Supporting Information

Palladium-Catalyzed [4+2] Cycloaddition of 2-Methylidenetrimethylene Carbonate or Methylene cyclic carbamate with Sulfamate-Derived Cyclic Imines

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General Information

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400, 600 or 800 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Melting points were determined by an X-4 digital micro melting point apparatus. Accurate mass measurements were performed using a SCIEX X500r instrument with the ESI-MS technique.

Starting materials and reagents were purchased directly from commercial suppliers and used without further purifications. All solvents used as reaction medium were distilled before the use. The 2-methylidenetrimethylene carbonate **1a**[1], *N*-tosyl carbamate **4a**[2] and Sulfamate-derived Cyclic Imines **2**[3] were synthesized using known literature procedures.

General Procedure for Preparation of [4+2] Products

Under argon atmosphere, to a mixture of 2-methylidenetrimethylene carbonate **1a** or *N*-tosyl carbamate **4a** (0.15 mmol), Sulfamate-derived cyclic imines **2** (0.10 mmol) and catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol%, 0.0025 mmol) / Xantphos (7.5 mol %, 0.0075 mmol)

[1] R. Shintani, K. Moriya, T. Hayashi, *Chem. Commun.* **2011**, *47*, 3057.

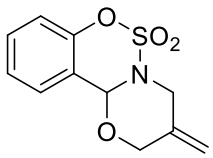
[2] Allen, B. D. W.; Connolly, M. J.; Harrity, J. P. A. *Chem. Eur. J.* **2016**, *22*, 13000.

[3] Wang, H.; Jiang, T.; Xu, M.-H. *J. Am. Chem. Soc.* **2013**, *135*, 971.

in a Schlenk tube, 1 mL of toluene were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc / PE) to afford the corresponding cycloaddition product **3** or **5**.

Characterization Data of the Products 3, 5

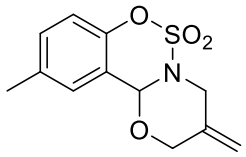
3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3aa)



3aa

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.17 (m, 3H), 7.01 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.04 (s, 1H), 5.08 (d, *J* = 19.0 Hz, 2H), 4.36 – 4.20 (m, 2H), 3.97 (t, *J* = 2.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 134.4, 131.3, 127.9, 126.0, 118.3, 118.2, 114.3, 85.8, 67.8, 49.0; HRMS (ESI) calcd for $C_{11}H_{11}NO_4S$ $[M+H]^+$:254.0482, found 254.0477.

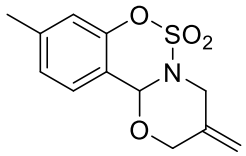
10-methyl-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ab)



3ab

Prepared according to the general procedure as described above in 93% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 118-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.07 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 1H), 5.07 (d, *J* = 18.6 Hz, 2H), 4.40 – 4.18 (m, 2H), 3.96 (d, *J* = 1.1 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 134.8, 133.5, 130.8, 126.9, 117.0, 116.9, 113.2, 84.9, 66.9, 48.0, 19.8; HRMS (ESI) calcd for $C_{12}H_{13}NO_4S$ $[M+H]^+$: 268.0638, found:268.0636.

9-methyl-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ac)

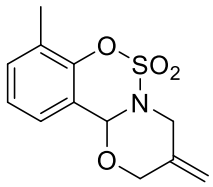


3ac

Prepared according to the general procedure as described above in 65% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 130-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.7 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.84 – 6.79 (m, 1H), 5.99 (s, 1H), 5.14 – 4.96 (m, 2H), 4.34 – 4.14 (m, 2H), 3.95 (q, *J* = 1.2 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 142.1, 134.6, 127.6, 126.8,

118.4, 115.3, 114.1, 85.8, 67.7, 49.0, 21.2; HRMS (ESI) calcd for $C_{12}H_{13}NO_4S$ $[M+H]^+$: 268.0638, found: 268.0639.

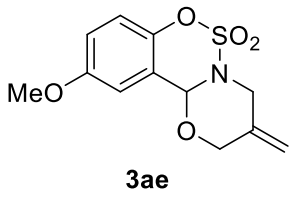
8-methyl-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ad)



3ad

Prepared according to the general procedure as described above in 75% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 110-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.06 (m, 3H), 6.00 (s, 1H), 5.07 (d, *J* = 19.4 Hz, 2H), 4.40 – 4.19 (m, 2H), 3.97 (d, *J* = 1.3 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 134.6, 132.6, 127.7, 125.4, 125.3, 118.2, 114.2, 86.1, 68.0, 49.1, 15.5; HRMS (ESI) calcd for $C_{12}H_{13}NO_4S$ $[M+H]^+$: 268.0638, found: 268.0635.

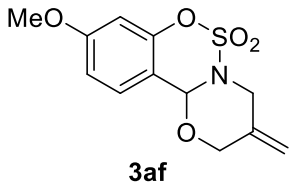
10-methoxy-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ae)



3ae

Prepared according to the general procedure as described above in 55% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a transparency liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.75 (m, 3H), 6.00 (s, 1H), 5.15 – 4.98 (m, 2H), 4.34 – 4.21 (m, 2H), 4.04 – 3.87 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 143.5, 134.4, 119.3, 119.0, 117.4, 114.3, 111.6, 85.8, 67.7, 55.9, 49.0; HRMS (ESI) calcd for $C_{12}H_{13}NO_5S$ $[M+H]^+$:284.0587, found:284.0578.

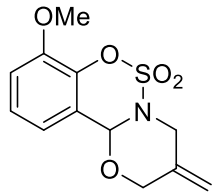
9-methoxy-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3af)



3af

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 124-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.6, 0.8 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.51 (d, *J* = 2.5 Hz, 1H), 5.97 (s, 1H), 5.19 – 4.98 (m, 2H), 4.35 – 4.16 (m, 2H), 3.95 (d, *J* = 1.2 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 150.6, 134.6, 128.7, 114.2, 112.8, 110.2, 103.0, 85.7, 67.6, 55.7, 49.0; HRMS (ESI) calcd for $C_{12}H_{13}NO_5S$ $[M+H]^+$: 284.0587, found: 284.0577.

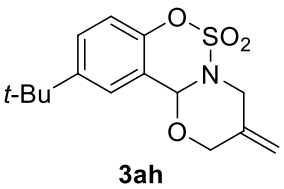
8-methoxy-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ag)



3ag

Prepared according to the general procedure as described above in 95% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 136-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 1H), 7.02 – 6.89 (m, 2H), 6.07 (s, 1H), 5.07 (d, *J* = 19.5 Hz, 2H), 4.36 – 4.16 (m, 2H), 4.05 – 3.88 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 139.5, 134.5, 125.7, 119.2, 118.6, 114.2, 113.4, 85.8, 67.5, 56.3, 49.0; HRMS (ESI) calcd for $C_{12}H_{13}NO_5S$ $[M+H]^+$: 284.0587, found: 284.0578.

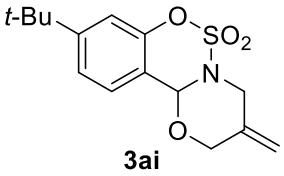
10-(tert-butyl)-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ah)



3ah

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 120-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 31.0, 8.0, 1.8 Hz, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 5.92 (s, 1H), 5.07 (d, *J* = 20.7 Hz, 2H), 4.41 – 4.26 (m, 2H), 4.17 – 3.91 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 138.5, 133.6, 127.7, 125.0, 124.4, 118.5, 113.1, 85.5, 67.9, 48.1, 33.9, 28.9; HRMS (ESI) calcd for $C_{15}H_{19}NO_4S$ $[M+H]^+$: 310.1108, found: 310.1109.

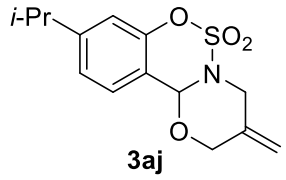
9-(tert-butyl)-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ai)



3ai

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 124-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 7.00 (d, *J* = 1.8 Hz, 1H), 6.01 (s, 1H), 5.06 (ddd, *J* = 18.7, 1.6, 0.8 Hz, 2H), 4.35 – 4.15 (m, 2H), 3.95 (dd, *J* = 3.0, 1.3 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 154.8, 148.9, 133.9, 126.7, 122.5, 114.5, 114.4, 113.4, 85.0, 66.9, 48.3, 34.3, 30.3; HRMS (ESI) calcd for $C_{15}H_{19}NO_4S$ $[M+H]^+$: 310.1108, found: 310.1109.

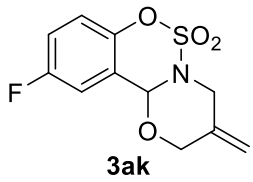
9-isopropyl-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3aj)



3aj

Prepared according to the general procedure as described above in 85% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 112-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 1H), 7.12 – 6.98 (m, 1H), 6.85 (d, *J* = 1.7 Hz, 1H), 6.00 (s, 1H), 5.06 (d, *J* = 18.7 Hz, 2H), 4.37 – 4.16 (m, 2H), 3.95 (q, *J* = 1.3 Hz, 2H), 2.85 (p, *J* = 6.9 Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.07, 149.76, 134.61, 127.70, 124.35, 115.94, 115.56, 114.11, 85.81, 67.63, 49.01, 33.92, 23.63; HRMS (ESI) calcd for $C_{14}H_{17}NO_4S$ $[M+H]^+$: 296.0951, found: 296.0952.

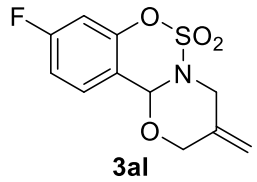
10-fluoro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ak)



3ak

Prepared according to the general procedure as described above in 50% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 132-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 6.96 (m, 3H), 6.01 (s, 1H), 5.16 – 5.05 (m, 2H), 4.26 (s, 2H), 4.10 – 3.77 (m, 2H); 13C NMR (201 MHz, CDCl3) δ 159.3 (d, *J* = 246.7 Hz), 145.2, 133.5, 119.5, 119.4, 117.9 (d, *J* = 23.8 Hz), 114.1, 113.9 (d, *J* = 25.2 Hz), 84.8, 67.2, 48.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.94. HRMS (ESI) calcd for $C_{11}H_{10}FNO_4S$ $[M+H]^+$: 272.0387, found: 272.0391.

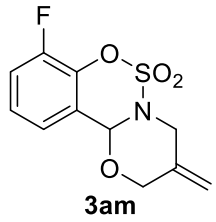
9-fluoro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3al)



3al

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 122-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 8.7, 6.0, 0.8 Hz, 1H), 7.03 – 6.68 (m, 2H), 6.01 (t, *J* = 1.1 Hz, 1H), 5.08 (d, *J* = 18.9 Hz, 2H), 4.25 (s, 2H), 4.06 – 3.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 252.0 Hz), 149.5 (d, *J* = 12.2 Hz), 133.1, 128.4 (d, *J* = 9.7 Hz), 113.5, 112.5 (d, *J* = 21.8 Hz), 105.1 (d, *J* = 25.9 Hz), 84.4, 66.5, 47.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -107.35. HRMS (ESI) calcd for $C_{11}H_{10}FNO_4S$ $[M+H]^+$: 272.0387, found: 272.0364.

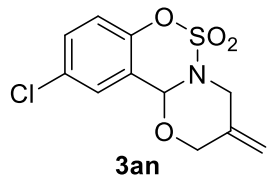
8-fluoro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3am)



3am

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 126-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 3H), 6.12 (s, 1H), 5.09 (d, *J* = 20.6 Hz, 2H), 4.24 (d, *J* = 0.9 Hz, 2H), 4.05 – 3.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, *J* = 252.7 Hz), 132.9, 124.7 (d, *J* = 7.0 Hz), 121.6 (d, *J* = 4.0 Hz), 119.3, 117.0 (d, *J* = 17.5 Hz), 113.6, 84.4 (d, *J* = 2.5 Hz), 66.2, 47.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -131.74. HRMS (ESI) calcd for $C_{11}H_{10}FNO_4S$ $[M+H]^+$: 272.0387, found: 272.0383.

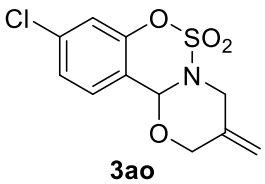
10-chloro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3an)



3an

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 118-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 2H), 7.05 – 6.89 (m, 1H), 6.01 (s, 1H), 5.09 (d, *J* = 17.2 Hz, 2H), 4.26 (s, 2H), 4.09 – 3.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 134.0, 131.4, 129.0, 127.8, 119.9, 119.8, 114.7, 85.2, 67.7, 49.0; HRMS (ESI) calcd for $C_{11}H_{10}ClNO_4S$ $[M+H]^+$: 288.0092, found: 288.0091.

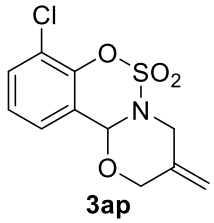
9-chloro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ao)



3ao

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 116-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 6.99 (m, 3H), 6.01 (d, *J* = 0.8 Hz, 1H), 5.08 (dt, *J* = 18.9, 1.2 Hz, 2H), 4.24 (t, *J* = 0.9 Hz, 2H), 4.05 – 3.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 135.6, 133.0, 127.9, 125.3, 117.6, 115.9, 113.6, 84.3, 66.5, 47.9; HRMS (ESI) calcd for $C_{11}H_{10}ClNO_4S$ $[M+H]^+$: 288.0092, found: 288.0082.

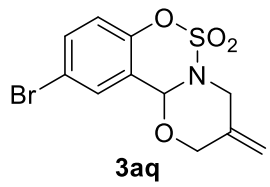
8-chloro-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ap)



3ap

Prepared according to the general procedure as described above in 51% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 1186-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.01 (s, 1H), 5.09 (d, *J* = 19.4 Hz, 2H), 4.24 (s, 2H), 4.01 – 3.87 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 136.7, 134.1, 128.9, 126.3, 118.7, 116.9, 114.6, 85.4, 67.6, 49.0; HRMS (ESI) calcd for $C_{11}H_{10}ClNO_4S$ $[M+H]^+$: 288.0092, found: 288.0085.

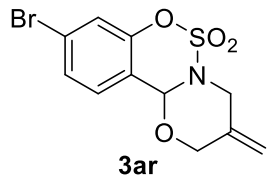
10-bromo-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3aq)



3aq

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.28 (m, 3H), 7.07 – 6.83 (m, 1H), 6.01 (s, 1H), 5.17 – 4.97 (m, 2H), 4.26 (s, 2H), 4.01 – 3.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 142.3, 133.2, 132.9, 129.6, 129.4, 127.9, 127.3, 124.3, 119.2, 119.0, 117.6, 113.6, 84.0, 66.6, 47.9; HRMS (ESI) calcd for $C_{11}H_{10}BrNO_4S$ $[M+H]^+$: 331.9587, found: 331.9571.

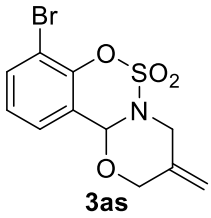
9-bromo-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3ar)



3ar

Prepared according to the general procedure as described above in 80% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 118-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 3H), 5.99 (s, 1H), 5.08 (d, *J* = 19.2 Hz, 2H), 4.24 (s, 2H), 4.04 – 3.85 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 134.0, 129.2, 129.1, 124.3, 121.5, 117.4, 114.6, 85.4, 67.5, 49.0; HRMS (ESI) calcd for $C_{11}H_{10}BrNO_4S$ $[M+H]^+$: 331.9587, found: 331.9575.

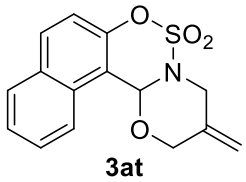
8-bromo-3-methylene-3,4-dihydro-2H,11bH-benzo[e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3as)



3as

Prepared according to the general procedure as described above in 50% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 130-134 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.71 – 7.10 (m, 4H), 6.15 (s, 1H), 5.16 (d, *J* = 41.5 Hz, 2H), 4.31 (s, 2H), 4.03 (dd, *J* = 78.7, 13.3 Hz, 2H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 145.5, 133.7, 132.7, 125.6, 125.1, 118.8, 113.3, 110.7, 84.2, 66.1, 47.7; HRMS (ESI) calcd for $C_{11}H_{10}BrNO_4S$ $[M+H]^+$: 331.9587, found: 331.9574.

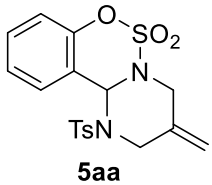
3-methylene-3,4-dihydro-2H,13cH-naphtho[1,2-e][1,3]oxazino[3,2-c][1,2,3]oxathiazine 6,6-dioxide (3at)



3at

Prepared according to the general procedure as described above in 83% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 210-216 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.02 – 7.81 (m, 3H), 7.58 (dddd, *J* = 69.9, 8.1, 6.8, 1.2 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 1H), 6.37 (s, 1H), 5.20 (d, *J* = 48.1 Hz, 2H), 4.74 – 4.52 (m, 3H), 4.18 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 134.9, 132.6, 131.2, 130.6, 128.7, 128.0, 126.0, 123.7, 117.5, 114.2, 112.4, 86.5, 70.9, 49.8; HRMS (ESI) calcd for $C_{15}H_{13}NO_4S$ $[M+H]^+$: 304.0638, found: 304.0634.

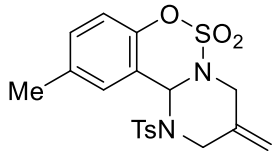
3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5aa)



5aa

Prepared according to the general procedure as described above in 96% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 168-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.24 (m, 7H), 7.08 – 6.88 (m, 2H), 4.73 (d, *J* = 10.9 Hz, 2H), 4.27 (d, *J* = 15.9 Hz, 1H), 3.70 – 3.52 (m, 2H), 3.28 (d, *J* = 12.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 144.5, 135.8, 131.5, 131.3, 129.7, 128.1, 127.6, 126.4, 118.3, 115.6, 115.6, 69.6, 48.7, 45.3, 21.6; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_5S_2$ $[M+H]^+$: 407.0730, found: .407.0730

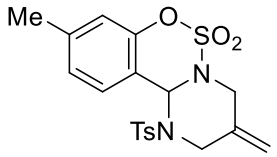
10-methyl-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ab)



5ab

Prepared according to the general procedure as described above in 78% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 220-226 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.41 – 7.20 (m, 4H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.86 – 4.74 (m, 2H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.72 – 3.66 (m, 2H), 3.34 (d, *J* = 12.7 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 148.3, 144.5, 136.5, 135.9, 132.0, 131.4, 129.7, 128.1, 127.5, 118.0, 115.4, 115.1, 69.6, 48.7, 45.3, 21.6, 20.8; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_5S_2$ $[M+H]^+$: 421.0886, found: 421.0885.

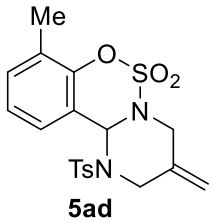
9-methyl-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ac)



5ac

Prepared according to the general procedure as described above in 53% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 170-176 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.47 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.13 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.97 – 6.80 (m, 2H), 4.79 (dt, *J* = 22.4, 1.6 Hz, 2H), 4.33 (d, *J* = 16.0 Hz, 1H), 3.67 (ddd, *J* = 17.7, 14.4, 1.5 Hz, 2H), 3.35 (dd, *J* = 12.7, 1.8 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 150.2, 144.5, 142.3, 135.9, 131.5, 129.7, 128.1, 127.3, 127.3, 118.5, 115.4, 112.4, 69.5, 48.6, 45.2, 21.6, 21.1; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_5S_2$ $[M+H]^+$: 421.0886, found: 421.0884.

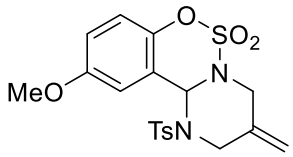
8-methyl-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ad)



5ad

Prepared according to the general procedure as described above in 90% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 180-186 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.11 (m, 4H), 6.91 (s, 1H), 4.72 (dt, *J* = 23.3, 1.6 Hz, 2H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.65 – 3.57 (m, 2H), 3.28 (dd, *J* = 12.8, 1.9 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 147.8, 143.4, 134.9, 131.9, 130.4, 128.6, 127.1, 126.7, 124.6, 124.0, 114.3, 114.2, 68.6, 47.7, 44.2, 20.6, 14.5; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_5S_2$ $[M+H]^+$: 421.0886, found: 421.0884.

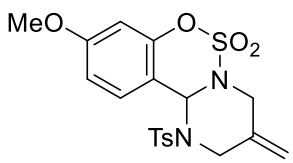
10-methoxy-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ae)



5ae

Prepared according to the general procedure as described above in 83% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 210-216 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.05 – 6.74 (m, 4H), 4.74 (d, *J* = 28.3 Hz, 2H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.76 (d, *J* = 0.9 Hz, 3H), 3.61 (d, *J* = 13.9 Hz, 2H), 3.27 (d, *J* = 12.7 Hz, 1H), 2.37 (s, 3H);^{13}C NMR (201 MHz, $CDCl_3$) δ 156.7, 143.5, 142.9, 134.8, 130.3, 128.6, 127.1, 118.3, 116.3, 115.4, 114.5, 110.3, 68.6, 54.9, 47.7, 44.3, 20.6; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_6S_2$ $[M+H]^+$: 437.0835, found: 437.0833.

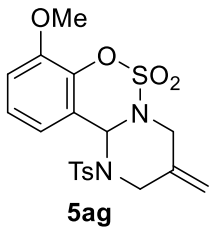
9-methoxy-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5af)



5af

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 168-176 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.46 – 7.21 (m, 3H), 6.90 – 6.75 (m, 2H), 6.51 (d, *J* = 2.5 Hz, 1H), 4.80 – 4.63 (m, 2H), 4.25 (d, *J* = 15.9 Hz, 1H), 3.74 (s, 3H), 3.59 (t, *J* = 14.4 Hz, 2H), 3.39 – 3.26 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 160.8, 150.1, 143.4, 134.9, 130.4, 128.6, 127.3, 127.0, 114.4, 111.8, 106.0, 102.3, 68.3, 54.7, 47.6, 44.1, 20.6; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_6S_2$ $[M+H]^+$: 437.0835, found: 437.0831.

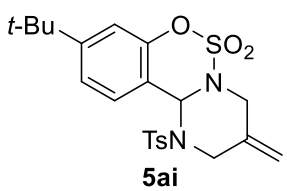
8-methoxy-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ag)



5ag

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 190-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 2H), 7.27 – 6.87 (m, 6H), 4.73 (dt, *J* = 10.9, 1.6 Hz, 2H), 4.26 (d, *J* = 15.9 Hz, 1H), 3.82 (s, 3H), 3.76 – 3.44 (m, 2H), 3.31 (dd, *J* = 12.6, 1.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 148.4, 144.5, 139.9, 135.9, 131.4, 129.7, 128.1, 125.9, 118.2, 116.5, 115.5, 113.7, 69.7, 56.3, 48.7, 45.3, 21.6; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_6S_2$ $[M+H]^+$: 437.0835, found: 437.0826.

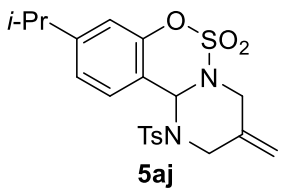
9-(tert-butyl)-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ai)



5ai

Prepared according to the general procedure as described above in 98% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 212-218 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.51 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.38 – 7.23 (m, 3H), 7.10 – 6.88 (m, 2H), 4.79 (dt, *J* = 25.2, 1.6 Hz, 2H), 4.34 (d, *J* = 15.9 Hz, 1H), 3.76 – 3.63 (m, 2H), 3.37 (dd, *J* = 12.6, 2.0 Hz, 1H), 2.44 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 155.8, 150.2, 144.4, 136.0, 131.5, 129.7, 129.6, 128.1, 127.1, 123.6, 115.4, 115.2, 112.4, 69.5, 48.7, 45.2, 35.0, 31.0, 21.6; HRMS (ESI) calcd for $C_{22}H_{26}N_2O_5S_2$ $[M+H]^+$: 463.1355, found: 463.1356.

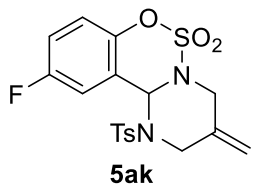
9-isopropyl-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5aj)



5aj

Prepared according to the general procedure as described above in 80% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a transparency liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.90 – 6.82 (m, 2H), 4.72 (d, *J* = 12.4 Hz, 2H), 4.26 (d, *J* = 15.9 Hz, 1H), 3.61 (dd, *J* = 14.3, 8.1 Hz, 2H), 3.29 (d, *J* = 12.6 Hz, 1H), 2.86 (p, *J* = 6.9 Hz, 1H), 2.37 (s, 3H), 1.18 (dd, *J* = 6.9, 1.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 149.3, 143.4, 134.9, 130.5, 128.6, 127.1, 126.3, 123.7, 115.0, 114.3, 111.6, 68.5, 47.6, 44.2, 32.8, 22.6, 22.5, 20.6; HRMS (ESI) calcd for $C_{21}H_{24}N_2O_5S_2$ $[M+H]^+$: 449.1199, found: 449.1196.

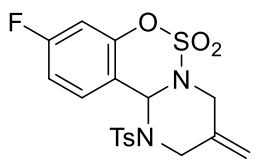
10-fluoro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ak)



5ak

Prepared according to the general procedure as described above in 73% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 198-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.31 – 7.22 (m, 3H), 7.12 – 6.81 (m, 3H), 4.76 (dt, *J* = 12.5, 1.5 Hz, 2H), 4.29 (d, *J* = 16.0 Hz, 1H), 3.70 – 3.52 (m, 2H), 3.26 (dd, *J* = 13.0, 1.9 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ δ 159.1 (d, J = 247.6 Hz), 145.1 (d, J = 2.8 Hz), 143.7, 134.6, 130.0, 128.7, 127.0, 119.0 (d, J = 8.1 Hz), 117.6, 117.4, 116.6 (d, J = 6.9 Hz), 114.8, 113.1 (d, J = 25.5 Hz), 68.3, 68.3, 47.7, 44.3, 20.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.97; HRMS (ESI) calcd for $C_{18}H_{17}FN_2O_5S_2$ $[M+H]^+$: 425.0635, found: 425.0631.

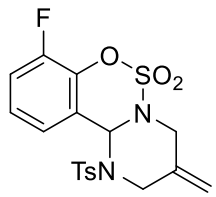
9-fluoro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5al)



5al

Prepared according to the general procedure as described above in 92% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 250-256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.40 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.08 – 6.61 (m, 3H), 4.75 (dt, *J* = 10.2, 1.5 Hz, 2H), 4.27 (d, *J* = 15.9 Hz, 1H), 3.69 – 3.49 (m, 2H), 3.28 (dd, *J* = 12.6, 1.7 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (d, J = 252.3 Hz), 151.0 (d, J = 12.1 Hz), 144.7, 135.7, 131.1, 129.7, 129.2, 129.1, 128.1, 115.8, 113.8 (d, J = 21.7 Hz), 111.5 (d, J = 3.6 Hz), 106.2 (d, J = 26.3 Hz), 69.2, 48.6, 45.2, 21.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -107.27; HRMS (ESI) calcd for $C_{18}H_{17}FN_2O_5S_2$ $[M+H]^+$: 425.0635, found: 425.0605.

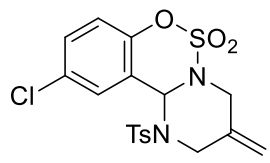
8-fluoro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5am)



5am

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 158-162 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.47 – 7.20 (m, 5H), 7.01 (s, 1H), 4.88 – 4.77 (m, 2H), 4.36 (d, *J* = 16.0 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.65 (d, *J* = 16.0 Hz, 1H), 3.40 (d, *J* = 12.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 150.7 (d, *J* = 252.7 Hz), 144.7, 138.8 (d, *J* = 13.5 Hz), 135.7, 131.0, 129.8, 128.1, 125.9 (d, *J* = 7.0 Hz), 122.3 (d, *J* = 3.6 Hz), 118.3 (d, *J* = 17.8 Hz), 118.0, 115.9, 69.6, 69.6, 48.8, 45.3, 21.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -131.51; HRMS (ESI) calcd for $C_{18}H_{17}FN_2O_5S_2$ $[M+H]^+$: 425.0635, found: 425.0636.

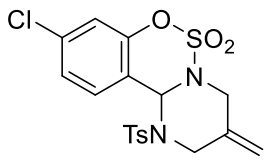
10-chloro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5an)



5an

Prepared according to the general procedure as described above in 50% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 250-252 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.86 – 7.21 (m, 6H), 7.10 – 6.87 (m, 2H), 4.83 (dt, *J* = 29.1, 1.6 Hz, 2H), 4.37 (d, *J* = 16.0 Hz, 1H), 3.72 – 3.55 (m, 2H), 3.33 (dd, *J* = 13.0, 2.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 148.8, 144.7, 135.6, 131.9, 131.6, 130.9, 129.8, 128.1, 127.3, 119.8, 117.5, 115.9, 69.3, 48.7, 45.4, 21.6; HRMS (ESI) calcd for $C_{18}H_{17}ClN_2O_5S_2$ $[M+H]^+$: 441.0340, found: 441.0339.

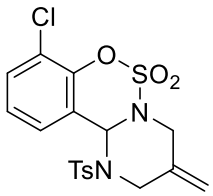
9-chloro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ao)



5ao

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 140-148 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.86 – 7.53 (m, 3H), 7.37 – 7.24 (m, 3H), 7.17 – 6.85 (m, 2H), 4.82 (dt, *J* = 19.9, 1.6 Hz, 2H), 4.34 (d, *J* = 16.0 Hz, 1H), 3.77 – 3.54 (m, 2H), 3.36 – 3.33 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 150.6, 144.7, 136.9, 135.7, 131.0, 129.8, 128.7, 128.1, 126.7, 118.6, 115.9, 114.3, 69.3, 48.7, 45.2, 21.6; HRMS (ESI) calcd for $C_{18}H_{17}ClN_2O_5S_2$ $[M+H]^+$: 441.0340, found: 441.0350.

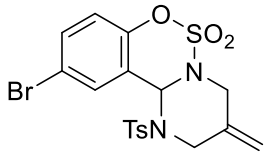
8-chloro-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ap)



5ap

Prepared according to the general procedure as described above in 74% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 186-192 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.96 – 6.88 (m, 8H), 4.95 – 4.75 (m, 2H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.72 (d, *J* = 12.8 Hz, 1H), 3.63 (d, *J* = 16.0 Hz, 1H), 3.37 (d, *J* = 12.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 146.3, 144.7, 135.7, 132.2, 130.9, 129.8, 128.1, 126.2, 125.9, 123.5, 117.6, 115.9, 69.6, 48.8, 45.3, 21.6; HRMS (ESI) calcd for $C_{18}H_{17}ClN_2O_5S_2$ $[M+H]^+$: 441.0340, found: 441.0353.

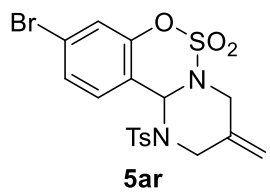
10-bromo-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5aq)



5aq

Prepared according to the general procedure as described above in 52% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 250-256 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.86 – 7.30 (m, 6H), 7.00 – 6.93 (m, 2H), 4.83 (d, *J* = 31.2 Hz, 2H), 4.38 (d, *J* = 16.1 Hz, 1H), 3.68 (dd, *J* = 25.2, 14.4 Hz, 2H), 3.33 (d, *J* = 12.7 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 149.4, 144.7, 135.6, 134.5, 130.9, 130.2, 129.8, 128.1, 120.0, 119.2, 117.8, 115.9, 69.2, 48.7, 45.4, 21.6; HRMS (ESI) calcd for $C_{18}H_{17}BrN_2O_5S_2$ $[M+H]^+$: 484.9835, found: 484.9821.

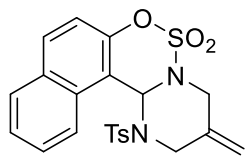
9-bromo-3-methylene-1-tosyl-1,3,4,11b-tetrahydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5ar)



5ar

Prepared according to the general procedure as described above in 99% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 200-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.58 (m, 2H), 7.47 – 7.35 (m, 2H), 7.32 – 7.13 (m, 3H), 6.84 (s, 1H), 4.75 (dt, *J* = 9.9, 1.5 Hz, 2H), 4.27 (d, *J* = 16.0 Hz, 1H), 3.68 – 3.48 (m, 2H), 3.30 – 3.21 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 144.7, 135.7, 131.0, 129.8, 129.6, 128.9, 128.1, 124.5, 121.5, 115.9, 114.8, 69.3, 48.7, 45.2, 21.6; HRMS (ESI) calcd for $C_{18}H_{17}BrN_2O_5S_2$ $[M+H]^+$: 484.9835, found: 484.9799.

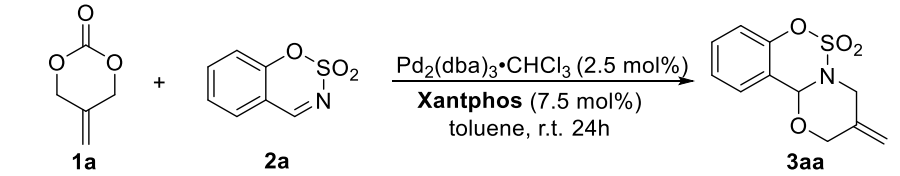
3-methylene-1-tosyl-1,3,4,13c-tetrahydro-2H-naphtho[1,2-e]pyrimido[1,2-c][1,2,3]oxathiazine 6,6-dioxide (5at)



5at

Prepared according to the general procedure as described above in 67% yield. It was purified by flash chromatography (6.7% EtOAc/PE) to afford a white solid. mp = 212-216 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.7 Hz, 1H), 8.04 – 7.02 (m, 9H), 4.76 (d, *J* = 58.5 Hz, 2H), 4.30 (d, *J* = 16.6 Hz, 1H), 3.63 (d, *J* = 13.7 Hz, 1H), 3.34 (dd, *J* = 15.2, 12.4 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 149.7, 144.8, 135.6, 132.7, 131.9, 131.7, 130.5, 129.7, 128.8, 128.5, 128.3, 126.1, 124.1, 117.7, 114.9, 109.1, 70.7, 49.2, 45.8, 21.7; HRMS (ESI) calcd for $C_{22}H_{20}N_2O_5S_2$ $[M+H]^+$: 457.0886, found: 457.0880.

Scaled-up Synthesis of the Product 3aa and 5aa



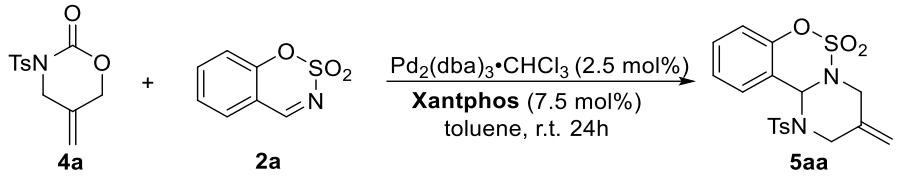
1a 7.5 mmol, 855 mg

2a 5 mmol, 915 mg

3aa 1.12 g, 89% yield

Under argon atmosphere, to a mixture of 2-methylidenetrimethylene carbonate **1a** (7.5 mmol) , Sulfamate-derived cyclic imine **2a** (5.0 mmol) and catalyst $Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%, 0.125 mmol) / **Xantphos** (7.5 mol %, 0.375 mmol) in a Schlenk tube, 75 mL of toluene were added at room temperature. The resulting mixture was stirred until the starting

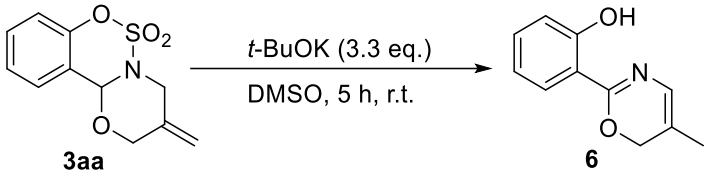
material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (6.7% EtOAc / PE) to afford the corresponding cycloaddition product **3aa** with 89% yield (1.12 g).



4a 3 mmol, 801 mg　　**2a** 2 mmol, 366 mg　　**5aa** 0.80 g, 99% yield

Under argon atmosphere, to a mixture of *N*-tosyl carbamate **4a** (3.0 mmol) , Sulfamate-derived cyclic imine **2a** (2.0 mmol) and catalyst $Pd_2(dba)_3$·$CHCl_3$ (2.5 mol%, 0.075 mmol) / **Xantphos** (7.5 mol %, 0.225 mmol) in a Schlenk tube, 30 mL of toluene were added at room temperature. The resulting mixture was stirred until the starting material were completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (6.7% EtOAc / PE) to afford the corresponding cycloaddition product **5aa** with 99% yield (0.80 g).

