Supporting Information

Palladium-Catalyzed [5 + 2] Cycloaddition of Vinyloxiranes with Sulfamate-Derived Cyclic Imines to Construct 1,3-Oxazepine Heterocycles

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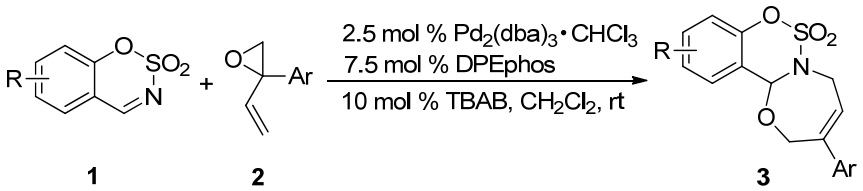
General Information

All reactions were performed under N_2 atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Dichloromethane employed in the reactions was freshly distilled from CaH_2. sulfamate-derived cyclic imines[1] and vinyl epoxides[2] were prepared according to the literature procedures. 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. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 300 MHz NMR instrument (referenced internally to Me_4Si). Chemical shifts (δ, ppm) are relative to tetramethylsilane (TMS) with the resonance of the non-deuterated solvent or TMS as the internal standard. ^1H 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. Optical rotation was obtained on an Autopol V Plus polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique.

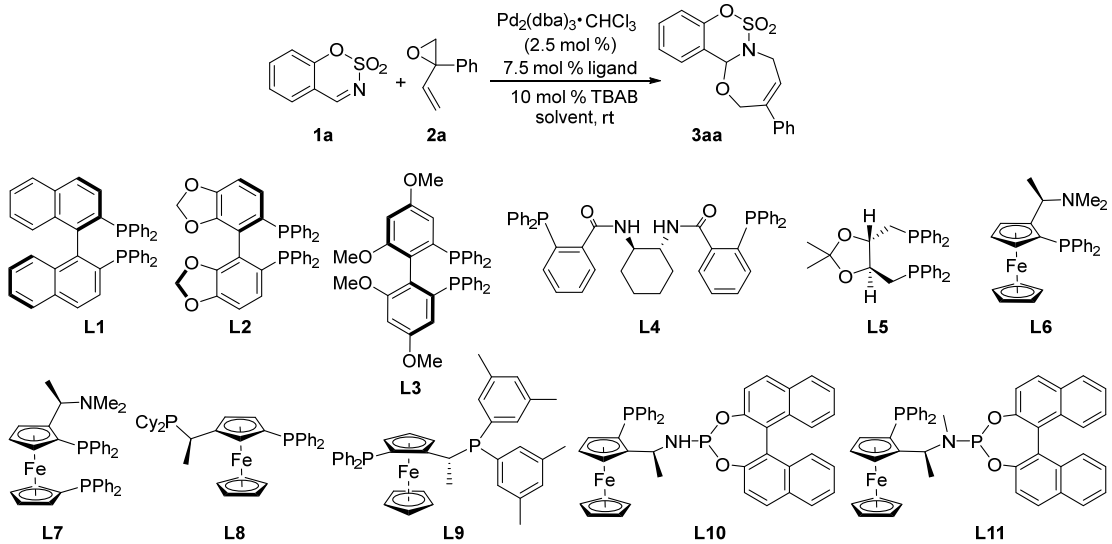
1. Wang, H.; Jiang, T.; Xu, M.-H. *J. Am. Chem. Soc.* **2013**, *135*, 971.
2. Trost, B. M.; Brown, B. S.; McEachern, E. J.; Kuhn, O. *Chem. Eur. J.* **2003**, *9*, 4442.

General Procedure for Pd (0)-Catalyzed [5 + 2] Cycloaddition



An oven-dried 10 mL of Schlenk tube was charged with sulfamate-derived cyclic imines **1** (0.2 mmol), 2-aryl-2-vinyloxiranes **2** (0.32 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 equiv, 5.2 mg), DPEphos (0.075 equiv, 8.0 mg) and TBAB (0.1 equiv, 6.4 mg) in 2 mL of CH_2Cl_2 for corresponding time under nitrogen atmosphere at room temperature. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (ethyl acetate/ petroleum ether = 1/30) to afford the corresponding cycloaddition product **3**.

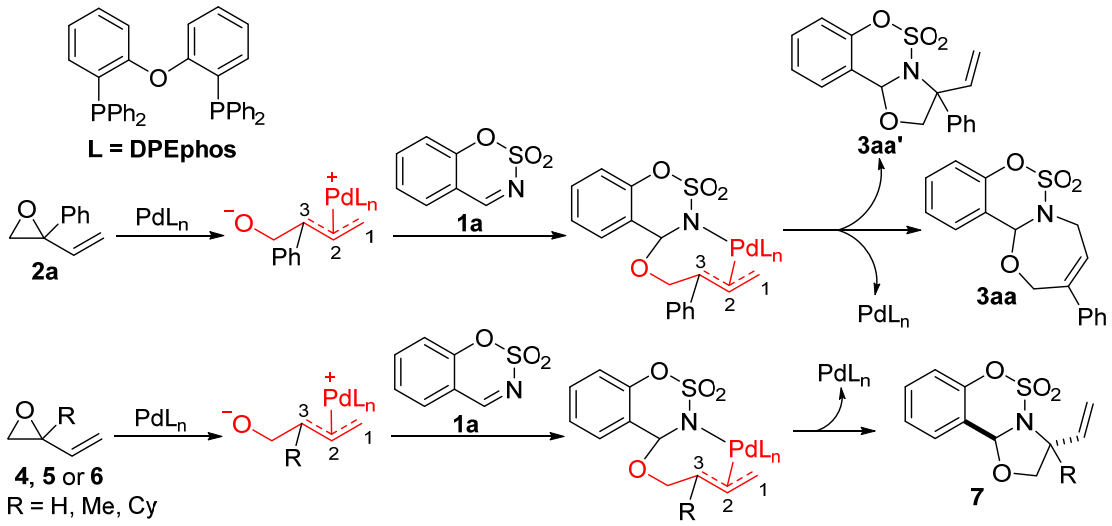
Table S1. Screening Reaction Conditions for Pd-Catalyzed Asymmetric [5 + 2] Cycloaddition



entry	ligand	*T*/°C	*t*/h	yield (%)[a]	ee (%)[b]	entry	ligand	*T*/°C	*t*/h	yield (%)[a]	ee (%)[b]
1	**L1**	25	24	13	20	8	**L8**	25	48	NR	-
2	**L2**	25	24	15	35	9	**L9**	25	48	NR	-
3	**L3**	25	24	15	-39	10	**L10**	25	16	69	0
4	**L4**	25	48	NR	-	11	**L11**	25	10	92	0
5	**L5**	25	5	86	15	12	**L5**	0	24	37	8
6	**L6**	25	48	NR	-	13	**L10**	0	24	37	4
7	**L7**	25	24	11	-18	14	**L11**	0	24	53	5

[a]Isolated yield. [b]Determined by chiral HPLC analysis.

Scheme S1. A Plausible Mechanism



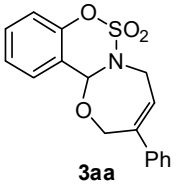
As shown in the Scheme S1, the ring-opening of the oxirane gives an electron-deficient C_3, which is stabilized by the neighboring C=C bond via delocalization of the π electrons. The presence of a Ph group on the C_3 enhances its stability with the C_3 adopting a planar conformation, and the deformation at this site costs energy. This results in the preference of the [5+2] pathway over the [3+2] one. The presence of the Ph group on C_3 also affects the stability of the product. According to calculations, the [5+2] product is about 11 kcal/mol more stable than the [3+2] product.

For the 2-vinyloxirane without a Ph group such as **4**, **5** or **6**, after the ring-opening of the oxirane, the electron-deficient region, which includes C_1, C_2 and C_3 atoms, is more active to interact with the electron-rich Pd^0 atom and the N atom. This to some extent weakens the conjugation in the area of the three C atoms, and makes it easier to deform the C_3 unit and form covalent bond with N atom. In contrast, the stronger interaction between Pd and the C=C bond impairs its access to the N atom of **2a**, leading to higher energy barrier to the [5+2] ring closure than the [3+2] one. According to calculations, the [3+2] cycloadduct from the substrate **4** is about 0.6 kcal/mol more stable than the [5+2] cycloadduct from the substrate **4**.

In conclusion, the chemical selectivity in the presence of a Ph group in the substrates **2** is the consequence of thermodynamic control. For the 2-vinyloxirane without a Ph group, the regioselectivity is the result of kinetic control.

