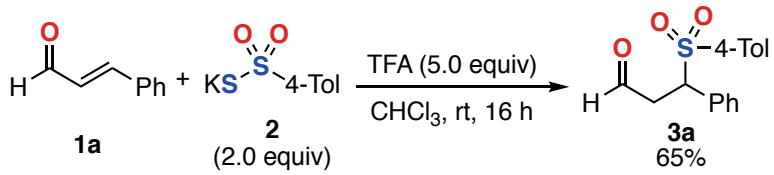
### General Remarks

All reactions were performed with dry glassware under atmosphere of nitrogen unless otherwise noted. The $^{1}$H NMR spectra were obtained with a Varian Mercury 400 NMR spectrometer at 400 MHz. $^{13}$C NMR spectra were obtained with a Varian Mercury 400 NMR spectrometer at 101 MHz or a JEOL ECZ-500R at 125 MHz. All NMR measurements were carried out at 25 ºC unless otherwise noted. Chemical shifts are reported in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for $^{1}$H NMR in $CDCl_3$) or the solvent peak (δ 77.16 for $^{13}$C NMR in $CDCl_3$). The abbreviations s, d, t, m, and br signify singlet, doublet, triplet, multiplet, and broad, respectively. ESI-MS was recorded on a JEOL JMS-T100LC AccuTOF under positive electrospray ionization ($ESI^+$) conditions. Column chromatography was performed with silica gel (Fuji Silysia, PSQ60B). Preparative thin layer chromatography was conducted using a 20×20 cm glass sheet coated with a 1mm thick layer of silica gel (Wako Pure Chemical Industries, Ltd., Wakogel® B-5F, Cat. No. 230-00043).

α,β-Unsaturated aldehyde **1b**, [13] α,β-unsaturated ketones **1f**, **1g**, **1h**, **1i**, **1k** [14] and nitroolefin **1m** [15] were prepared according to the reported methods. All other chemical reagents used were commercial grade and used as received.

### Experimental Procedures

*A typical procedure for TFA-mediated sulfonylation of α,β-unsaturated aldehyde (**1**) with potassium 4-toluenethiosulfonate (**2**)*

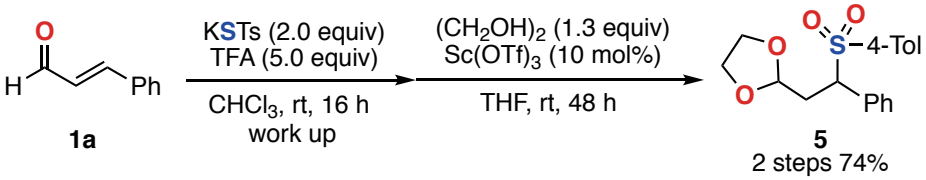



To a mixture of *trans*-cinnamaldehyde (**1a**) (37.8 μL, 0.300 mmol, 1.00 equiv) and potassium *p*-toluenethiosulfonate (**2**) (136 mg, 0.601 mmol, 2.00 equiv) suspended in $CHCl_3$ (4.5 mL) was added TFA (114 μL, 1.49 mmol, 4.96 equiv) at room temperature. After stirring for 16 h at the same temperature, to the mixture was added aqueous saturated solution of sodium bicarbonate (10 mL). The mixture was extracted with $CHCl_3$ (10 mL × 3), and the combined organic extract was washed with brine (10 mL), dried ($MgSO_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 15 g, *n*-hexane/$CHCl_3$ = 3/2) to give 3-phenyl-3-tosylpropanal (**3a**) (56.5 mg, 0.196 mmol, 65.3%) as a colorless solid.