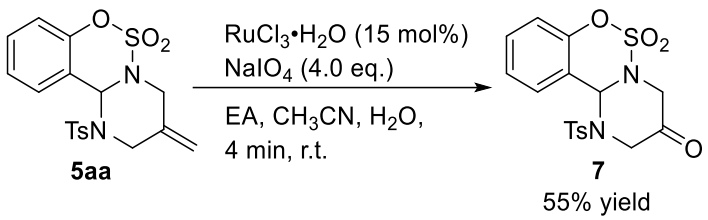
Transformations of the Product 3aa and 5aa



3aa　　**6** 35% yield

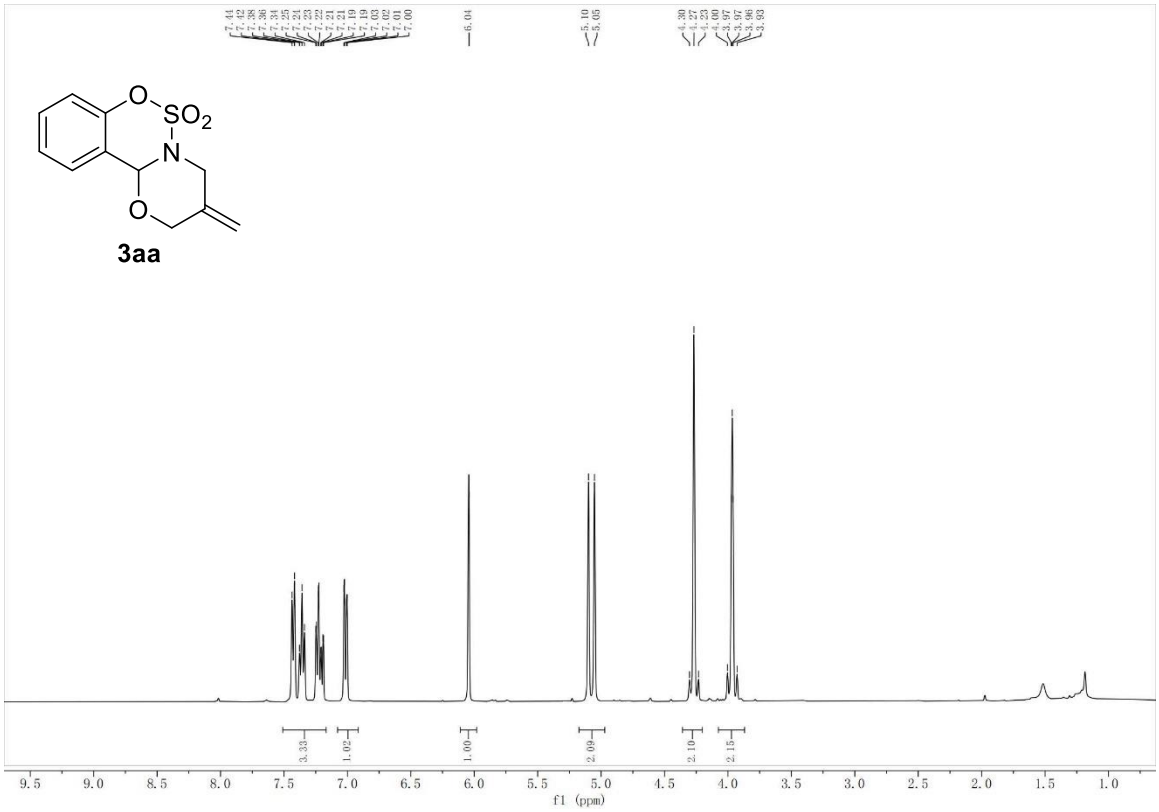
To a dry tube equipped with a stirring bar added **3aa** (0.10 mmol), KO*t*-Bu (0.33 mmol) and anhydrous DMSO (1 mL). The reaction mixture was stirred under an atmosphere of argon at r.t. for 5 h. The reaction was quenched with H_2O and extracted with DCM three times. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. Then, the crude mixture was purified by flash chromatography (16.7% EtOAc/PE) to afford a white solid **6** (6.6 mg, 35% yield). **6: 2-(5-methyl-6H-1,3-oxazin-2-yl)phenol**, mp = 110-114 °C; ^{1}H NMR (800 MHz, $CDCl_3$) δ 13.46 (s, 1H), 7.68 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.32 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.01 – 6.74 (m, 2H), 6.26 – 6.23 (m, 1H), 4.81 (q, *J* = 1.4 Hz, 2H), 1.69 (q, *J* = 1.4 Hz, 3H); ^{13}C NMR (201 MHz,

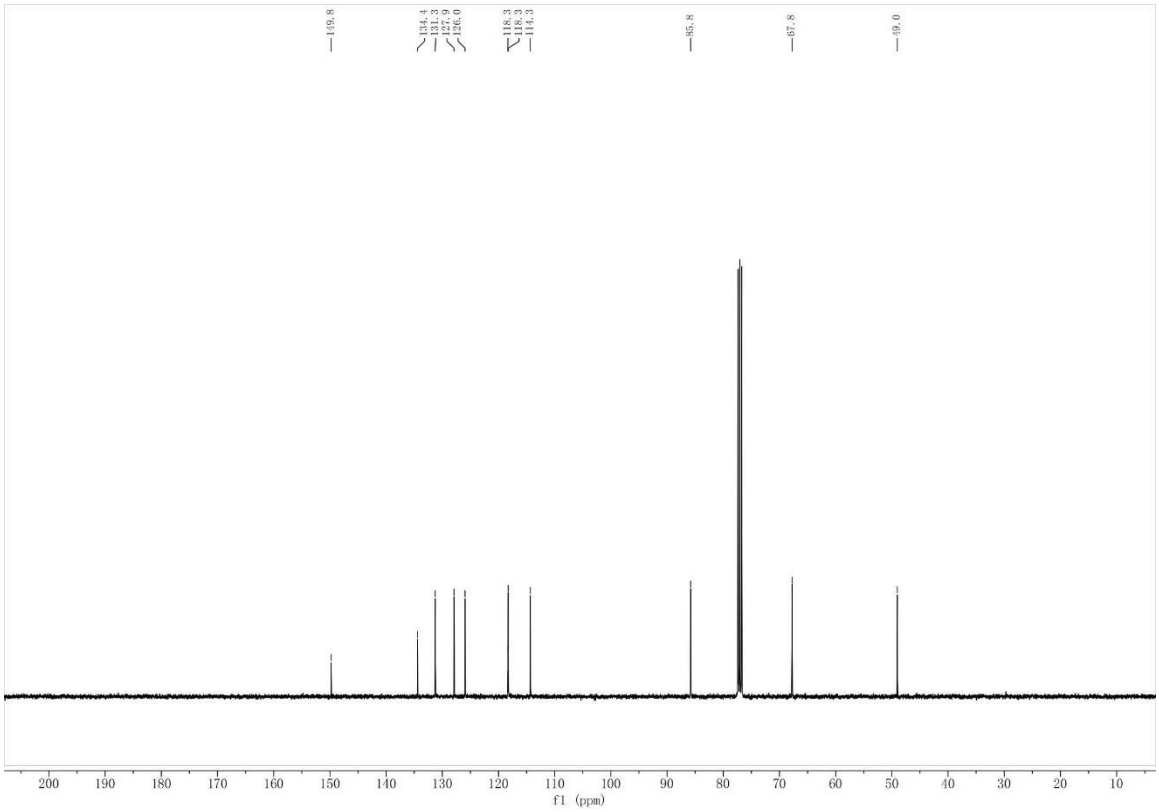
$CDCl_3$) δ 161.0, 158.1, 133.1, 127.2, 124.5, 118.2, 117.4, 117.2, 113.6, 67.6, 16.1.HRMS (ESI) calcd for $C_{11}H_{11}NO_2$ $[M+H]^+$: 190.0863, found: 190.0861.

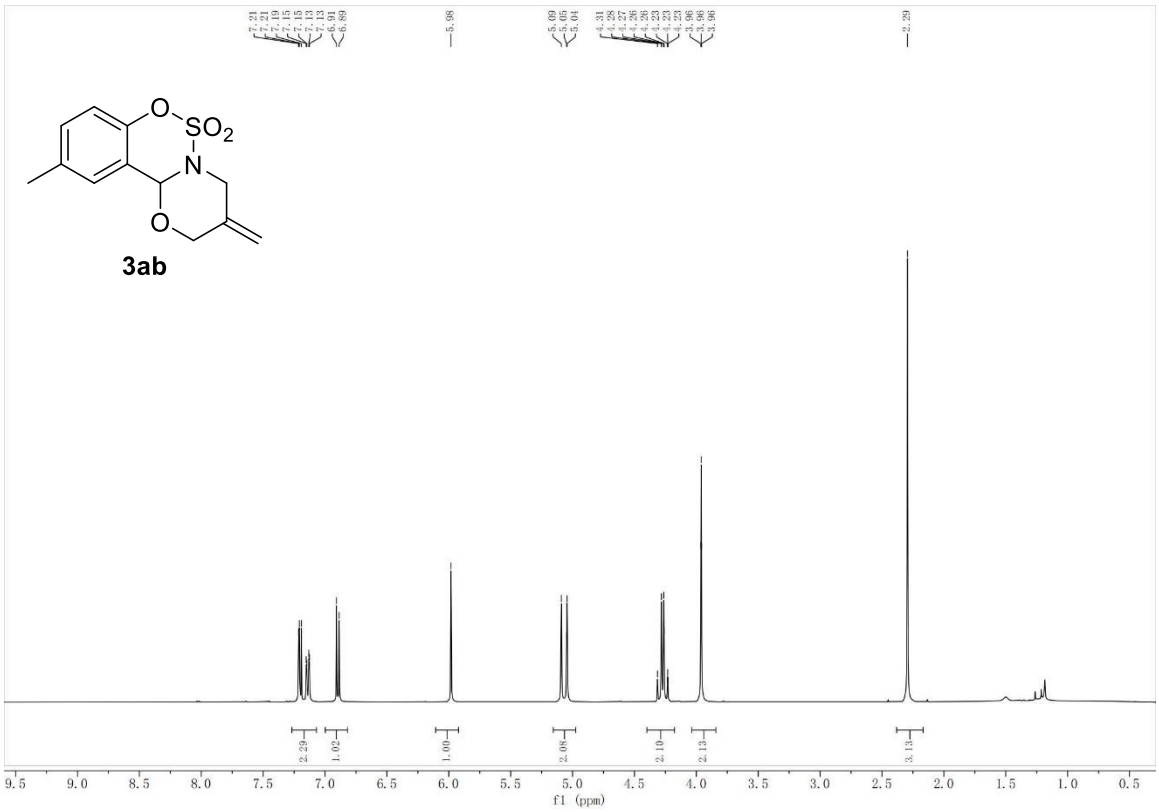


A solution of $NaIO_4$ (85 mg, 0.4 mmol) in water (0.6 mL) was added to a solution of $RuCl_3$•H_2O (3.1 mg, 15 mol%) in MeCN (0.8 mL). This mixture was stirred 2 minutes and then a solution of the **5aa** (0.1 mmol) in EA (0.8 mL) was added. The mixture was stirred for 10 minutes until TLC indicates complete consumption of the starting material. $MgSO_4$ was added and the resulting heterogeneous mixture was washed with EA, and finally evaporated under reduced pressure. Purified by flash chromatography (6.7% EtOAc/PE) to afford a transparency liquid **7** (22.4 mg, 55% yield). **7: 1-tosyl-1,11b-dihydro-2H-benzo[e]pyrimido[1,2-c][1,2,3]oxathiazin-3(4H)-one 6,6-dioxide**, ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.65 – 7.01 (m, 6H), 4.35 (d, *J* = 19.1 Hz, 1H), 3.71 (d, *J* = 19.2 Hz, 1H), 3.53 (d, *J* = 17.7 Hz, 1H), 3.31 (d, *J* = 17.7 Hz, 1H), 2.48 (d, *J* = 2.0 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 194.8, 150.6, 145.7, 134.4, 132.1, 130.4, 127.9, 127.3, 126.9, 118.9, 115.0, 68.9, 52.6, 49.3, 21.7; HRMS (ESI) calcd for $C_{17}H_{16}N_2O_6S_2$ $[M+H]^+$: 409.0523, found: 409.0519.

^{1}H, ^{13}C and ^{19}F NMR Spectra of All Products






7.21
7.21
7.19
7.15
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7.13
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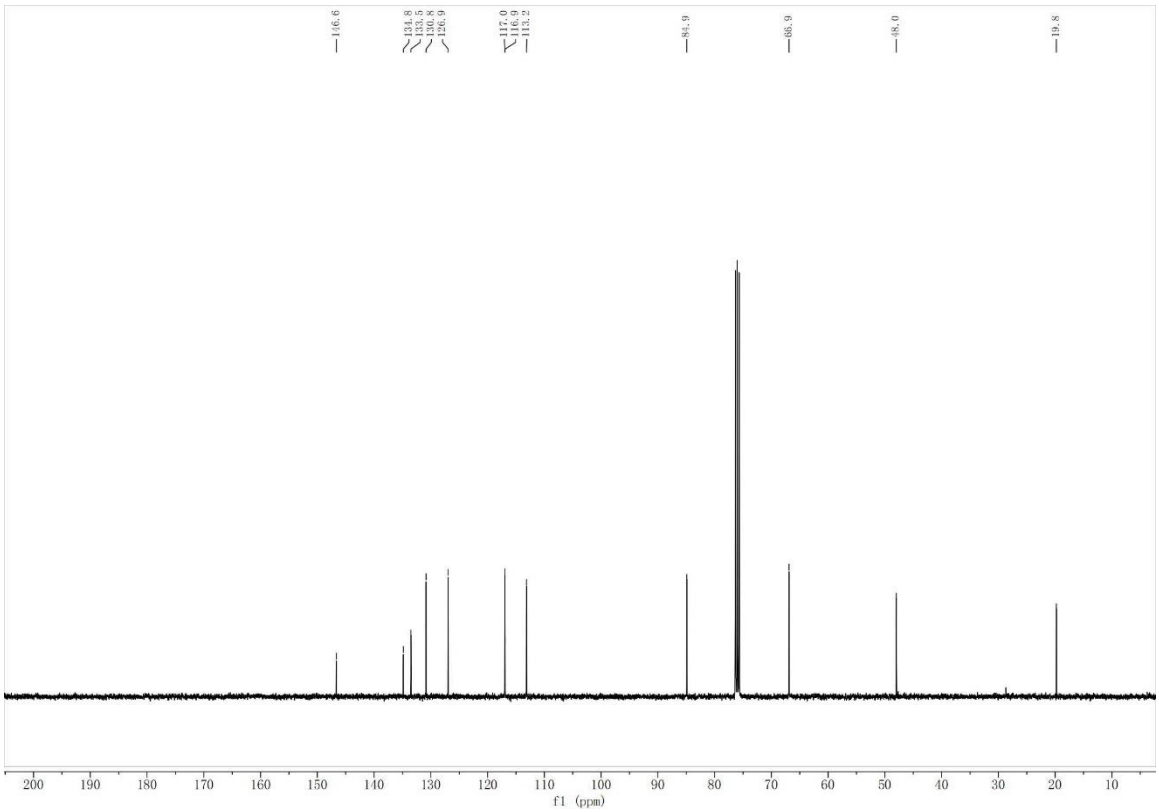
6.89
5.98
5.69
5.65
5.61
4.31
4.28
4.27
4.26
4.26
4.23
4.23
3.98
3.96
3.96
2.29
O
SO2
N
O
3ab
2.29
1.02
1.09
2.08
2.10
2.13
3.13
f1 (ppm)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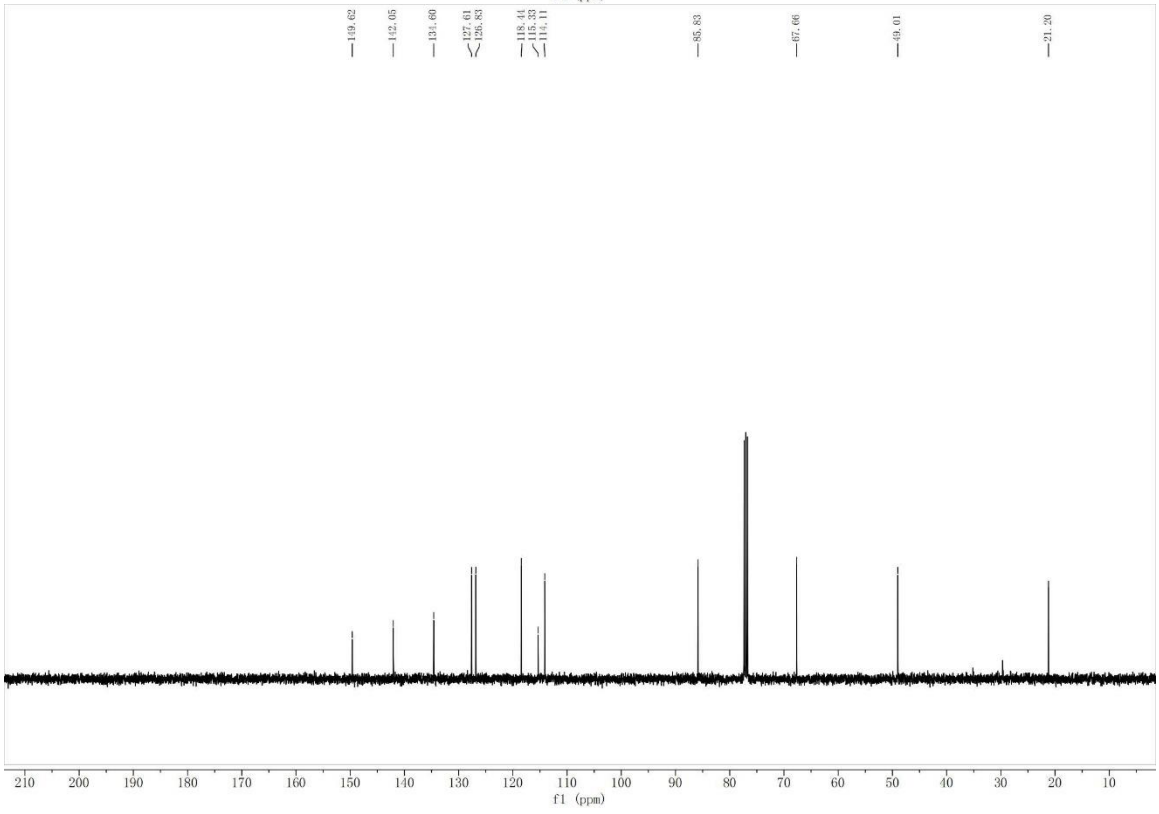
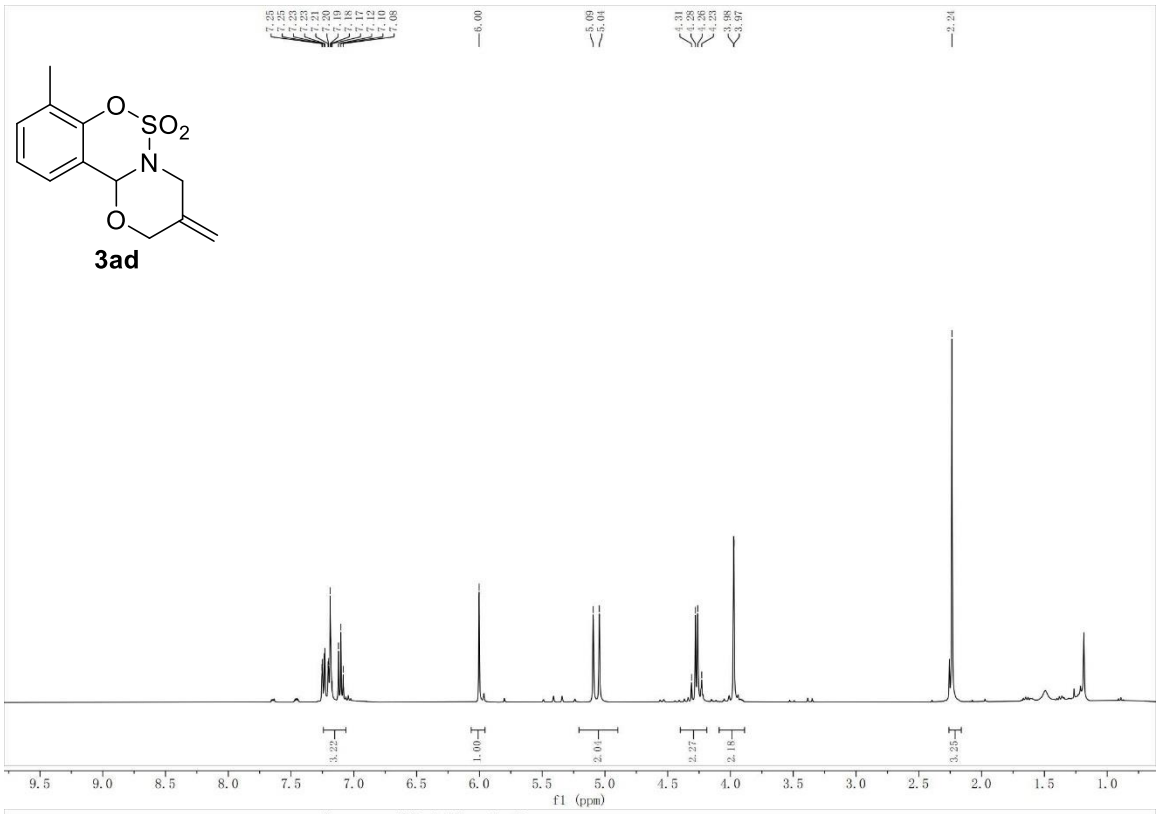
134.8
133.5
130.8
126.9
117.0
116.9
113.2
84.9
66.9
48.0
19.8
f1 (ppm)

3ac




7.25
7.25
7.23
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7.19
7.18
7.17
7.12
7.10
7.08
6.00
5.09
5.04
4.31
4.28
4.26
4.23
3.98
3.97
2.24
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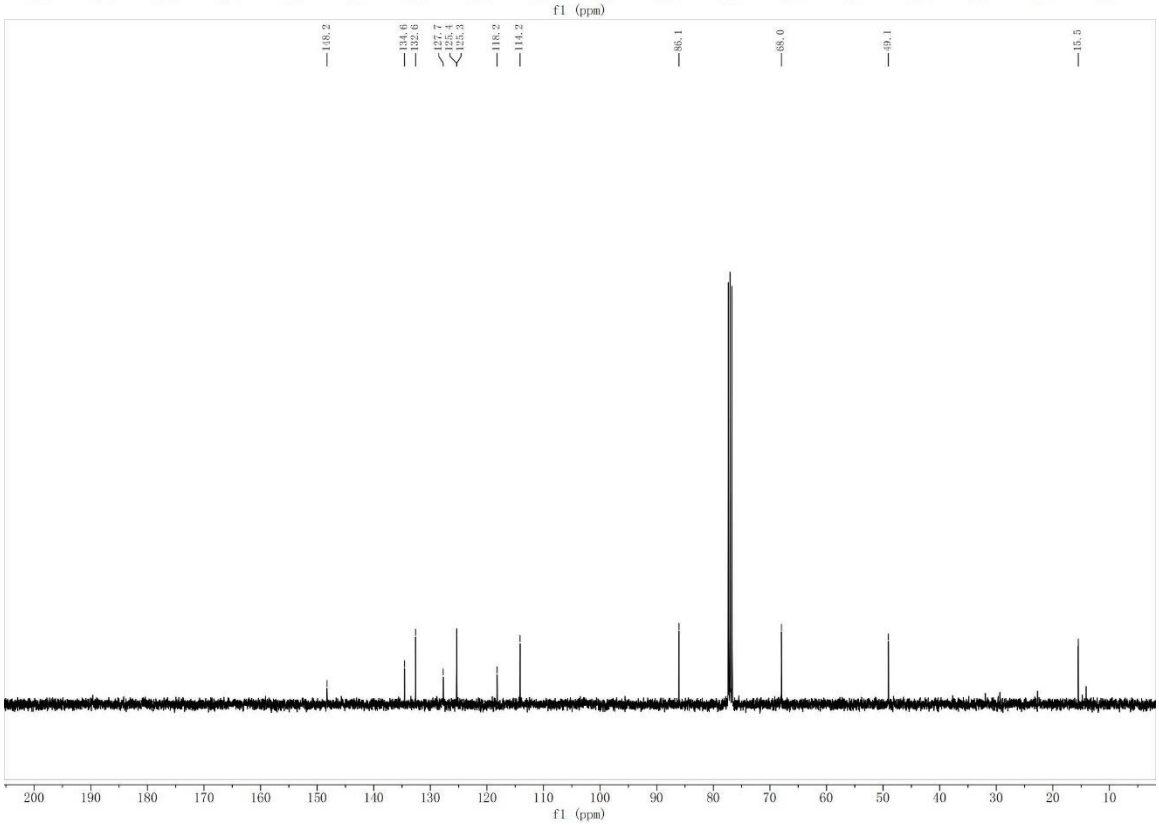
SO2
N
O
3ad
3.22
1.00
2.04
2.27
2.18
3.25
f1 (ppm)


148.2
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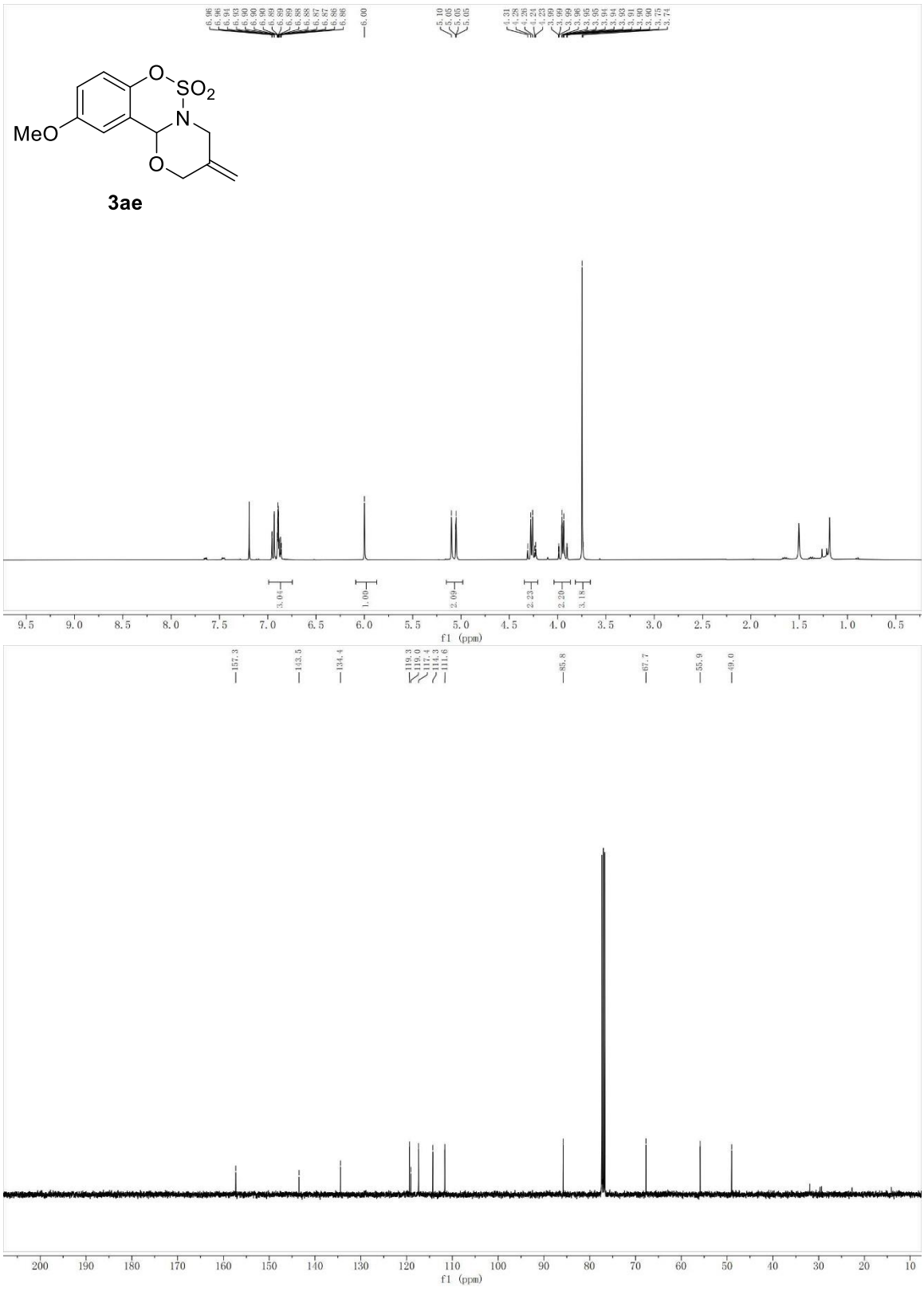
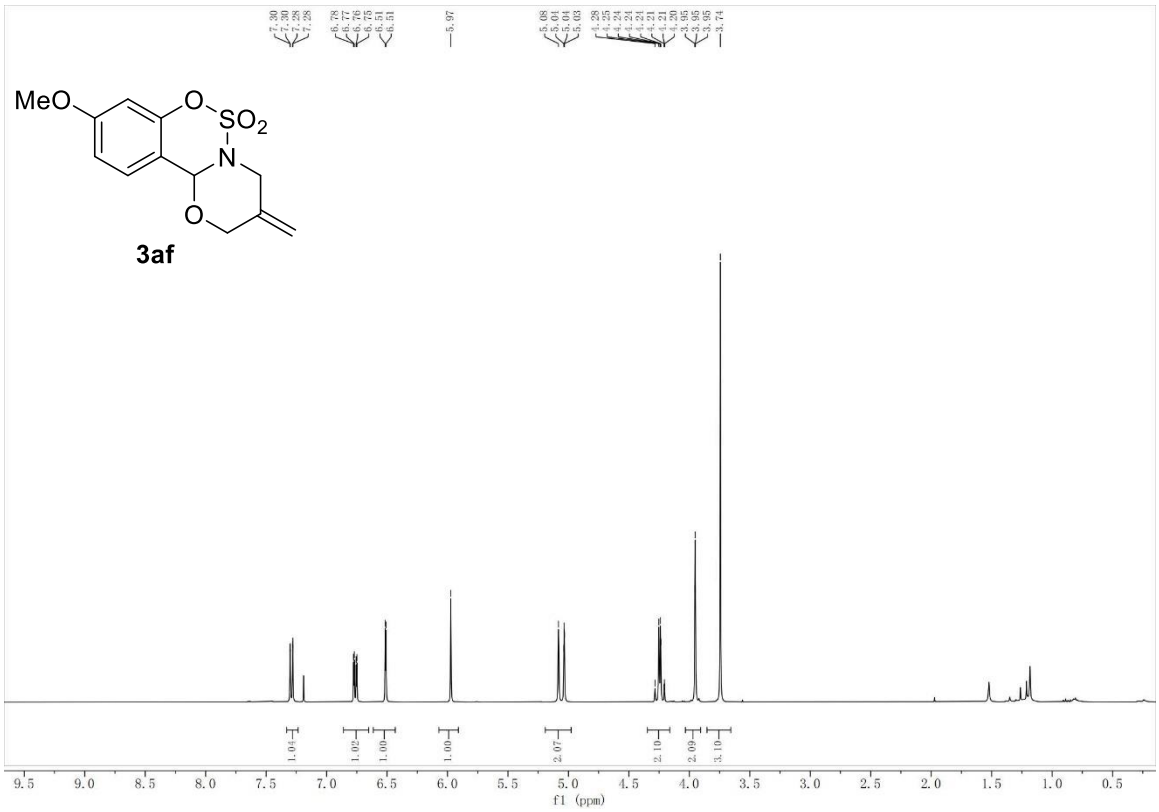
132.6
127.7
125.4
125.3
118.2
114.2
86.1
68.0
49.1
15.5
f1 (ppm)


MeO
O
SO2
N
O
3ae
f1 (ppm)
f1 (ppm)