Characterization Data for the Products 3

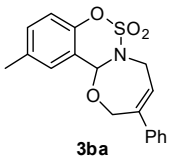
3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3aa)



3aa

Prepared according to the general procedure as described above in 96% yield (63.4 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 117 – 119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.23 (m, 7H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.30 (s, 1H), 5.96 (d, *J* = 7.3 Hz, 1H), 4.99 (q, *J* = 16.0 Hz, 2H), 4.20 (dd, *J* = 16.3, 7.3 Hz, 1H), 4.05 – 3.76 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 141.6, 138.3, 130.8, 128.3, 128.0, 127.7, 125.8, 125.3, 122.5, 118.3, 117.6, 89.9, 71.0, 43.0; IR (film) ν_{max} 1455, 1403, 1265, 1205, 1173, 1145, 1098, 908, 890, 834, 804, 749, 698, 628, 597, 566; HRMS (ESI) calcd for $C_{17}H_{16}NO_4S^+(M+H)^+$ 330.0795, found 330.0790.

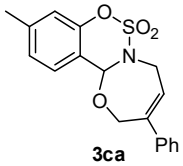
11-methyl-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]ox azepine 7,7-dioxide (3ba)



3ba

Prepared according to the general procedure as described above in 88% yield (60.6 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless crystal, m.p. 135 – 137 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.42 – 7.28 (m, 5H), 7.24 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.26 (s, 1H), 5.95 (dd, *J* = 5.1, 2.2 Hz, 1H), 4.98 (q, *J* = 16.0 Hz, 2H), 4.19 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.93 (dd, *J* = 16.3, 1.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 141.6, 138.4, 135.2, 131.4, 128.3, 128.1, 127.7, 125.8, 122.6, 117.8, 117.3, 89.9, 70.9, 43.0, 20.5; IR (film) ν_{max} 2926, 1489, 1403, 1266, 1207, 1183, 1139, 1109, 1017, 844, 808, 740, 704, 665, 615, 594; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S^+(M+H)^+$ 344.0951, found 344.0948.

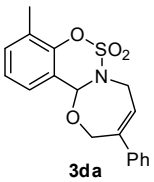
10-methyl-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ca)



3ca

Prepared according to the general procedure as described above in 86% yield (59.2 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 169 – 171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.26 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.88 (s, 1H), 6.26 (s, 1H), 5.95 (d, *J* = 6.8 Hz, 1H), 4.97 (q, *J* = 15.9 Hz, 2H), 4.18 (dd, *J* = 16.3, 7.2 Hz, 1H), 3.93 (d, *J* = 16.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 141.6, 141.5, 138.4, 128.3, 127.7, 127.7, 126.2, 125.8, 122.6, 117.8, 115.3, 89.9, 70.9, 42.9, 20.9; IR (film) ν_{max} 1627, 1446, 1403, 1354, 1336, 1269, 1194, 1146, 1104, 1048, 1016, 950, 894, 859, 809, 783, 749, 699, 647, 601, 569; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S^+$(M+H)$^+$ 344.0951, found 344.0948.

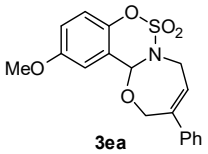
9-methyl-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3da)



3da

Prepared according to the general procedure as described above in 93% yield (64.0 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 118 – 119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.25 (m, 6H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.29 (s, 1H), 5.96 (dd, *J* = 4.4, 2.7 Hz, 1H), 4.97 (q, *J* = 16.1 Hz, 2H), 4.20 (dd, *J* = 16.3, 7.1 Hz, 1H), 3.96 (dd, *J* = 16.3, 1.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 141.7, 138.4, 132.2, 128.3, 127.7, 127.0, 125.8, 125.4, 124.6, 122.6, 118.1, 90.0, 70.8, 43.1, 15.2; IR (film) ν_{max} 1496, 1464, 1445, 1403, 1353, 1336, 1265, 1248, 1202, 1153, 1113, 1079, 1051, 1017, 880, 860, 801, 777, 748, 700, 683, 659, 606, 582; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S^+$(M+H)$^+$ 344.0951, found 344.0952.

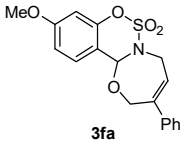
11-methoxy-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ea)



3ea

Prepared according to the general procedure as described above in 54% yield (38.9 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 122 –123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 5H), 7.10 (d, *J* = 2.6 Hz, 1H), 7.06 – 6.89 (m, 2H), 6.22 (s, 1H), 6.02 – 5.84 (m, 1H), 4.96 (q, *J* = 16.0 Hz, 2H), 4.17 (dd, *J* = 16.3, 7.2 Hz, 1H), 3.93 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 143.1, 141.6, 138.3, 128.3, 127.7, 125.8, 122.6, 118.9, 118.6, 117.1, 111.7, 89.8, 70.9, 55.5, 43.0; IR (film) ν_{max} 1489, 1402, 1281, 1205, 1173, 1141, 1108, 1034, 881, 844, 807, 750, 698, 617, 597; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+(M+H)^+$ 360.0900, found 360.0899.

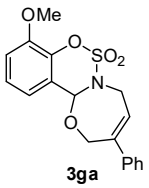
10-methoxy-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3fa)



3fa

Prepared according to the general procedure as described above in 72% yield (51.9 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.27 (m, 5H), 6.85 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 6.23 (s, 1H), 5.96 (d, *J* = 7.0 Hz, 1H), 4.96 (q, *J* = 15.9 Hz, 2H), 4.18 (dd, *J* = 16.2, 7.2 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.88 (d, *J* = 21.4 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 161.3, 150.0, 141.5, 138.3, 129.6, 128.7, 128.1, 125.9, 122.7, 112.8, 110.5, 102.8, 89.8, 70.7, 56.0, 43.0; IR (film) ν_{max} 1523, 1333, 1245, 1189, 1167, 1095, 1011, 908, 855, 807, 774, 690, 623, 545, 443; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+(M+H)^+$ 360.0900, found 360.0896.

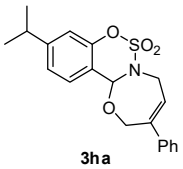
10-methoxy-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ga)



3ga

Prepared according to the general procedure as described above in 91% yield (65.5 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 168 – 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 7.25 – 7.16 (m, 2H), 7.02 (dd, *J* = 7.1, 2.1 Hz, 1H), 6.29 (s, 1H), 5.95 (d, *J* = 6.9 Hz, 1H), 4.96 (q, *J* = 16.0 Hz, 2H), 4.20 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.98 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 141.6, 139.2, 138.3, 128.3, 127.7, 125.8, 124.9, 122.5, 119.2, 118.9, 113.1, 90.0, 71.0, 56.0, 43.1; IR (film) ν_{max} 1585, 1483, 1441, 1403, 1354, 1319, 1276, 1244, 1203, 1162, 1080, 1016, 877, 857, 800, 775, 747, 700, 606, 554; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+$(M+H)$^+$360.0900, found 360.0898.

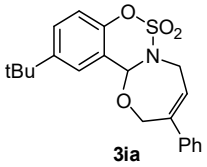
10-isopropyl-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ha)



3ha

Prepared according to the general procedure as described above in 80% yield (59.5 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.29 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 6.27 (s, 1H), 5.96 (d, *J* = 7.0 Hz, 1H), 4.97 (q, *J* = 16.0 Hz, 2H), 4.19 (dd, *J* = 16.3, 7.2 Hz, 1H), 3.95 (d, *J* = 16.2 Hz, 1H), 2.96 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 149.4, 141.6, 138.4, 128.3, 127.8, 127.7, 125.8, 123.7, 122.6, 115.6, 115.3, 89.9, 70.9, 43.0, 33.6, 23.3; IR (film) ν_{max} 1505, 1483, 1435, 1403, 1251, 1201, 1152, 1129, 1074, 1037, 864, 821, 740, 699, 606, 567; HRMS (ESI) calcd for $C_{20}H_{22}NO_4S^+$(M+H)$^+$ 372.1264, found 372.1262.

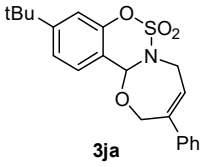
11-(tert-butyl)-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1, 3]oxazepine 7,7-dioxide (3ia)



3ia

Prepared according to the general procedure as described above in 95% yield (73.4 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 168 – 169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.42 – 7.31 (m, 5H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.30 (s, 1H), 6.02 – 5.88 (m, 1H), 5.01 (q, *J* = 16.0 Hz, 2H), 4.21 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.95 (dd, *J* = 16.3, 1.5 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 147.2, 141.6, 138.4, 128.3, 128.0, 127.7, 125.8, 124.6, 122.6, 117.4, 117.1, 90.2, 71.0, 43.0, 34.4, 31.0; IR (film) ν_{max} 2965, 1494, 1404, 1366, 1264, 1181, 1151, 1121, 1095, 1017, 846, 803, 776, 749, 611, 600; HRMS (ESI) calcd for $C_{21}H_{24}NO_4S^+(M+H)^+$ 386.1421, found 386.1417.