According to the procedure for preparing 3-phenyl-3-tosylpropanal (**3a**), 3-(2-naphthyl)-3-tosylpropanal (**3b**) (90.3 mg, 88.9%), 4-tosylpentan-2-one (**3c**) (74.6%, $^{1}$H NMR yield based on 1,1,2,2-tetrachloroethane), 3-tosylcyclopentan-1-one (**3d**) (71.0 mg, 99.3%), 4-phenyl-4-tosylbutan-

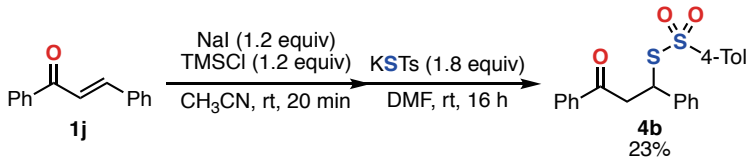
2-one (**3e**) (75.7 mg, 83.4%), 4-(4-tolyl)-4-tosylbutan-2-one (**3f**) (70.8%, $^1$H NMR yield based on 1,1,2,2-tetrachloroethane), 4-(4-chlorophenyl)-4-tosylbutan-2-one (**3g**) (89.6 mg, 88.6%), 4-(2-tolyl)-4-tosylbutan-2-one (**3h**) (83.9 mg, 88.3%), 3-(4-methoxyphenyl)-1-phenyl-3-tosylpropan-1-one (**3i**) (87.4 mg, 73.9%, isolated by recrystallization), 1,3-diphenyl-3-tosylpropan-1-one (**3j**) (104 mg, 92.1%, isolated by recrystallization), 3-(4-chlorophenyl)-1-phenyl-3-tosylpropan-1-one (**3k**) (89.0 mg, 74.3%, isolated by recrystallization), and 1-nitro-2-phenyl-3-tosylethane (**3l**) (83.1%, $^1$H NMR yield based on 1,1,2,2-tetrachloroethane) were prepared from the corresponding activated olefin **1** and potassium *p*-toluenethiosulfonate (**2**).

*Synthesis of 2-(2-phenyl-2-tosylethyl)-1,3-dioxolane (**5**) from trans-cinnamaldehyde (**1a**) via the sulfonylation and subsequent acetalization* [11e]



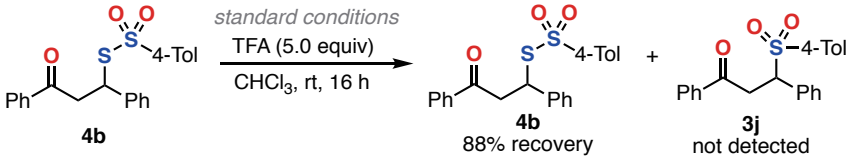

To a mixture of *trans*-cinnamaldehyde (**1a**) (37.8 μL, 0.300 mmol, 1.00 equiv) and potassium *p*-toluenethiosulfonate (136 mg, 0.601 mmol, 2.00 equiv) suspended in $CHCl_3$ (4.5 mL) was added TFA (114 μL, 1.49 mmol, 4.96 equiv) at room temperature. After stirring for 16 h at the same temperature, to the mixture was added aqueous saturated solution of sodium bicarbonate (10 mL). The mixture was extracted with $CHCl_3$ (10 mL × 3), and the combined organic extract was washed with brine (10 mL), dried ($MgSO_4$), and after filtration, the filtrate was concentrated under reduced pressure to afford the crude 3-phenyl-3-tosylpropanal (**3a**) as a yellow solid, and was used for next reaction without further purification. To a mixture of crude 3-phenyl-3-tosylpropanal (**3a**) and $Sc(OTf)_3$ (14.7 mg, 0.0299 mmol, 9.95 mol %) suspended in THF (1.00 mL) was added ethylene glycol (22.0 μL, 0.397 mmol, 1.32 equiv) at room temperature. After stirring for 48 h at the same temperature, to the mixture was added aqueous saturated solution of sodium bicarbonate (10 mL). The mixture was extracted with EtOAc (10 mL × 3), and the combined organic extract was washed with brine (10 mL × 3), dried ($MgSO_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 22 g, *n*-hexane/EtOAc = 3/1) to give 2-(2-phenyl-2-tosylethyl)-1,3-dioxolane (**5**) (73.8 mg, 0.222 mmol, 73.9%) as a colorless solid.