MeO
O
SO2
N
O
3af
7.30
7.30
7.28
7.28
6.78
6.77
6.76
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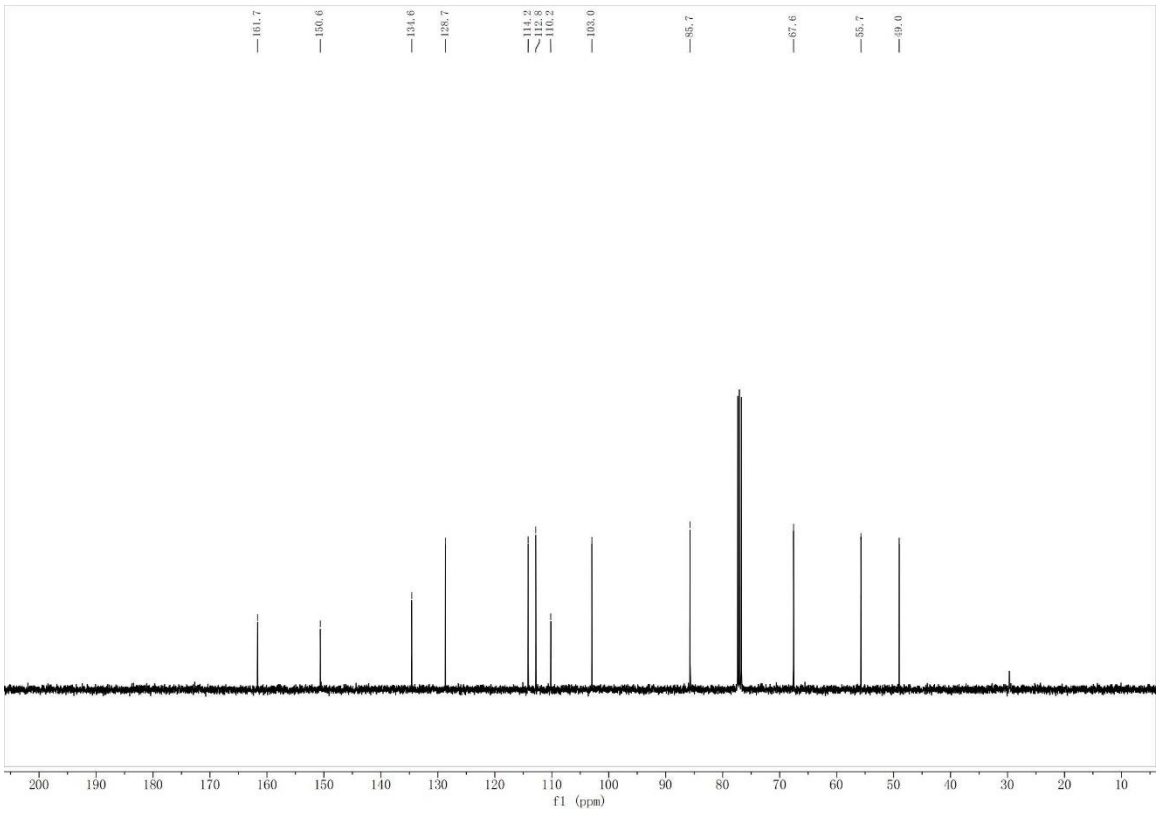
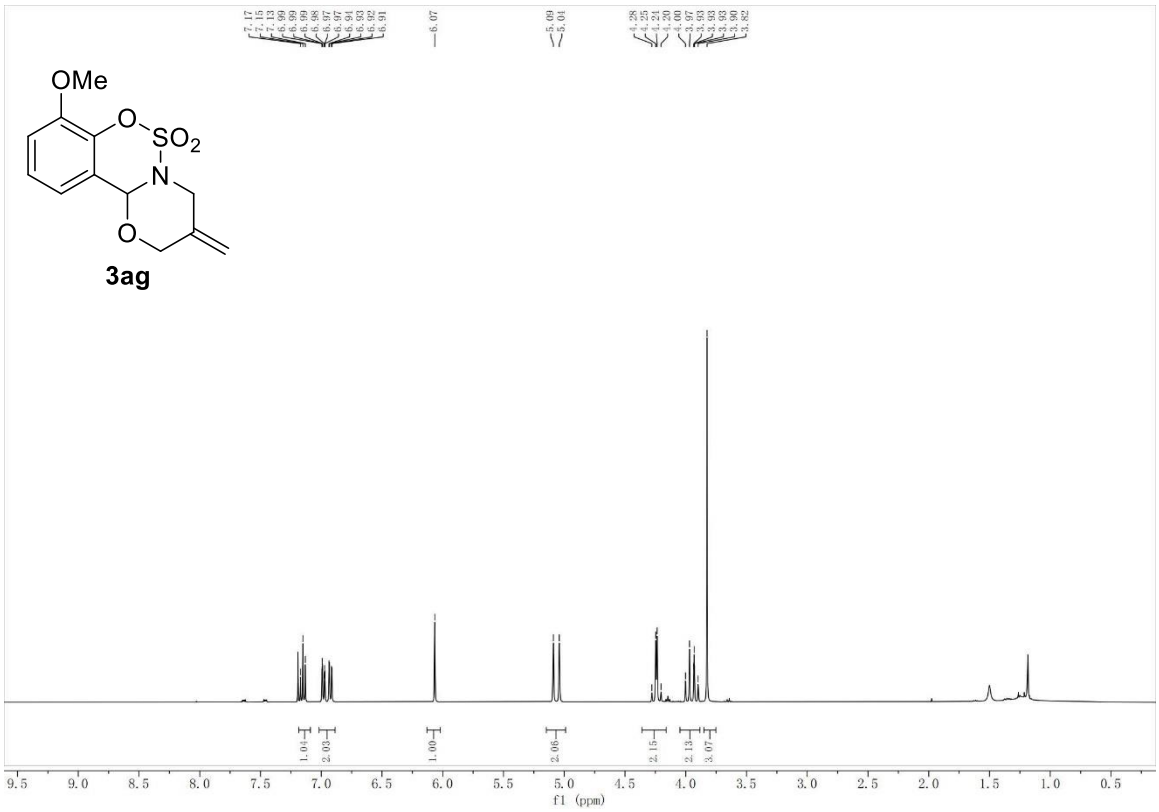
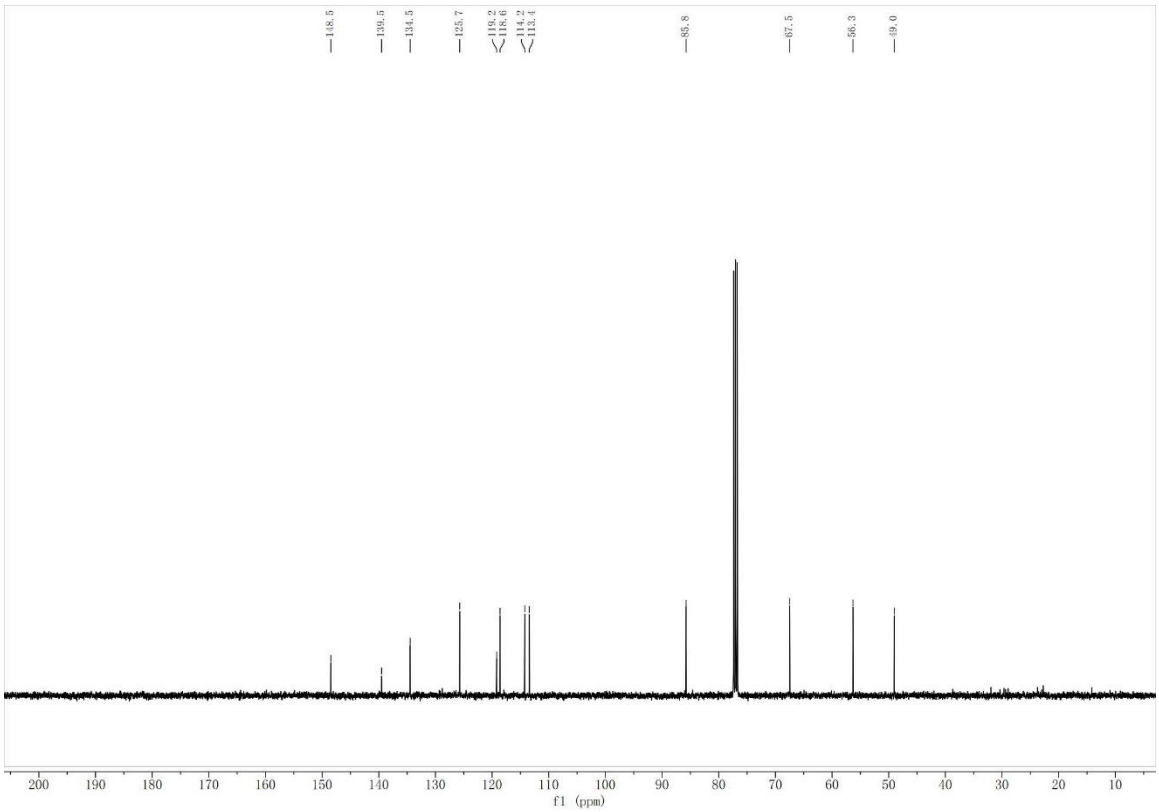
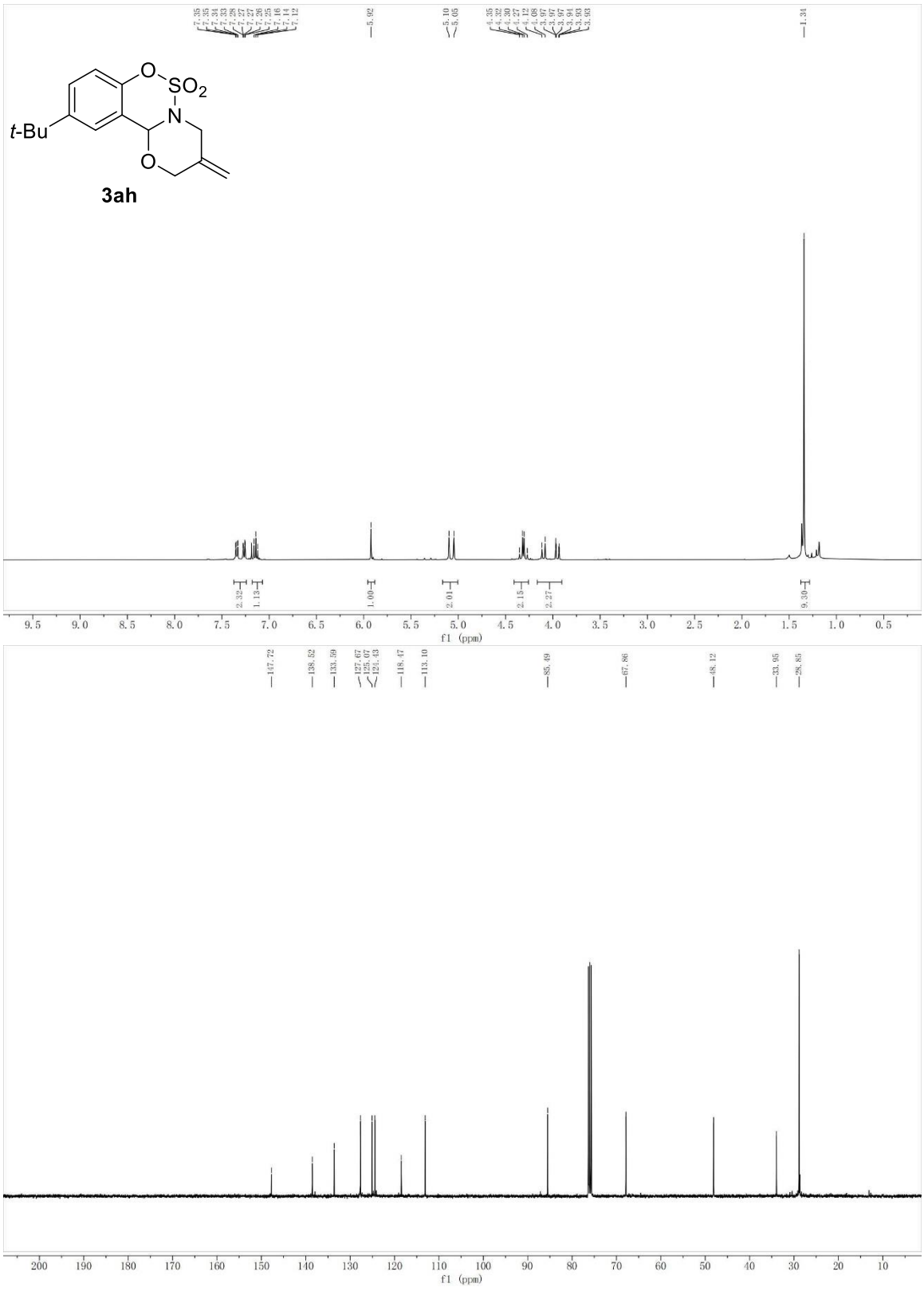
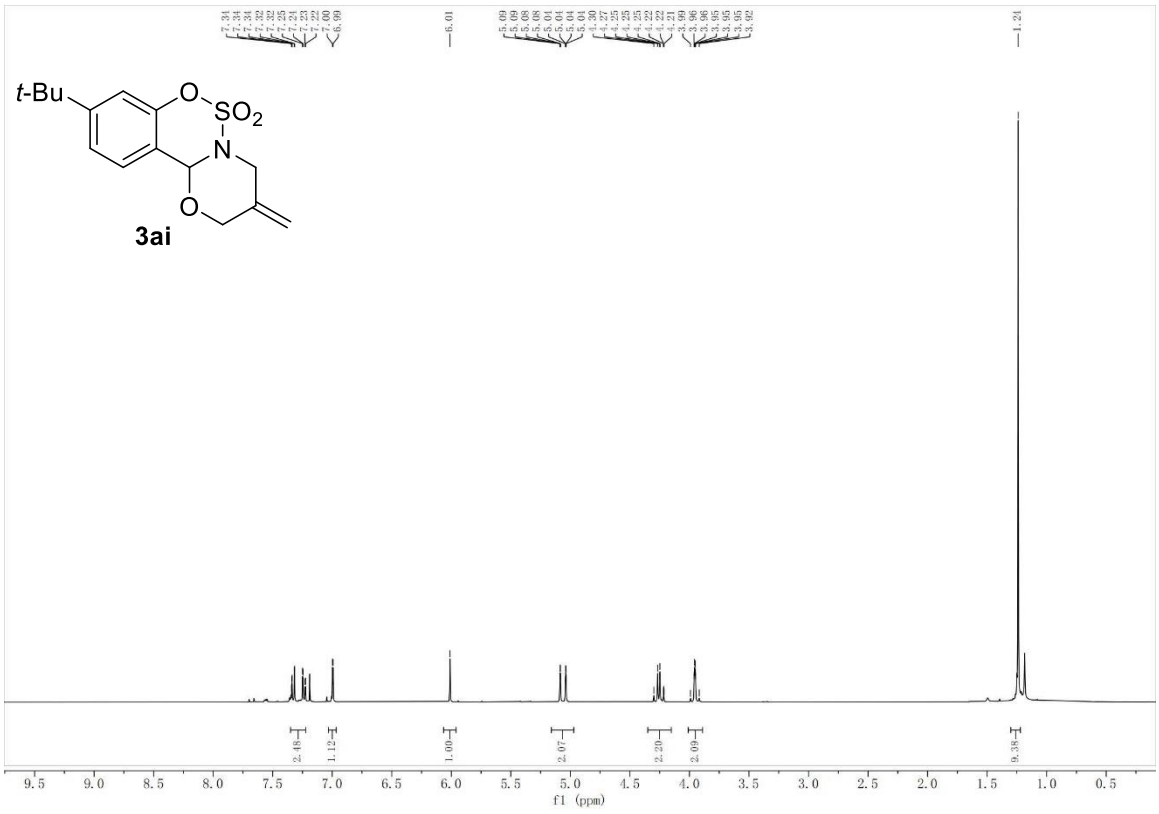
6.51
6.51
5.97
5.08
5.01
5.04
5.03
4.28
4.25
4.24
4.21
4.21
4.21
4.20
3.95
3.95
3.74
1.04
1.02
1.09
1.00
2.07
2.10
2.09
3.10
f1 (ppm)

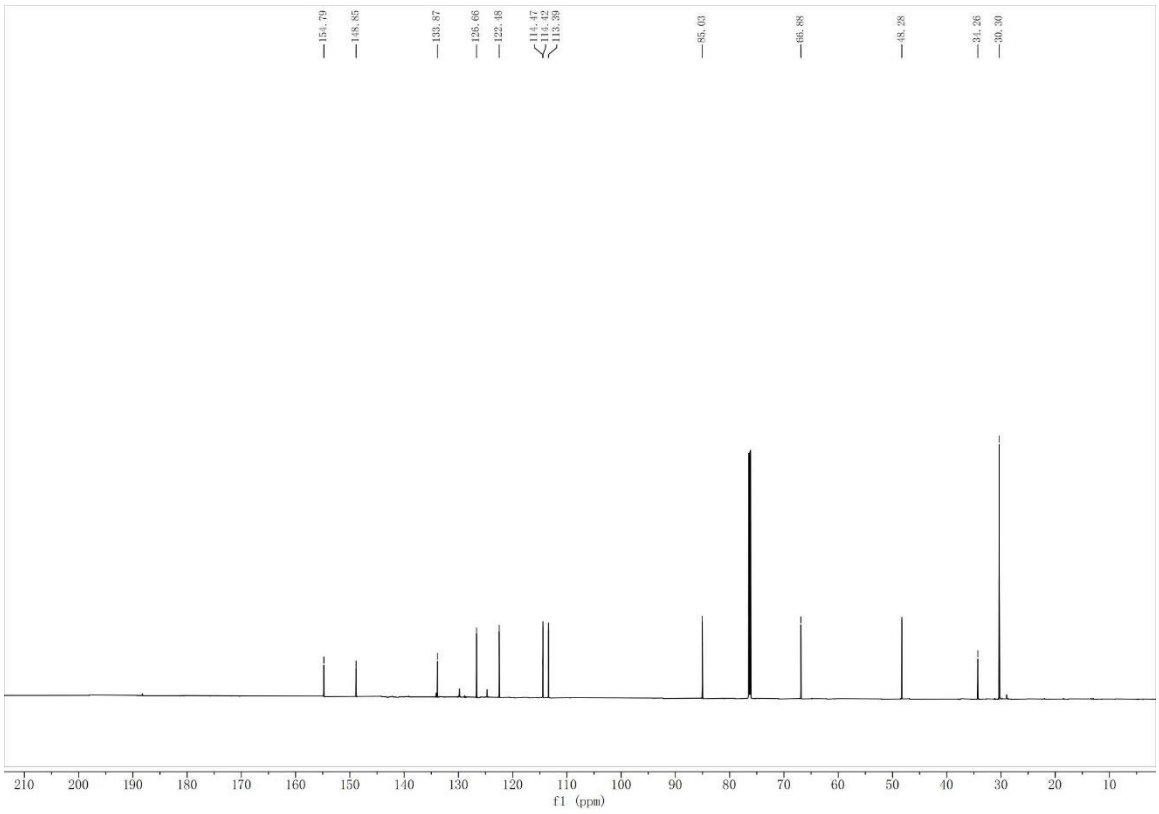

161.7
150.6
134.6
128.7
114.2
112.8
110.2
103.0
85.7
67.6
55.7
49.0
f1 (ppm)

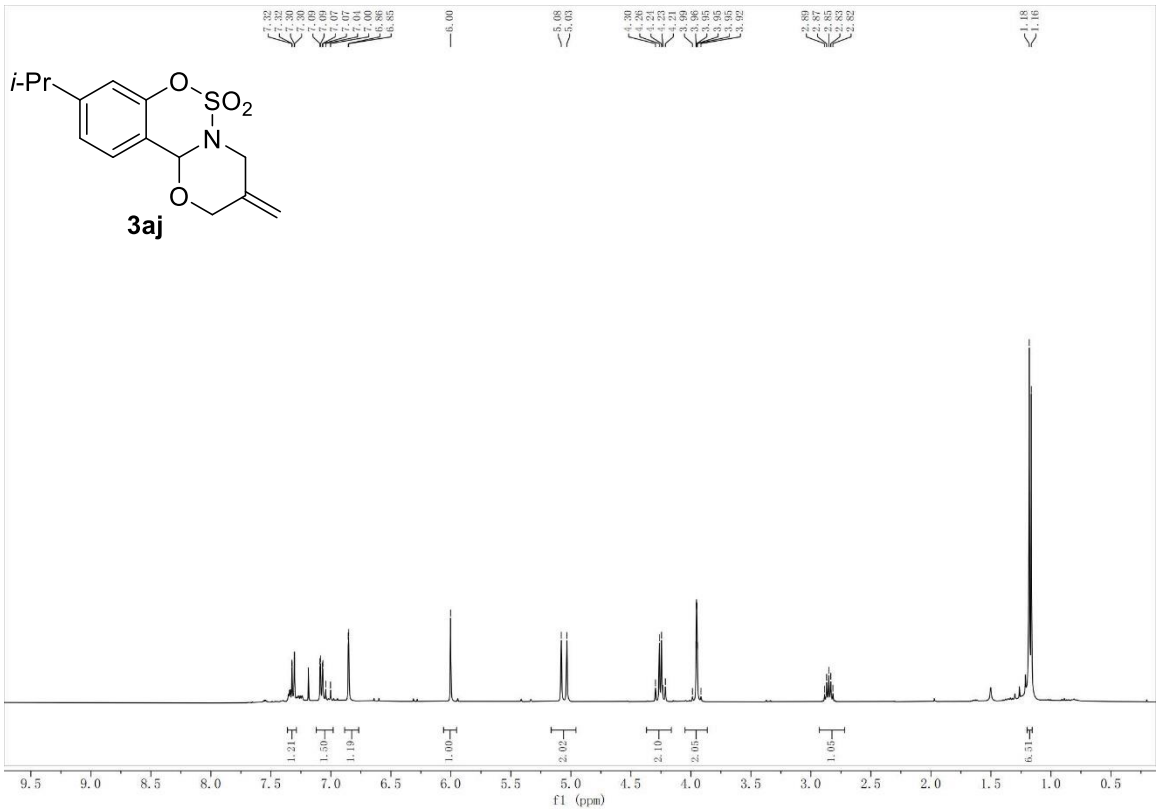

OMe
O
SO2
N
O
3ag
7.17
7.15
7.13
6.99
6.99
6.98
6.97
6.97
6.91
6.93
6.92
6.91
6.07
5.69
5.61
4.28
4.25
4.24
4.20
4.00
3.97
3.95
3.93
3.90
3.82
1.04
2.03
1.09
2.06
2.15
2.13
3.07
f1 (ppm)

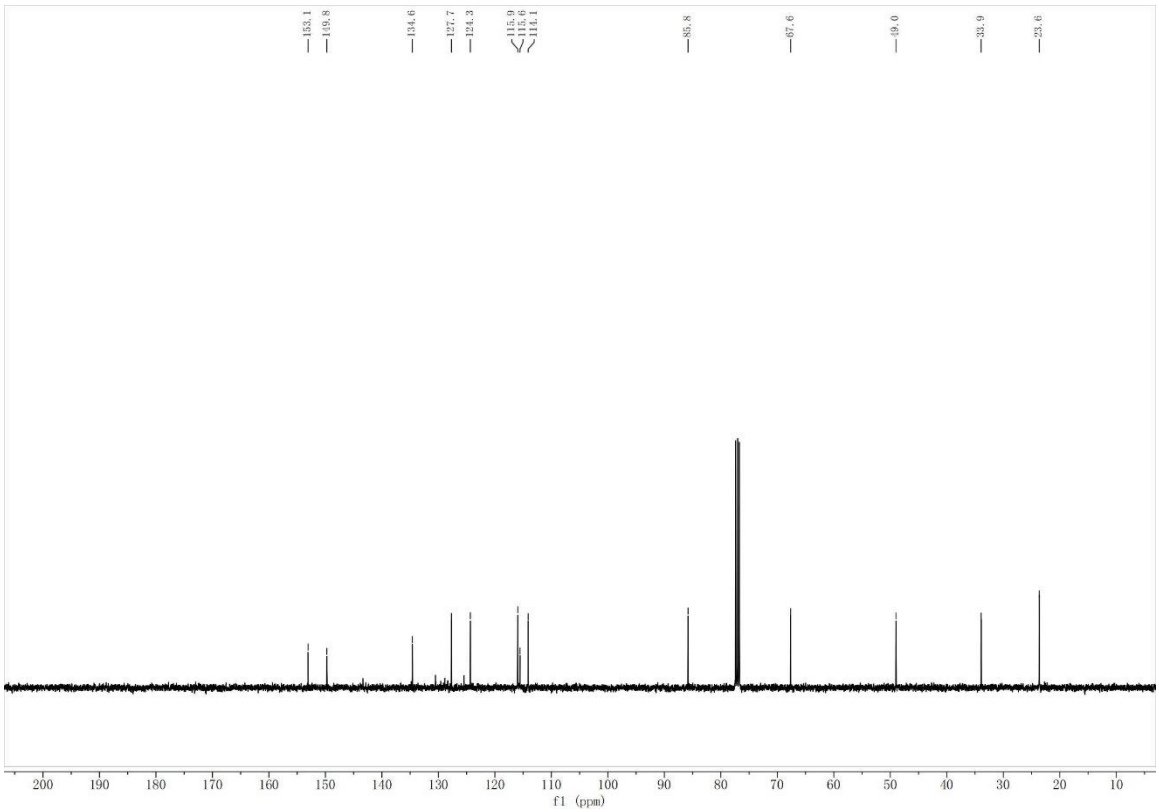

148.5
139.5
134.5
125.7
119.2
118.6
114.2
113.4
85.8
67.5
56.3
49.0
f1 (ppm)

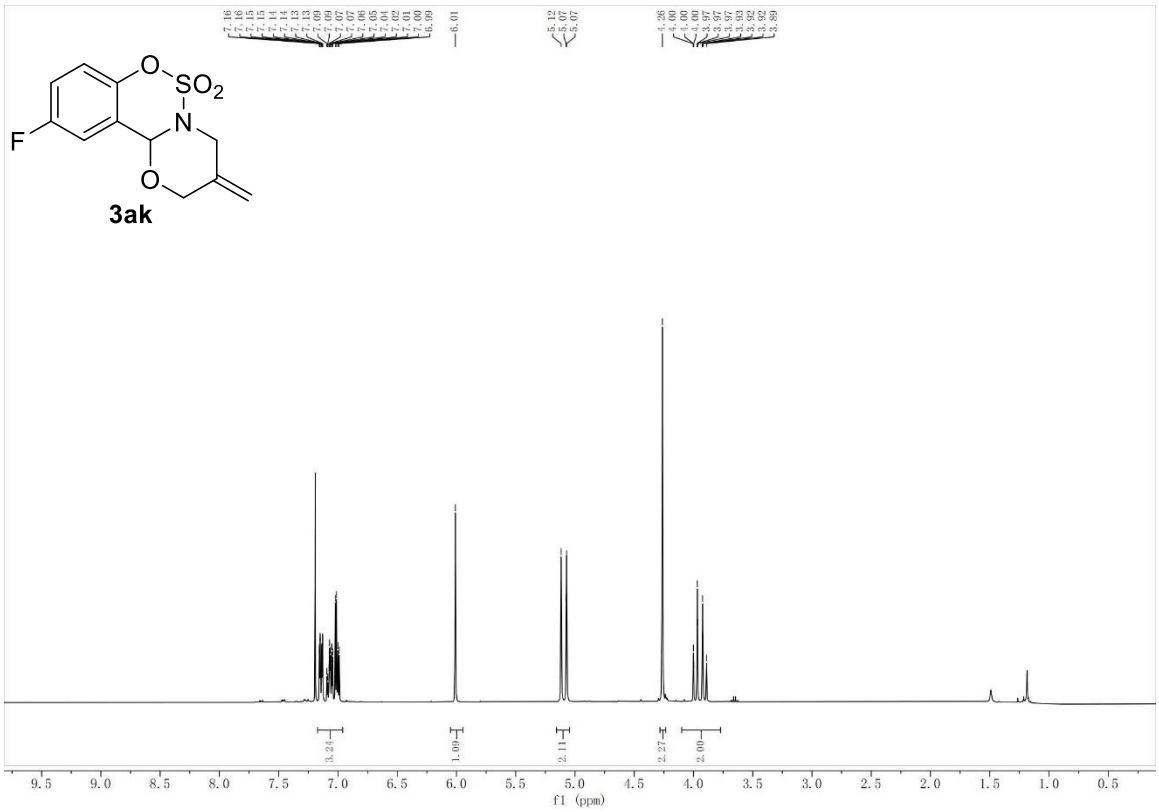

t-Bu
O
SO2
N
O
3ah
f1 (ppm)
f1 (ppm)

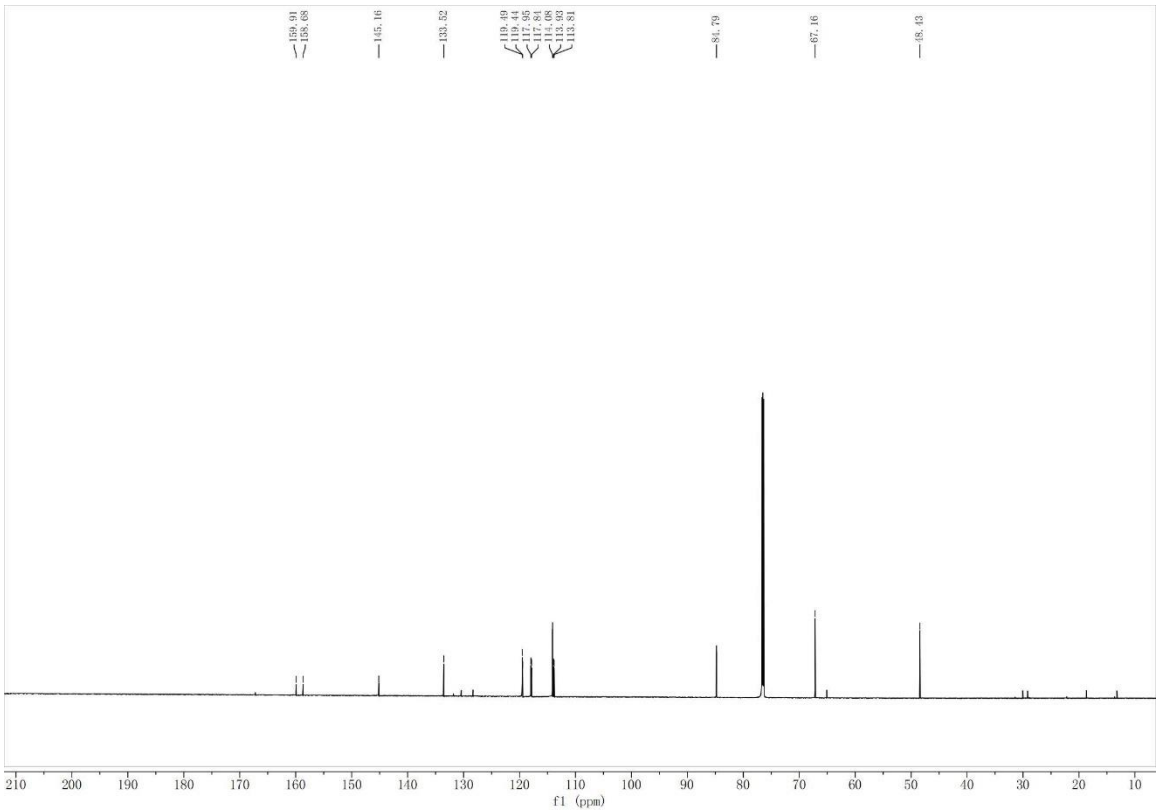

t-Bu
O
SO2
N
O
3ai
f1 (ppm)

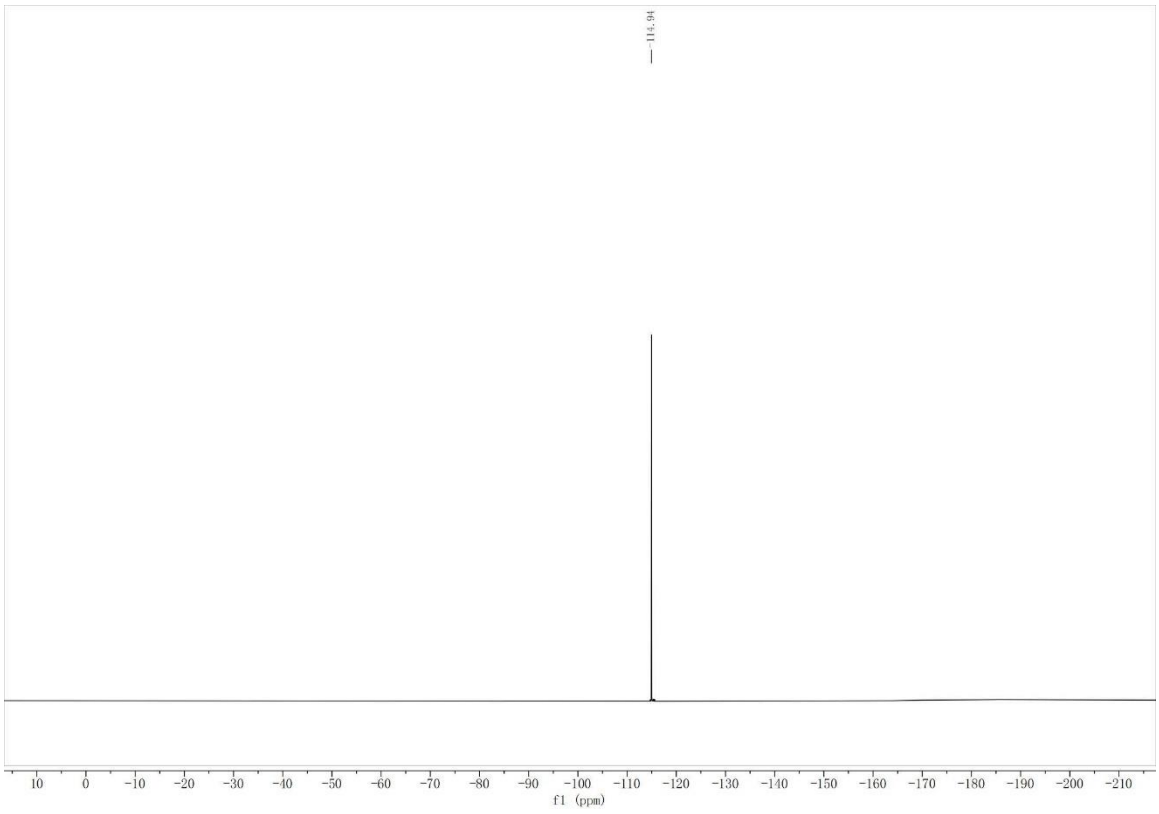

f1 (ppm)

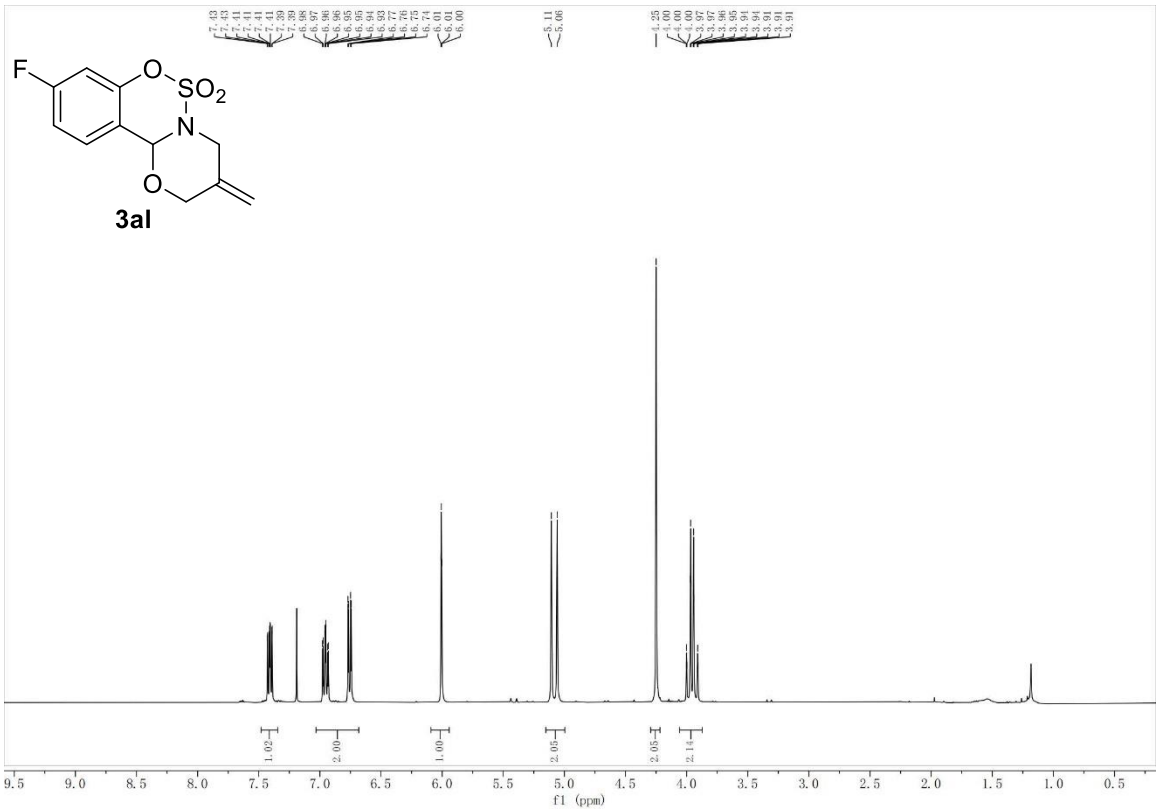

i-Pr
O
SO2
N
O
3aj
f1 (ppm)


f1 (ppm)


F
O
SO2
N
O
3ak
f1 (ppm)


f1 (ppm)