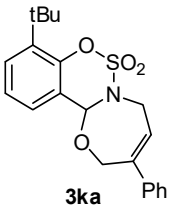
10-(tert-butyl)-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1, 3]oxazepine 7,7-dioxide (3ja)



3ja

Prepared according to the general procedure as described above in 82% yield (63.3 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.29 (m, 6H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.28 (s, 1H), 5.96 (dd, *J* = 5.1, 2.1 Hz, 1H), 4.98 (q, *J* = 16.0 Hz, 2H), 4.20 (dd, *J* = 16.3, 7.3 Hz, 1H), 3.95 (dd, *J* = 16.3, 1.7 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 149.2, 141.6, 138.4, 128.3, 127.7, 127.6, 125.8, 122.6, 115.3, 114.5, 89.9, 70.9, 43.0, 34.6, 30.7; IR (film) ν_{max} 2965, 1625, 1567, 1497, 1445, 1403, 1337, 1272, 1199, 1177, 1152, 1128, 1088, 1017, 943, 866, 827, 804, 770, 749, 708, 655, 627, 602, 566; HRMS (ESI) calcd for $C_{21}H_{24}NO_4S^+(M+H)^+$ 386.1421, found 386.1417.

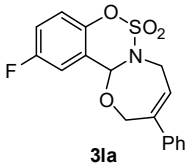
10-(tert-butyl)-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ka)



3ka

Prepared according to the general procedure as described above in 83% yield (64.1 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 2H), 7.39 – 7.22 (m, 6H), 6.27 (s, 1H), 6.04 – 5.86 (m, 1H), 4.95 (q, *J* = 16.0 Hz, 2H), 4.23 (dd, *J* = 16.5, 6.6 Hz, 1H), 4.06 (dd, *J* = 16.4, 1.6 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6, 141.8, 138.9, 138.5, 128.3, 128.3, 127.7, 125.9, 125.8, 124.8, 122.6, 119.3, 89.9, 70.4, 43.3, 34.7, 29.6; IR (film)ν_{max} 2963, 1429, 1404, 1267, 1200, 1165, 1134, 1088, 1051, 1017, 916, 880, 861, 827, 802, 746, 698, 658, 607, 593, 563; HRMS (ESI) calcd for $C_{21}H_{24}NO_4S^+(M+H)^+$ 386.1421, found 386.1416.

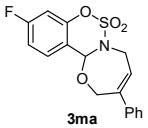
11-fluoro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3la)



3la

Prepared according to the general procedure as described above in 42% yield (29.2 mg). Reaction time = 36 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 166 – 167 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.25 (m, 6H), 7.09 (d, *J* = 1.9 Hz, 1H), 6.25 (s, 1H), 6.03 – 5.90 (m, 1H), 4.98 (q, *J* = 16.1 Hz, 2H), 4.19 (dd, *J* = 16.3, 7.4 Hz, 1H), 3.90 (dd, *J* = 16.2, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (d, *J* = 244.5 Hz), 145.3 (d, *J* = 3.0 Hz), 141.6, 138.2, 128.3, 127.8, 125.8, 122.3, 119.8 (d, *J* = 6.8 Hz), 119.2 (d, *J* = 8.3 Hz), 117.9 (d, *J* = 24.0 Hz), 114.6 (d, *J* = 24.8 Hz), 89.42, 71.15, 42.98; IR (film) ν_{max} 1486, 1429, 1404, 1261, 1205, 1163, 1134, 1095, 884, 843, 808. 748, 698, 665, 616, 594; HRMS (ESI) calcd for $C_{17}H_{15}FNO_4S^+(M+H)^+$ 348.0700, found 348.0699.

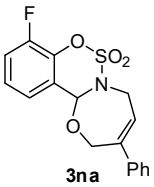
10-fluoro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ma)



3ma

Prepared according to the general procedure as described above in 83% yield (57.8 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 156 – 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.6, 6.3 Hz, 1H), 7.49 – 7.25 (m, 5H), 7.03 (td, *J* = 8.4, 2.5 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.26 (s, 1H), 6.10 – 5.82 (m, 1H), 4.99 (q, *J* = 16.0 Hz, 2H), 4.20 (dd, *J* = 16.3, 7.4 Hz, 1H), 3.91 (dd, *J* = 16.3, 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (d, *J* = 250.0 Hz), 150.2 (d, *J* = 4.5 Hz), 141.6, 138.2, 129.6 (d, *J* = 9.8 Hz), 128.3, 127.8, 125.8, 122.3, 114.3 (d, *J* = 3.0 Hz), 112.7 (d, *J* = 21.0 Hz), 105.3 (d, *J* = 25.5 Hz), 89.5, 71.1, 42.9; IR (film) ν_{max} 1621, 1597, 1500, 1407, 1267, 1243, 1195, 1136, 1091, 973, 897, 863, 809, 784, 744, 697, 648, 603, 563; HRMS (ESI) calcd for $C_{17}H_{15}FNO_4S^+(M+H)^+$ 348.0700, found 348.0700.

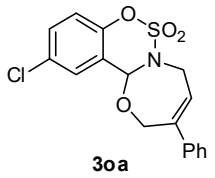
9-fluoro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3na)



3na

Prepared according to the general procedure as described above in 79% yield (55.0 mg). Reaction time = 36 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 114 – 116 °C.°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.03 (m, 8H), 6.32 (s, 1H), 5.96 (d, *J* = 7.2 Hz, 1H), 5.00 (q, *J* = 16.1 Hz, 2H), 4.22 (dd, *J* = 16.4, 7.3 Hz, 1H), 3.95 (d, J = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1 (d, *J* = 250.0 Hz), 141.6, 138.1, 128.3, 127.8, 125.8, 124.9 (d, *J* = 6.8 Hz), 122.9 (d, *J* = 3.8 Hz), 122.3, 120.3, 117.6 (d, *J* = 17.3 Hz), 89.8 (d, *J* = 2.3Hz), 71.27, 43.04; IR (film) ν_{max} 1480, 1409, 1336, 1271, 1206, 1180, 1153, 1050, 1017, 879, 859, 807, 775, 747, 699, 607, 592; HRMS (ESI) calcd for $C_{17}H_{15}FNO_4S^+(M+H)^+$ 348.0700, found 348.0698.

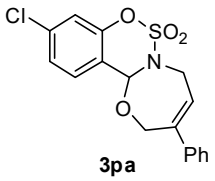
11-chloro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3oa)



3oa

Prepared according to the general procedure as described above in 73% yield (53.0 mg). Reaction time = 36 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 138 – 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.4 Hz, 1H), 7.46 – 7.28 (m, 6H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.25 (s, 1H), 5.95 (d, *J* = 7.3 Hz, 1H), 4.99 (q, *J* = 16.1 Hz, 2H), 4.19 (dd, *J* = 16.2, 7.5 Hz, 1H), 3.90 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 141.6, 138.1, 130.9, 130.6, 128.3, 128.0, 127.8, 125.8, 122.2, 119.8, 119.0, 89.3, 71.2, 43.0; IR (film) ν_{max} 1474, 1408, 1203, 1174, 1150, 1110, 885, 836, 776, 749, 698, 647, 604, 588; HRMS (ESI) calcd for $C_{17}H_{13}ClNO_4S^-$ $(M-H)^-$ 362.0259, found 362.0263.

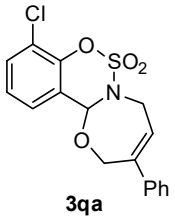
10-chloro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3pa)



3pa

Prepared according to the general procedure as described above in 70% yield (51.0 mg). Reaction time = 48 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 142 – 143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.23 (m, 6H), 7.10 (d, *J* = 1.9 Hz, 1H), 6.25 (s, 1H), 5.95 (dd, *J* = 5.3, 2.1 Hz, 1H), 4.98 (q, *J* = 16.0 Hz, 2H), 4.19 (dd, *J* = 16.2, 7.4 Hz, 1H), 3.90 (dd, *J* = 16.2, 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 141.6, 138.1, 136.1, 129.2, 128.3, 127.8, 125.8, 125.6, 122.3, 117.9, 116.8, 89.5, 71.2, 42.9; IR (film) ν_{max} 1609, 1481, 1407, 1207, 1177, 1149, 1116, 1080, 926, 894, 859, 801, 749, 695, 601, 567; HRMS (ESI) calcd for $C_{17}H_{15}ClNO_4S^+$ $(M+H)^+$ 364.0405, found 364.0403.

