

## Supplementary Material

### **Cobalt(II) catalytic oxidation of arylmethyl sulfonyl imines to arylcarbonyl analogues**

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## General information

All experiments were conducted with a sealed pressure vessel.  $^1\text{H}$ -NMR spectra were obtained at 500 MHz in  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm). Coupling constants are given in hertz.  $^{13}\text{C}$ -NMR spectra were recorded at 126 MHz in  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm). Chemical shifts are given in  $\delta$  (ppm) and are measured relative to tetramethylsilane (TMS) as internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. HRMS was recorded by using Q-TOF mass spectrometer. Flash column chromatography was performed over silica gel (200–300 mesh).

## Synthesis of substrates

### General procedure for the synthesis of 3-arylmethylbenzo[d]isothiazole 1,1-dioxide **1**

The Grignard reagent was typically prepared according known literature<sup>[1]</sup>. To a 50-mL three-neck flask, metallic magnesium in the form of chips (20.7 mmol, 1.1 equiv),  $\text{I}_2$  (1.0 mg) were added and exchanged with  $\text{N}_2$  for three times, then 7.0 mL of dry ether was injected by a syringe and the reaction mixture was warmed to  $40^\circ\text{C}$  followed by add 0.75 mmol of halide derivative to initiate the reaction (the color of iodine disappears). Then the remaining 18.0 mmol of halide derivative was diluted with 7.0 mL of ether and dropped into the cooled reaction solution with ice water bath. After completion of the addition, the grey–black mixture was warmed to room temperature and stirred for further 2 h.

To a flame-dried flask were added saccharin (0.92 g, 5.0 mmol) and anhydrous diethyl ether (10 mL) and the solution was then cooled to  $-30^\circ\text{C}$ . Fresh benzylmagnesium chloride (15 mmol, in 15 mL  $\text{Et}_2\text{O}$ ) was added dropwise to the above solution over 20 min. The reaction mixture was stirred at  $-30^\circ\text{C}$  for 24 h, then quenched with a solution of saturated aqueous  $\text{NH}_4\text{Cl}$  and diluted with water (30 mL). The mixture was extracted with  $\text{EtOAc}$  ( $3 \times 50$  mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The corresponding residue was purified by column chromatography on silica gel (petroleum ether/ $\text{EtOAc} = 4/1$ ) to give benzyl cyclic *N*-sulfonylimines **1**.<sup>[2]</sup>

## Synthesis of products

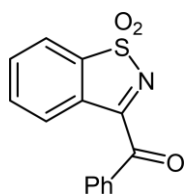
### General procedure for the synthesis of (1,1-dioxidobenzo[d]isothiazol-3-yl)(aryl)methanone **2**

A 10-mL sealed tube was charged with  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1.0 mg, 0.004 mmol), *N*-hydroxyphthalimide (13.2 mg, 0.08 mmol), substrate **1** (0.4 mmol) and exchanged with  $\text{O}_2$  for three times and  $\text{BuOAc}:\text{Pyridine}$  (1 mL, 7:3 v/v) was injected by a syringe. The mixture was stirred at  $90^\circ\text{C}$  for 10 h under  $\text{O}_2$  atmosphere (1 atm). Once completed, the reaction mixture was cooled, evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ $\text{EtOAc}$

or petroleum ether/dichloromethane) followed by crystallization with EtOAc to give target product **2**.

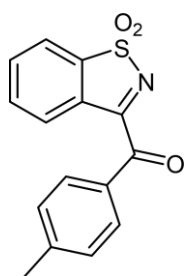
### Characterization data of the products:

#### (1,1-Dioxidobenzo[d]isothiazol-3-yl)(phenyl)methanone (**2a**, CAS:2095061-21-3)<sup>[3]</sup>



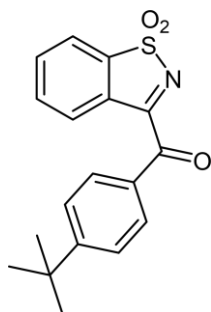
Light yellow crystal (89%, 97 mg); Silica gel column chromatography (petroleum ether/ethyl acetate = 9:1);  $T_{mp}$  99–101°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.22 (d,  $J$  = 7.6 Hz, 2H), 8.00 (d,  $J$  = 7.5 Hz, 1H), 7.92 (d,  $J$  = 7.6 Hz, 1H), 7.81 (t,  $J$  = 7.5 Hz, 1H), 7.72–7.77 (m, 2H), 7.55–7.58 (m, 2H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  187.4, 164.2, 139.7, 135.7, 134.3, 134.2, 133.5, 130.6, 129.1, 129.0, 127.0, 123.0.