-114.94
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


F
O
SO2
N
O
3al
7.43
7.43
7.41
7.41
7.41
7.41
7.39
7.39
6.98
6.97
6.96
6.96
6.95
6.95
6.94
6.93
6.77
6.76
6.75
6.74
6.01
6.01
6.00
5.11
5.06
4.25
4.00
4.00
3.97
3.97
3.96
3.95
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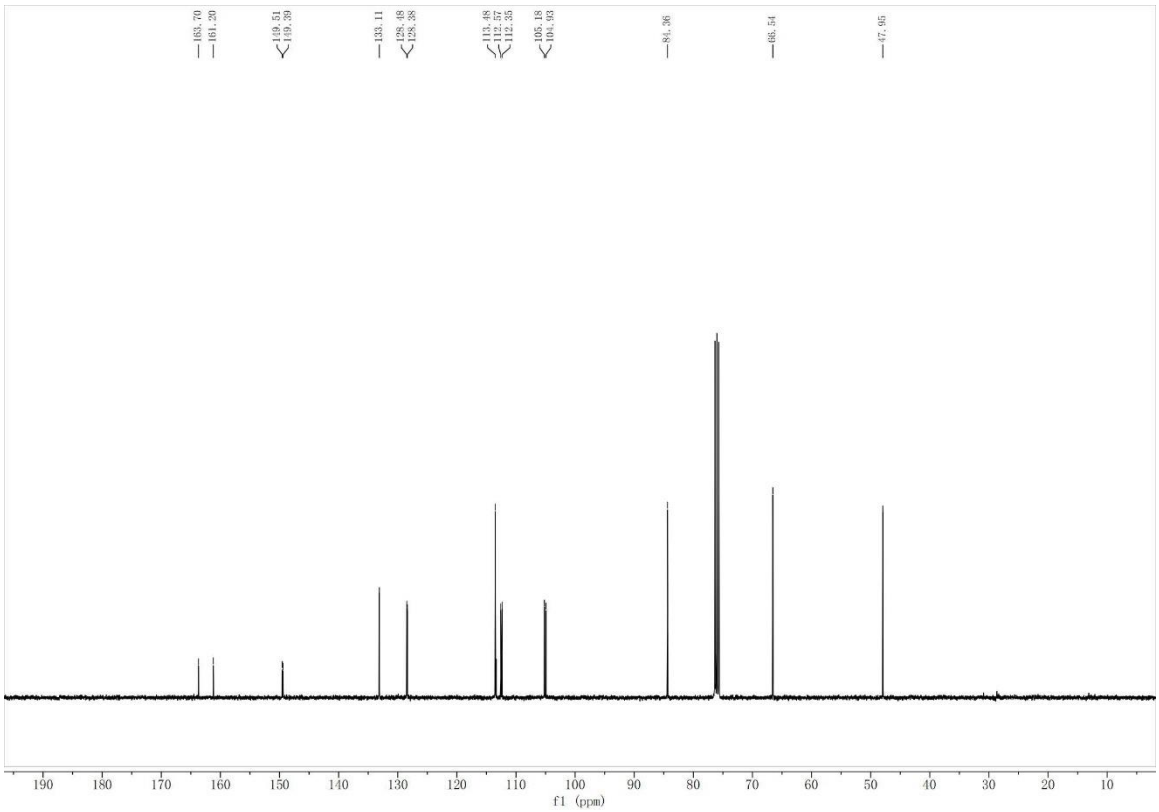
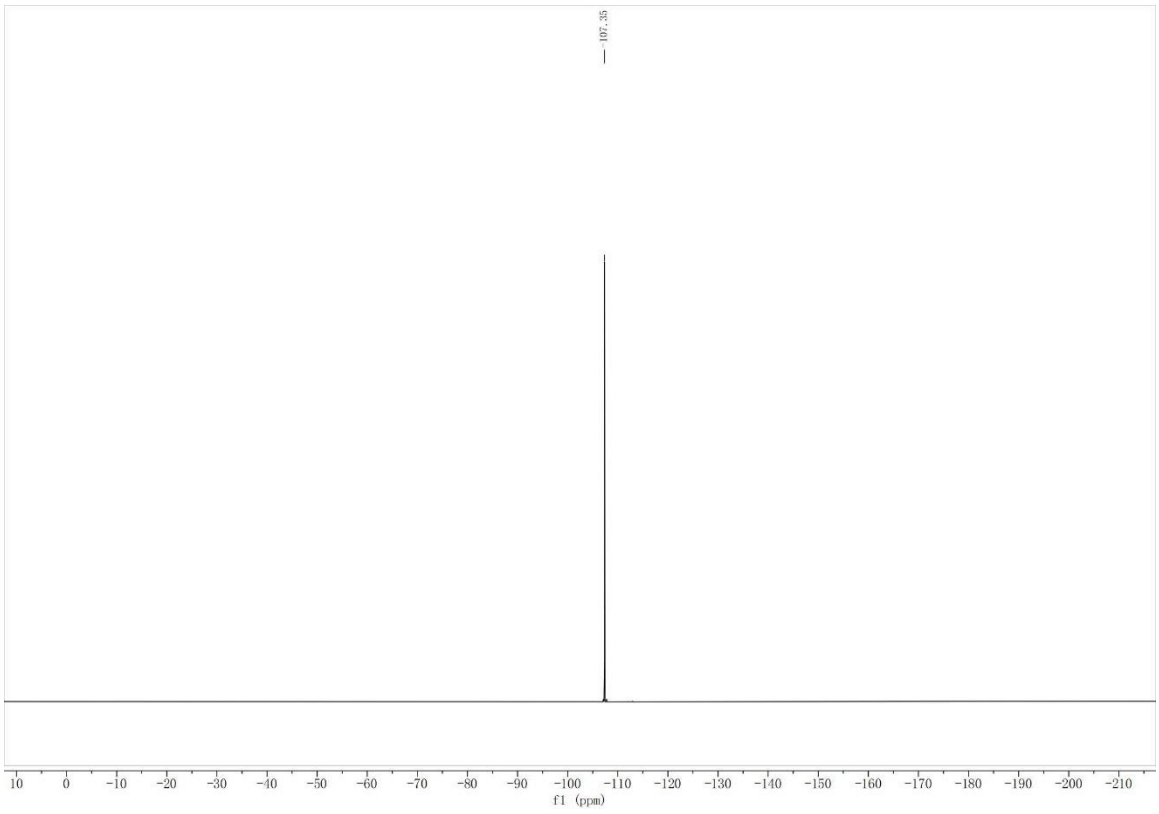
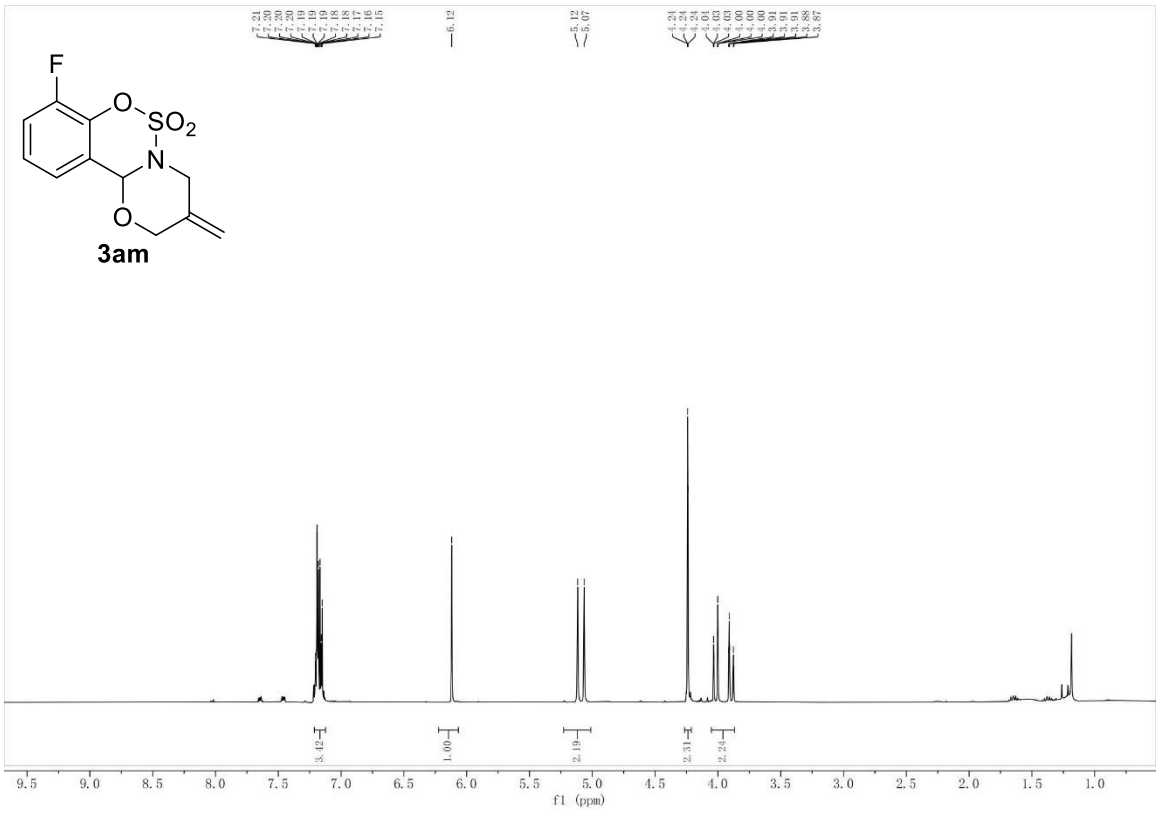
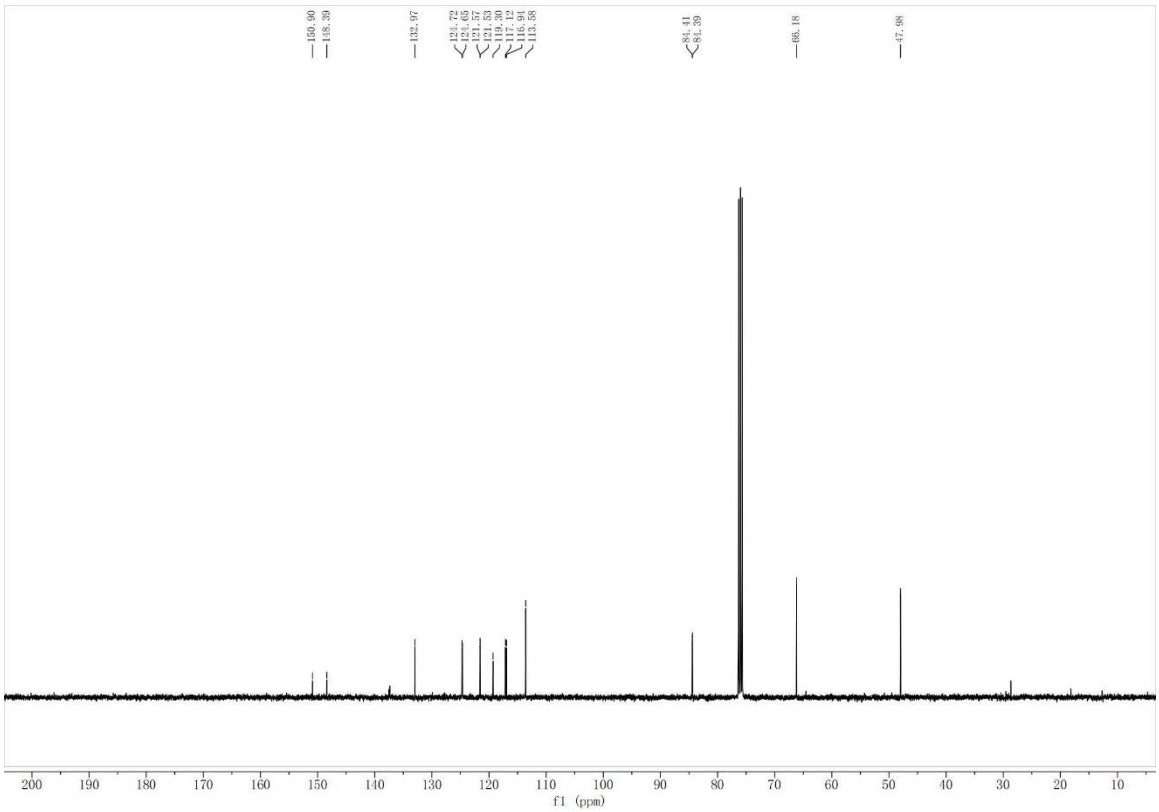
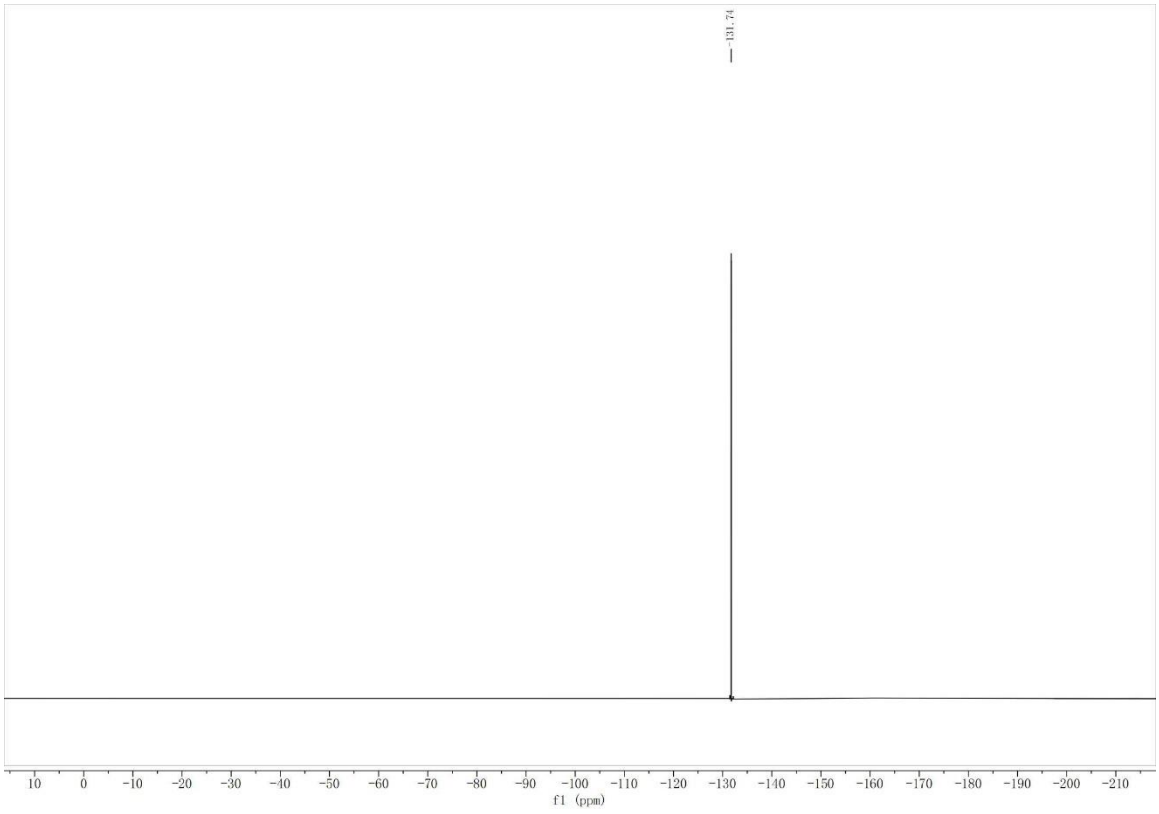
2.00
1.00
2.05
2.05
2.14
f1 (ppm)

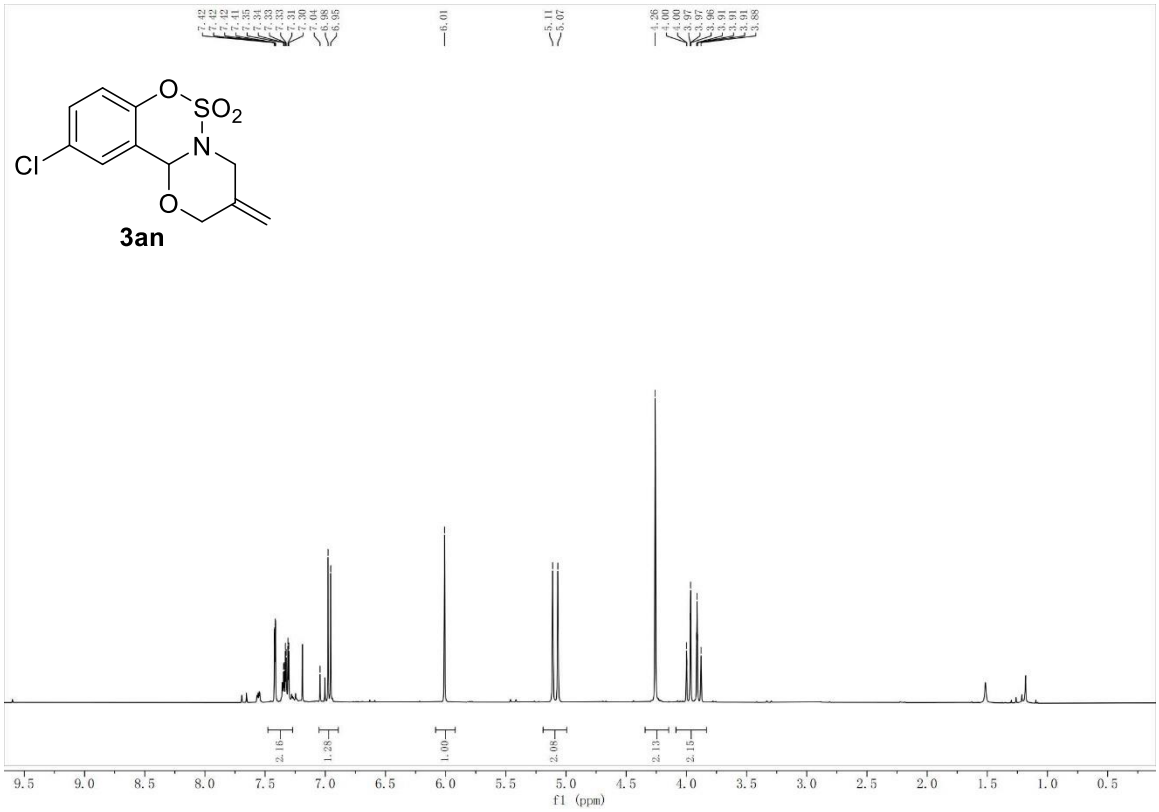

163.70
161.20
149.51
149.39
133.11
128.48
128.38
113.48
112.57
112.35
105.18
104.93
84.36
68.54
47.95
f1 (ppm)

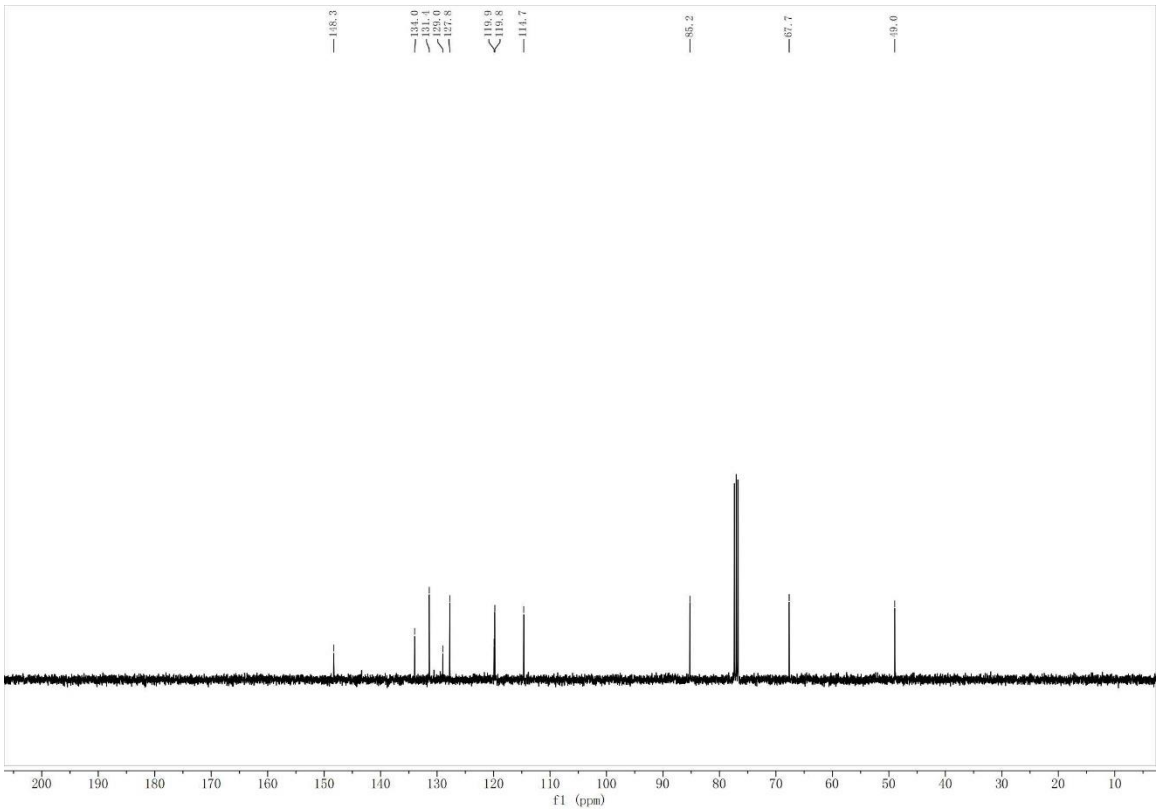

107.35
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

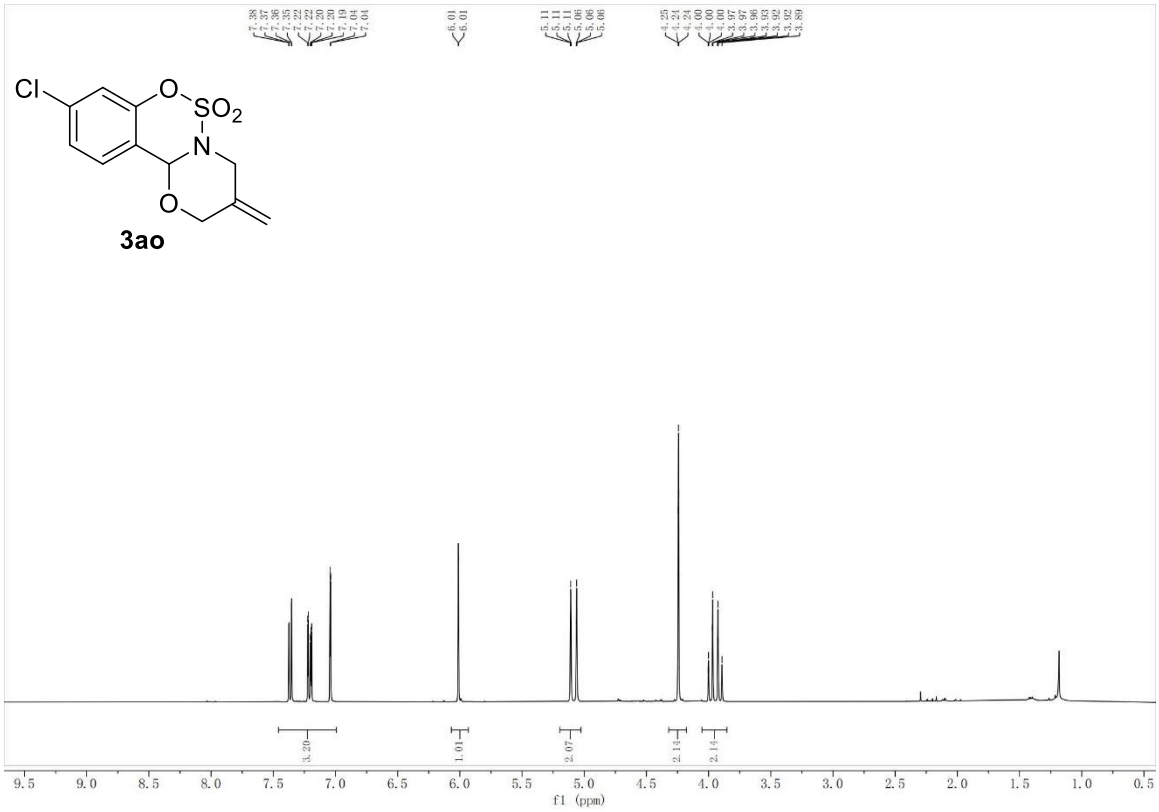

F
O
SO2
N
O
3am
7.21
7.20
7.19
7.18
7.17
7.16
7.15
6.12
5.12
5.07
4.24
4.01
4.00
3.91
3.88
3.87
3.42
1.00
2.19
2.31
2.24
f1 (ppm)

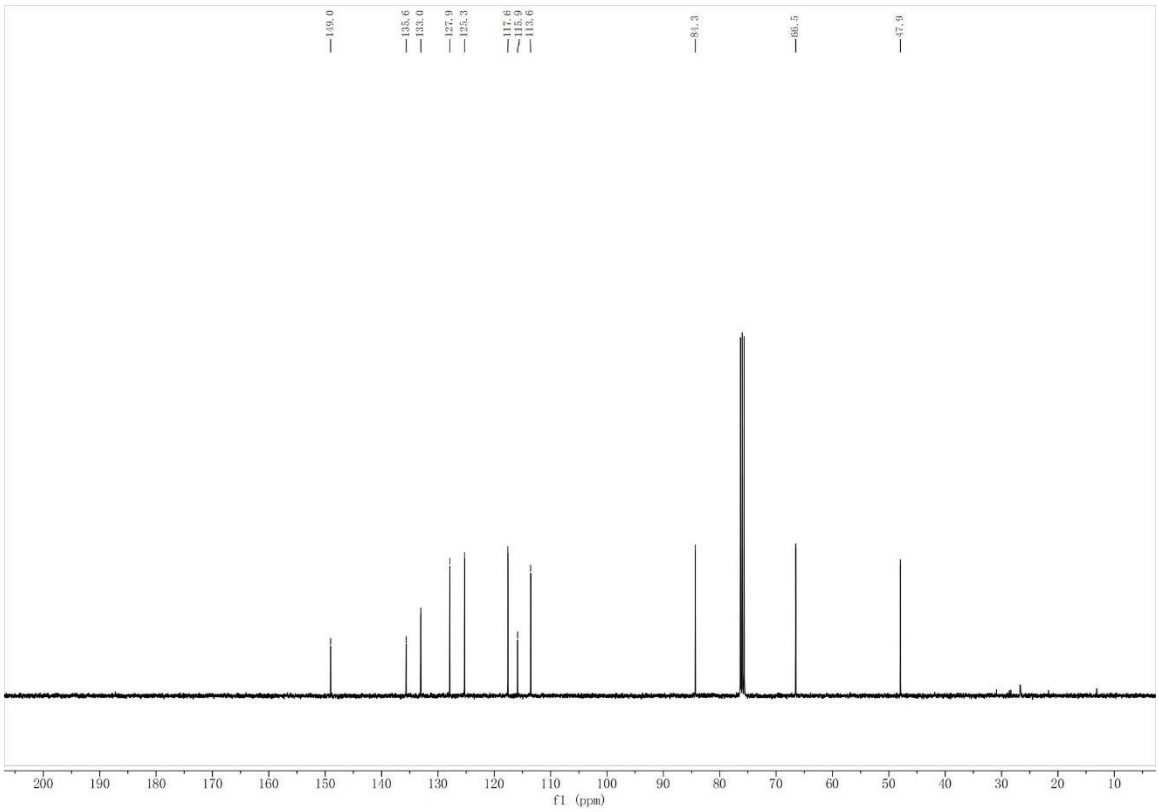

150.90
148.39
132.97
124.72
124.65
121.75
121.53
119.30
117.12
116.94
114.98
84.41
82.39
66.18
47.98
f1 (ppm)

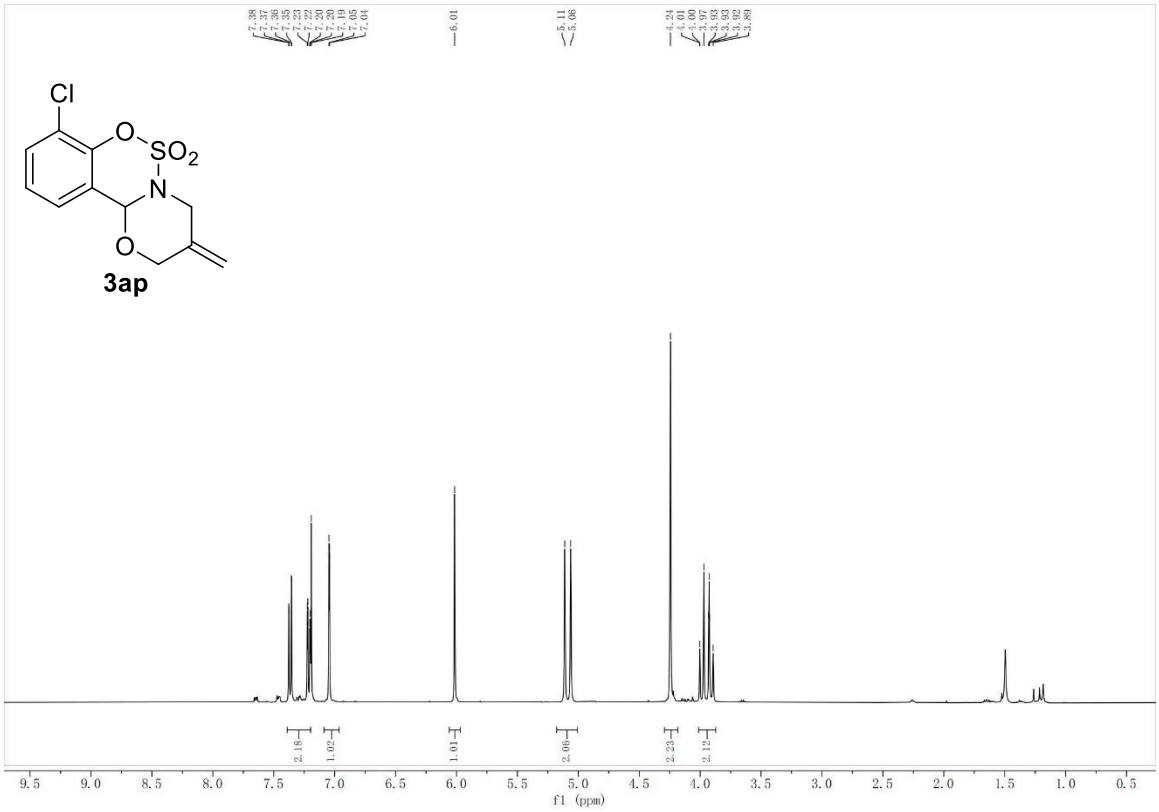

131.74
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

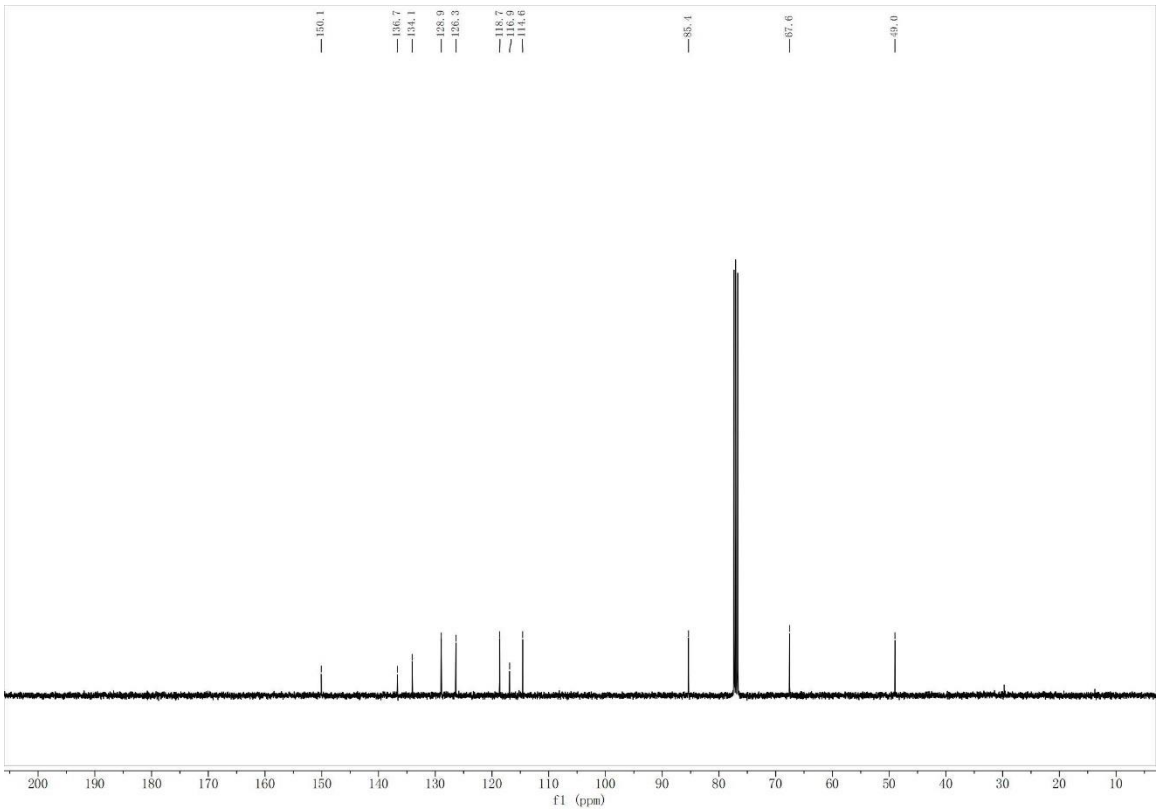

7.42
7.42
7.42
7.41
7.35
7.34
7.33
7.33
7.31
7.30
7.04
6.98
6.95
6.01
5.11
5.07
4.26
4.00
4.00
3.97
3.96
3.91
3.91
3.88
O
SO2
N
Cl
O
3an
2.16
1.28
1.09
2.08
2.13
2.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

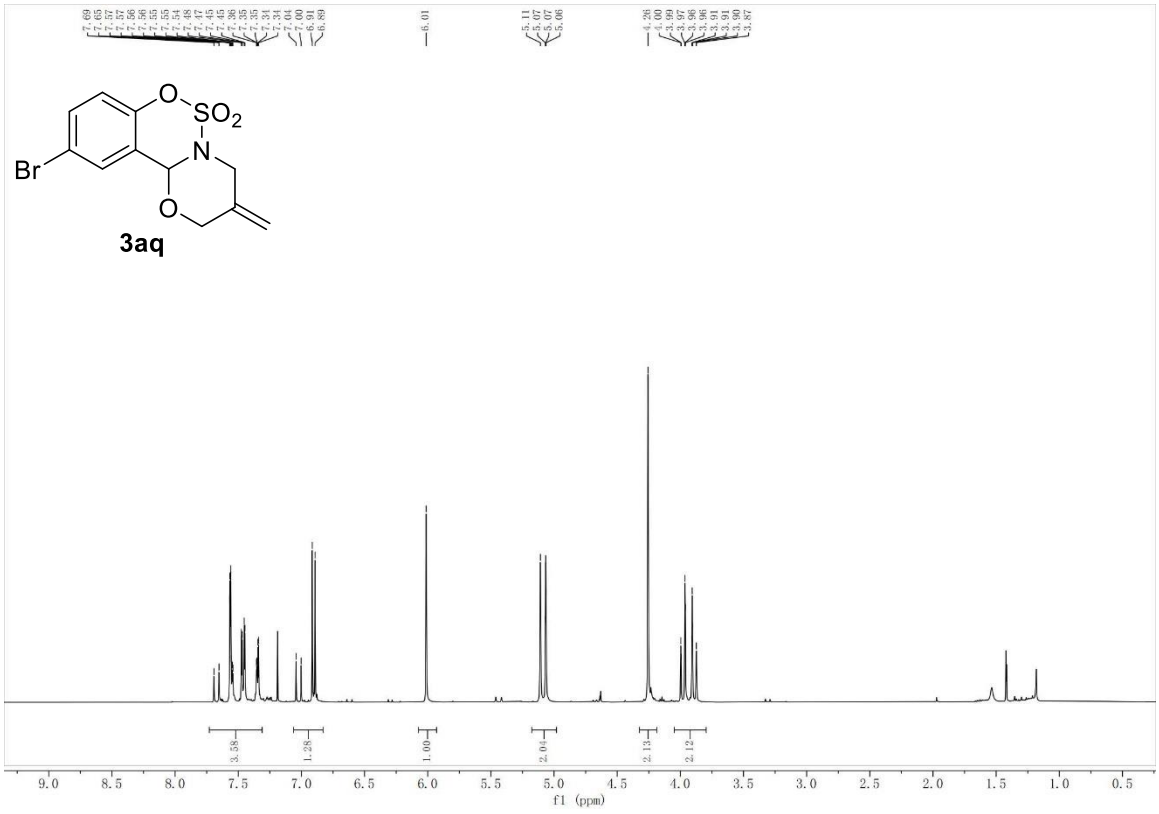

148.3
134.0
131.4
129.0
127.8
119.9
119.8
114.7
85.2
67.7
49.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

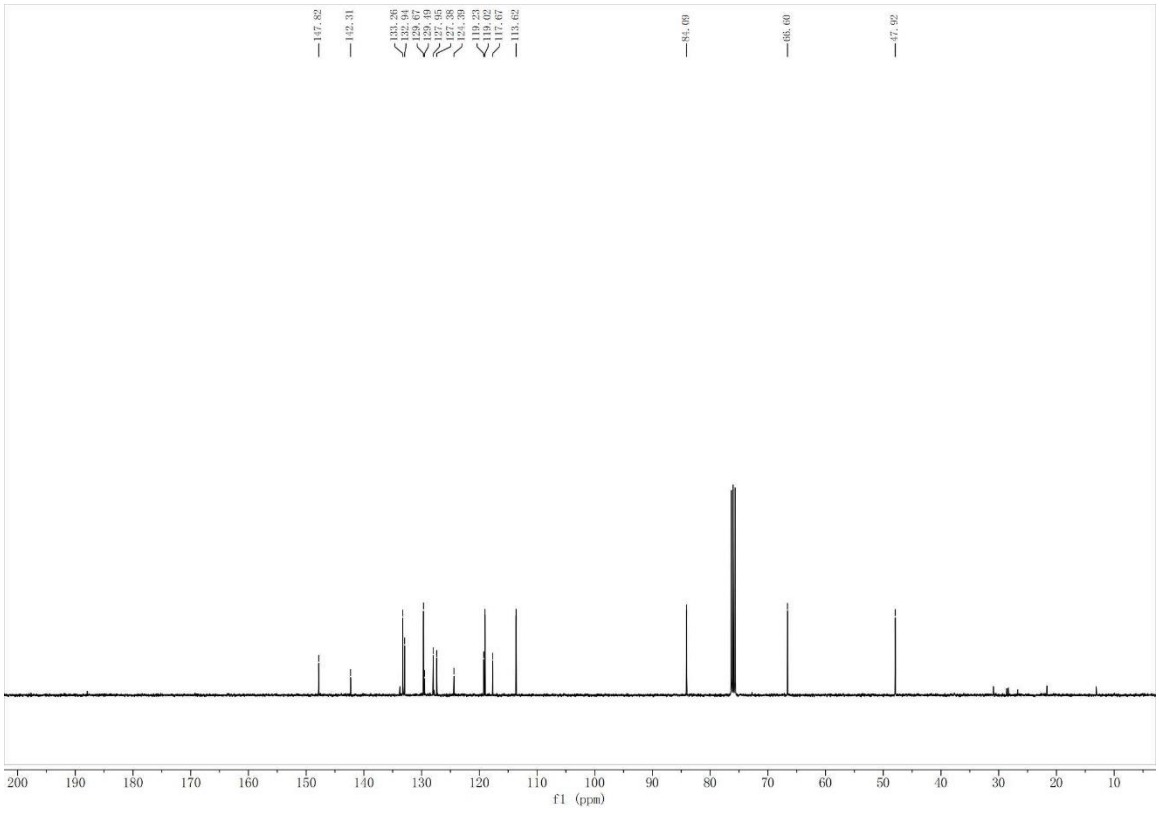

Cl
O
SO2
N
O
3ao
7.38
7.37
7.36
7.35
7.22
7.22
7.20
7.20
7.19
7.04
7.04
6.01
6.01
5.11
5.11
5.06
5.06
5.06
4.25
4.24
4.24
4.00
4.00
3.97
3.97
3.96
3.93
3.92
3.92
3.89
3.20
1.01
2.07
2.14
2.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