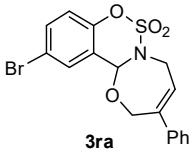
9-chloro-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3qa)



3qa

Prepared according to the general procedure as described above in 35% yield (25.5 mg). Reaction time = 72 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 130 – 131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.46 (m, 2H), 7.38 – 7.27 (m, 5H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.28 (s, 1H), 6.02 – 5.82 (m, 1H), 4.97 (q, *J* = 16.0 Hz, 2H), 4.20 (dd, *J* = 16.4, 7.4 Hz, 1H), 3.91 (dd, *J* = 16.3, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 141.6, 138.1, 131.5, 128.3, 127.8, 126.4, 125.8, 125.1, 122.6, 122.3, 120.0, 89.8, 71.2, 43.1; IR (film) ν_{max} 1446, 1408, 1200, 1178, 1155, 1136, 1049, 1017, 875, 854, 790, 749, 690, 604, 576; HRMS (ESI) calcd for $C_{17}H_{15}ClNO_4S^+$ $(M+H)^+$ 364.0405, found 364.0406.

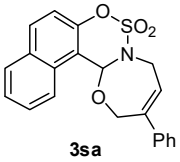
11-bromo-3-phenyl-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ra)



3ra

Prepared according to the general procedure as described above in 61% yield (50.2 mg). Reaction time = 72 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 142 – 143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.2 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.51 – 7.23 (m, 5H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.26 (s, 1H), 5.95 (d, *J* = 7.2 Hz, 1H), 4.99 (q, *J* = 15.9 Hz, 2H), 4.19 (dd, *J* = 16.3, 7.5 Hz, 1H), 3.89 (d, J = 16.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 141.6, 138.1, 133.8, 131.0, 128.3, 127.8, 125.8, 122.2, 120.1, 119.3, 118.0, 89.3, 71.2, 43.0; IR (film) ν_{max} 1472, 1404, 1330, 1258, 1203, 1176, 1150, 1109, 1053, 1017, 902, 884, 834, 769, 749, 694, 640, 600, 582; HRMS (ESI) calcd for $C_{17}H_{13}BrNO_4S^-$ $(M-H)^-$ 405.9754, found 405.9752.

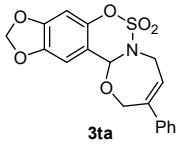
3-phenyl-5,14c-dihydro-2*H*-naphtho[1',2':5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3sa)



3sa

Prepared according to the general procedure as described above in 87% yield (66.1 mg). Reaction time = 18 h. It was purified by flash chromatography (Ether/PE=1/20) to afford yellow solid, m.p. 118 – 119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.91 (t, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 7.7, 6.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.29 (m, 5H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.73 (s, 1H), 6.05 (t, *J* = 5.0 Hz, 1H), 5.01 (q, *J* = 15.9 Hz, 2H), 4.32 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 141.7, 138.2, 132.2, 131.4, 130.9, 128.7, 1286, 128.3, 128.1, 127.8, 127.4, 125.7, 125.6, 124.5, 122.9, 117.4, 112.3, 90.7, 70.7, 44.1; IR (film) ν_{max} 1597, 1515, 1435, 1404, 1350, 1266, 1190, 1141, 1075, 1015, 953, 930, 889, 826, 749, 716, 698, 658, 644, 610, 588; HRMS (ESI) calcd for $C_{21}H_{18}NO_4S^+(M+H)^+$ 380.0951, found 380.0949.

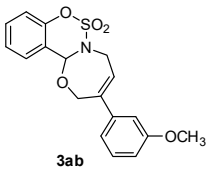
3-phenyl-5,13b-dihydro-2*H*-[1,3]dioxolo[4'',5'':4',5']benzo[1',2':5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ta)



3ta

Prepared according to the general procedure as described above in 68% yield (50.9 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 156 – 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 18.1, 7.3 Hz, 5H), 7.01 (s, 1H), 6.56 (s, 1H), 6.16 (s, 1H), 6.01 (t, *J* = 10.9 Hz, 1H), 5.95 (d, *J* = 6.2 Hz, 1H), 4.94 (q, *J* = 16.0 Hz, 2H), 4.16 (dd, *J* = 16.3, 7.1 Hz, 1H), 3.94 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 145.1, 144.2, 141.6, 138.3, 128.3, 127.7, 125.8, 122.5, 110.7, 106.2, 101.8, 99.1, 89.8, 70.8, 43.0; IR (film) ν_{max} 1505, 1483, 1435, 1403, 1251, 1201, 1152, 1129, 1074, 1037, 864, 821, 740, 699, 606, 567; HRMS (ESI) calcd for $C_{18}H_{15}NO_6S^+(M+H)^+$ 374.0693, found 374.0693.

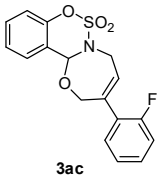
3-(3-methoxyphenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ab)



3ab

Prepared according to the general procedure as described above in 70% yield (50.4 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 134 – 135 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.44 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.01 – 6.81 (m, 3H), 6.29 (s, 1H), 5.96 (d, *J* = 7.1 Hz, 1H), 4.95 (dt, *J* = 18.4, 9.1 Hz, 2H), 4.19 (dd, *J* = 16.3, 7.4 Hz, 1H), 3.92 (dd, *J* = 16.4, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 149.4, 141.5, 139.7, 130.8, 129.3, 128.0, 125.3, 122.6, 118.3, 118.2, 117.6, 113.1, 111.7, 89.8, 71.0, 55.0, 42.9; IR (film) ν_{max} 1580, 1455, 1403, 1289, 1266, 1205, 1173, 1145, 1098, 893, 860, 838, 802, 759, 566; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+(M+H)^+$ 360.0900, found 360.0899.

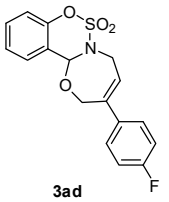
3-(2-fluorophenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ac)



3ac

Prepared according to the general procedure as described above in 25% yield (17.4 mg). Reaction time = 48 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 89 – 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.29 (dd, *J* = 12.6, 6.3 Hz, 3H), 7.18 – 6.94 (m, 3H), 6.30 (s, 1H), 5.92 (d, *J* = 7.0 Hz, 1H), 4.92 (dd, *J* = 36.7, 15.9 Hz, 2H), 4.21 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.92 (d, *J* = 16.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.02, 157.74, 159.4 (d, *J* = 24.8 Hz), 149.4, 138.1, 130.8, 129.5 (d, *J* = 3.8 Hz), 129.4, 128.0, 126.4 (d, *J* = 15.0 Hz), 125.4, 125.3, 124.1 (d, *J* = 3.0 Hz), 118.2, 117.5, 115.5 (d, *J* = 21.8 Hz), 90.0 70.8, 70.7, 43.0; IR (film) ν_{max} 1487, 1454, 1404, 1265, 1206, 1174, 1146, 1097, 1035, 909, 892, 857, 835, 802, 757, 676, 599, 568; HRMS (ESI) calcd for $C_{17}H_{15}FNO_4S^+(M+H)^+$ 348.0700, found 348.0699.

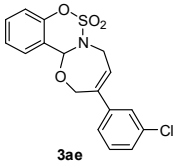
3-(4-fluorophenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ad)



3ad

Prepared according to the general procedure as described above in 75% yield (52.2 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 131 – 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.20 (m, 3H), 7.06 (t, *J* = 8.6 Hz, 3H), 6.29 (s, 1H), 5.91 (d, *J* = 7.0 Hz, 1H), 5.15 – 4.83 (m, 2H), 4.18 (dd, *J* = 16.3, 7.1 Hz, 1H), 3.92 (dd, *J* = 16.3, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.8 Hz), 149.4, 140.7, 134.4 (d, *J* = 3.0 Hz), 130.8, 128.0, 127.6, 127.4, 125.3, 122.6, 118.2, 117.6, 115.4, 115.1, 89.8, 70.9, 42.9; IR (film) ν_{max} 1511, 1455, 1404, 1266, 1206, 1175, 1146, 1099, 909, 891, 857, 835, 790, 761, 673, 633, 597, 565; HRMS (ESI) calcd for $C_{17}H_{15}FNO_4S^+(M+H)^+$ 348.0700, found 348.0697.