#### (1,1-Dioxidobenzo[d]isothiazol-3-yl)(*p*-tolyl)methanone (**2b**)



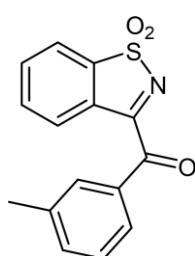
Light yellow crystal (87%, 99 mg); Silica gel column chromatography (petroleum ether/ethyl acetate = 9:1);  $T_{mp}$  139–141°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  8.11 (d,  $J$  = 8.3 Hz, 2H), 7.98 (d,  $J$  = 7.5 Hz, 1H), 7.88 (d,  $J$  = 7.6 Hz, 1H), 7.79 (t,  $J$  = 7.5 Hz, 1H), 7.72–7.75 (m, 2H), 7.35 (d,  $J$  = 8.1 Hz, 2H), 2.46 (s, 1H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ ):  $\delta$  186.9, 164.4, 147.3, 139.7, 134.2, 134.1, 131.1, 130.7, 129.8, 129.1, 127.0, 122.8, 22.0.

#### (4-(*tert*-Butyl)phenyl)(1,1-dioxidobenzo[d]isothiazol-3-yl)methanone (**2c**)



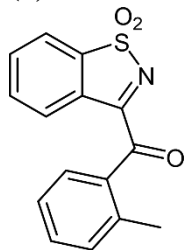
Light yellow crystal (83%, 109 mg); Silica gel column chromatography (petroleum ether/ethyl acetate = 15:1);  $T_{mp}$  120–121°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  8.15 (d,  $J$  = 8.6 Hz, 2H), 7.98 (d,  $J$  = 7.5 Hz, 1H), 7.89 (d,  $J$  = 7.6 Hz, 1H), 7.97 (t,  $J$  = 7.4 Hz, 1H), 7.73 (t,  $J$  = 7.5 Hz, 1H), 7.58 (d,  $J$  = 8.6 Hz, 2H), 1.36 (s, 9H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ ):  $\delta$  186.9, 164.5, 160.0, 139.7, 134.2, 134.1, 131.0, 130.6, 129.1, 126.9, 126.1, 122.9, 35.5, 30.9.

#### (1,1-Dioxidobenzo[d]isothiazol-3-yl)(*m*-tolyl)methanone (**2d**)



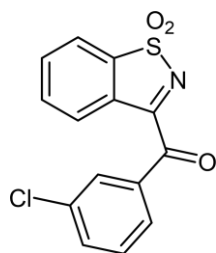
Yellow crystal (85%, 97 mg); Silica gel column chromatography (petroleum ether/ethyl acetate = 7:1);  $T_{mp}$  123–124°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.97–8.01 (m, 3H), 7.88 (d,  $J$  = 7.6 Hz, 1H), 7.79–7.82 (m, 1H), 7.72–7.75 (m, 1H), 7.54 (d,  $J$  = 7.6 Hz, 1H), 7.42–7.45 (m, 1H), 2.44 (s, 1H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  187.6, 164.4, 139.7, 139.1, 136.5, 134.2, 134.1, 133.5, 130.6, 129.1, 128.9, 128.0, 126.9, 122.9, 21.3.