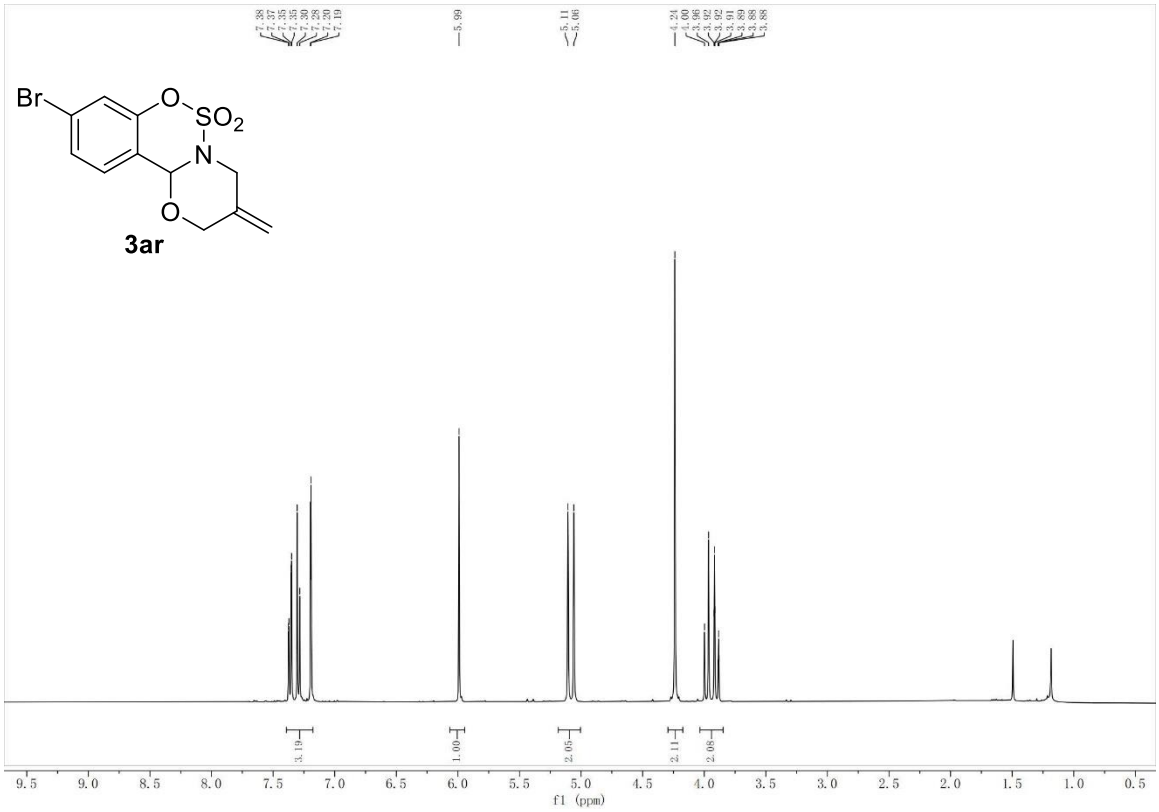

149.0
135.6
133.0
127.9
125.3
117.6
115.9
113.6
84.3
66.5
47.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

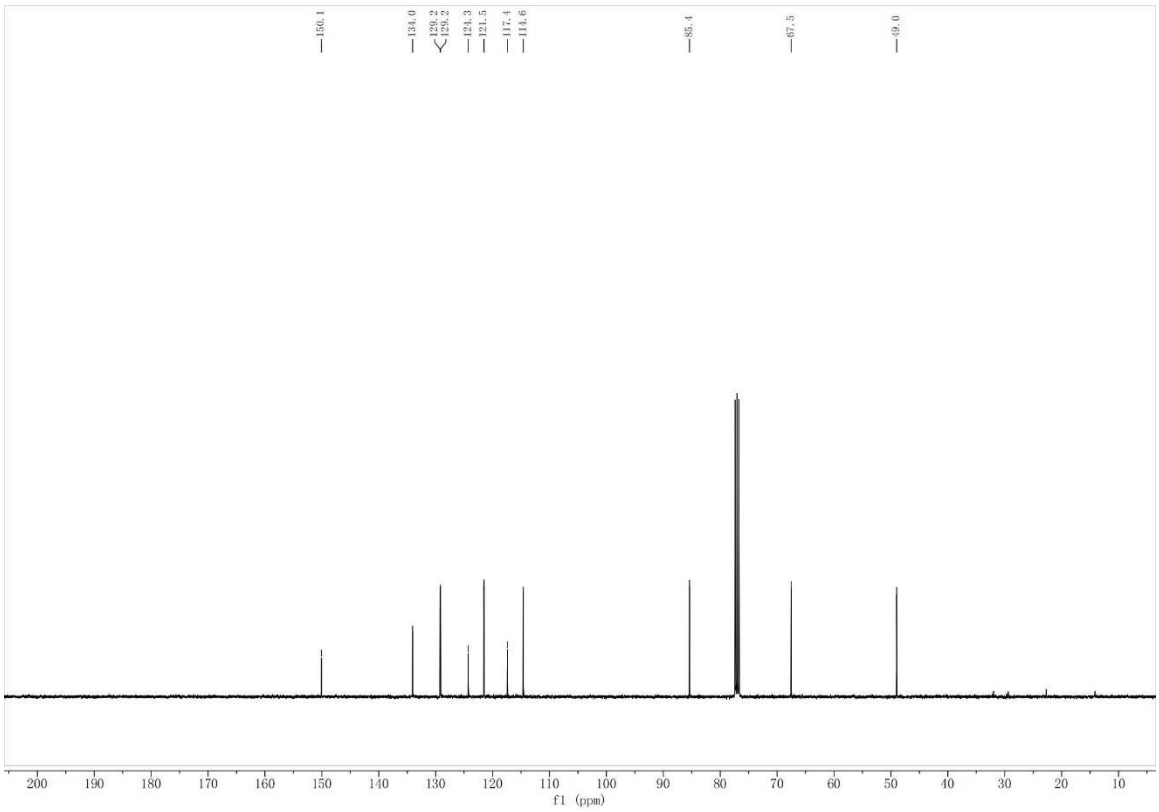

7.38
7.37
7.36
7.35
7.23
7.22
7.20
7.19
7.05
7.04
6.01
5.11
5.06
4.24
4.01
4.00
3.97
3.95
3.93
3.92
3.89
Cl
O
SO2
N
O
3ap
2.18
1.02
1.01
2.06
2.23
2.12
f1 (ppm)

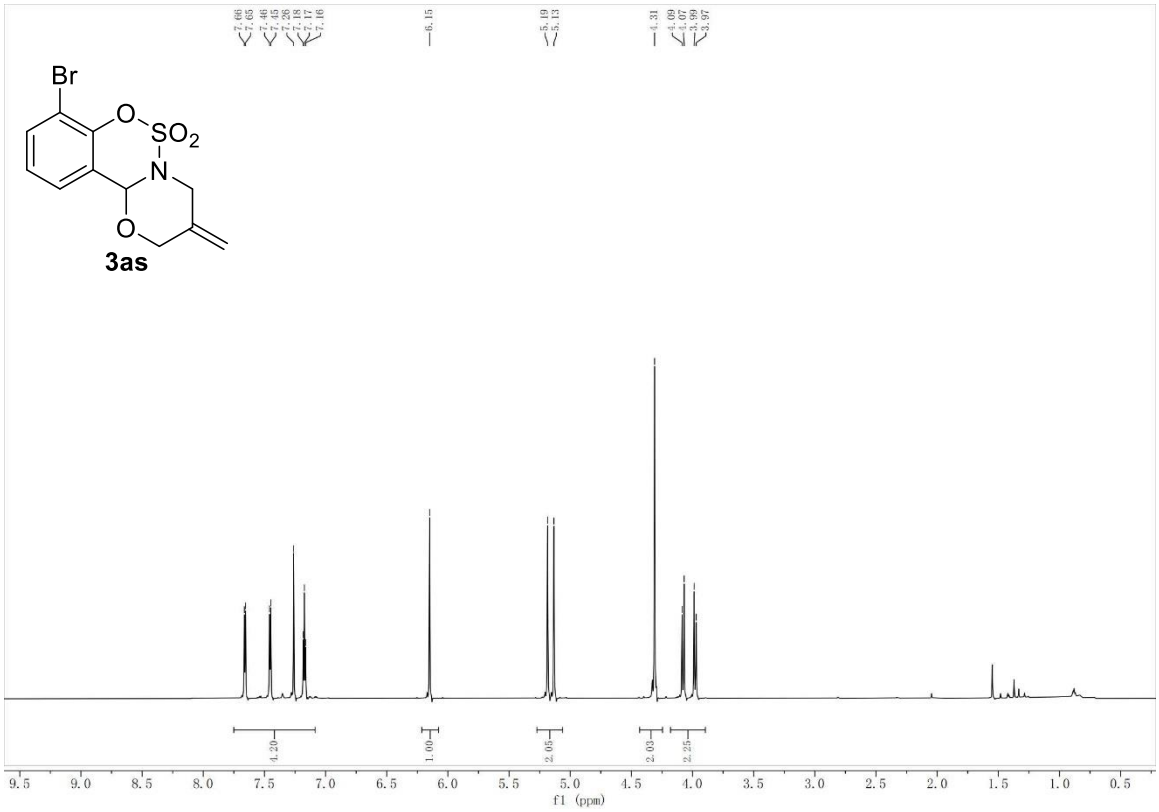

150.1
136.7
134.1
128.9
126.3
118.7
116.9
114.6
85.4
67.6
49.0
f1 (ppm)

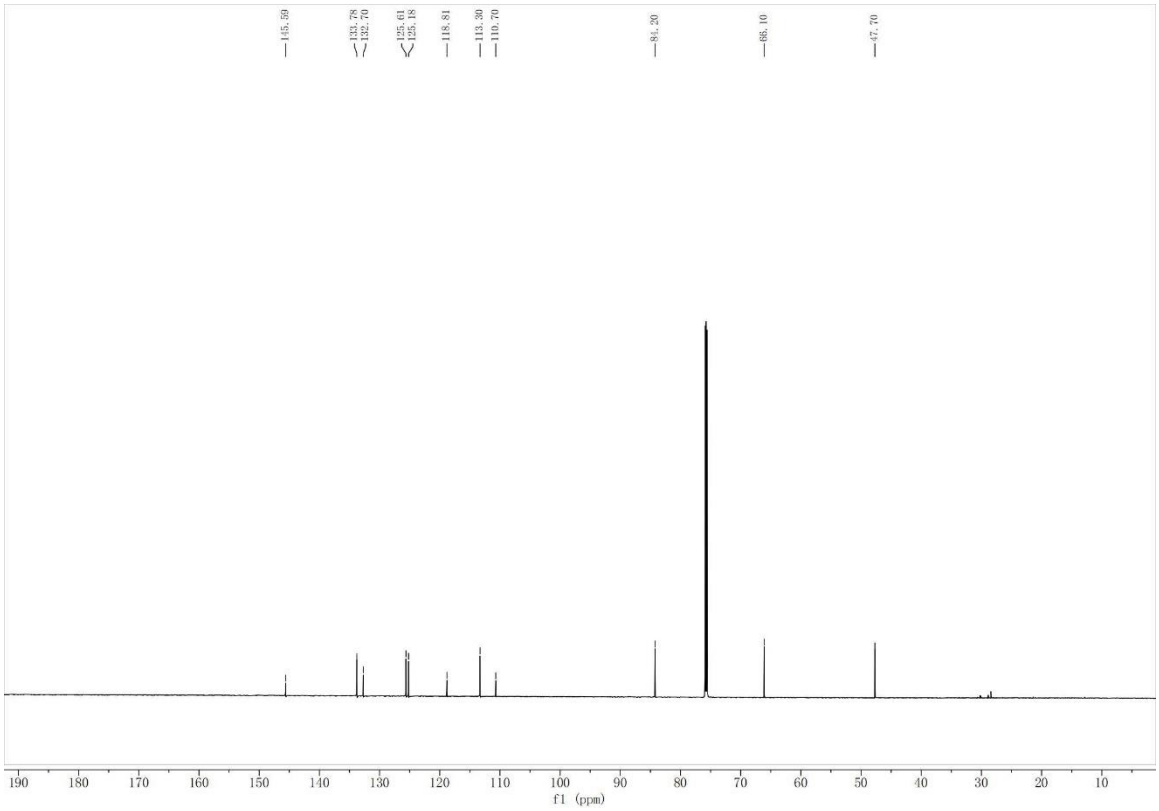

Br
O
SO2
N
O
3aq
f1 (ppm)

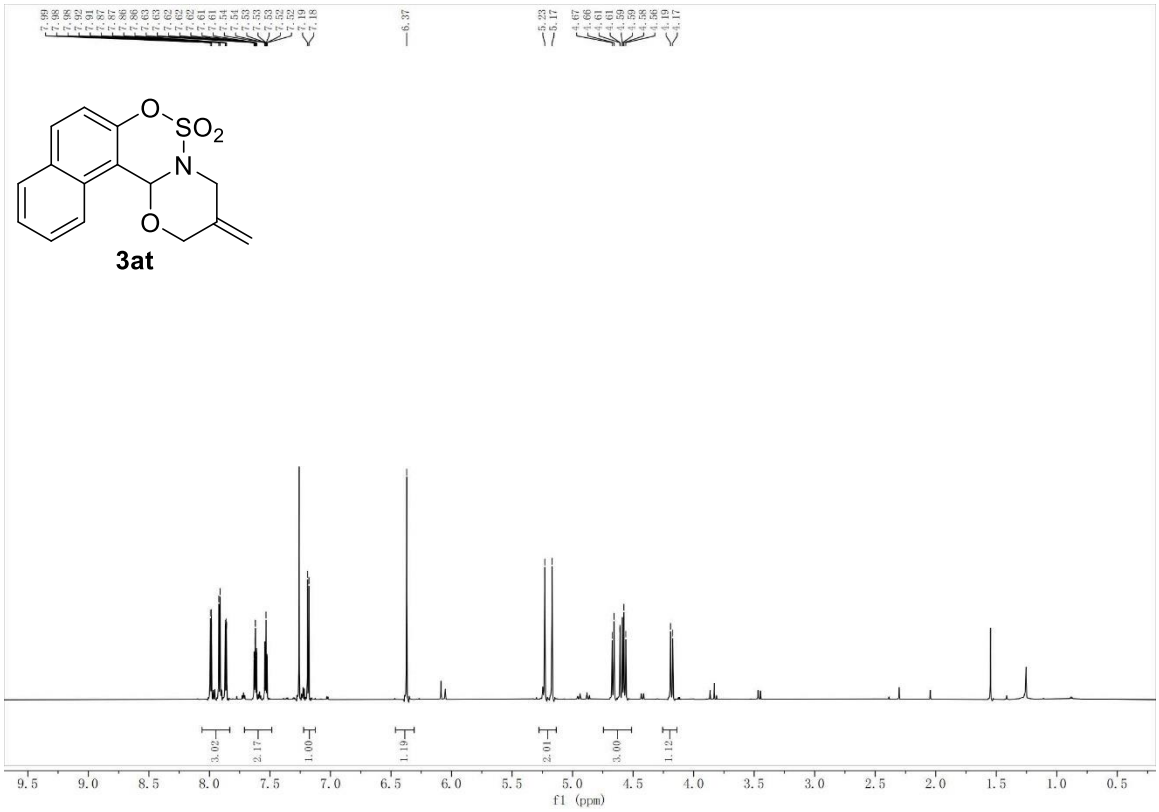

f1 (ppm)

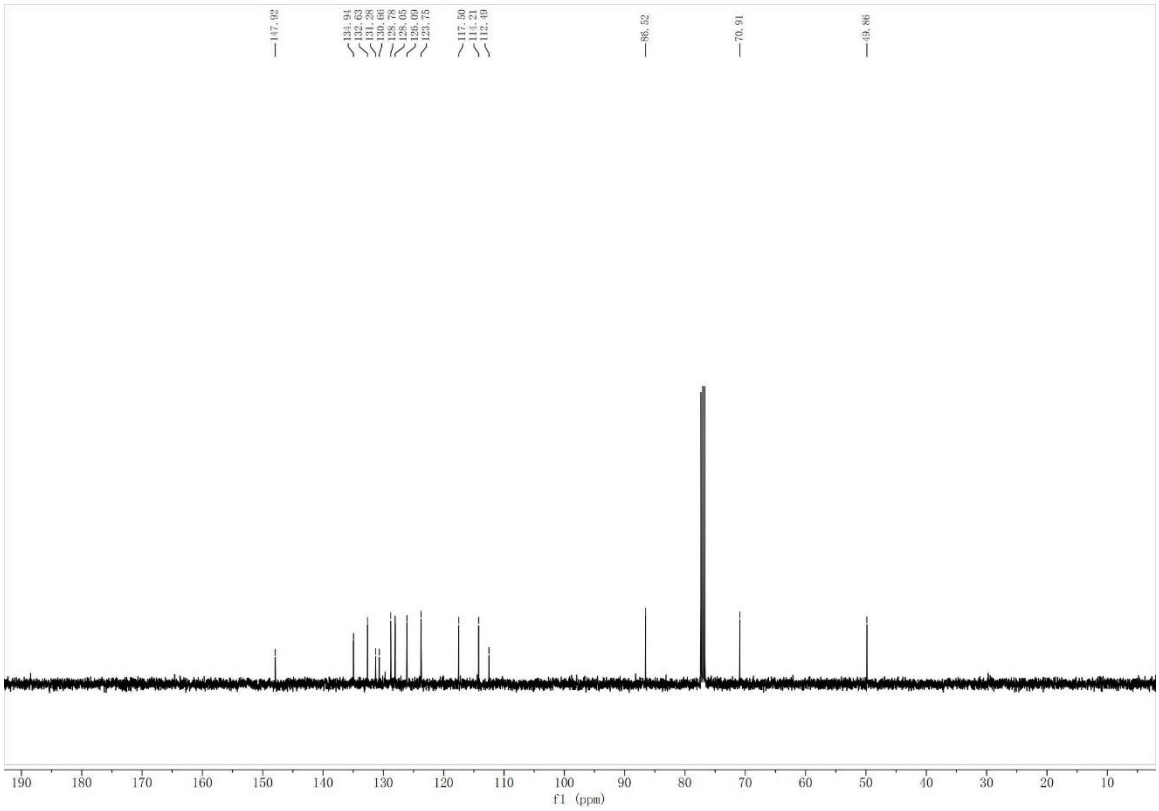

7.38
7.37
7.35
7.35
7.30
7.28
7.20
7.19
5.99
5.11
5.06
4.24
4.00
3.96
3.92
3.92
3.91
3.89
3.88
3.88
Br
O
SO2
N
O
3ar
3.19
1.00
2.05
2.11
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

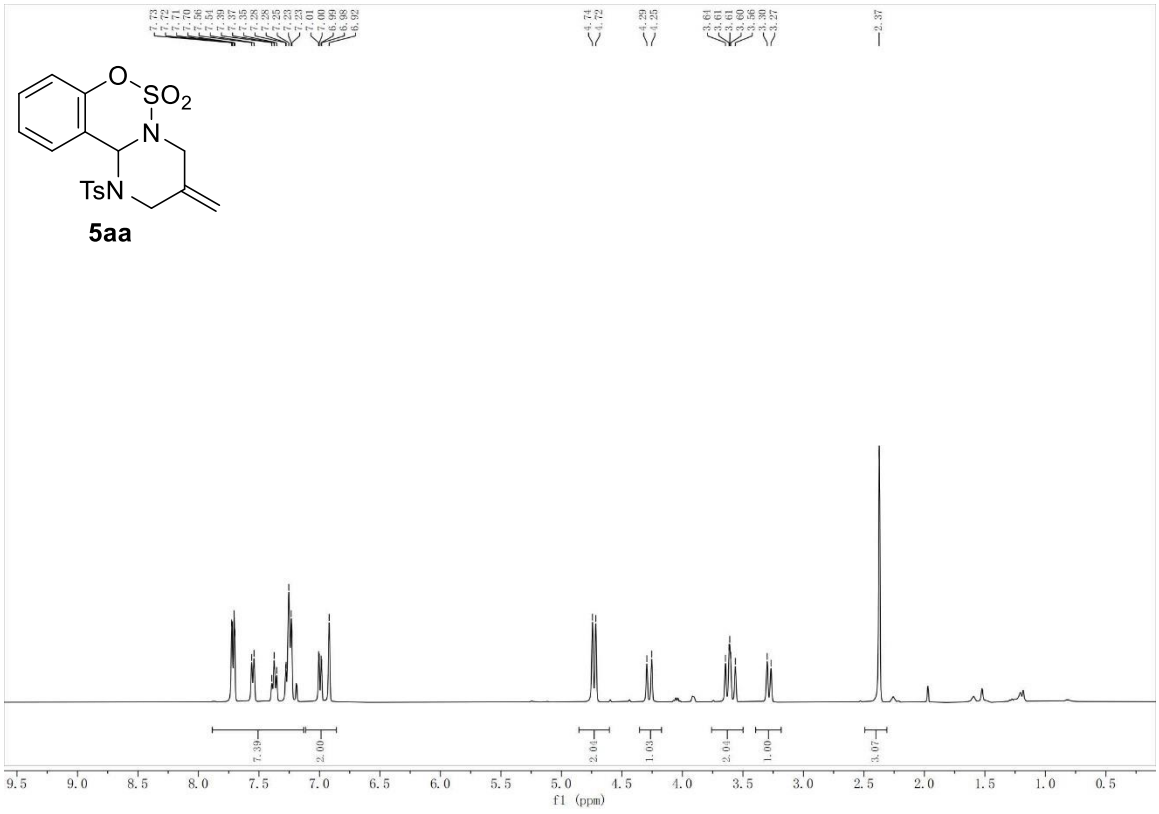

150.1
134.0
129.2
129.2
124.3
121.5
117.4
114.6
85.4
67.5
49.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

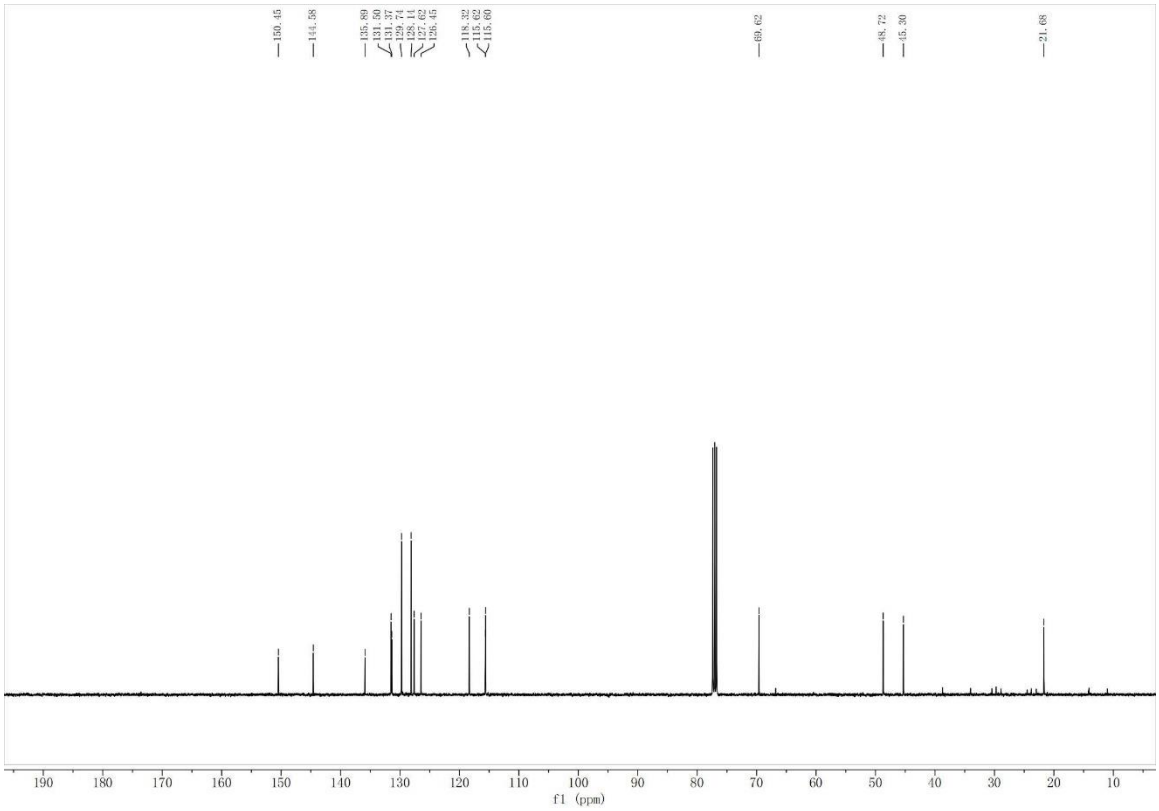

7.66
7.65
7.46
7.45
7.26
7.18
7.17
7.16
6.15
5.19
5.13
4.31
4.09
4.07
3.99
3.97
Br
O
SO2
N
O
3as
4.20
1.00
2.05
2.03
2.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


145.59
133.78
132.70
125.61
125.18
118.81
113.30
110.70
84.20
68.10
47.70
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.99
7.98
7.98
7.92
7.91
7.87
7.87
7.86
7.63
7.63
7.62
7.62
7.62
7.61
7.61
7.54
7.54
7.53
7.53
7.52
7.52
7.19
7.18
6.37
5.23
5.17
4.67
4.66
4.61
4.61
4.59
4.59
4.58
4.56
4.19
4.17
O
SO2
N
O
3at
3.02
2.17
1.00
1.19
2.01
3.00
1.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


147.92
134.94
132.63
131.28
130.66
128.78
128.05
126.09
123.75
117.50
114.21
112.49
86.52
70.91
49.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
SO2
N
TsN
5aa
7.73
7.72
7.71
7.70
7.56
7.54
7.39
7.37
7.35
7.28
7.25
7.23
7.03
7.01
7.00
6.99
6.98
6.92
4.74
4.72
4.29
4.25
3.64
3.61
3.61
3.60
3.56
3.30
3.27
2.37
7.39
2.09
2.04
1.03
2.04
1.09
3.07
f1 (ppm)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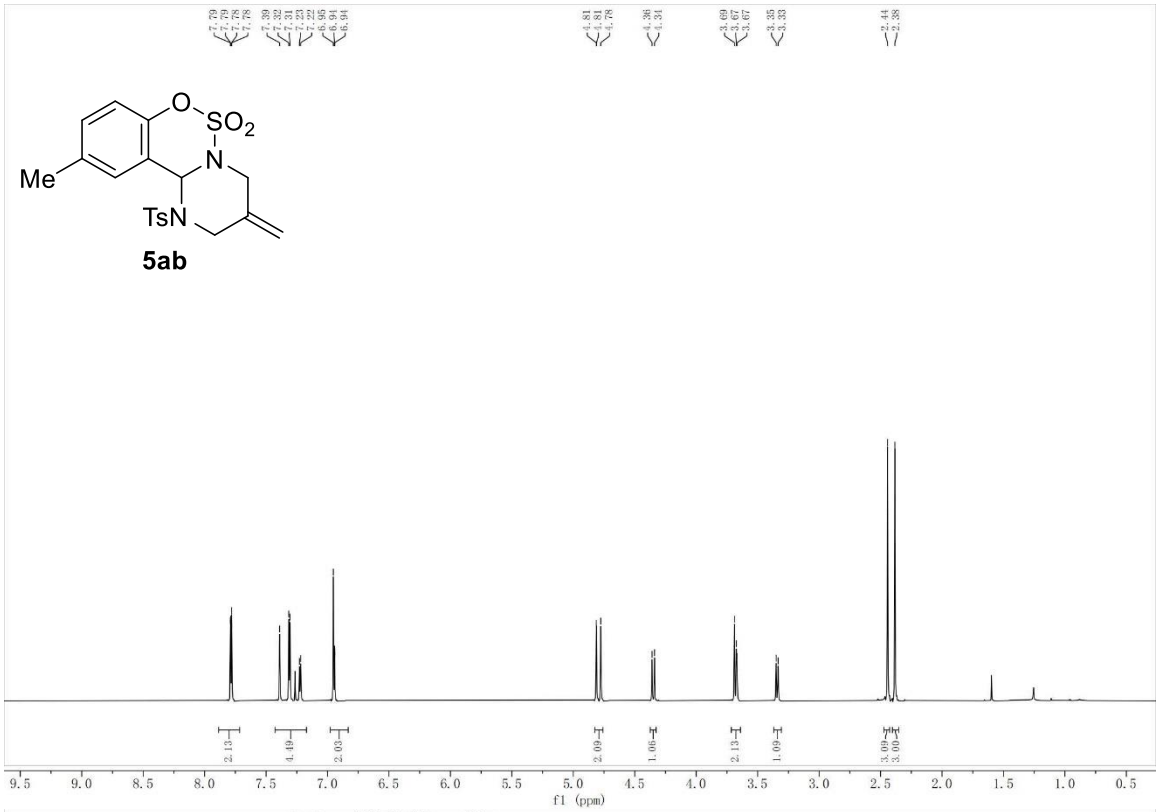
69.62
48.72
45.30
21.68
f1 (ppm)