*Synthesis of S-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) from chalcone (**1j**) via iodination and subsequent sulfonylthiolation* [12]




To a mixture of sodium iodide (540 mg, 3.60 mmol, 1.20 equiv) and TMSCl (390 mg, 1.20 equiv) suspended in anhydrous $CH_3CN$ (4.0 mL) was added a solution of chalcone (**1j**) (624 mg, 3.00 mmol, 1.00 equiv) dissolved in anhydrous $CH_3CN$ (0.60 mL) at room temperature. After stirring for 20 min at the same temperature, to the mixture was added $Et_2O$ (10 mL), washed with aqueous solution of $Na_2SO_3$ and brine (10 mL), and dried ($MgSO_4$). After filtration, the filtrate was concentrated under reduced pressure to give crude 3-iodo-1,3-diphenylpropan-1-one as a brown solid, and were used for next reaction without further purification. A mixture of crude 3-iodo-1,3-diphenylpropan-1-one and potassium *p*-toluenethiosulfonate (1.20 g, 5.30 mmol, 1.77 equiv) was suspended in DMF (10 mL) at room temperature. After stirring for 16 h at the same temperature, to the mixture was added $H_2O$ (10 mL). The mixture was extracted with EtOAc (10 mL × 3), washed with brine (10 mL × 3), dried ($MgSO_4$), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from $CH_2Cl_2$/*n*-heaxane to give *S*-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) (277 mg, 0.699 mmol, 23.3%) as a colorless solid.

*Conversion of S-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) in the presence of TFA*

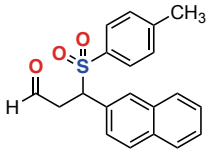



To a mixture of *S*-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) (59.4 mg, 0.150 mmol, 1.00 equiv) dissolved in $CHCl_3$ (4.5 mL) was added TFA (57 μL, 0.75 mmol, 4.97 equiv) at room temperature. After stirring for 16 h at the same temperature, to the mixture was added aqueous saturated solution of sodium bicarbonate (10 mL). The mixture was extracted with $CHCl_3$ (10 mL × 3), washed with brine (10 mL × 3), dried ($MgSO_4$), and after filtration, the filtrate was concentrated under reduced pressure. Recovery of *S*-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) and formation of 1,3-diphenyl-3-tosylpropan-1-one (**3j**) were confirmed by $^1H$ NMR analysis based on 1,1,2,2-tetrachloroethane.

## Characterization Data of New Compounds

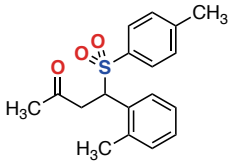
3-Phenyl-3-tosylpropanal (**3a**), [16] 4-tosylpentan-2-one (**3c**), [17] 3-tosylcyclopentan-1-one (**3d**), [17] 4-phenyl-4-tosylbutan-2-one (**3e**), [18] 4-(4-tolyl)-4-tosylbutan-2-one (**3f**), [18] 4-(4-chlorophenyl)-4-tosylbutan-2-one (**3g**), [18] 3-(4-methoxyphenyl)-1-phenyl-3-tosylpropan-1-one (**3i**), [19] 1,3-diphenyl-3-tosylpropan-1-one (**3j**), [17] 3-(4-chlorophenyl)-1-phenyl-3-tosylpropan-1-one (**3k**), [19] and 1-nitro-2-phenyl-3-tosylethane (**3l**) [19] were identical in spectra data with those reported in the literature.

*3-(2-Naphthyl)-3-tosylpropanal (**3b**)*



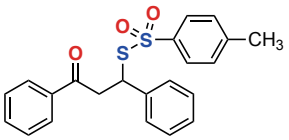

Yellow solid; mp 90–93 ºC; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 9.73 (s, 1H), 7.76–7.84 (m, 1H), 7.70–7.76 (m, 2H), 7.58 (s, 1H), 7.45–7.54 (m, 2H), 7.34–7.44 (AA′BB′, 2H), 7.24 (dd, 1H, $J$ = 8.6, 1.8 Hz), 7.10–7.18 (AA′BB′, 2H), 4.88 (dd, 1H, $J$ = 9.2, 4.7 Hz), 3.67 (dd, 1H, $J$ = 18.2, 4.7 Hz), 3.41 (dd, 1H, $J$ = 18.2, 9.2 Hz), 2.35 (s, 3H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 101 MHz) δ 197.0 (1C), 145.2 (1C), 133.5 (1C), 133.3 (1C), 133.0 (1C), 129.60 (2C), 129.57 (1C), 129.5 (1C), 129.2 (2C), 128.5 (1C), 128.2 (1C), 127.7 (1C), 126.9 (1C), 126.7 (1C), 126.6 (1C), 65.2 (1C), 42.4 (1C), 21.7 (1C); HRMS (ESI$^+$) *m*/*z*: ([M+K]$^+$, calcd for $C_{20}H_{18}KO_3S^+$, 377.0608; found, 377.0608).