**(1,1-Dioxidobenzo[d]isothiazol-3-yl)(*o*-tolyl)methanone (2e)**



Yellow crystal (84%, 96 mg); Silica gel column chromatography (petroleum ether/dichloromethane = 1:2);  $T_{mp}$  170–171°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.99 (d,  $J = 7.5$  Hz, 1H), 7.91 (d,  $J = 7.6$  Hz, 1H), 7.87–7.78 (m, 2H), 7.75 (t,  $J = 8.0$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.40–7.32 (m, 2H), 2.65 (s, 3H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  190.0, 165.3, 141.2, 140.11, 134.3, 134.2, 134.1, 132.9, 132.7, 132.4, 129.1, 126.9, 126.1, 123.0, 21.7.

**(1,1-Dioxidobenzo[d]isothiazol-3-yl)(3-chlorophenyl)methanone (2f)**



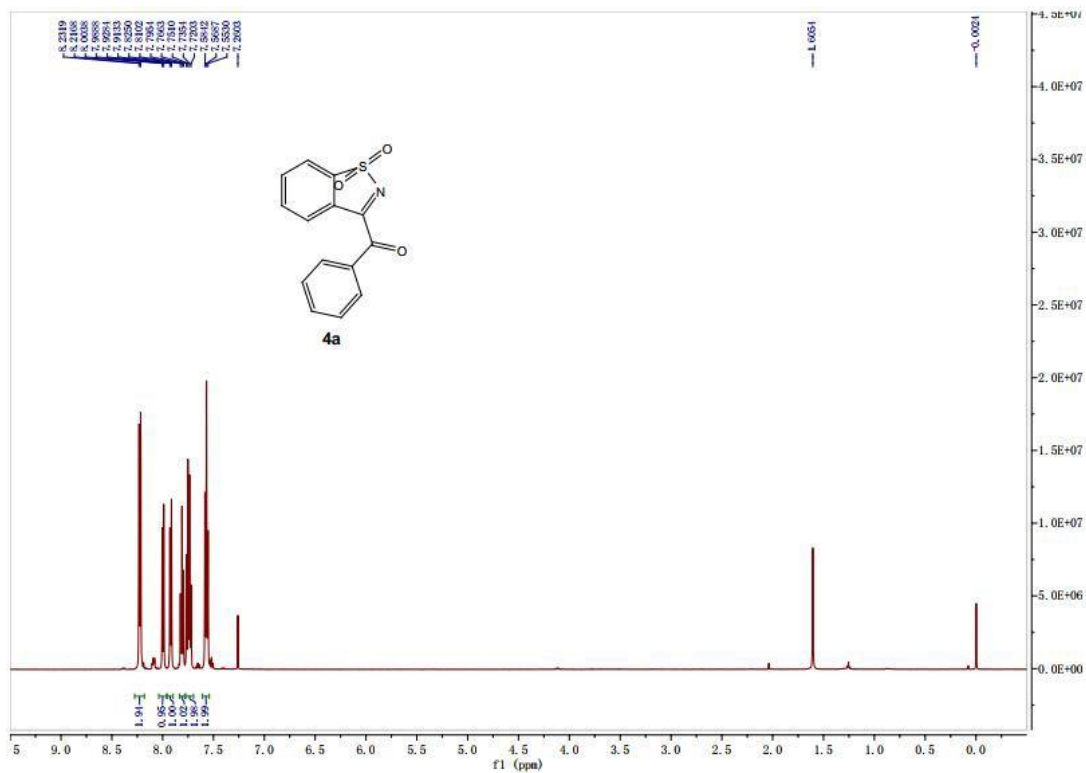
Yellow crystal (76%, 93 mg); Silica gel column chromatography (petroleum ether/ethyl acetate = 7:1);  $T_{mp}$  140–142°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.19–8.20 (m, 1H), 8.13 (d,  $J = 7.9$  Hz, 1H), 7.95–7.99 (m, 2H), 7.82 (t,  $J = 7.4$  Hz, 1H), 7.76 (t,  $J = 7.6$  Hz, 1H), 7.68 (d,  $J = 8.0$  Hz, 1H), 7.50 (t,  $J = 7.9$  Hz, 1H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  x