Me
TsN
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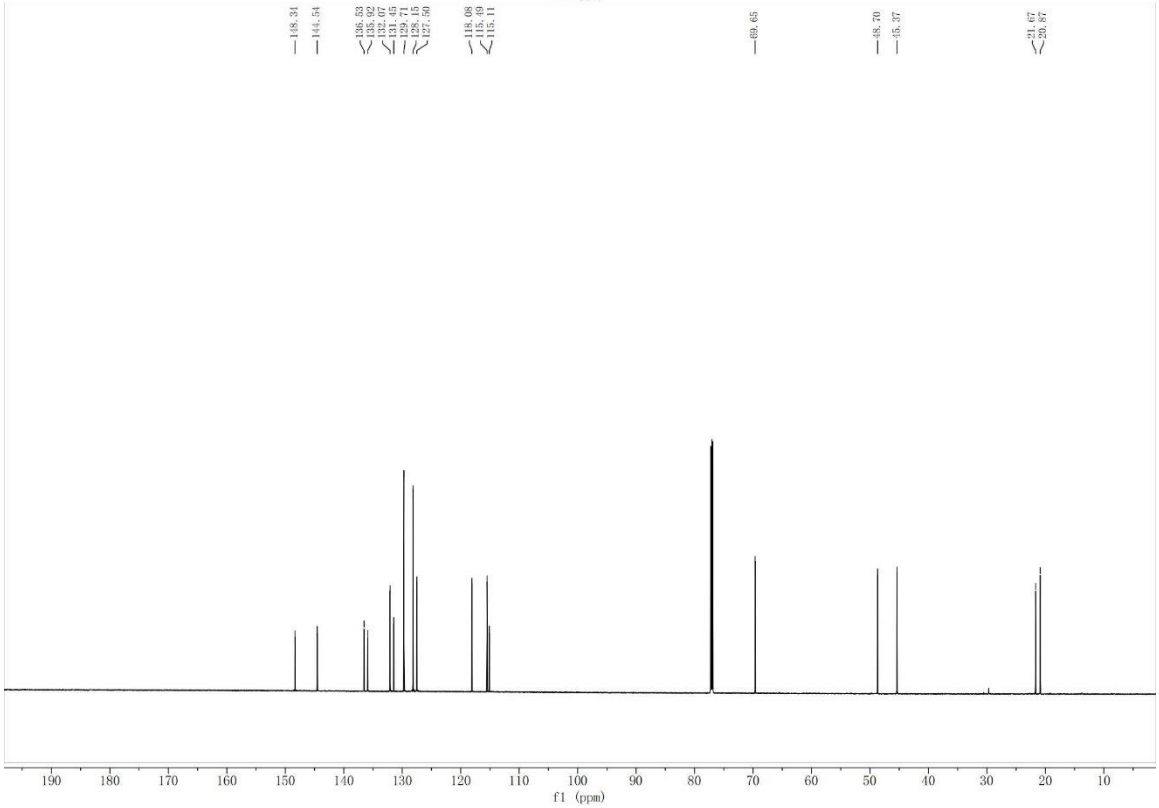
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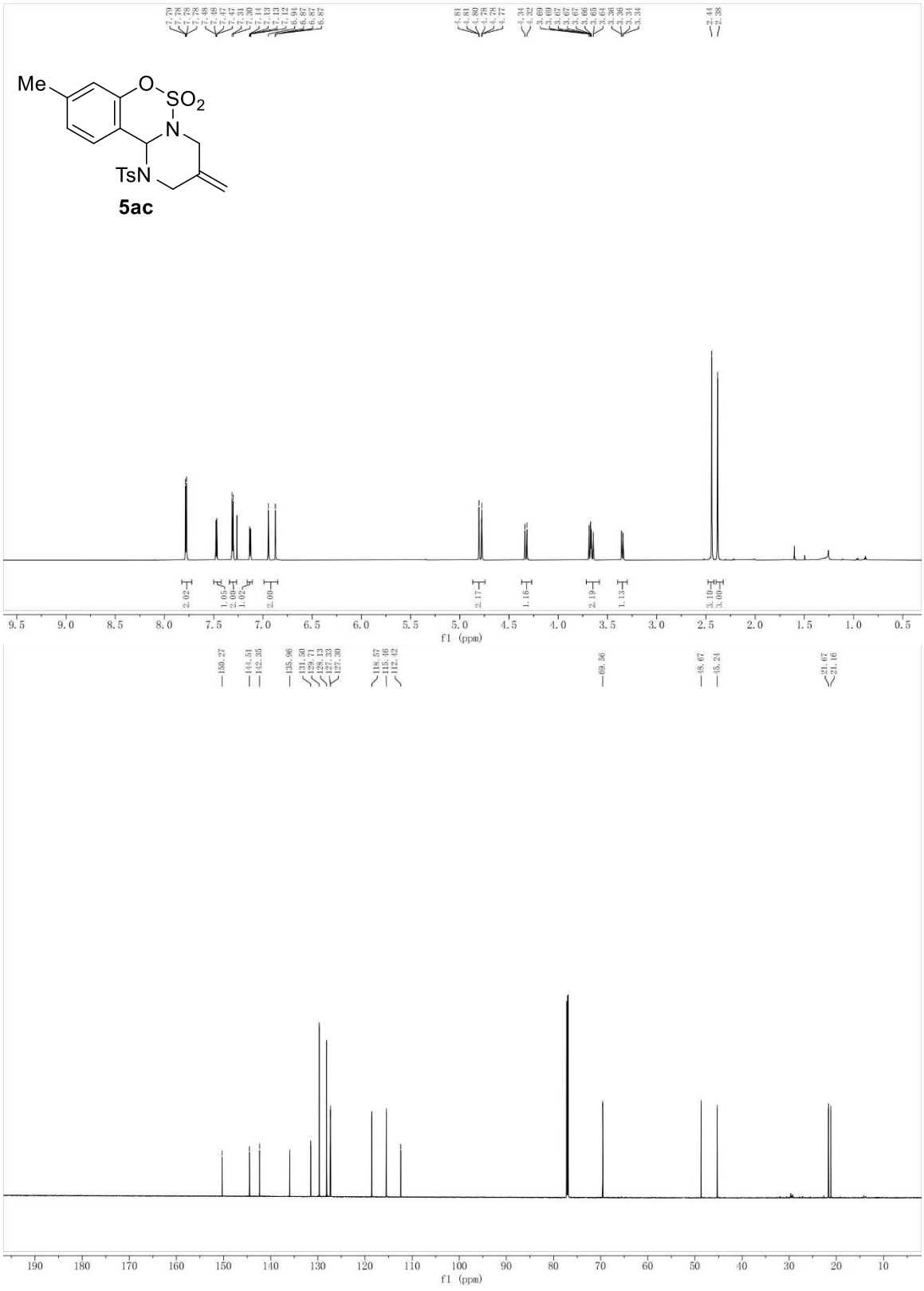
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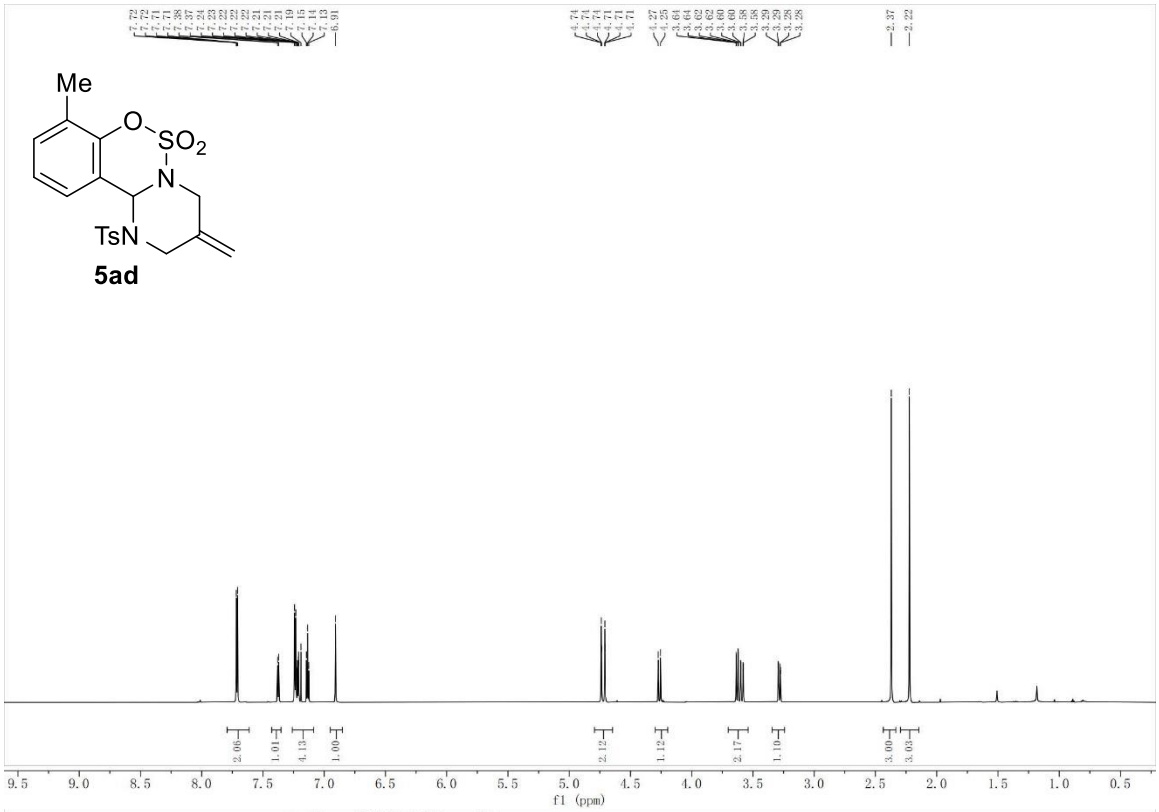
SO2
N
TsN
5ac
f1 (ppm)
f1 (ppm)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N
TsN
5ad
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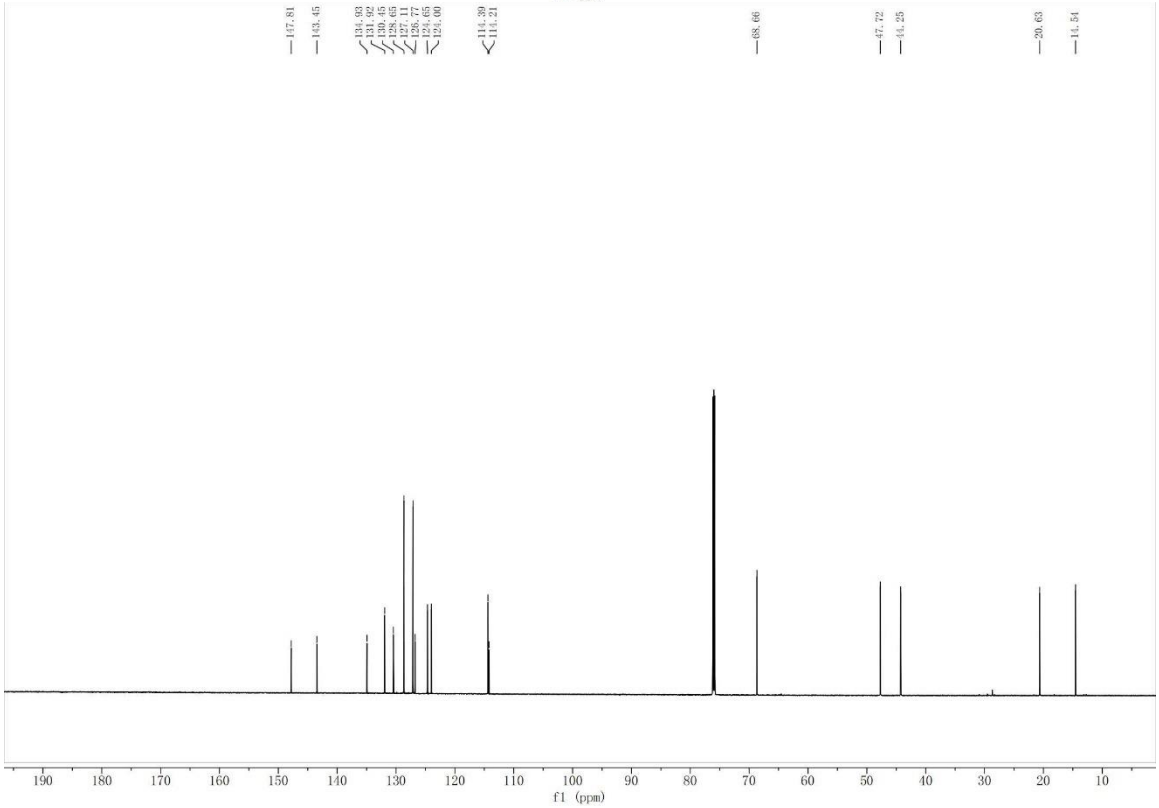
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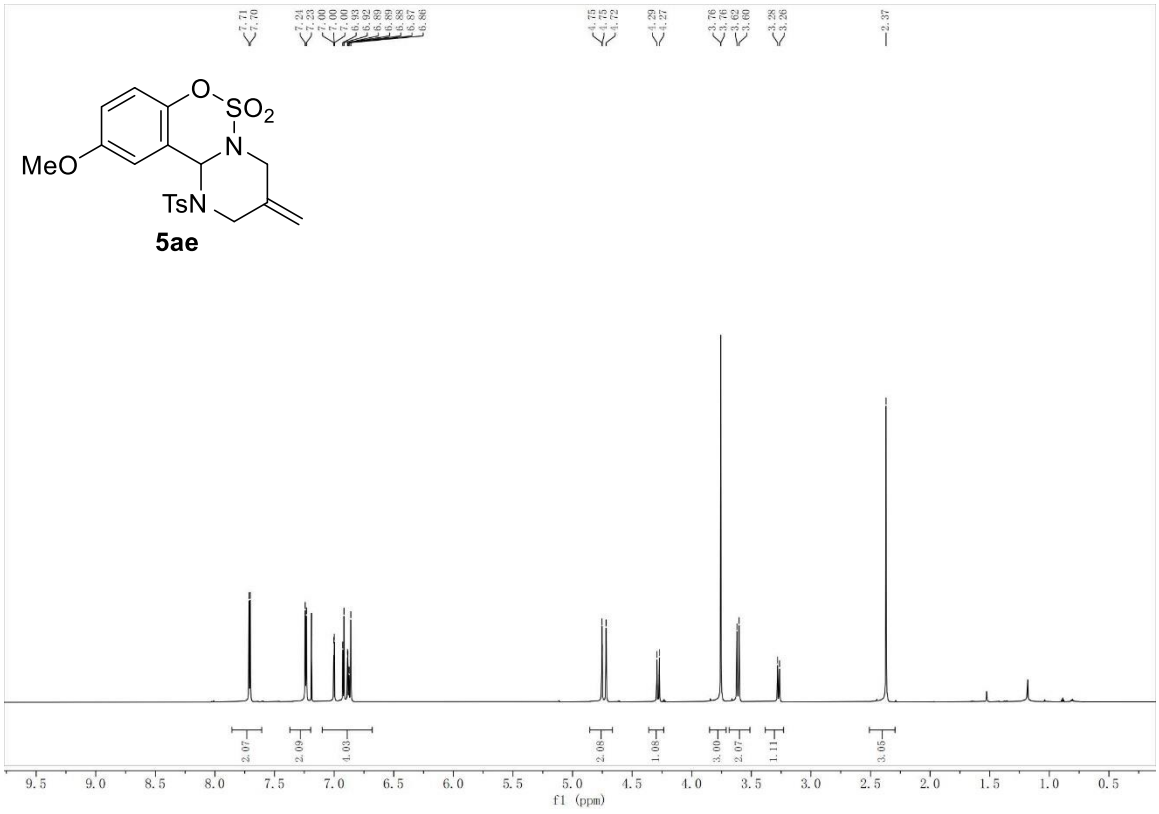
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O
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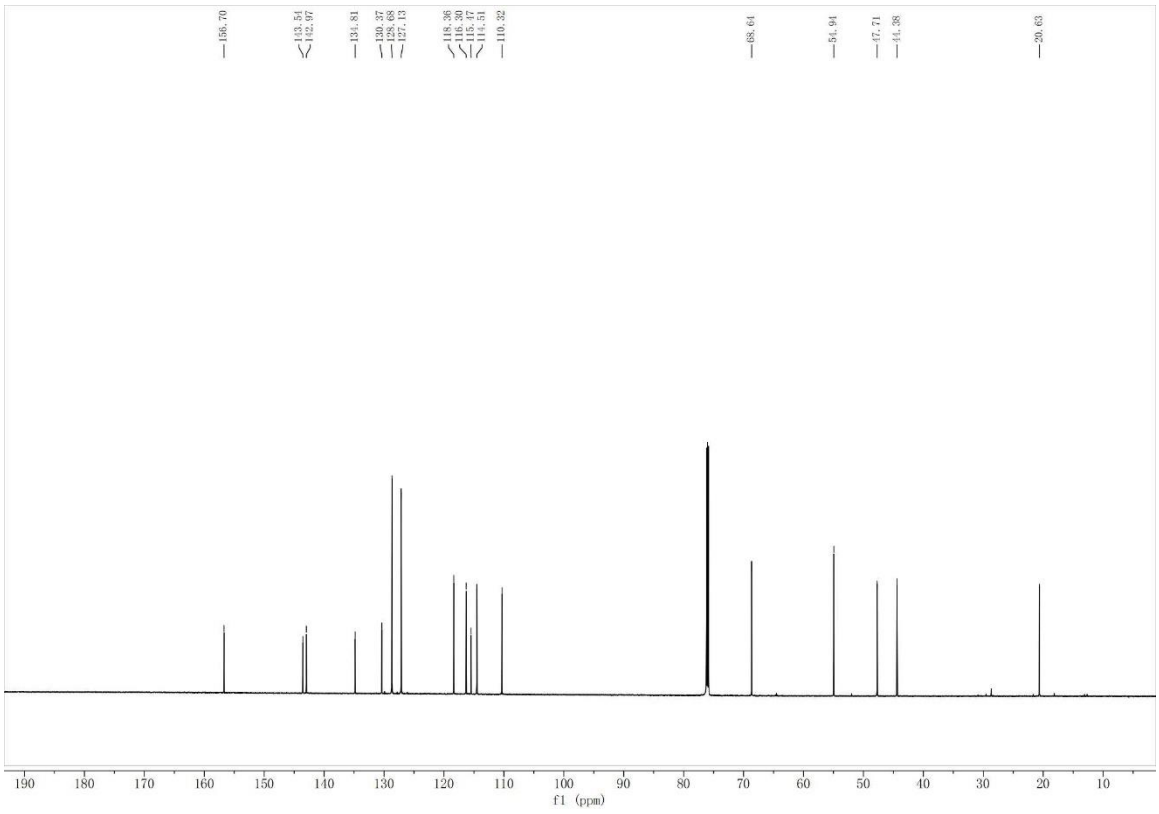
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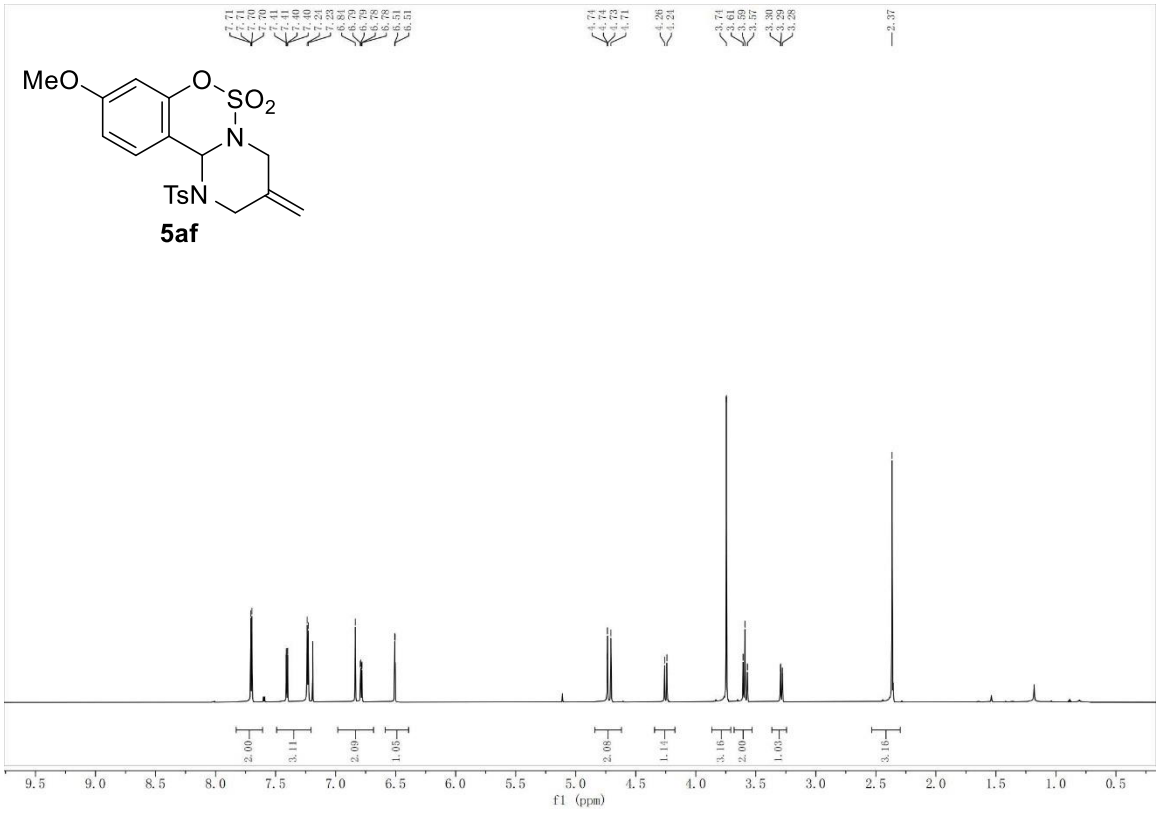
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SO2
N
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7.41
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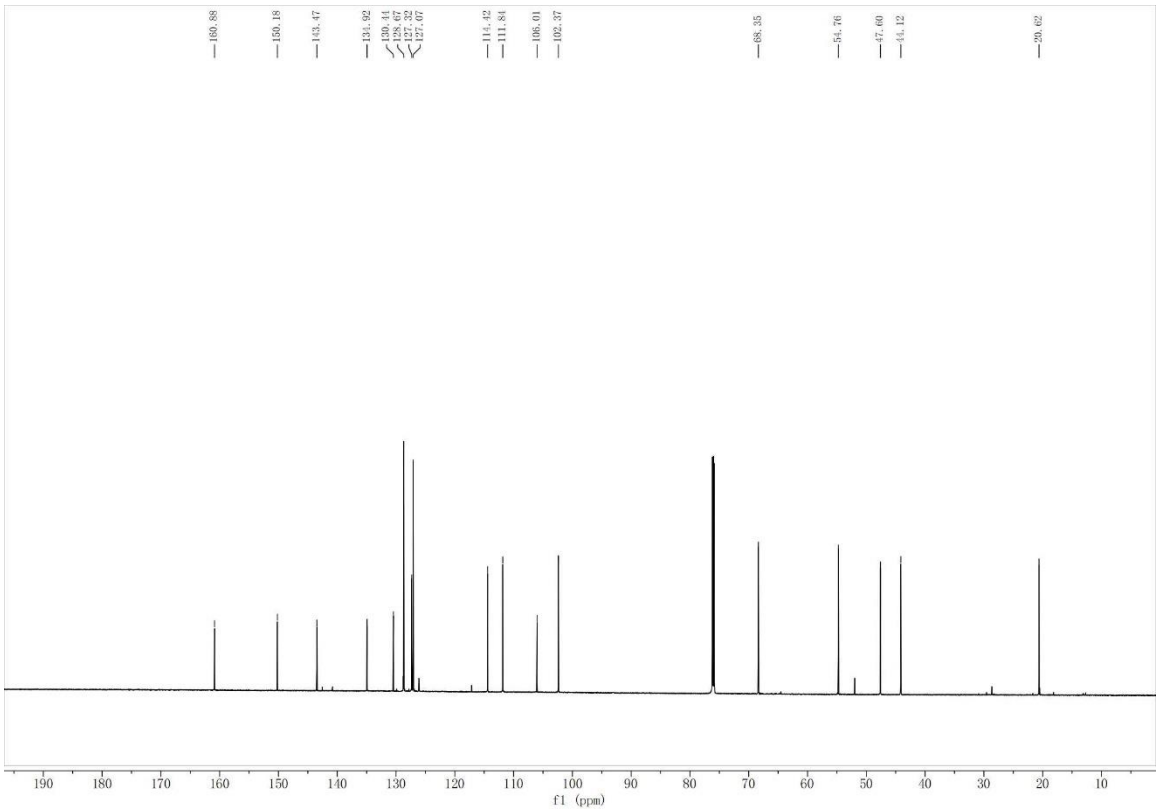
7.40
7.24
7.23
6.81
6.79
6.79
6.78
6.78
6.51
6.51
4.74
4.74
4.73
4.71
4.28
4.21
3.74
3.64
3.59
3.57
3.30
3.29
3.28
2.37
2.09
3.11
2.09
1.05
2.08
1.14
3.16
2.00
1.03
3.16
f1 (ppm)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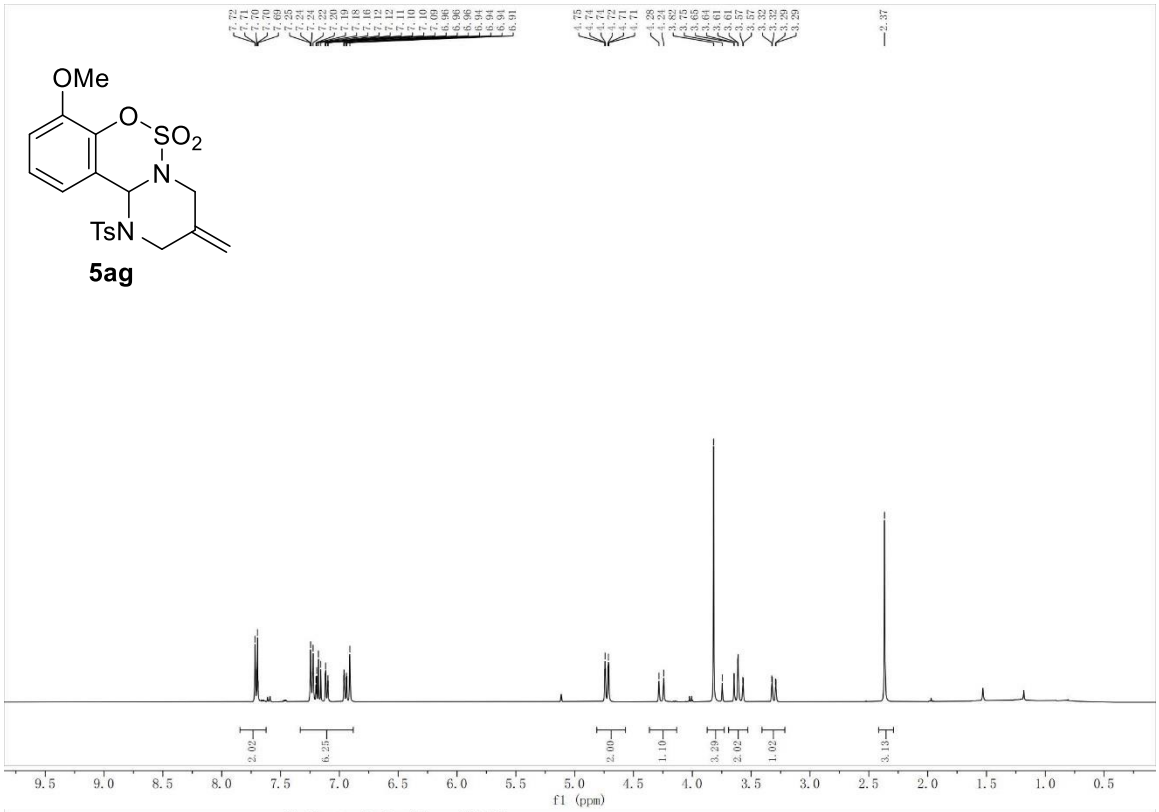
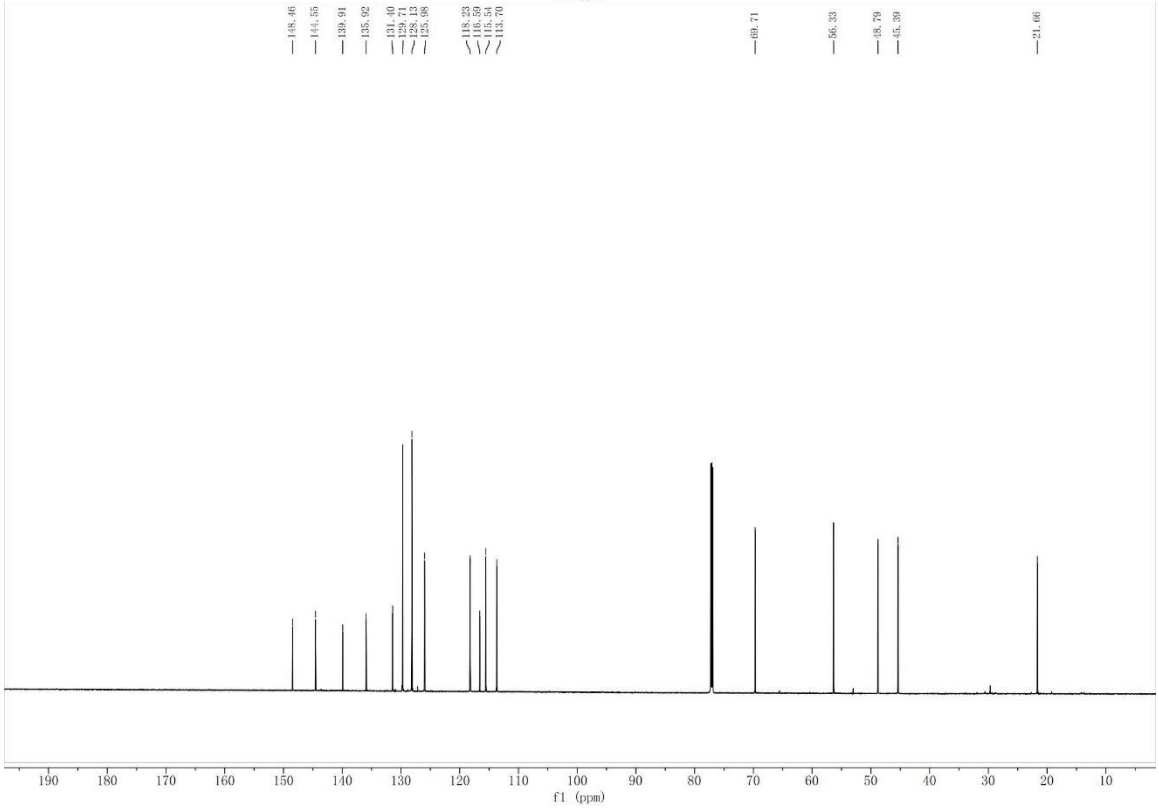
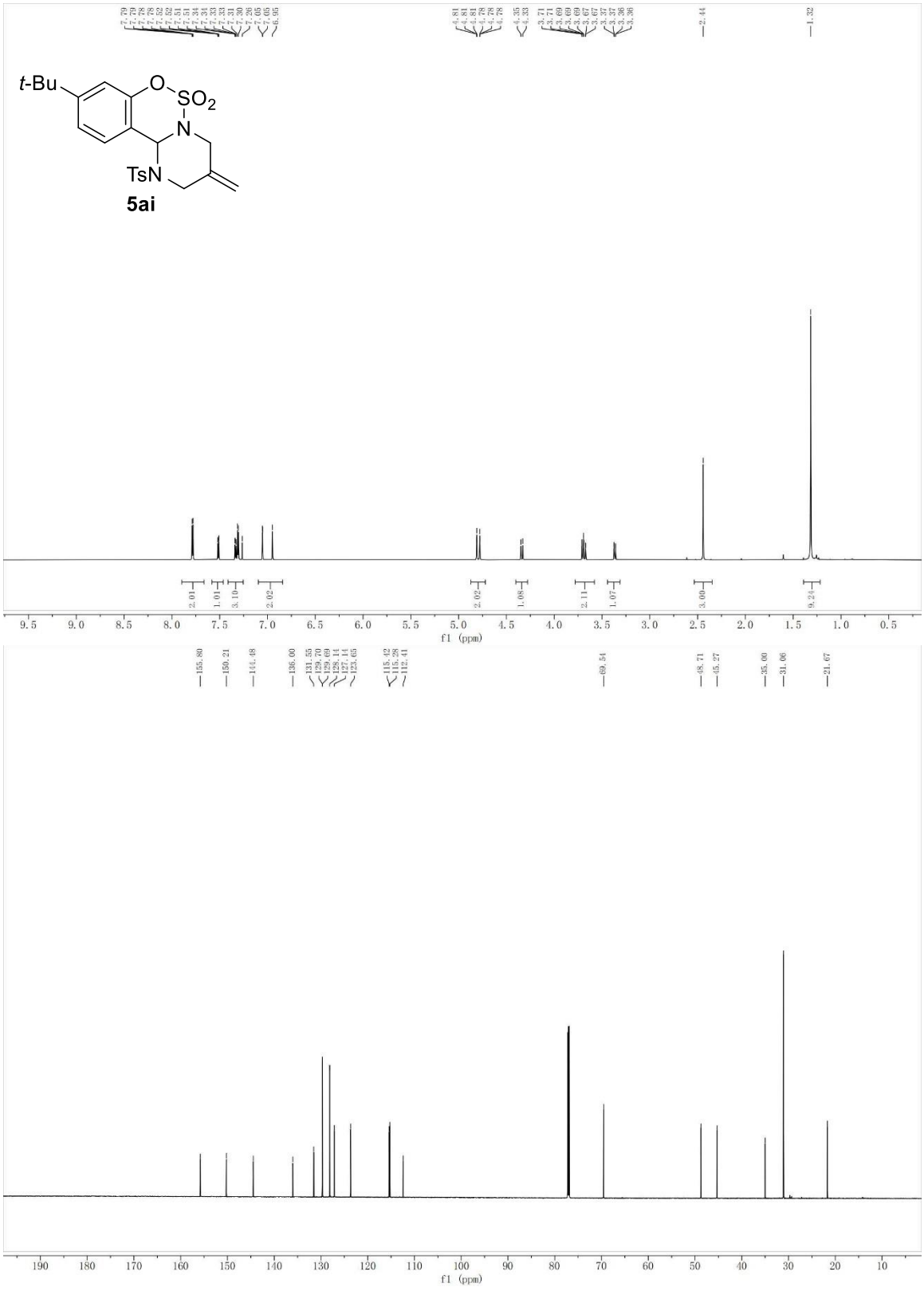
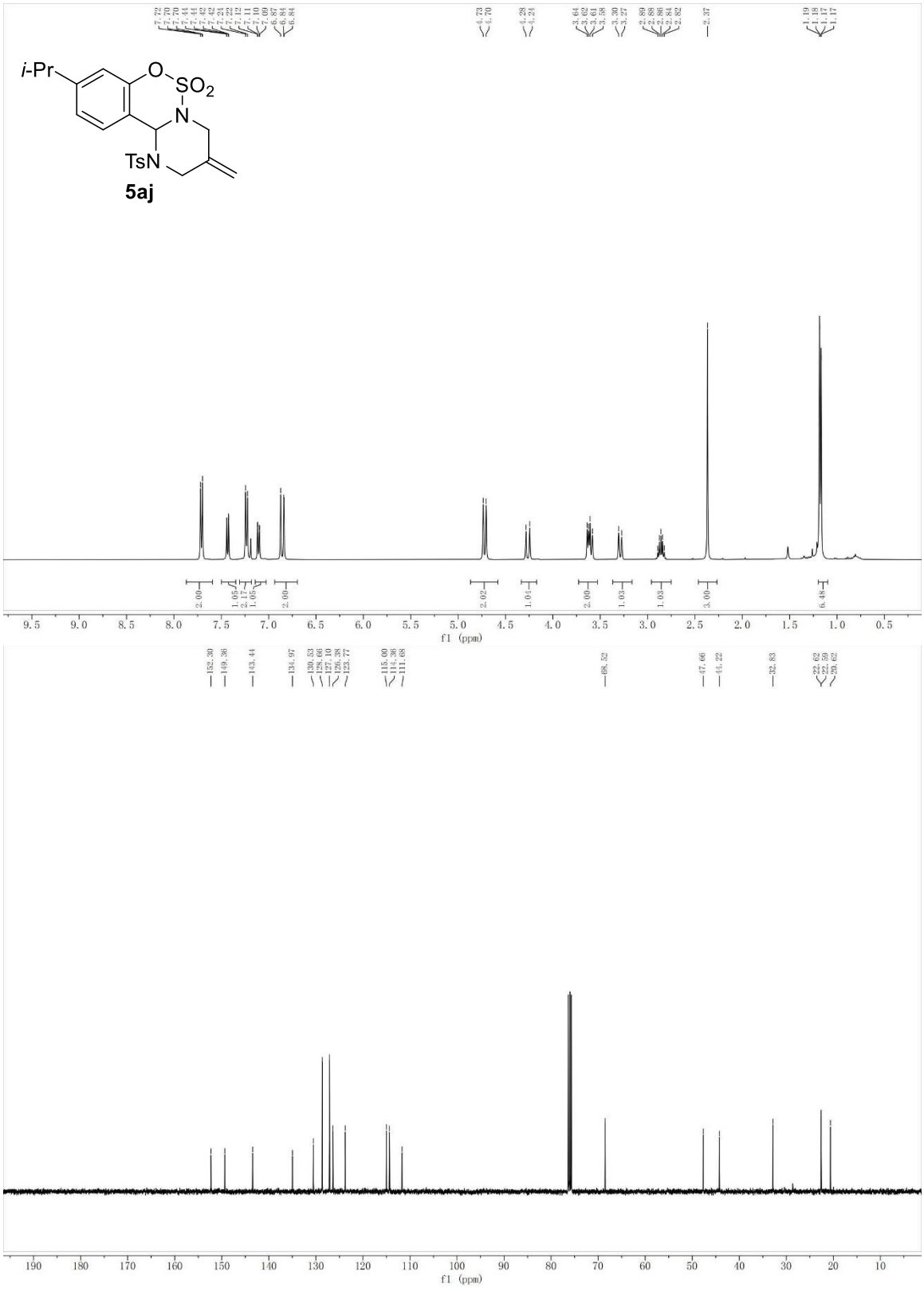
47.60
45.12
29.62
f1 (ppm)

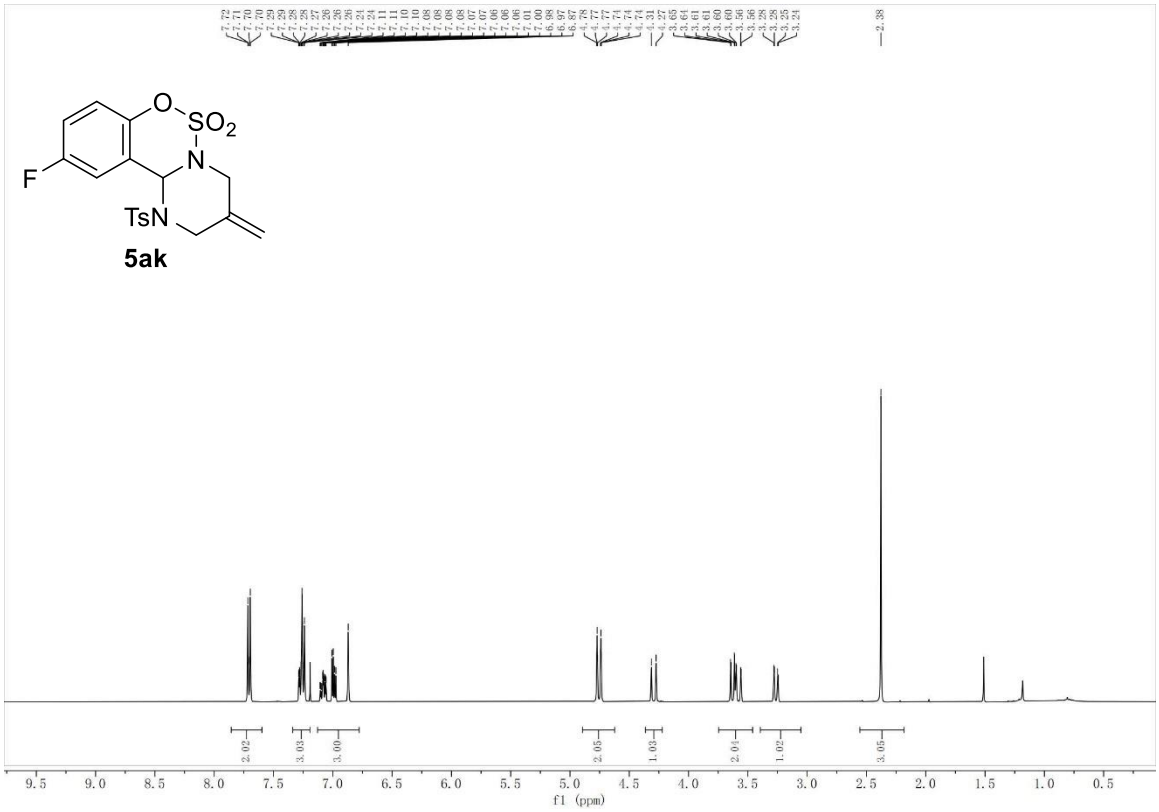


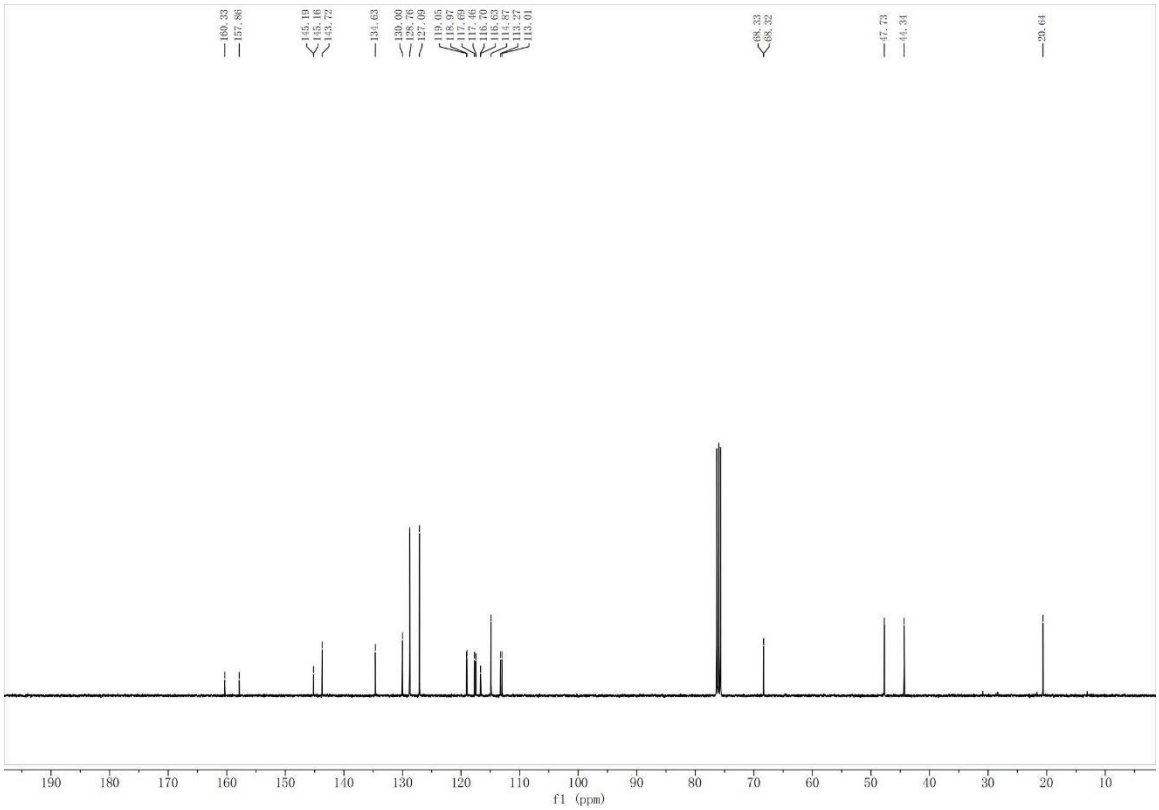
5ag

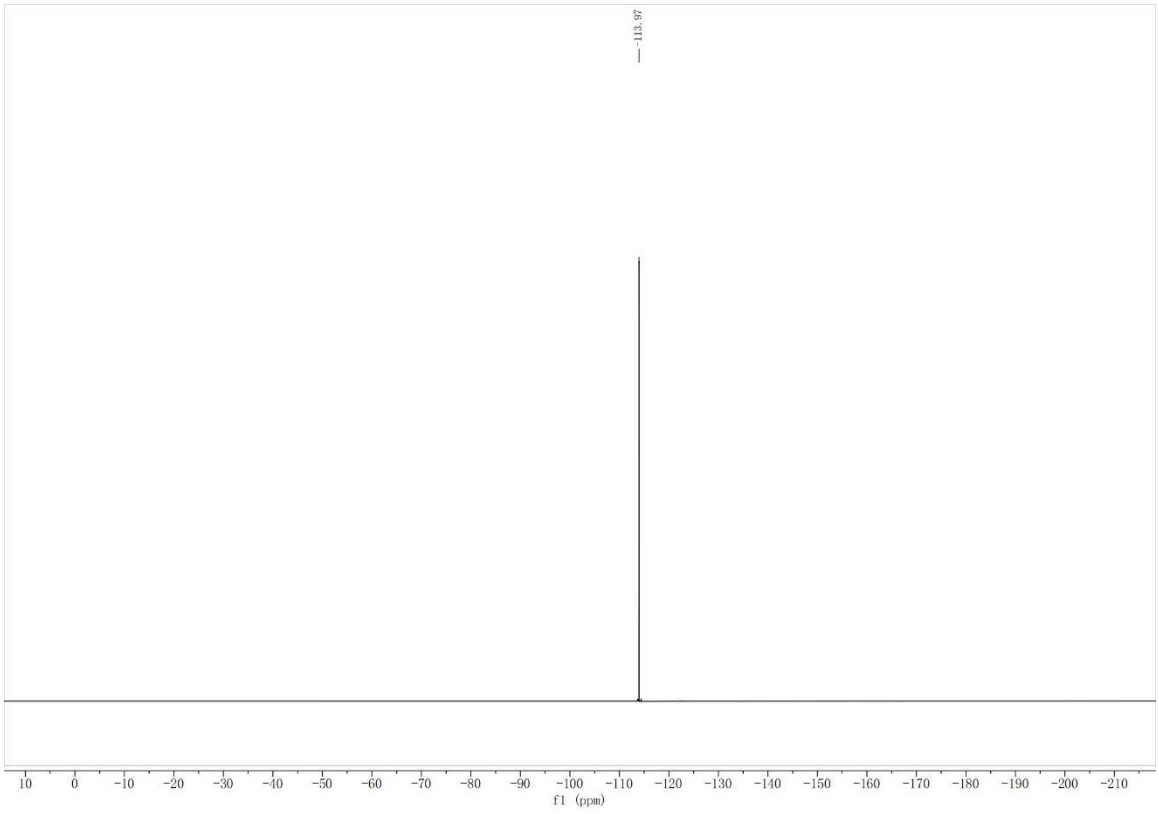


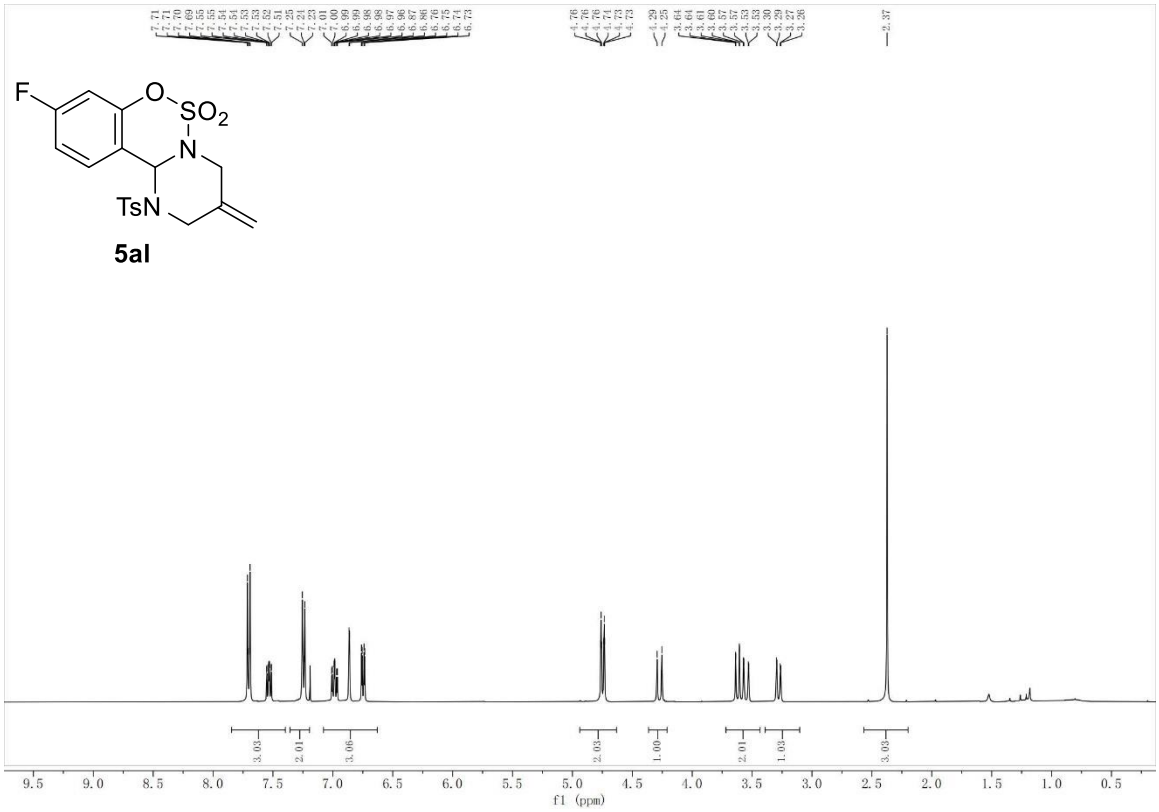

t-Bu
O
SO2
N
TsN
5ai
f1 (ppm)
f1 (ppm)


i-Pr
O
SO2
N
TsN
5aj
f1 (ppm)
f1 (ppm)