*4-(2-Tolyl)-4-tosylbutan-2-one (**3h**)*



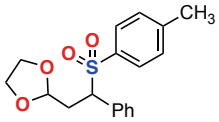

Colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, 1H, $J$ = 7.6 Hz), 7.35–7.40 (AA′BB′, 2H), 7.14–7.21 (m, 4H), 6.97 (d, 1H, $J$ = 7.4 Hz), 5.01 (dd, 1H, $J$ = 9.6, 3.7 Hz), 3.60 (dd, 1H, $J$ = 18.0, 3.7 Hz), 3.33 (dd, 1H, $J$ = 18.0, 9.6 Hz), 2.38 (s, 3H), 2.12 (s, 3H), 1.94 (s, 3H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) δ 203.6 (1C), 144.9 (1C), 138.8 (1C), 134.4 (1C), 131.1 (1C), 130.4 (1C), 129.4 (2C), 129.1 (2C), 128.7 (1C), 128.0 (1C), 126.3 (1C), 61.0 (1C), 42.6 (1C), 30.5 (1C), 21.7 (1C), 19.3 (1C); HRMS (ESI$^+$) *m*/*z*: ([M+Na]$^+$, calcd for $C_{18}H_{20}NaO_3S^+$, 339.1025; found, 339.1025).

*S-(3-Oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**)*



Colorless solid; mp 99–102 ºC; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.86–7.89 (AA′BB′C, 2H), 7.65–7.70 (AA′BB′, 2H), 7.54–7.59 (AA′BB′C, 1H), 7.42–7.47 (AA′BB′C, 2H), 7.20–7.24 (AA′BB′, 2H), 7.14–7.20 (m, 5H), 5.06 (dd, 1H, $J$ = 8.5, 5.4 Hz), 3.85 (d, 1H, $J$ = 5.4 Hz), 3.84 (d, 1H, $J$ = 8.5 Hz), 2.41 (s, 3H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 125 MHz) δ 196.0 (1C), 144.8 (1C), 141.9 (1C), 138.4 (1C), 136.2 (1C), 133.7 (1C), 129.8 (2C), 128.9 (2C), 128.8 (2C), 128.2 (2C), 128.1 (1C), 127.9 (2C), 127.2 (2C), 50.3 (1C), 45.2 (1C), 21.8 (1C); HRMS (ESI$^+$) *m*/*z*: ([M+K]$^+$, calcd for $C_{22}H_{20}KO_3S_2^+$, 435.0485; found, 435.0.486).