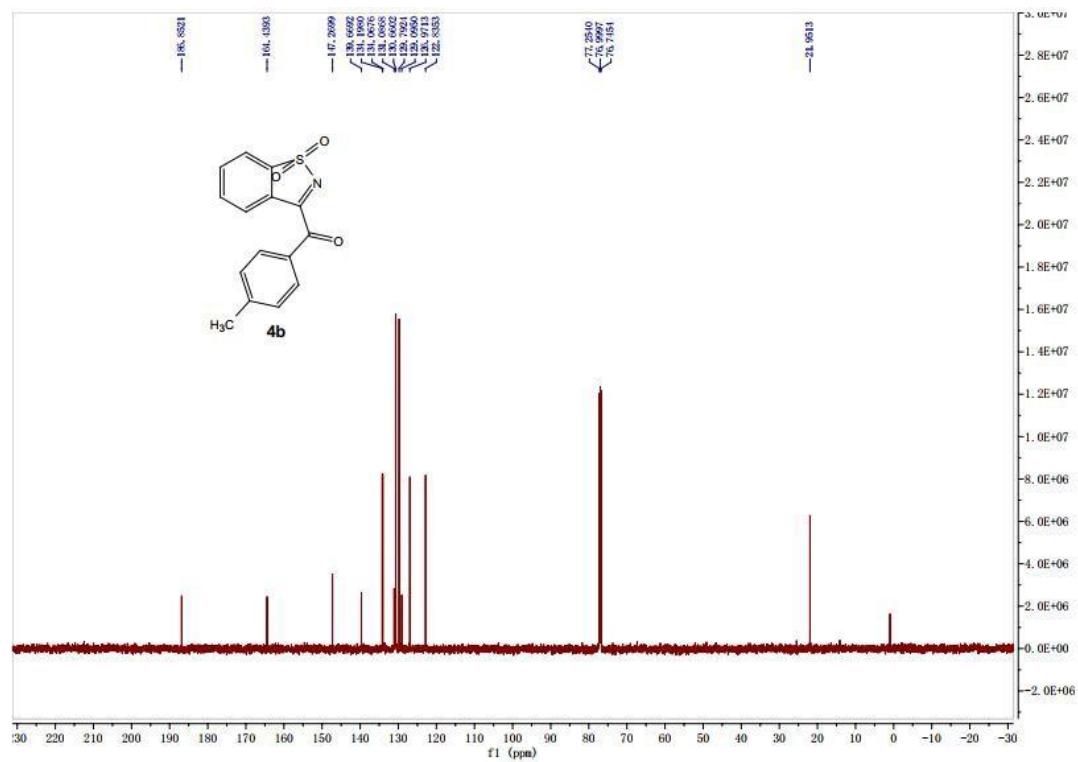
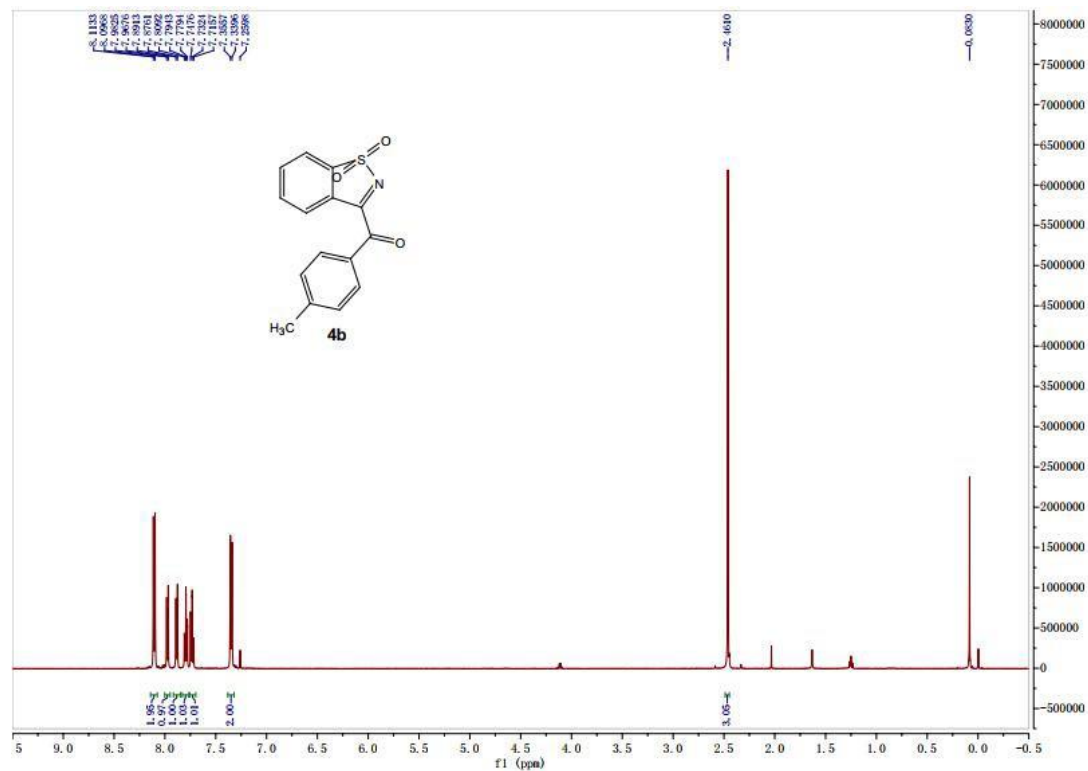
**References**