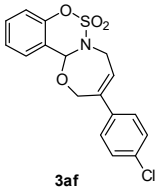
3-(3-chlorophenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ae)



3ae

Prepared according to the general procedure as described above in 48% yield (35.1 mg). Reaction time = 48 h. It was purified by flash chromatography (Ether/PE=1/20) to afford yellow semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.18 (dd, *J* = 6.3, 3.7 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 5.99 (dd, *J* = 6.7, 3.6 Hz, 1H), 5.05 – 4.84 (m, 2H), 4.20 (dd, *J* = 16.5, 7.2 Hz, 1H), 3.93 (dd, *J* = 16.4, 2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 140.5, 140.1, 134.3, 130.9, 129.6, 128.0, 127.8, 126.0, 125.3, 123.9, 123.7, 118.2, 117.6, 89.8, 70.6, 42.9; IR (film) ν_{max} 1484, 1455, 1404, 1338, 1266, 1206, 1174, 1146, 1100, 913, 891, 858, 835, 803, 763, 738, 673, 628, 599, 566; HRMS (ESI) calcd for $C_{17}H_{13}ClNO_4S^-(M-H)^-$ 362.0259, found 362.0260.

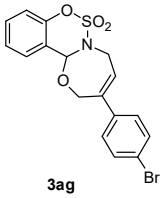
3-(4-chlorophenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3af)



3af

Prepared according to the general procedure as described above in 71% yield (51.8 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 140 – 141 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.29 (dt, *J* = 18.5, 8.3 Hz, 5H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 5.95 (d, *J* = 6.5 Hz, 1H), 5.09 – 4.82 (m, 2H), 4.19 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.92 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 140.5, 136.7, 133.6, 130.9, 128.5, 128.0, 127.1, 125.3, 123.1, 118.2, 117.6, 89.8, 70.7, 42.9; IR (film) ν_{max} 1494, 1455, 1404, 1266, 1206, 1174, 1146, 1098, 1013, 909, 891, 833, 807, 761, 672, 630, 598; HRMS (ESI) calcd for $C_{17}H_{13}ClNO_4S^-$(M-H)$^-$ 362.0259, found 362.0265.

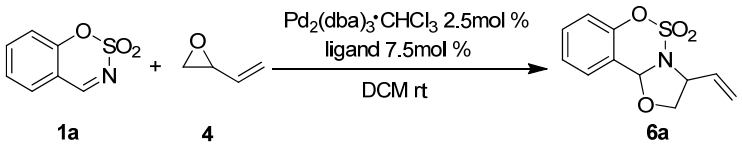
3-(4-bromophenyl)-5,12b-dihydro-2*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*][1,3]oxazepine 7,7-dioxide (3ag)



3ag

Prepared according to the general procedure as described above in 61% yield (49.5 mg). Reaction time = 72 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 149 – 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.28 (s, 1H), 5.95 (d, *J* = 7.1 Hz, 1H), 5.05 – 4.84 (m, 2H), 4.19 (dd, *J* = 16.5, 7.3 Hz, 1H), 3.91 (dd, *J* = 16.4, 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 140.6, 137.2, 131.4, 130.9, 128.0, 127.4, 125.3, 123.2, 121.8, 118.2, 117.6, 89.8, 70.6, 42.9; IR (film) ν_{max} 1488, 1403, 1266, 1205, 1173, 1146, 1099, 1009, 909, 891, 832, 806, 760, 671, 629, 598, 567; HRMS (ESI) calcd for $C_{17}H_{13}BrNO_4S^-$ (M-H)$^-$ 405.9754, found 405.9756.

Table S2. Screening Reaction Conditions for Pd-Catalyzed [3 + 2] Cycloaddition

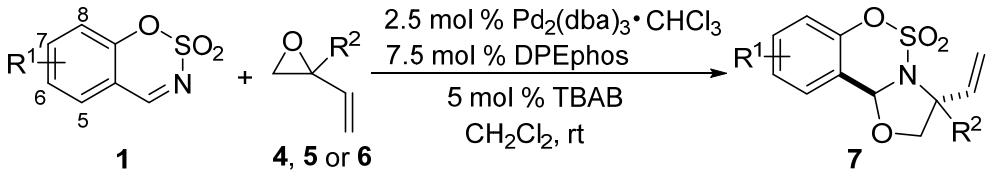


1a **4** **6a**

entry	ligand	*t*/h	yield (%)[a]	dr[b]
1	no ligand	24	NR	-
2	PPh_3	10	95	2:1
3	dppe	4	98	2.3:1
4	dppp	5	95	20:1
5	dppbz	5	94	20:1
6	DPEphos	10	94	25:1
7	Xantphos	10	86	25:1
8[c]	DPEphos	6	95	25:1

[a]Isolated yield. [b]Determined by ^{1}HNMR. [c]5 mol% TBAB (Tetrabutylammonium bromide) was added.

General Procedure for Pd-Catalyzed [3 + 2] Cycloaddition

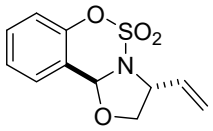


1 **4**, **5** or **6** **7**

An oven-dried 10 mL of Schlenk tube was charged with sulfamate-derived cyclic imines **1** (0.2 mmol), vinyl epoxides **4**, **5** or **6** (0.30 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 equiv, 5.2 mg), DPEphos (0.075 equiv, 8.0 mg) and TBAB (0.05equiv, 3.2 mg) in 2 mL of CH_2Cl_2 for corresponding time under nitrogen atmosphere at room temperature. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (ethyl acetate/ petroleum ether = 1/20) to afford the corresponding cycloaddition product **7**.

Characterization Data for the Products 7

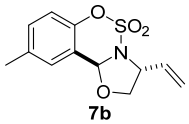
3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7a)



7a

Prepared according to the general procedure as described above in 96% yield (48.8 mg). Reaction time = 4 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 60 – 61 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 6.1 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.33 (s, 1H), 5.93 (ddd, *J* = 17.2, 9.2, 4.2 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 4.42 (dd, *J* = 11.3, 7.0 Hz, 1H), 4.07 – 3.97 (m, 1H), 3.90 (dd, *J* = 9.0, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 134.4, 130.9, 127.8, 125.8, 119.3, 118.4, 118.0, 90.9, 70.3, 61.5; IR (film) ν_{max} 1484, 1455, 1404, 1203, 1176, 1121, 1032, 987, 941, 889, 863, 822, 760, 703, 634, 590, 563; HRMS (ESI) calcd for $C_{11}H_{12}NO_4S^+(M+H)^+$ 254.0481, found 254.0481.

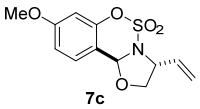
9-methyl-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7b)



7b

Prepared according to the general procedure as described above in 97% yield (52.0 mg). Reaction time = 6 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless crystal, m.p. 98 – 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 6.1 Hz, 2H), 7.12 – 6.76 (m, 1H), 6.28 (s, 1H), 5.91 (ddd, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.40 – 5.20 (m, 1H), 4.41 (td, *J* = 7.1, 4.3 Hz, 1H), 4.02 (dd, *J* = 8.9, 7.2 Hz, 1H), 3.89 (dd, *J* = 9.0, 4.3 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 135.7, 134.4, 131.5, 127.9, 118.8, 118.4, 117.7, 90.9, 70.3, 61.5, 20.4; IR (film) ν_{max} 2924, 1492, 1404, 1328, 1260, 1206, 1184, 1157, 1128, 1102, 987, 941, 836, 763, 672, 648, 620, 587, 513; HRMS (ESI) calcd for $C_{12}H_{14}NO_4S^+(M+H)^+$ 268.0638, found 268.0636.

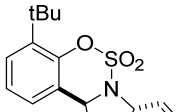
8-methoxy-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7c)



7c

Prepared according to the general procedure as described above in 88% yield (50.0 mg). Reaction time = 10 h. It was purified by flash chromatography (Ether/PE=1/20) to afford pale yellow solid, m.p. 79 – 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, *J* = 6.5 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.55 (d, *J* = 2.4 Hz, 1H), 6.26 (s, 1H), 5.90 (ddd, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.42 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 4.40 (dd, *J* = 11.2, 7.0 Hz, 1H), 4.11 – 3.92 (m, 1H), 3.87 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 151.4, 134.6, 128.6, 118.3, 112.6, 111.0, 102.8, 90.8, 70.1, 61.5, 55.4; IR (film) ν_{max} 1627, 1581, 1505, 1404, 1275, 1239, 1201, 1153, 1118, 1030, 942, 790, 745, 606, 578; HRMS (ESI) calcd for $C_{12}H_{14}NO_5S^+(M+H)^+$ 284.0578, found 284.0586.