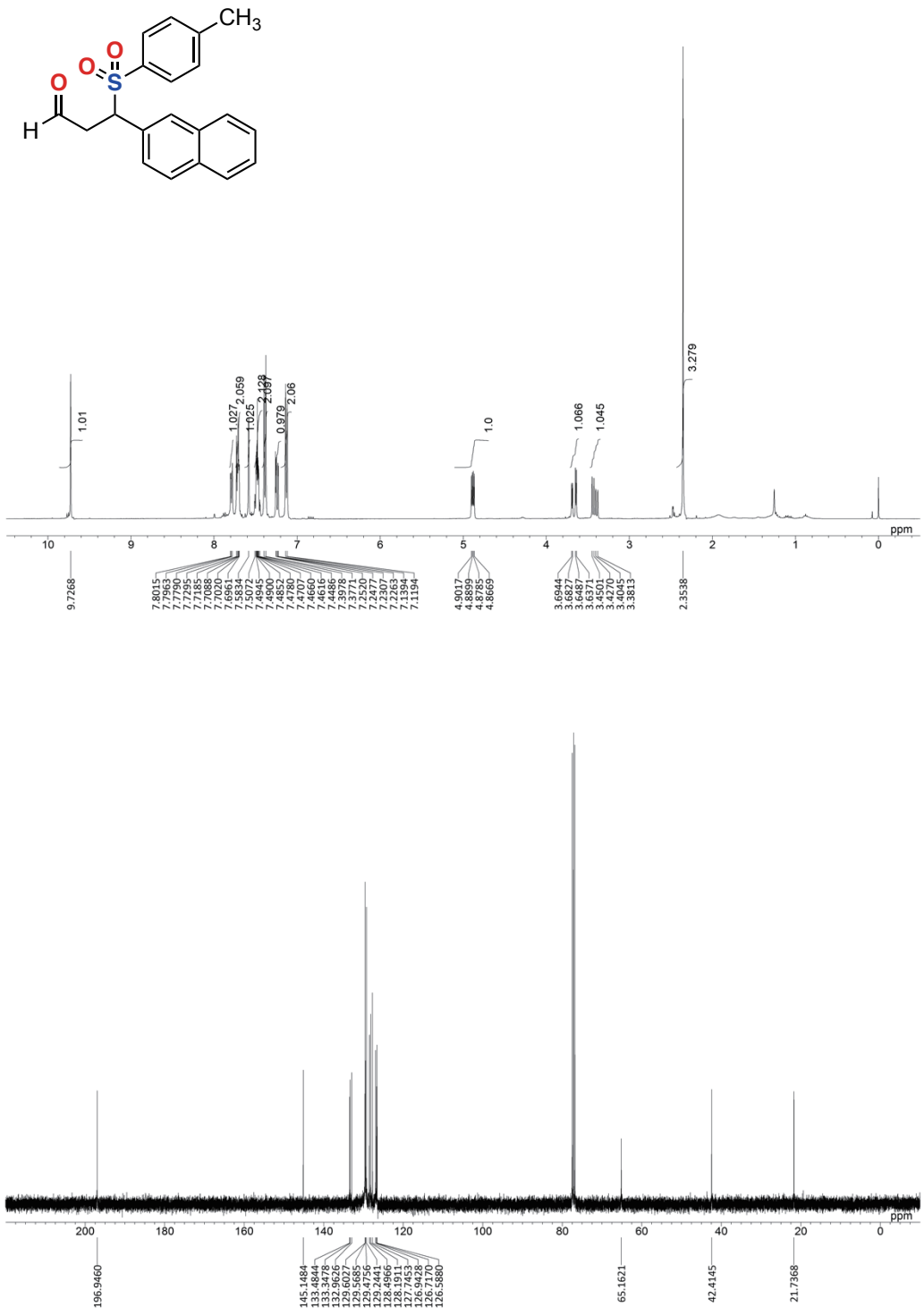
*2-(2-Phenyl-2-tosylethyl)-1,3-dioxolane (**5**)*