- [1] Wang, M.-S., Gong, Y., Yu, Z.-C., Tian, Y.-G., Zhuo, L.-S., Huang, W., She, N.-F., *Molecules*, 2020, vol. 25, p. 5667. <http://doi.org/10.3390/molecules25235667>
- [2] An, Q., Liu, D., Shen, J., Liu, Y., Zhang, W., *Org. Lett.*, 2017, vol. 19, p. 238-241. <http://doi.org/10.1021/acs.orglett.6b03529>
- [3] Jeran, M., Cotman, A.E., Stephan, M., Mohar, B., *Org. Lett.*, 2017, vol. 19, p. 2042-2045. <http://doi.org/10.1021/acs.orglett.7b00670>

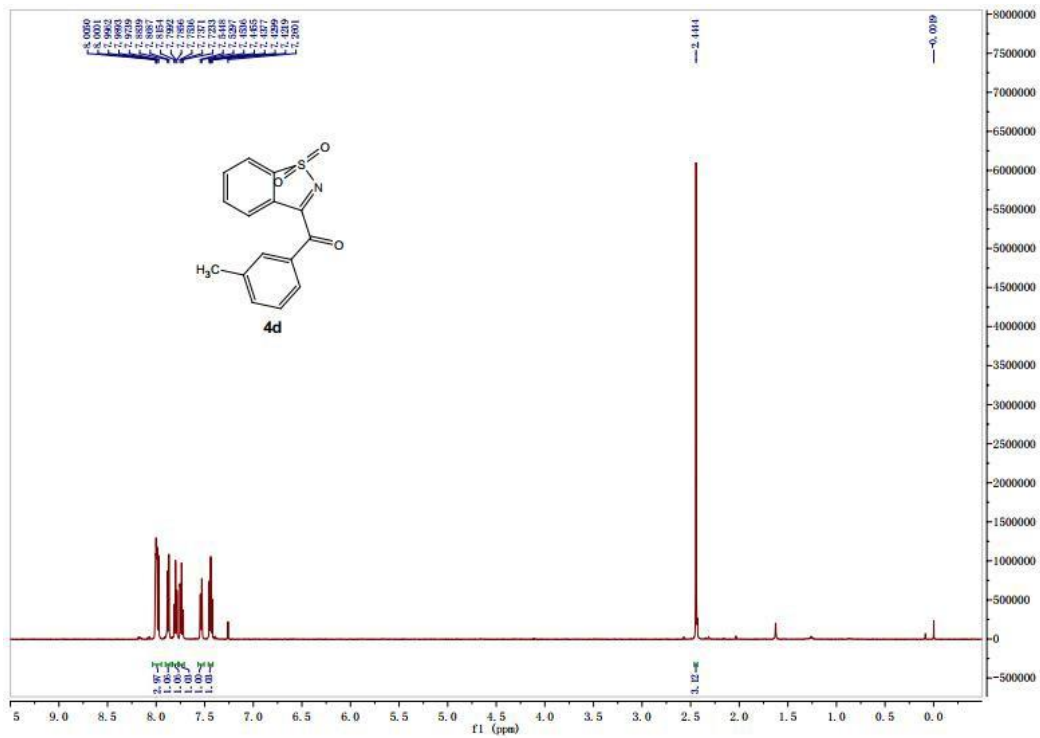
# Copies of $^1\text{H}$ , $^{13}\text{C}$ -NMR spectra of the products