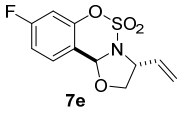
7-(tert-butyl)-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7d)



7d

Prepared according to the general procedure as described above in 94% yield (58.3 mg). Reaction time = 6 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.32 – 7.17 (m, 2H), 6.22 (s, 1H), 5.92 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.47 (d, *J* = 17.0 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 4.52 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.12 (dd, *J* = 8.9, 7.1 Hz, 1H), 3.84 (dd, *J* = 9.0, 5.5 Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 134.0, 128.4, 126.1, 125.3, 120.1, 118.6, 91.3, 70.2, 62.5, 34.6, 29.7; IR (film) ν_{max} 2963, 1481, 1434, 1405, 1199, 1169, 1147, 1116, 1020, 985, 936, 864, 801, 771, 745, 597; HRMS (ESI) calcd for $C_{15}H_{20}NO_4S^+(M+H)^+$ 310.1108, found 310.1106.

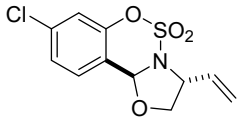
8-fluoro-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7e)



7e

Prepared according to the general procedure as described above in 95% yield (51.7 mg). Reaction time = 4 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 63 – 64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.00 (td, *J* = 8.4, 2.5 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.30 (s, 1H), 6.05 – 5.80 (m, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 4.41 (dt, *J* = 11.3, 5.7 Hz, 1H), 4.01 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.91 (dd, *J* = 9.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (d, *J* = 250.5Hz), 151.2 (d, *J* = 12.0Hz), 134.1, 129.4 (d, *J* = 2.3Hz), 118.6, 115.4 (d, *J* = 3.8Hz), 113.4 (d, *J* = 21.8Hz), 105.8 (d, *J* = 26.3Hz), 90.5, 70.3, 61.5; IR (film) ν_{max} 1621, 1599, 1500, 1410, 1268, 1237, 1203, 1139, 1094, 971, 941, 858, 792, 749, 606, 574; HRMS (ESI) calcd for $C_{11}H_{11}FNO_4S^+(M+H)^+$ 272.0387, found 272.0388.

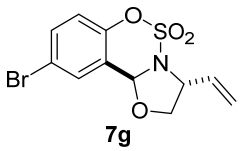
8-chloro-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7f)



7f

Prepared according to the general procedure as described above in 93% yield (53.6 mg). Reaction time = 4 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 62 – 63 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.20 (m, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 6.30 (s, 1H), 5.90 (ddd, *J* = 17.1, 10.2, 7.2 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 4.40 (td, *J* = 7.1, 4.3 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.91 (dd, *J* = 9.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 136.3, 134.1, 128.8, 126.1, 118.7, 118.4, 117.9, 90.4, 70.4, 61.5; IR (film) ν_{max} 1610, 1575, 1482, 1408, 1206, 1182, 1111, 1081, 917, 807, 778, 700, 599, 567; HRMS (ESI) calcd for $C_{11}H_{11}ClNO_4S^+(M+H)^+$ 288.0092, found 288.0090.

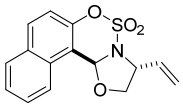
9-bromo-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7g)



7g

Prepared according to the general procedure as described above in 86% yield (57.1 mg). Reaction time = 12 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless crystal, m.p. 104 – 105 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.3 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.29 (s, 1H), 5.90 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.42 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 4.39 (td, *J* = 7.1, 4.2 Hz, 1H), 4.02 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.93 (dd, *J* = 9.1, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 134.0, 133.9, 130.6, 121.2, 119.8, 118.7, 118.4, 90.2, 70.5, 61.4; IR (film) ν_{max} 1471, 1410, 1178, 1129, 1106, 940, 824, 783, 698, 641, 597, 580; HRMS (ESI) calcd for $C_{11}H_{11}BrNO_4S^+(M+H)^+$ 331.9587, found 331.9589.

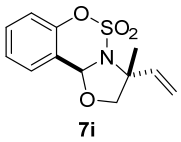
3-vinyl-3,12c-dihydro-2*H*-naphtho[1,2-e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7h)



7h

Prepared according to the general procedure as described above in 96% yield (58.4 mg). Reaction time = 6 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 82 – 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (t, *J* = 9.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 6.90 (s, 1H), 5.99 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.51 (d, *J* = 17.0 Hz, 1H), 5.36 (d, *J* = 10.2 Hz, 1H), 4.57 (dd, *J* = 11.3, 6.8 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.95 (dd, *J* = 9.0, 4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 134.4, 132.1, 131.2, 130.4, 128.4, 127.6, 125.8, 123.7, 118.5, 117.4, 112.5, 90.5, 70.3, 62.1; IR (film) ν_{max} 1515, 1408, 1192, 1123, 1076, 940, 877, 819, 750, 718, 641, 613; HRMS (ESI) calcd for $C_{15}H_{14}NO_4S^+(M+H)^+$ 304.0638, found 304.0638.

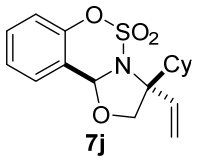
3-methyl-3-vinyl-3,10b-dihydro-2*H*-benzo[e]oxazolo[3,2-*c*][1,2,3]oxathiazine 5,5-dioxide (7i)



7i

Prepared according to the general procedure as described above in 92% yield (49.3 mg). Reaction time = 6 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.34 (m, 2H), 7.31 – 7.19 (m, 1H), 7.09 – 6.96 (m, 1H), 6.35 – 6.29 (s, 1H), 6.07 – 5.93 (m, 1H), 5.46 – 5.22 (m, 2H), 4.06 – 3.65 (m, 2H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.1, 138.4, 130.6, 127.2, 125.4, 120.2, 118.0, 116.1, 90.6, 77.9, 67.3, 19.0; IR (film) ν_{max} 2880, 1615, 1584, 1485, 1455, 1403, 1264, 1176, 1133, 1095, 974, 932, 887, 862, 820, 758, 702, 644, 591, 565; HRMS (ESI) calcd for $C_{12}H_{14}NO_4S^+(M+H)^+$ 268.0638, found 268.0638.

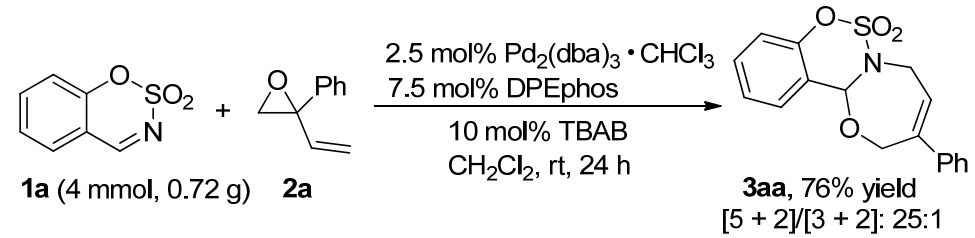
3-cyclohexyl-3-vinyl-3,10b-dihydro-2H-benzo[e]oxazolo[3,2-c][1,2,3]oxathiazine 5,5-dioxide (7j)



7j

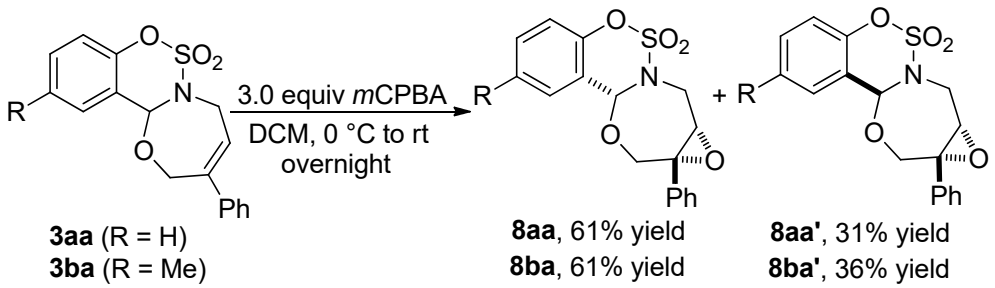
Prepared according to the general procedure as described above in 37% yield (24.8 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford colorless semi-solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 2H), 7.31 – 7.20 (m, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.27 (s, 1H), 6.17 (dd, *J* = 17.7, 11.2 Hz, 1H), 5.18 (dd, *J* = 37.3, 14.4 Hz, 2H), 4.08 (dd, J = 24.9, 9.2 Hz, 2H), 2.17 – 1.98 (m, 2H), 1.90 – 1.70 (m, 4H), 1.35 – 1.11 (m, 4H), 0.92 – 0.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 134.7, 130.3, 126.8, 125.1, 120.2, 117.7, 117.5, 90.7, 72.1, 70.7, 43.2, 28.1, 26.8, 26.2, 26.1, 25.9; IR (film) ν_{max} 2970, 1530, 1300, 1256, 1143, 1102, 932, 908, 842, 818, 725, 701, 673, 621, 566, 433; HRMS (ESI) calcd for $C_{17}H_{22}NO_4S^+(M+H)^+$ 336.1255, found 336.1264.