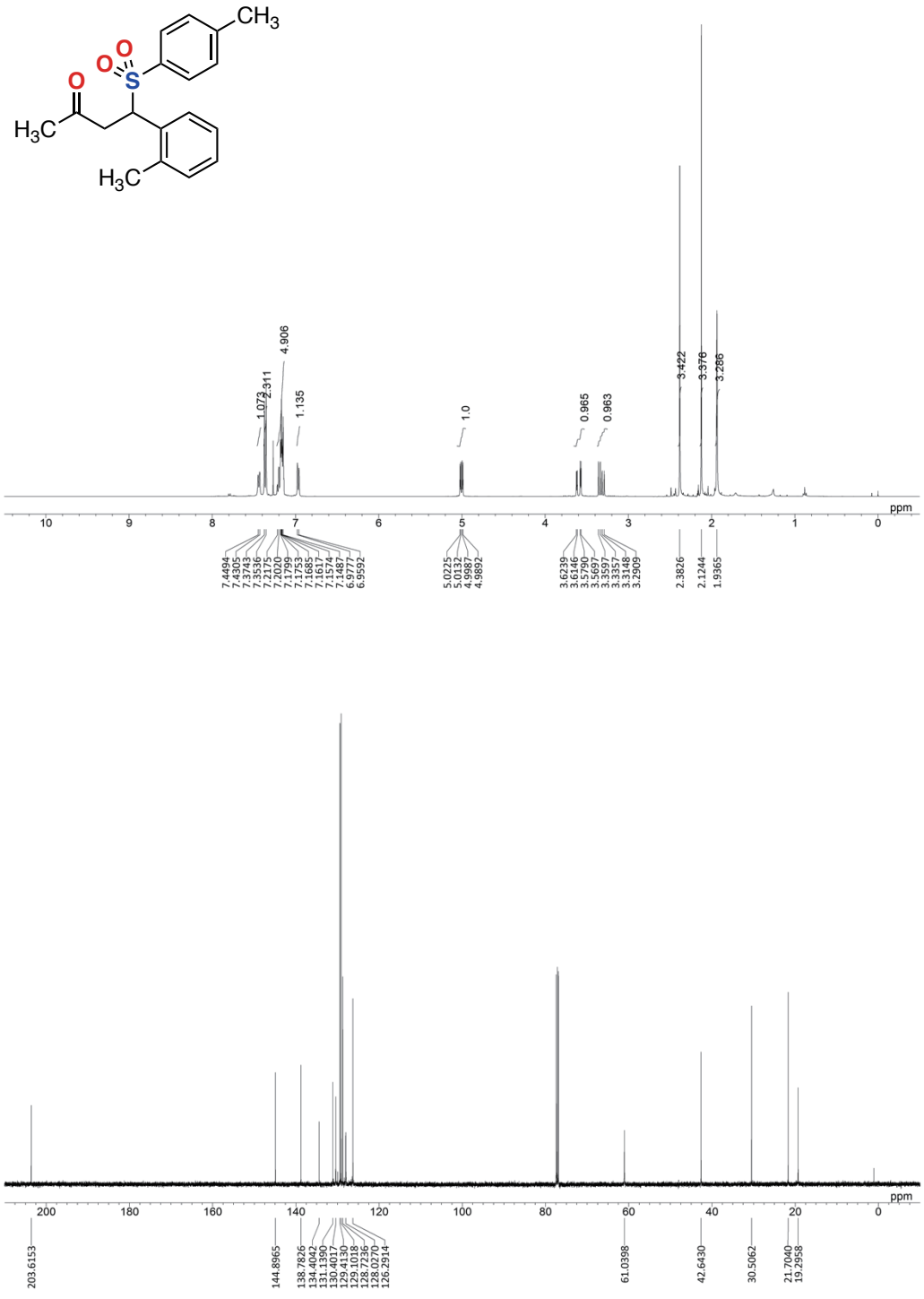
Brown solid; mp 162–165 ºC; $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.45 (AA′BB′, 2H), 7.22–7.33 (m, 3H), 7.10–7.21 (m, 4H), 4.73 (dd, 1H, $J$ = 7.0, 3.3 Hz), 4.30 (dd, 1H, $J$ = 11.0, 4.2 Hz), 3.70–3.96 (m, 4H), 2.46–2.66 (m, 2H), 2.38 (s, 3H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 101 MHz) δ 144.7 (1C), 134.1 (1C), 132.2 (1C), 130.0 (2C), 129.4 (2C), 129.3 (2C), 128.9 (1C), 128.6 (2C), 101.9 (1C), 67.6 (1C), 65.2 (1C), 64.9 (1C), 32.7 (1C), 21.8 (1C); HRMS (ESI$^+$) *m*/*z*: ([M+K]$^+$, calcd for $C_{18}H_{20}KO_4S^+$, 371.0714; found, 371.0719).