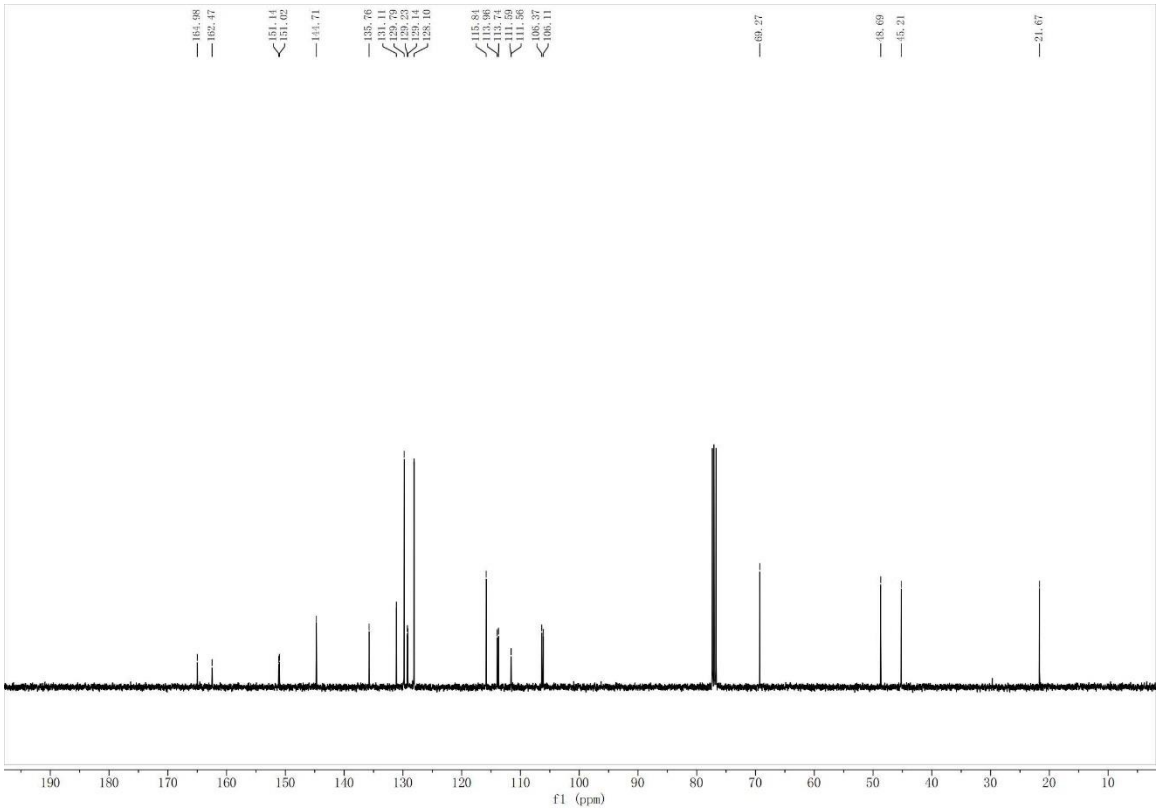

O
SO2
N
F
TsN
5ak
f1 (ppm)

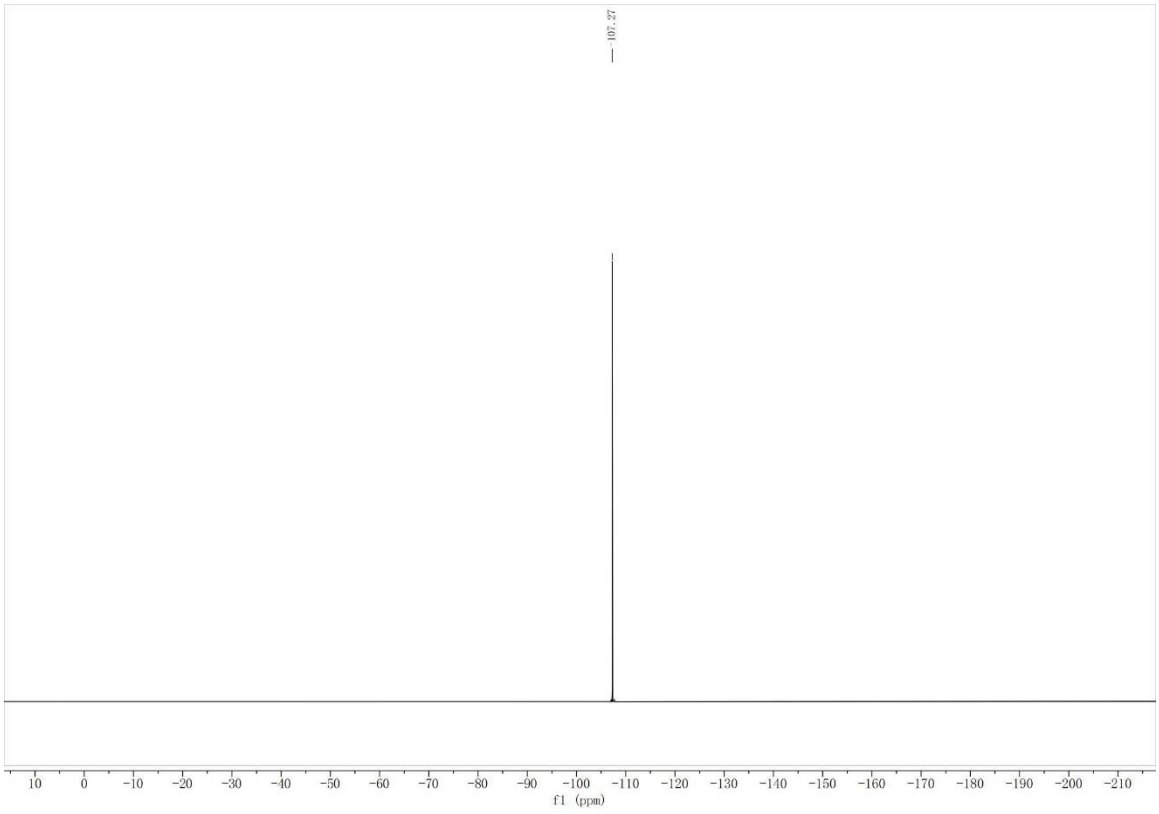

f1 (ppm)


-113.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



5al




-107.27
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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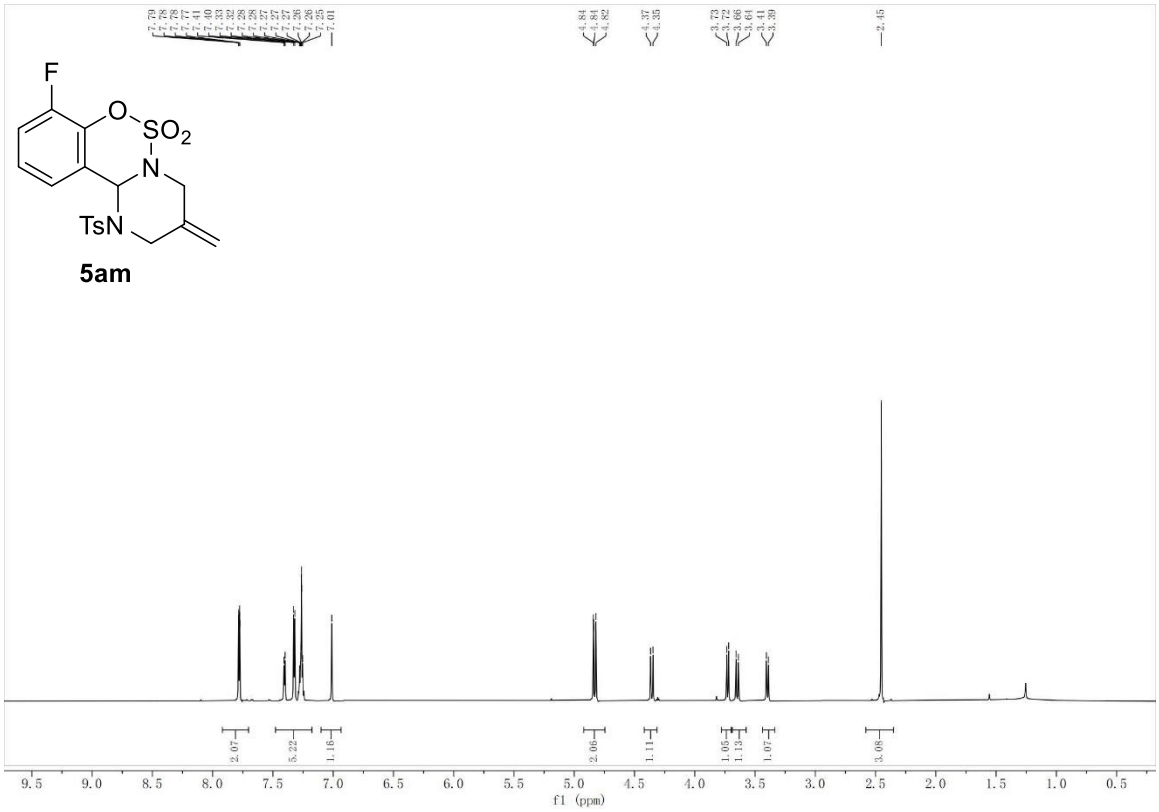
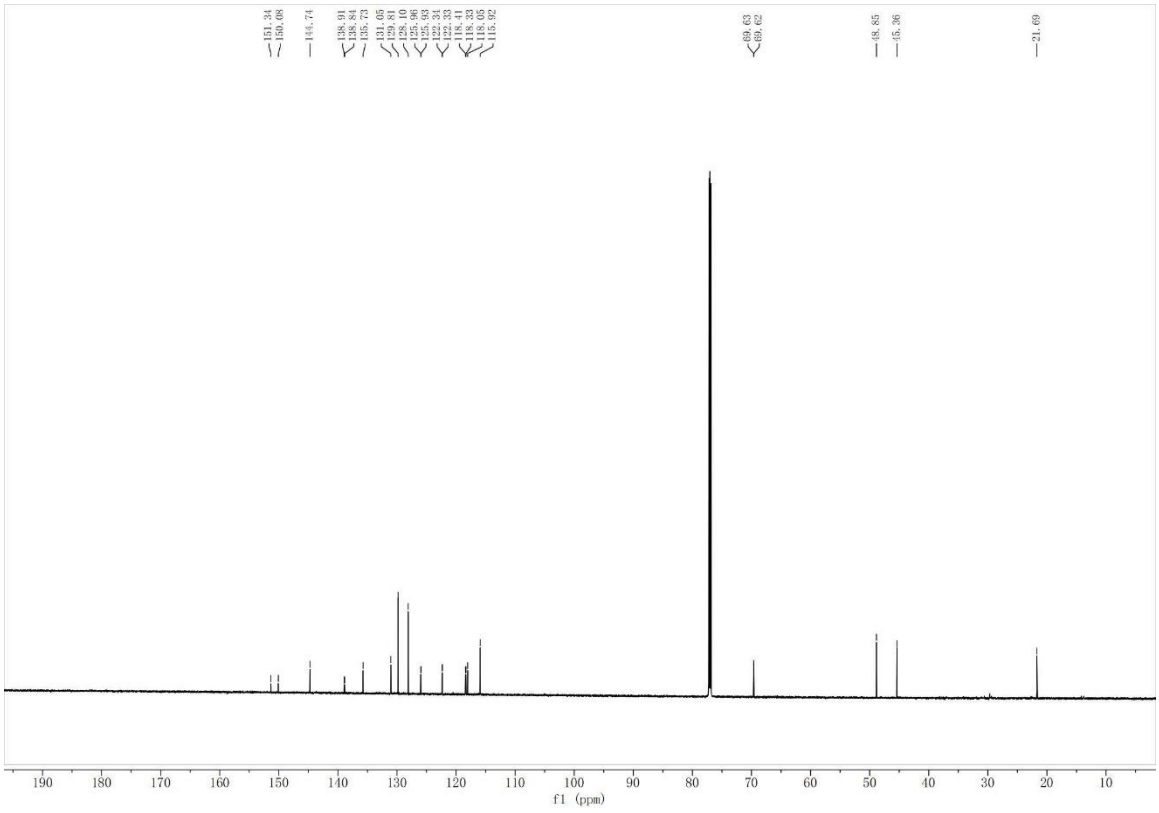
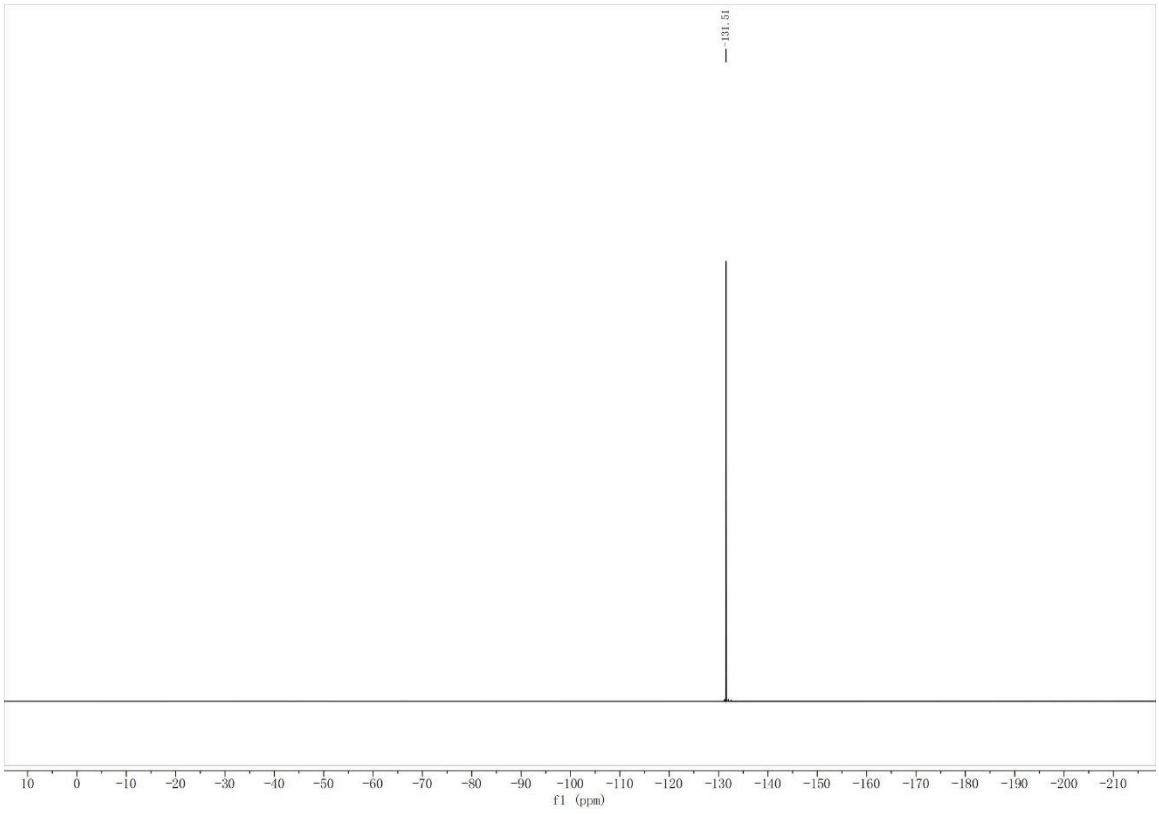
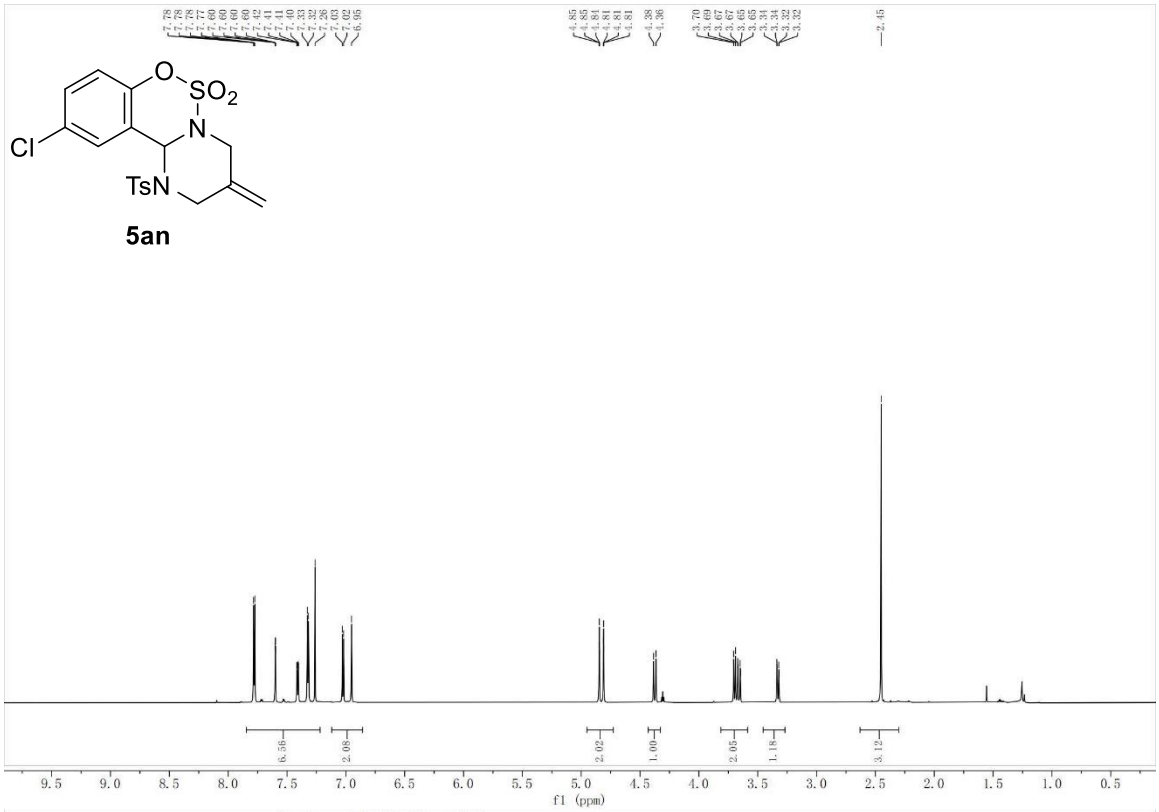
-160
-170
-180
-190
-200
-210
f1 (ppm)


F
O
SO2
N
TsN
5am
f1 (ppm)


f1 (ppm)


131.51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



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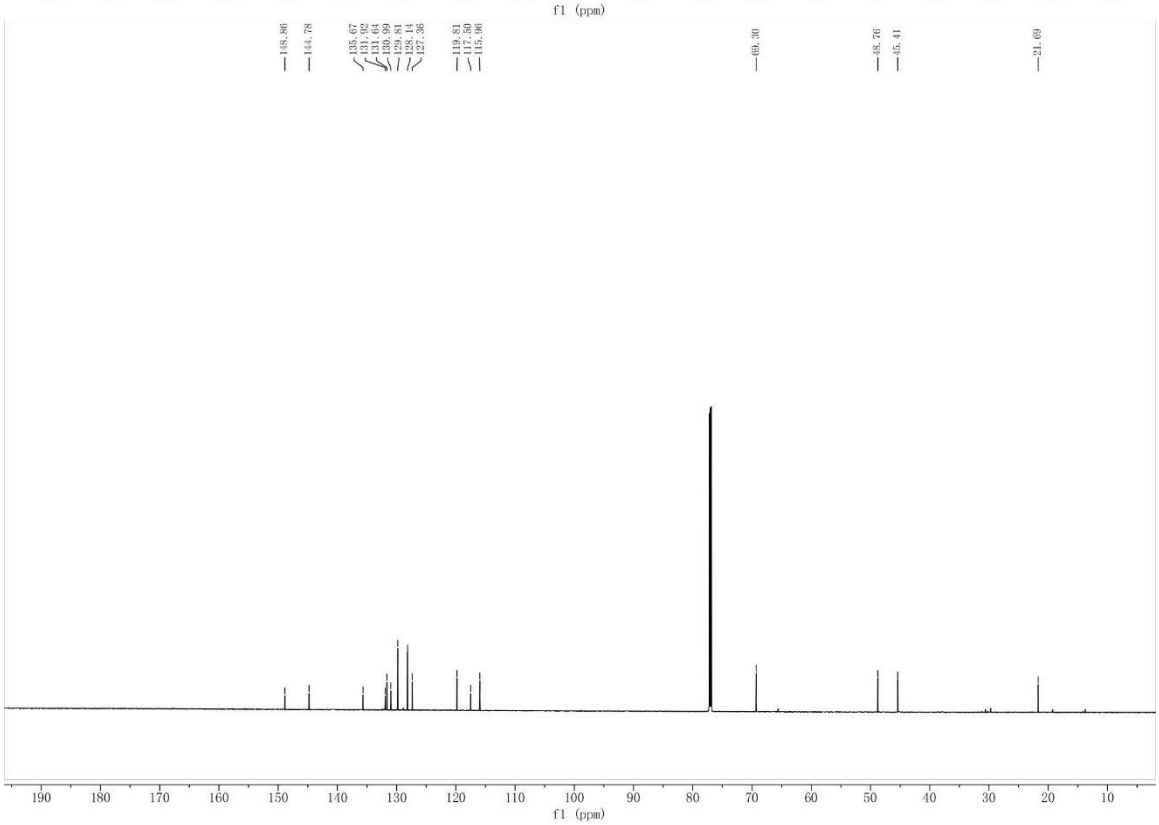
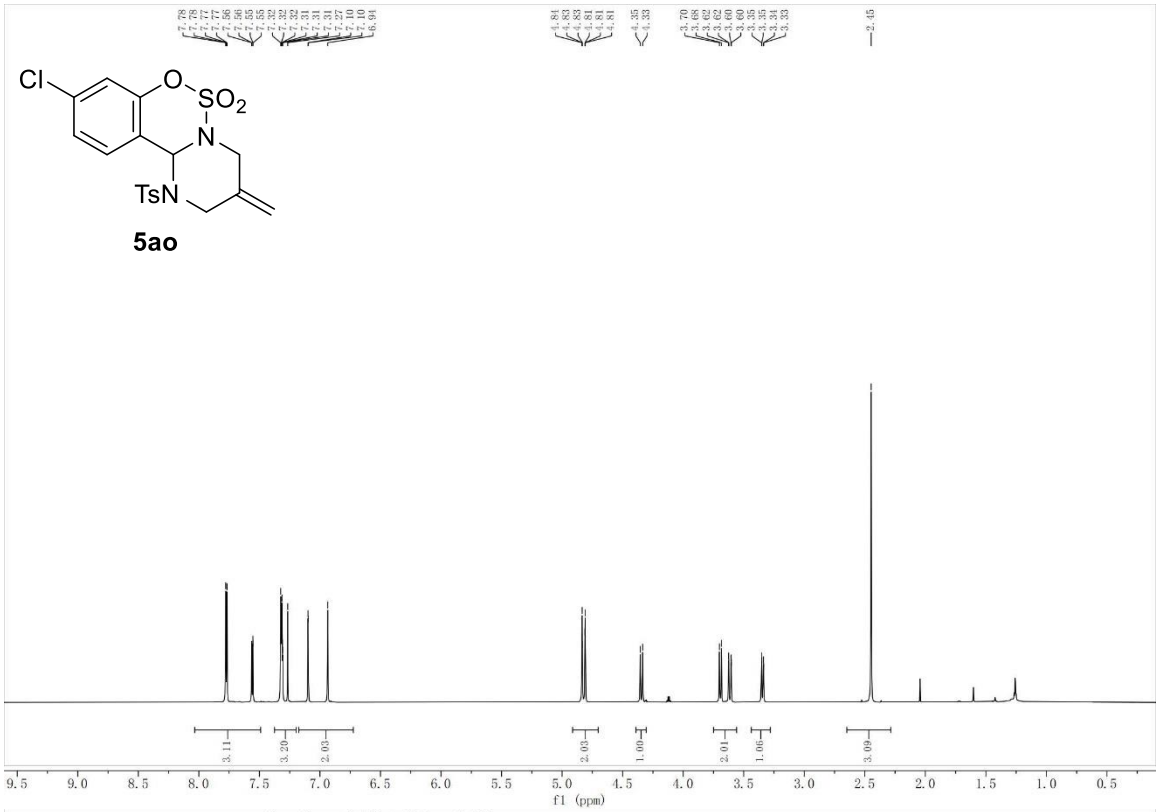
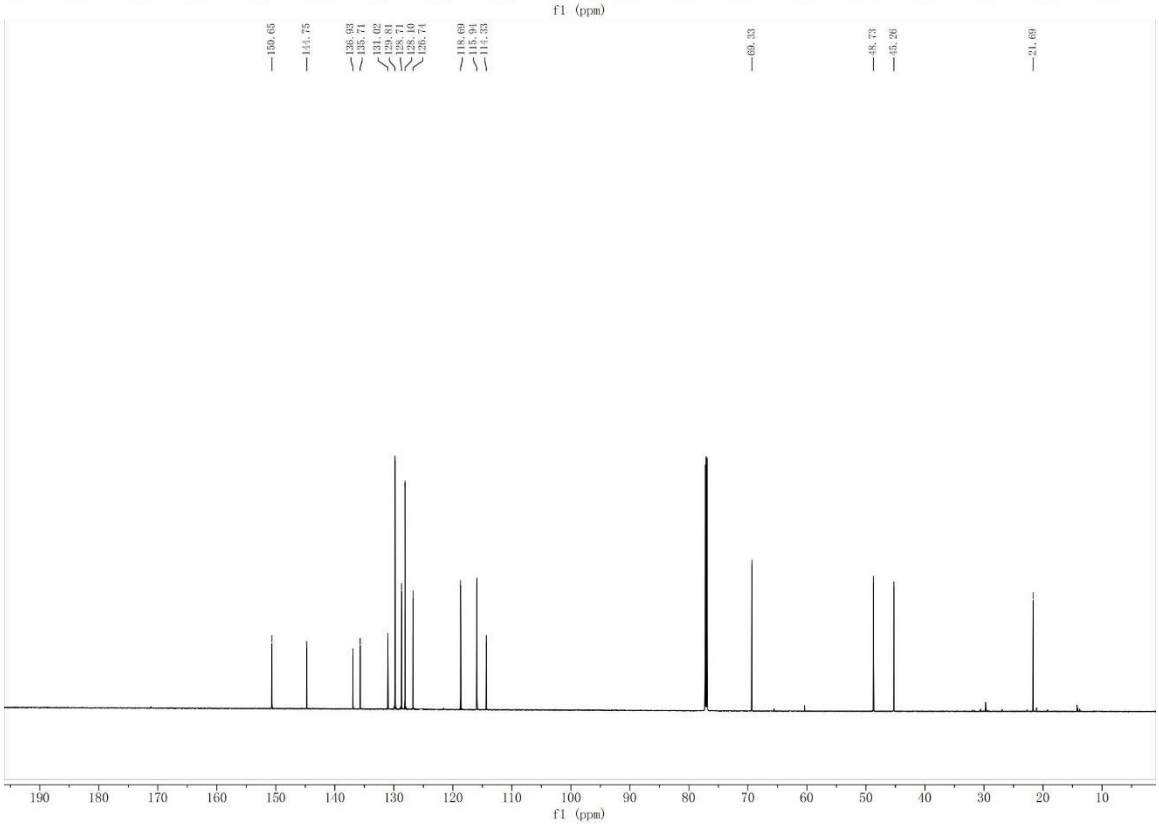
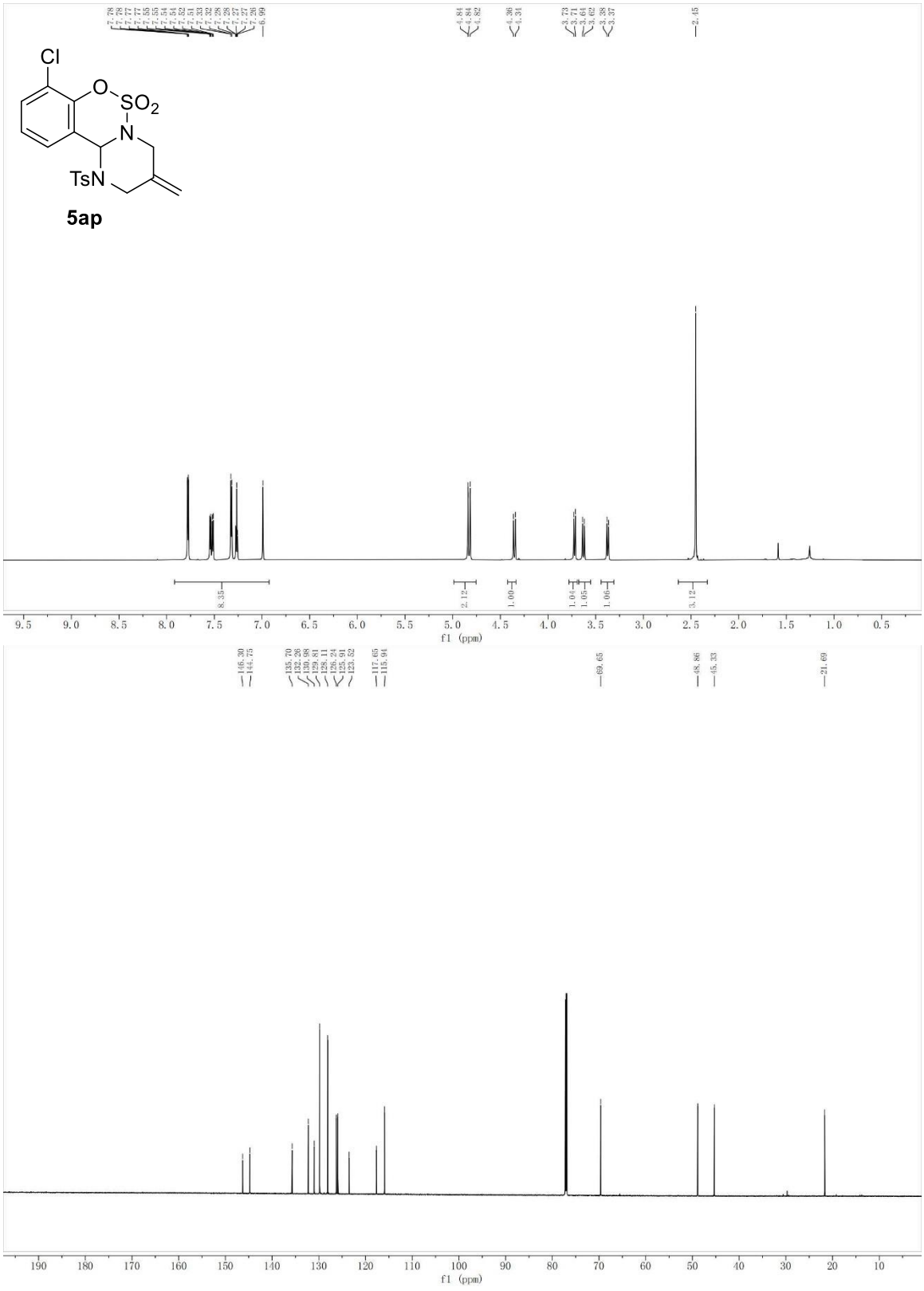
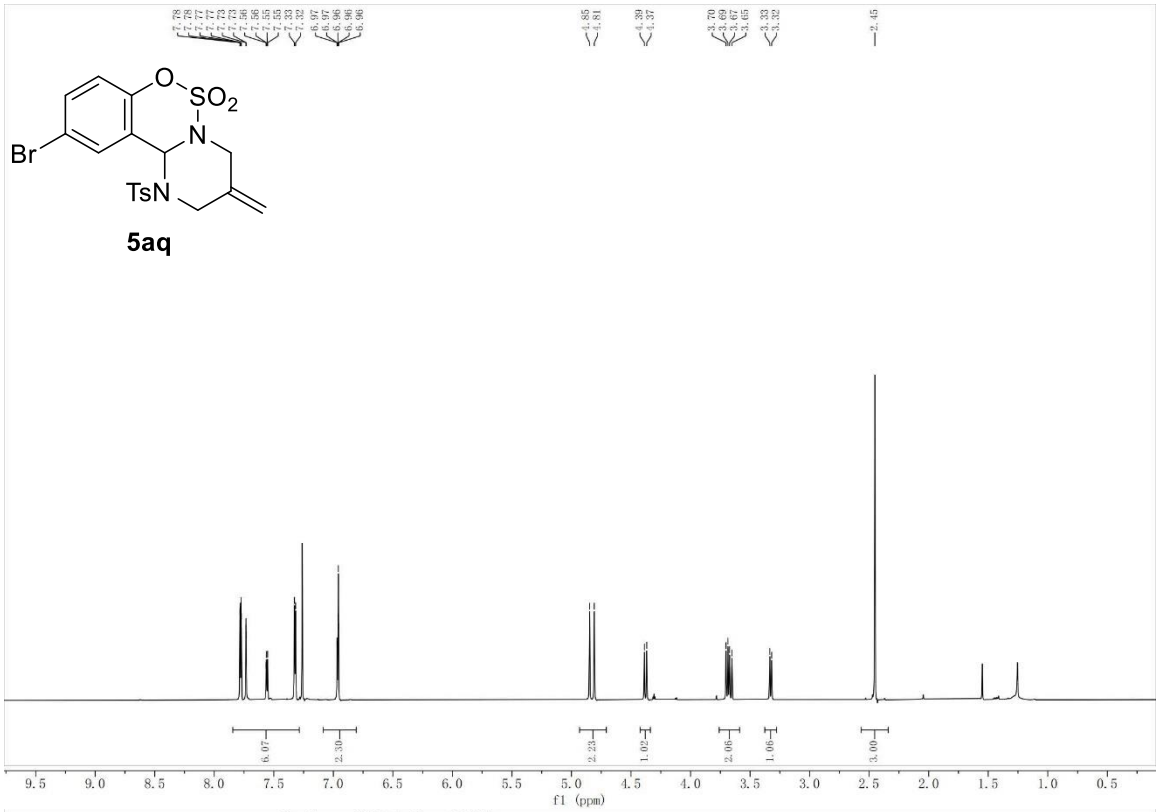