Synthesis of 1,3-oxazepine heterocycles on the gram scale



An oven-dried 100 mL of Schlenk tube was charged with sulfamate-derived cyclic imines **1a** (4 mmol, 0.72 g), vinyloxirane **2a** (6.4 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 equiv, 104 mg), DPEphos (0.075 equiv, 162 mg) and TBAB (0.1 equiv, 129 mg) in 40 mL of CH_2Cl_2 for corresponding time under nitrogen atmosphere at room temperature. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (ethyl acetate/ petroleum ether = 1/30) to afford the corresponding cycloaddition product **3aa**.

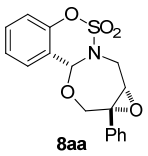
Representative procedure for the epoxidation



To a solution of seven-membered heterocycle **3** (0.10 mmol, 1.0 equiv.) in dichloromethane (2 mL) was added the dichloromethane solution of *m*CPBA (0.30 mmol, 0.30 M, 1.0 mL) dropwise at 0 ℃ under nitrogen. The reaction mixture was sealed under nitrogen and allowed to warm to room temperature and stir for 24 hours. The reaction was then quenched with saturated $NaHCO_3$ solution and extracted with dichloromethane. The combined organic phase was collected and dried with Na_2SO_4. After filtration and evaporation, the residue was purified by silica gel chromatography (hexanes/EA = 15:1).

Characterization Data for the Products 8

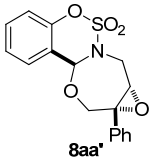
9a-phenyl-8a,9a,10,11a-tetrahydro-8*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*]oxireno [2,3-*e*][1,3]oxazepine 6,6-dioxide (8aa)



8aa

Prepared according to the general procedure as described above in 61% yield (21.1mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 138 – 139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.30 (m, 6H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.19 (s, 1H), 4.75 – 4.36 (m, 2H), 4.12 (dd, *J* = 14.2, 6.5 Hz, 1H), 3.50 – 3.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 135.9, 130.9, 128.4, 128.4, 125.7, 125.4, 117.6, 117.5, 90.1, 68.9, 64.7, 60.9, 44.0; IR (film) ν_{max} 1455, 1403, 1206, 1173, 1135, 1101, 917, 891, 865, 832, 757, 701, 675, 627, 589, 571; HRMS (ESI) calcd for $C_{17}H_{16}NO_5S^+(M+H)^+$ 346.0743, found 346.0739.

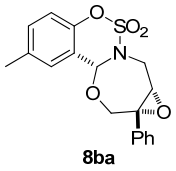
9a-phenyl-8a,9a,10,11a-tetrahydro-8*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*]oxireno [2,3-*e*][1,3]oxazepine 6,6-dioxide (8aa′)



8aa'

Prepared according to the general procedure as described above in 31% yield (10.7 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 145 – 147 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.38 – 7.29 (m, 4H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.00 (s, 1H), 4.60 (d, *J* = 14.0 Hz, 1H), 4.35 – 4.02 (m, 2H), 3.82 (dd, *J* = 15.5, 4.1 Hz, 1H), 3.29 (t, *J* = 4.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 137.6, 131.1, 128.2, 128.0, 127.9, 125.8, 125.2, 119.3, 117.9, 90.1, 69.9, 64.1, 62.3, 45.3; IR (film) ν_{max} 1456, 1387, 1208, 1175, 1078, 1011, 866, 833, 806, 760, 700, 630, 566; HRMS (ESI) calcd for $C_{17}H_{16}NO_5S^+(M+H)^+$ 346.0743, found 346.0736.

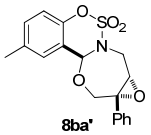
2-methyl-9a-phenyl-8a,9a,10,11a-tetrahydro-8*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*]oxireno[2,3-*e*][1,3]oxazepine 6,6-dioxide (8ba)



8ba

Prepared according to the general procedure as described above in 61% yield (22.0 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p.174 – 175 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.33 (m, 6H), 7.19 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.15 (s, 1H), 4.74 – 4.36 (m, 2H), 4.12 (dd, *J* = 14.5, 6.9 Hz, 1H), 3.38 (ddd, *J* = 18.2, 10.7, 3.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 135.9, 135.3, 131.5, 128.4, 128.3, 125.6, 117.2, 117.1, 90.1, 68.9, 64.7, 60.9, 44.0, 20.4; IR (film) ν_{max} 2922, 1489, 1403, 1349, 1266, 1207, 1185, 1111, 1017, 968, 911, 837, 748, 701, 666, 613, 587, 546, 475; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+$(M+H)$^+$ 360.0900, found 360.0893.

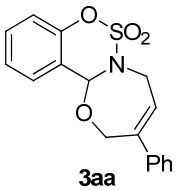
2-methyl-9a-phenyl-8a,9a,10,11a-tetrahydro-8*H*-benzo[5,6][1,2,3]oxathiazino[4,3-*b*]oxireno[2,3-*e*][1,3]oxazepine 6,6-dioxide (8ba′)



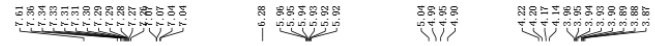
8ba'

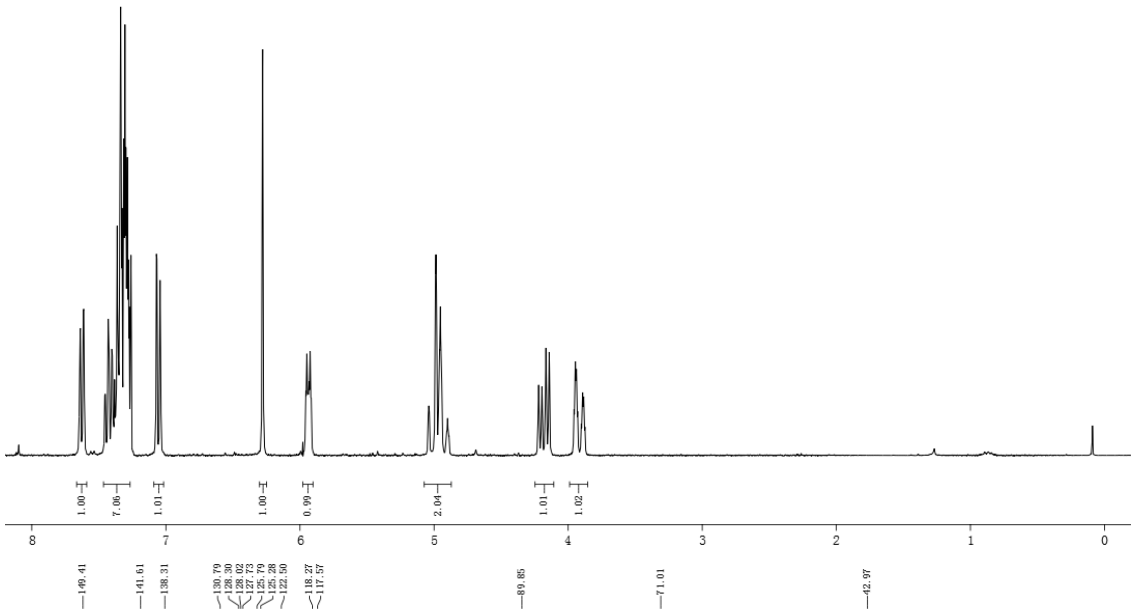
Prepared according to the general procedure as described above in 36% yield (13.0 mg). Reaction time = 24 h. It was purified by flash chromatography (Ether/PE=1/20) to afford white solid, m.p. 153 – 155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.34 (dd, *J* = 11.2, 5.1 Hz, 4H), 7.27 – 7.21 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 1H), 4.59 (d, *J* = 14.0 Hz, 1H), 4.36 – 4.11 (m, 2H), 3.80 (dd, J = 15.5, 4.2 Hz, 1H), 3.29 (t, J = 4.1 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 137.6, 135.7, 131.7, 128.2, 128.1, 127.9, 125.3, 118.9, 117.6, 90.1, 69.9, 64.2, 62.4, 45.4, 20.5; IR (film) ν_{max} 2923, 1495, 1385, 1264, 1209, 1180, 1080, 1015, 948, 871, 789, 760, 700, 665, 620, 599, 574, 541; HRMS (ESI) calcd for $C_{18}H_{18}NO_5S^+$ (M+H)$^+$ 360.0900, found 360.0891.