## $^{1}H$ and $^{13}C$ NMR Spectra of Compounds

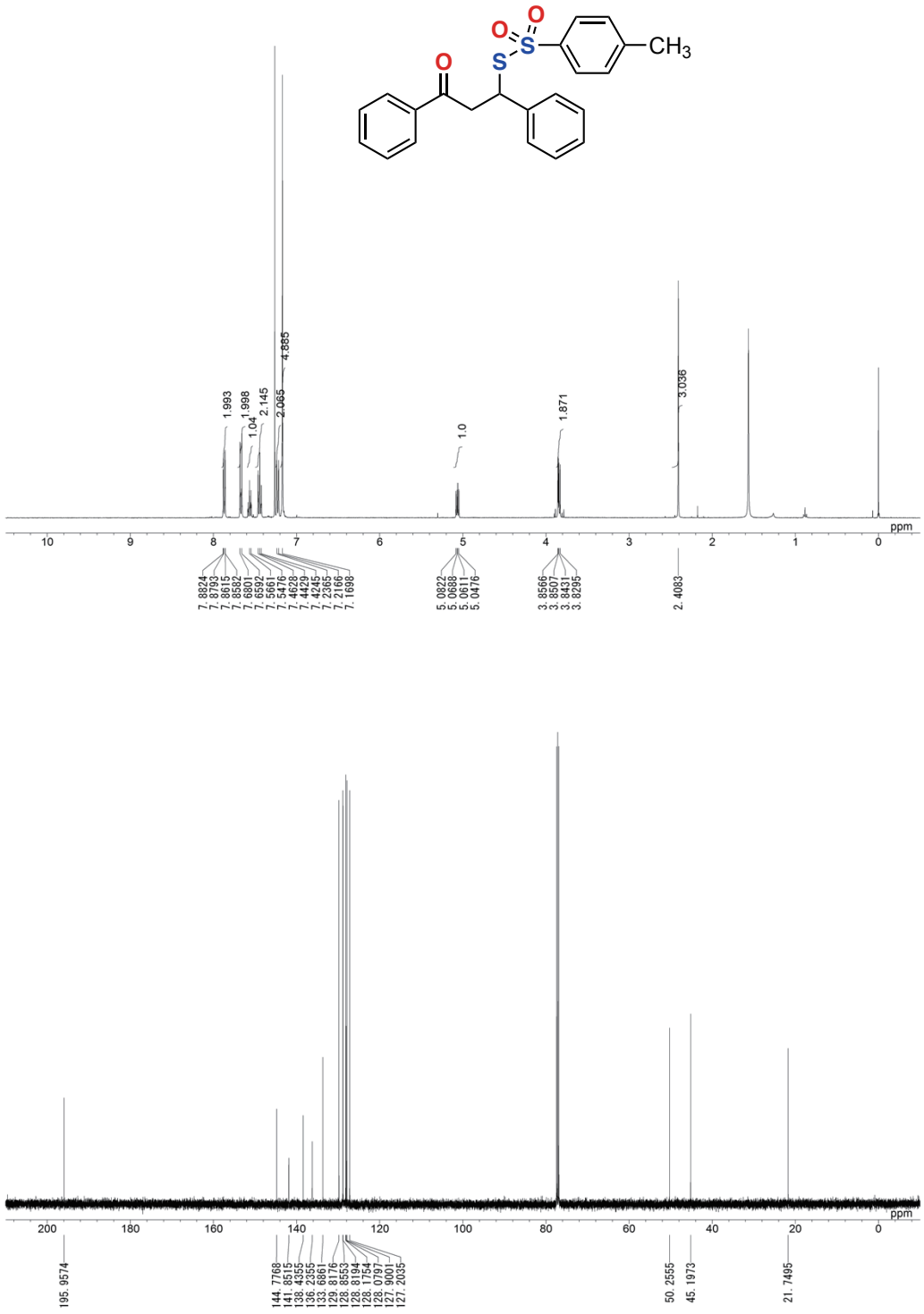
$^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (101 MHz) spectra of 3-(2-naphthyl)-3-tosylpropanal (**3b**) ($CDCl_3$)