## (1,1-Dioxidobenzo[d]isothiazol-3-yl)(aryl)methanone



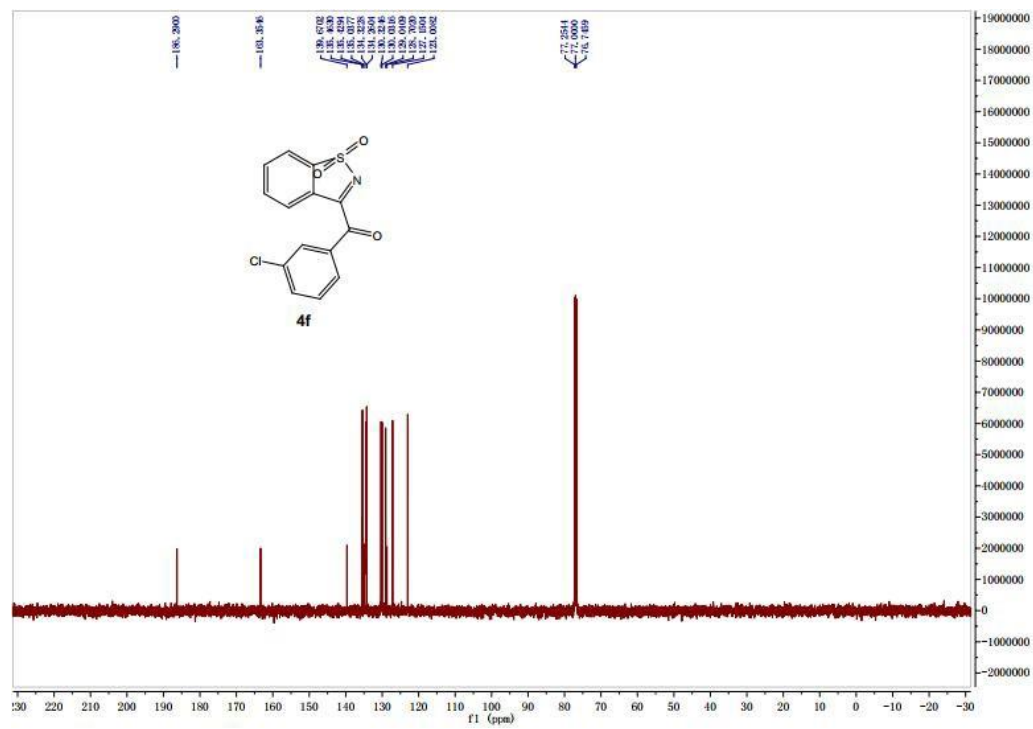
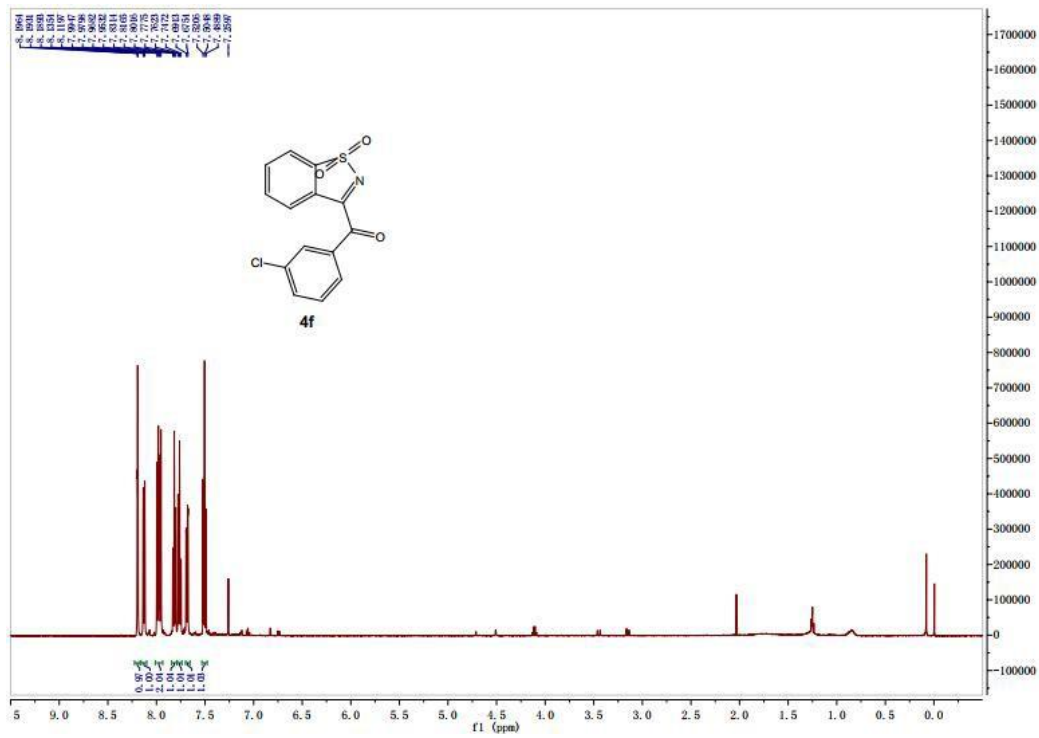