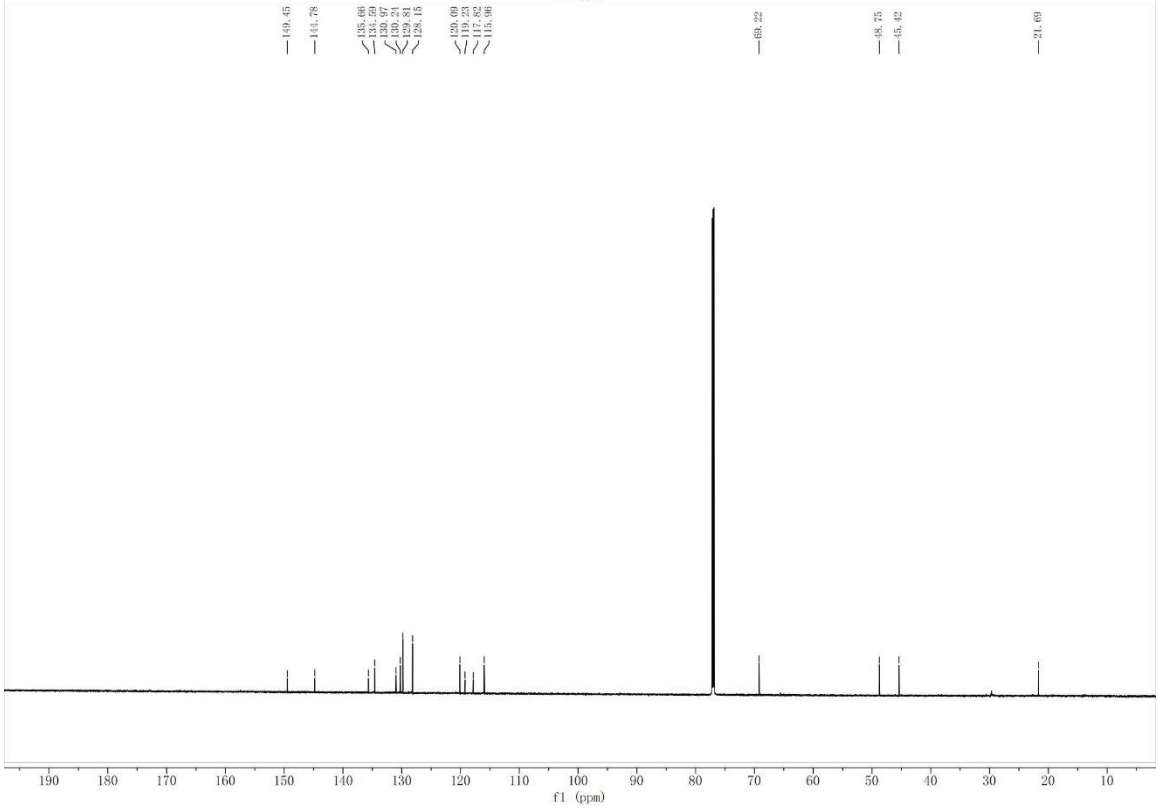
5ao

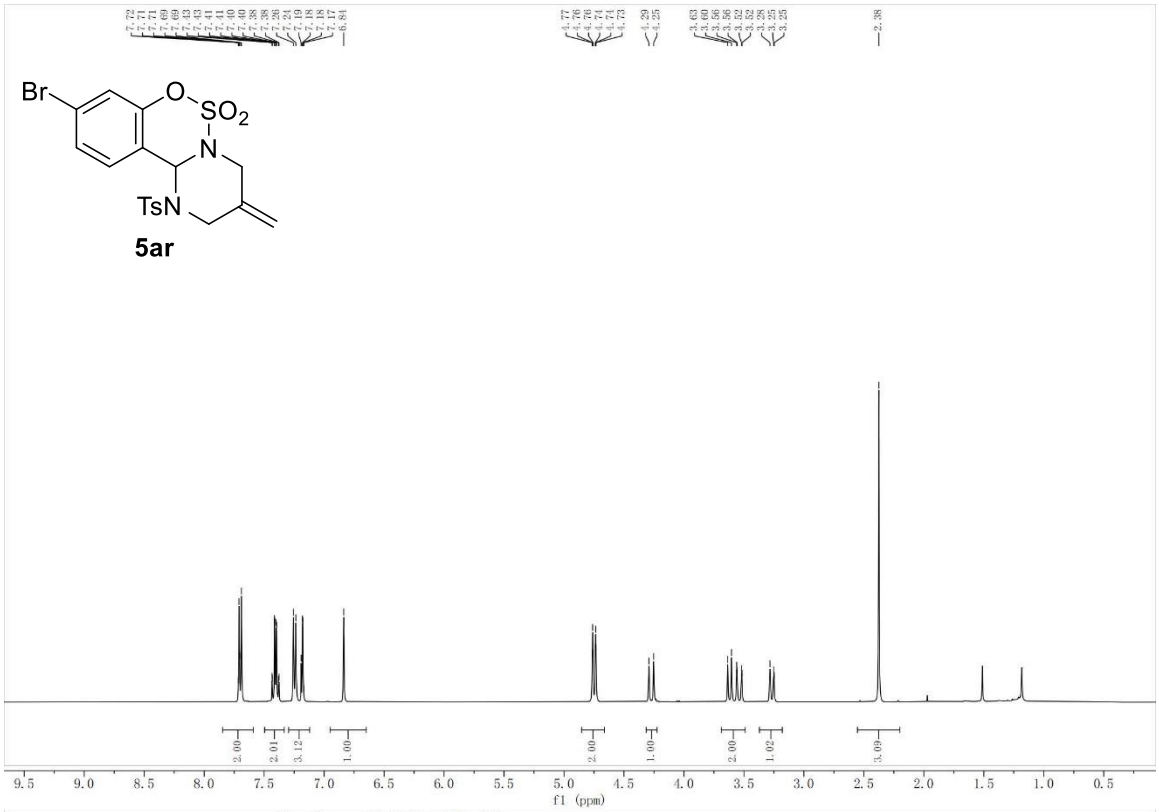


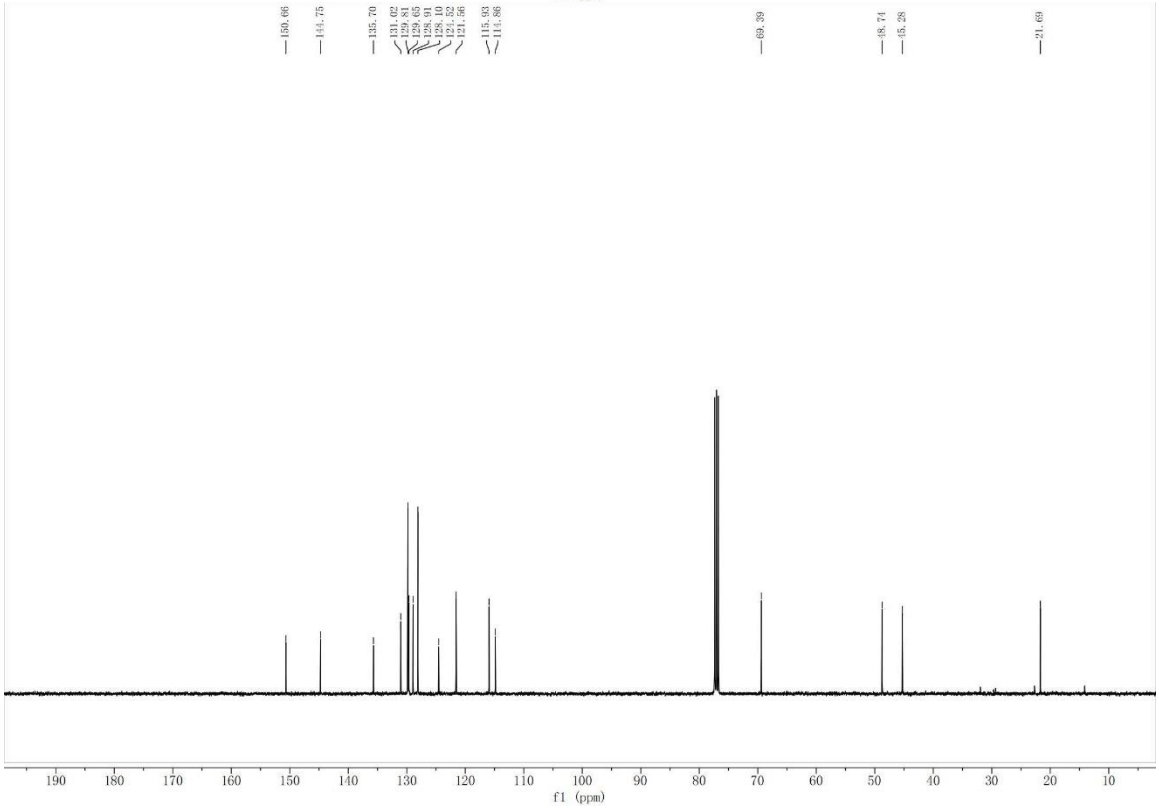

Cl
O
SO2
N
TsN
5ap
f1 (ppm)
f1 (ppm)

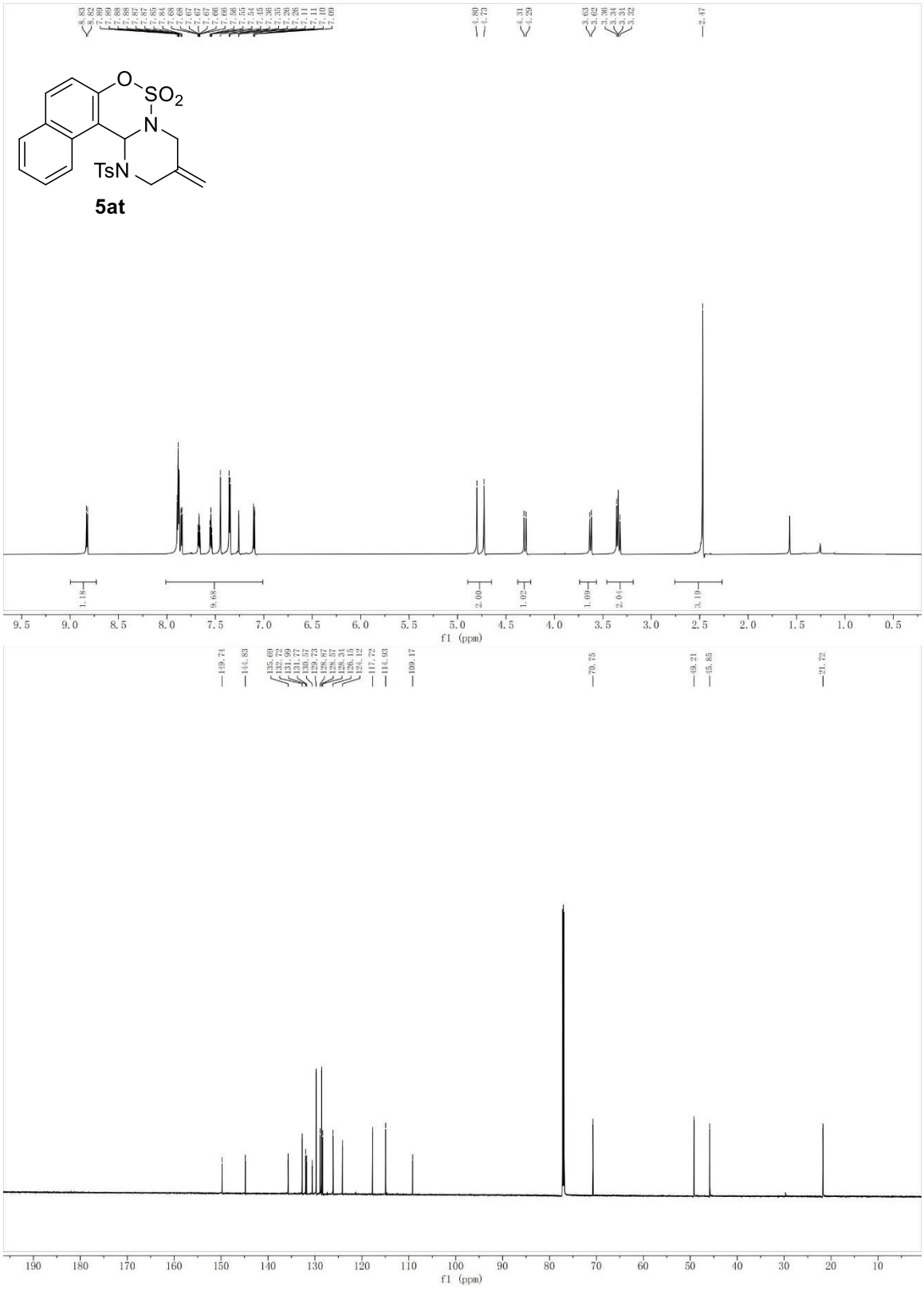


5aq

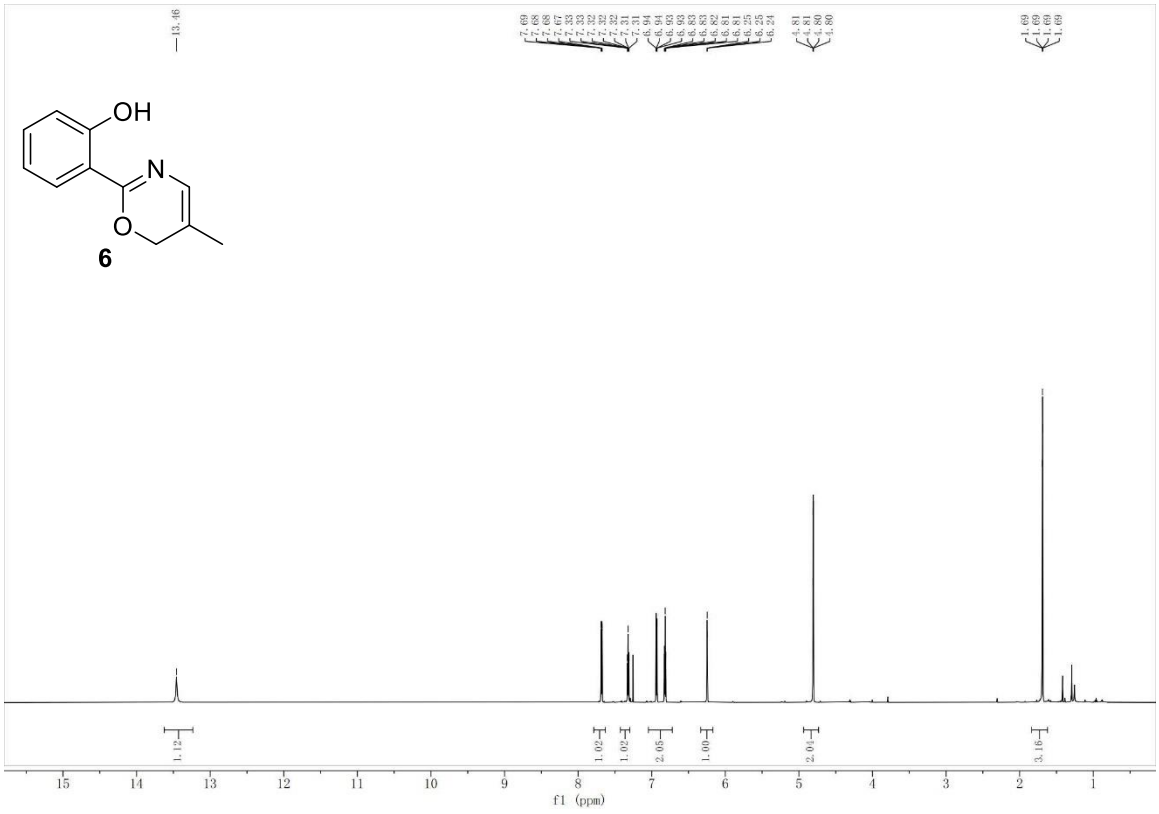


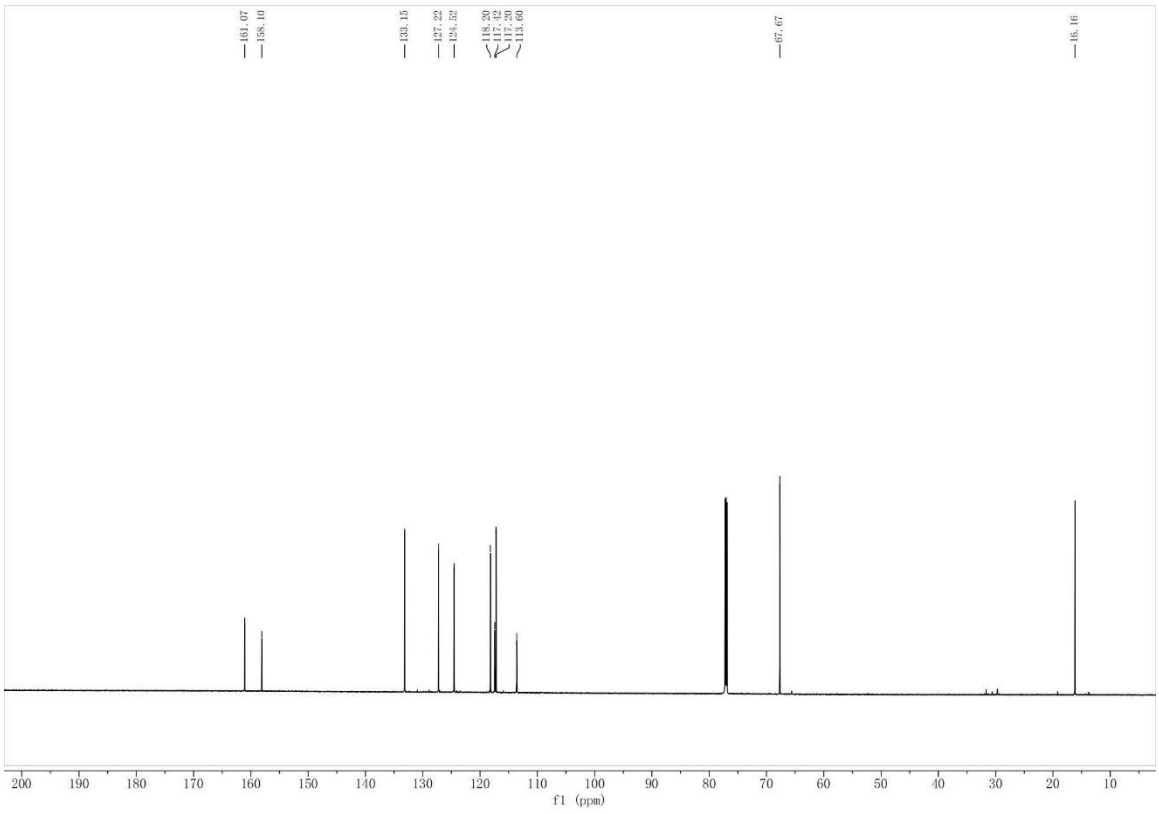

Br
O
SO2
N
TsN
5ar
f1 (ppm)

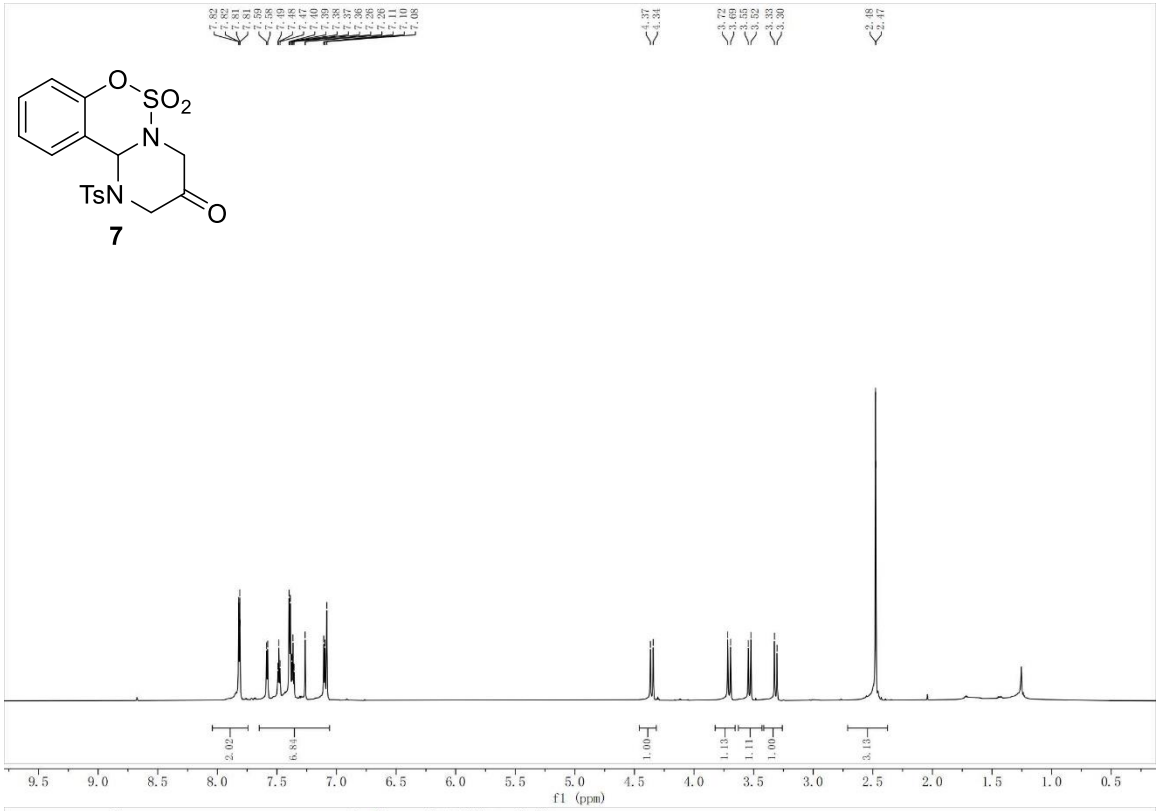

f1 (ppm)



5at


OH
N
O
6
f1 (ppm)


f1 (ppm)


7.82
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7.48
7.47
7.40
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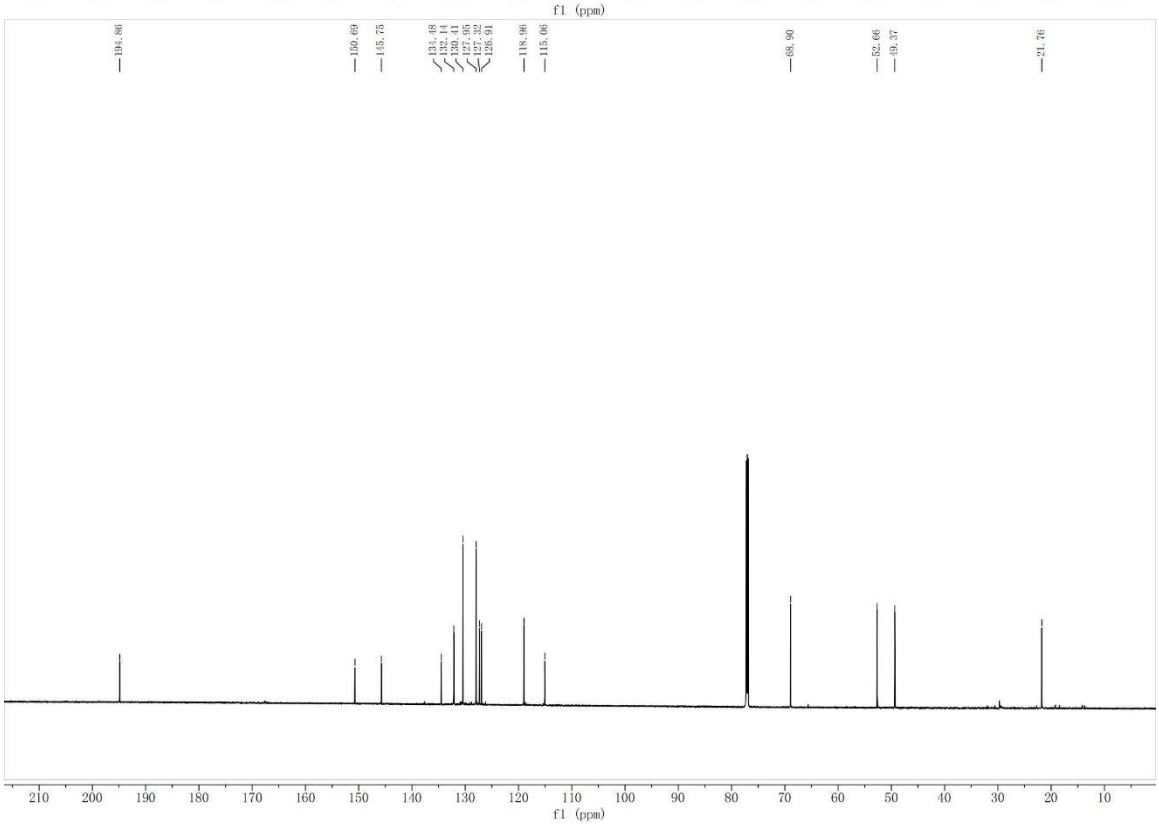
7.38
7.37
7.36
7.26
7.26
7.11
7.10
7.08
4.37
4.34
3.72
3.69
3.55
3.52
3.33
3.30
2.49
2.47
O
SO2
N
TsN
O
7
2.02
6.84
1.00
1.13
1.11
1.00
3.13
f1 (ppm)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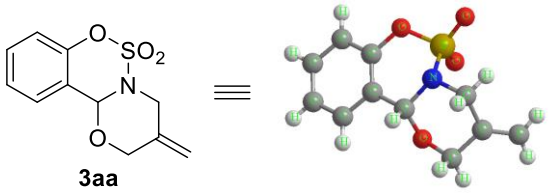
145.75
134.48
132.14
130.41
127.95
127.32
126.91
118.96
115.06
68.90
52.66
49.37
21.76
f1 (ppm)

X-Ray Crystallographic Data of 3aa

Crystallographic data for **3aa** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2278928. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3aa

Table 1. Crystal data and structure refinement for **3aa**.

Identification code	3aa
Empirical formula	$C_{11}H_{11}NO_4S$
Formula weight	253.27
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 12.9083(11) A alpha = 90 deg.
	b = 8.1492(7) A beta = 90 deg.
	c = 20.8706(18) A gamma = 90 deg.
Volume	2195.4(3) A^3
Z, Calculated density	8, 1.533 Mg/m^3
Absorption coefficient	0.297 mm^-1
F(000)	1056
Crystal size	0.45 x 0.33 x 0.14 mm
Theta range for data collection	2.51 to 25.02 deg.
Limiting indices	-14<=h<=15, -9<=k<=9, -24<=l<=18
Reflections collected / unique	10188 / 1931 [R(int) = 0.1011]
Completeness to theta = 25.02	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9596 and 0.8780

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1931 / 0 / 154
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0592, wR2 = 0.1499
R indices (all data)	R1 = 0.0880, wR2 = 0.1648
Largest diff. peak and hole	0.306 and -0.424 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3aa.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	6043(2)	-486(3)	6548(1)	34(1)
O(1)	5544(2)	885(4)	5574(1)	56(1)
O(2)	7667(2)	627(3)	6876(1)	40(1)
O(3)	5682(2)	2555(3)	6523(1)	52(1)
O(4)	4294(2)	593(4)	6389(1)	62(1)
S(1)	5332(1)	1008(1)	6308(1)	41(1)
C(1)	6584(3)	970(5)	5387(2)	41(1)
C(2)	6776(3)	1631(6)	4800(2)	56(1)
C(3)	7775(4)	1767(6)	4601(2)	66(1)
C(4)	8564(4)	1260(6)	4981(2)	64(1)
C(5)	8362(3)	564(5)	5568(2)	51(1)
C(6)	7352(3)	402(4)	5777(2)	36(1)
C(7)	7151(3)	-341(4)	6416(2)	34(1)
C(8)	7569(3)	-81(6)	7500(2)	54(1)
C(9)	6463(3)	-177(5)	7683(2)	46(1)
C(10)	5835(3)	-1092(5)	7206(2)	41(1)
C(11)	6085(4)	447(6)	8197(2)	74(2)

Table 3. Bond lengths [A] and angles [deg] for 3aa.

N(1)-C(7)	1.461(4)
N(1)-C(10)	1.484(4)
N(1)-S(1)	1.604(3)
O(1)-C(1)	1.400(4)
O(1)-S(1)	1.560(3)
O(2)-C(7)	1.410(4)
O(2)-C(8)	1.430(4)
O(3)-S(1)	1.412(3)
O(4)-S(1)	1.392(3)
C(1)-C(2)	1.360(5)
C(1)-C(6)	1.363(5)
C(2)-C(3)	1.360(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.356(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.374(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.381(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.489(5)
C(7)-H(7)	0.9800
C(8)-C(9)	1.480(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(11)	1.283(6)
C(9)-C(10)	1.485(5)

C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-H(11A)	0.9300
C(11)-H(11B)	0.9300
C(7)-N(1)-C(10)	112.2(3)
C(7)-N(1)-S(1)	116.1(2)
C(10)-N(1)-S(1)	115.9(2)
C(1)-O(1)-S(1)	116.1(2)
C(7)-O(2)-C(8)	110.6(3)
O(4)-S(1)-O(3)	119.08(18)
O(4)-S(1)-O(1)	105.78(16)
O(3)-S(1)-O(1)	108.24(16)
O(4)-S(1)-N(1)	109.16(17)
O(3)-S(1)-N(1)	113.35(15)
O(1)-S(1)-N(1)	99.05(15)
C(2)-C(1)-C(6)	122.6(4)
C(2)-C(1)-O(1)	116.5(3)
C(6)-C(1)-O(1)	120.9(3)
C(3)-C(2)-C(1)	118.8(4)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(4)-C(3)-C(2)	120.6(4)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.3(4)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	120.0(4)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0

C(1)-C(6)-C(5)	117.8(3)
C(1)-C(6)-C(7)	123.1(3)
C(5)-C(6)-C(7)	119.1(3)
O(2)-C(7)-N(1)	112.4(3)
O(2)-C(7)-C(6)	107.5(3)
N(1)-C(7)-C(6)	111.8(3)
O(2)-C(7)-H(7)	108.3
N(1)-C(7)-H(7)	108.3
C(6)-C(7)-H(7)	108.3
O(2)-C(8)-C(9)	109.9(3)
O(2)-C(8)-H(8A)	109.7
C(9)-C(8)-H(8A)	109.7
O(2)-C(8)-H(8B)	109.7
C(9)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2
C(11)-C(9)-C(8)	124.1(4)
C(11)-C(9)-C(10)	123.5(4)
C(8)-C(9)-C(10)	112.4(3)
N(1)-C(10)-C(9)	110.8(3)
N(1)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10A)	109.5
N(1)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
C(9)-C(11)-H(11A)	120.0
C(9)-C(11)-H(11B)	120.0
H(11A)-C(11)-H(11B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 3aa.

The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	34(2)	33(2)	35(2)	0(1)	0(1)	-3(1)
O(1)	40(2)	93(2)	34(2)	5(2)	-4(1)	-2(1)
O(2)	39(1)	40(2)	40(1)	4(1)	-10(1)	-10(1)
O(3)	58(2)	41(2)	58(2)	1(1)	8(1)	12(1)
O(4)	33(2)	99(3)	53(2)	18(2)	1(1)	3(2)
S(1)	32(1)	56(1)	36(1)	8(1)	1(1)	6(1)
C(1)	43(2)	49(2)	32(2)	1(2)	3(2)	1(2)
C(2)	67(3)	67(3)	34(2)	5(2)	5(2)	7(2)
C(3)	74(3)	77(4)	48(3)	13(2)	23(2)	2(3)
C(4)	58(3)	70(3)	63(3)	6(3)	22(2)	-1(2)
C(5)	41(2)	53(3)	60(3)	7(2)	6(2)	-1(2)
C(6)	41(2)	30(2)	36(2)	-5(2)	7(2)	-2(2)
C(7)	34(2)	29(2)	39(2)	1(2)	-1(2)	2(1)
C(8)	58(3)	58(3)	44(2)	16(2)	-21(2)	-13(2)
C(9)	60(3)	48(3)	31(2)	14(2)	-4(2)	-10(2)
C(10)	46(2)	37(2)	41(2)	13(2)	2(2)	-6(2)
C(11)	107(4)	71(4)	45(3)	-1(2)	7(3)	-28(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3aa.

	x	y	z	U(eq)
H(2)	6235	1984	4541	67
H(3)	7919	2210	4200	79

H(4)	9246	1385	4845	76
H(5)	8905	203	5824	61
H(7)	7455	-1443	6422	41
H(8A)	7942	584	7810	64
H(8B)	7870	-1172	7502	64
H(10A)	6000	-2252	7231	50
H(10B)	5105	-960	7304	50
H(11A)	6515	1002	8481	89
H(11B)	5382	345	8284	89

Table 6. Torsion angles [deg] for 3aa.

C(1)-O(1)-S(1)-O(4)	-169.2(3)
C(1)-O(1)-S(1)-O(3)	62.1(3)
C(1)-O(1)-S(1)-N(1)	-56.3(3)
C(7)-N(1)-S(1)-O(4)	172.0(2)
C(10)-N(1)-S(1)-O(4)	-53.1(3)
C(7)-N(1)-S(1)-O(3)	-52.7(3)
C(10)-N(1)-S(1)-O(3)	82.2(3)
C(7)-N(1)-S(1)-O(1)	61.8(3)
C(10)-N(1)-S(1)-O(1)	-163.4(2)
S(1)-O(1)-C(1)-C(2)	-149.8(3)
S(1)-O(1)-C(1)-C(6)	30.7(5)
C(6)-C(1)-C(2)-C(3)	-1.6(7)
O(1)-C(1)-C(2)-C(3)	178.9(4)
C(1)-C(2)-C(3)-C(4)	-0.4(7)
C(2)-C(3)-C(4)-C(5)	1.6(7)
C(3)-C(4)-C(5)-C(6)	-1.0(7)
C(2)-C(1)-C(6)-C(5)	2.1(6)

O(1)-C(1)-C(6)-C(5)	-178.3(3)
C(2)-C(1)-C(6)-C(7)	-179.3(4)
O(1)-C(1)-C(6)-C(7)	0.2(6)
C(4)-C(5)-C(6)-C(1)	-0.8(6)
C(4)-C(5)-C(6)-C(7)	-179.4(4)
C(8)-O(2)-C(7)-N(1)	60.6(4)
C(8)-O(2)-C(7)-C(6)	-175.9(3)
C(10)-N(1)-C(7)-O(2)	-54.1(4)
S(1)-N(1)-C(7)-O(2)	82.4(3)
C(10)-N(1)-C(7)-C(6)	-175.1(3)
S(1)-N(1)-C(7)-C(6)	-38.6(4)
C(1)-C(6)-C(7)-O(2)	-119.7(4)
C(5)-C(6)-C(7)-O(2)	58.8(4)
C(1)-C(6)-C(7)-N(1)	4.1(5)
C(5)-C(6)-C(7)-N(1)	-177.4(3)
C(7)-O(2)-C(8)-C(9)	-60.7(4)
O(2)-C(8)-C(9)-C(11)	-124.7(4)
O(2)-C(8)-C(9)-C(10)	55.7(4)
C(7)-N(1)-C(10)-C(9)	47.6(4)
S(1)-N(1)-C(10)-C(9)	-89.0(3)
C(11)-C(9)-C(10)-N(1)	131.3(4)
C(8)-C(9)-C(10)-N(1)	-49.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3aa [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)