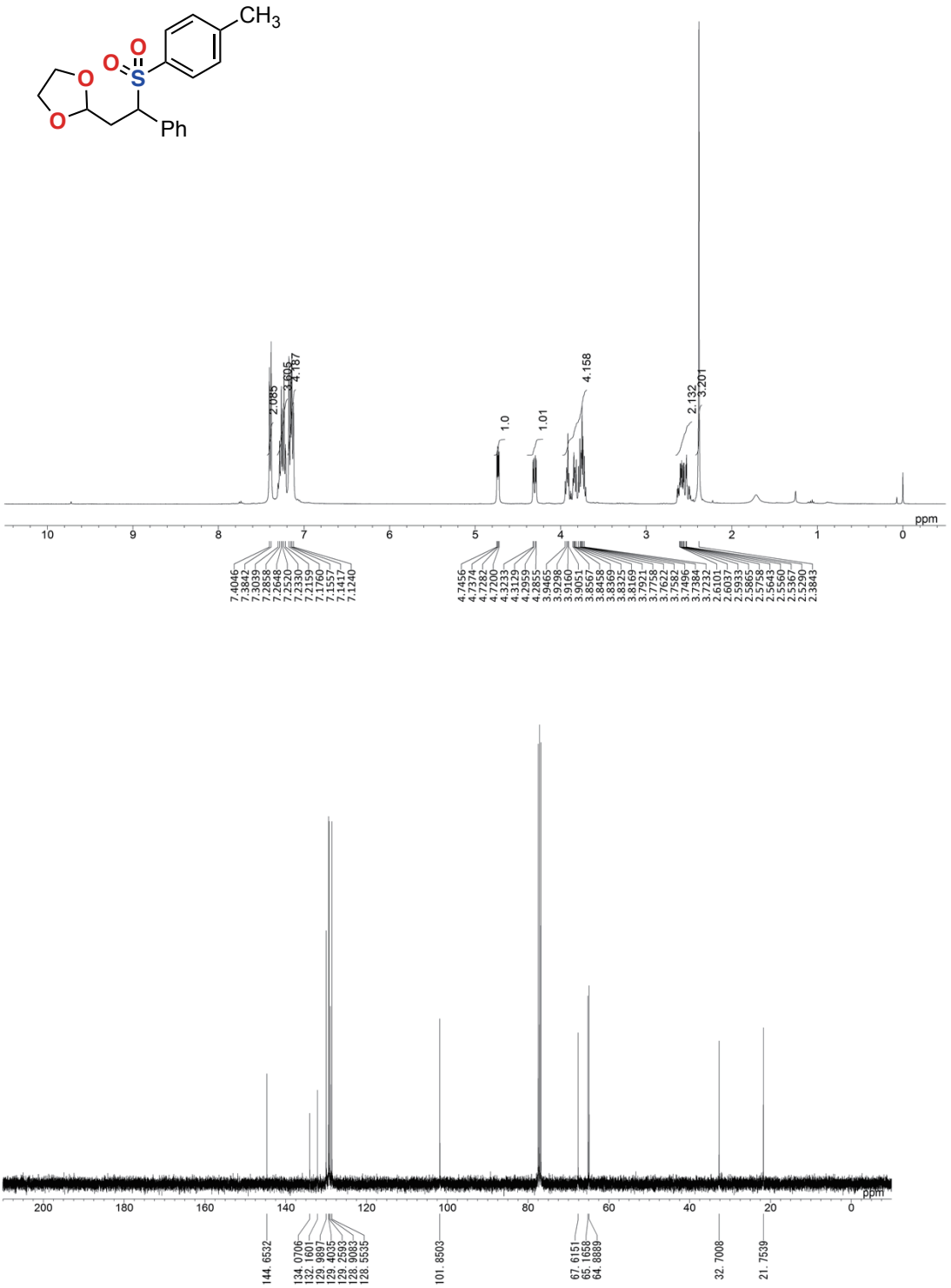
$^{1}$H NMR (400 MHz) and $^{13}$C NMR (125 MHz) spectra of 4-(2-tolyl)-4-tosylbutan-2-one (**3h**) ($CDCl_3$)



$^{1}$H NMR (400 MHz) and $^{13}$C NMR (125 MHz) spectra of *S*-(3-oxo-1,3-diphenylpropyl) 4-toluenethiosulfonate (**4b**) ($CDCl_3$)



$^{1}$H NMR (400 MHz) and $^{13}$C NMR (101 MHz) spectra of 2-(2-phenyl-2-tosylethyl)-1,3-dioxolane (**5**) ($CDCl_3$)



## Acknowledgement

This work was supported by Kato Memorial Bioscience Foundation (K.K.), Tokyo Biochemical Research Foundation (K.K.), Takahashi Industrial and Economic Research Foundation (K.K.), Meiji Seika Award in Synthetic Organic Chemistry, Japan (K.K.), JSPS KAKENHI Grant Number JP19K23637 (Research Activity Start-up; K.K.), JP20K15288 (Young Scientists; K.K.), JP21K05415 (Scientific Research (C); S.F.), and the Institute of Science and Engineering, Chuo University.

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