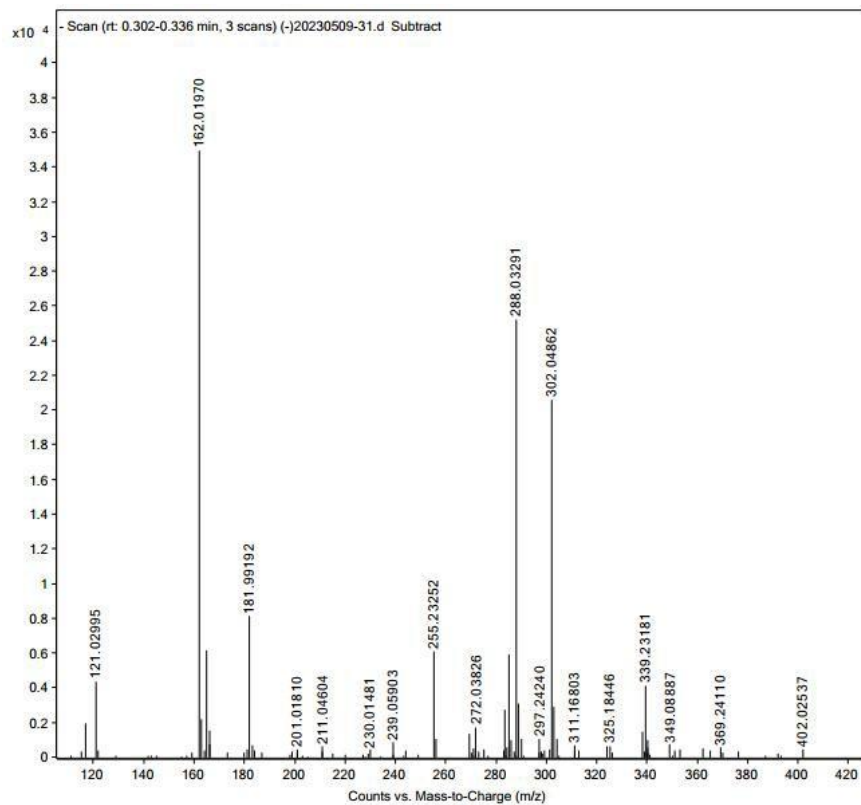












Intermediate A: MS (ESI, m/z)  $C_{14}H_{10}NO_4S$ :  $[M-H]^- = 288.03291$ .