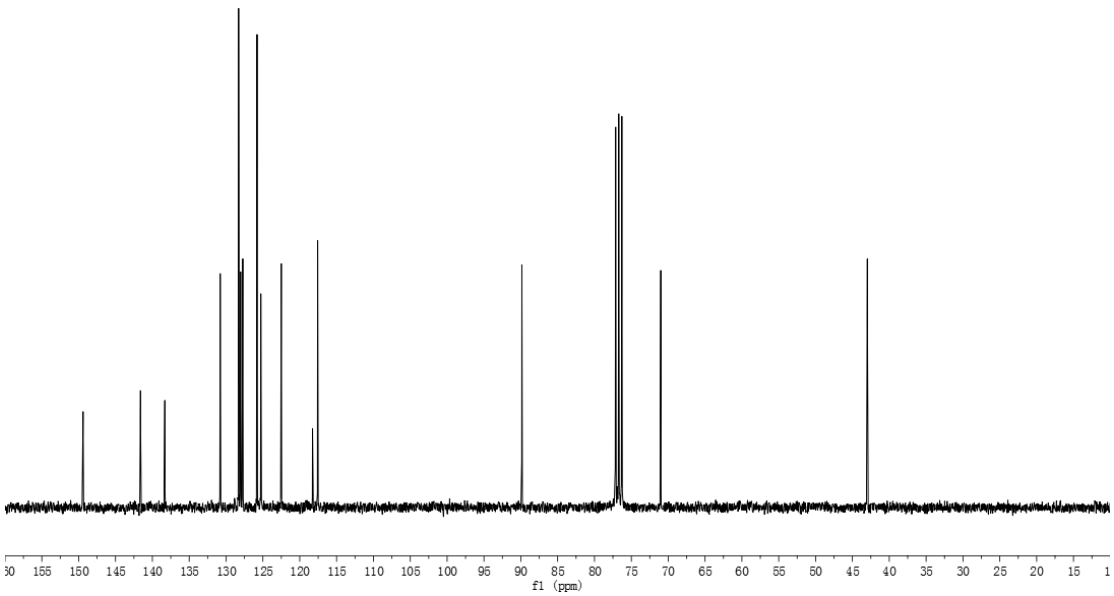
^{1}H and ^{13}C NMR Spectra of the Products 3, **5** and **8**

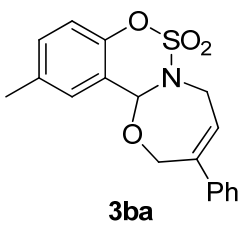


3aa





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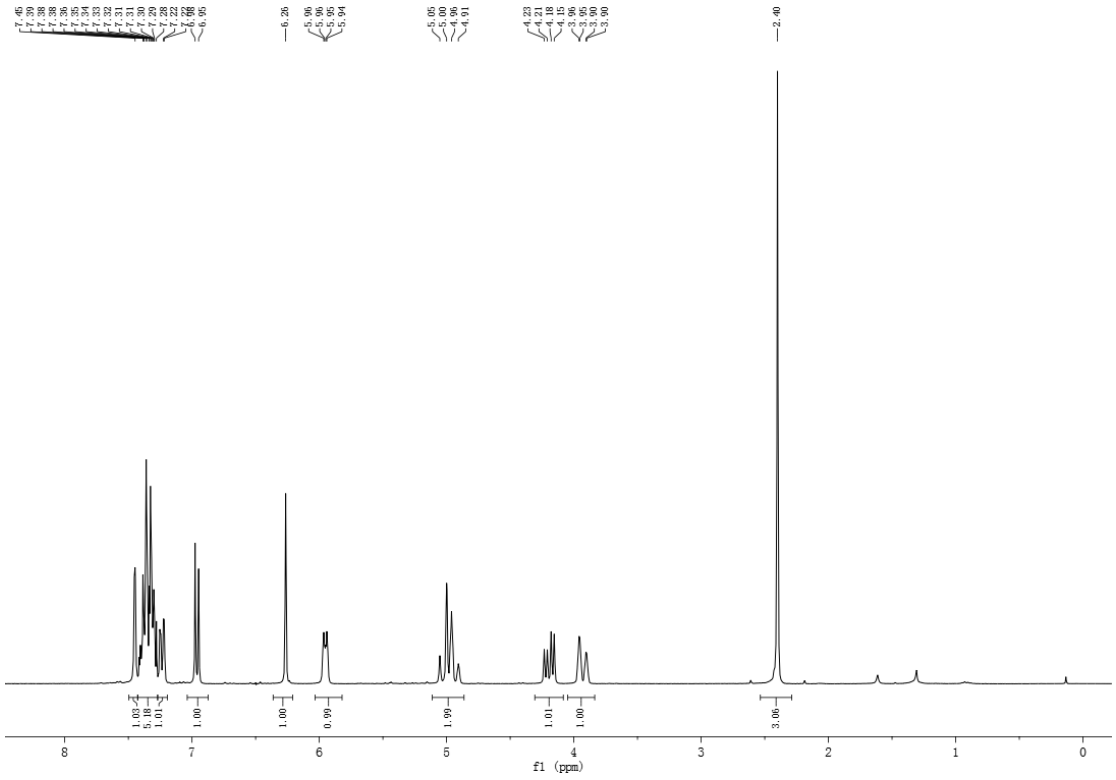
SO2
N
O
Ph

3ba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4.18
4.15
3.96
3.95
3.90
3.90
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1.00
0.99
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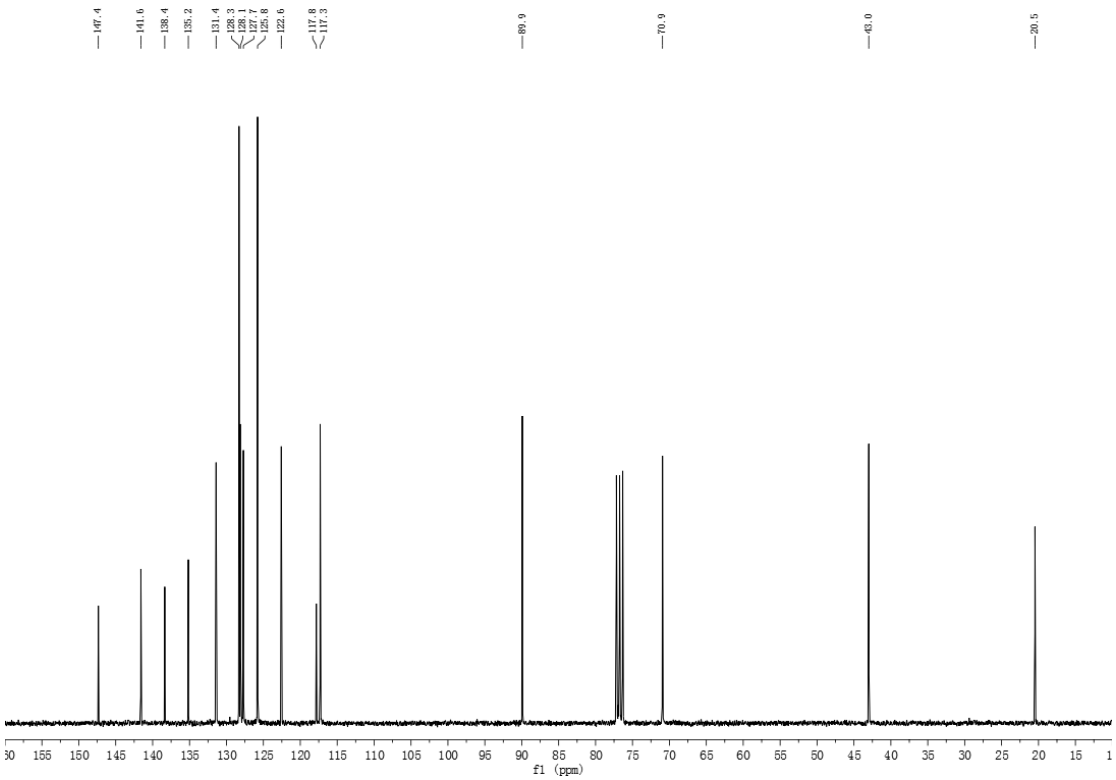
1.01
1.00
3.06
f1 (ppm)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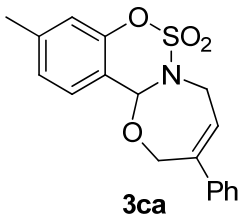
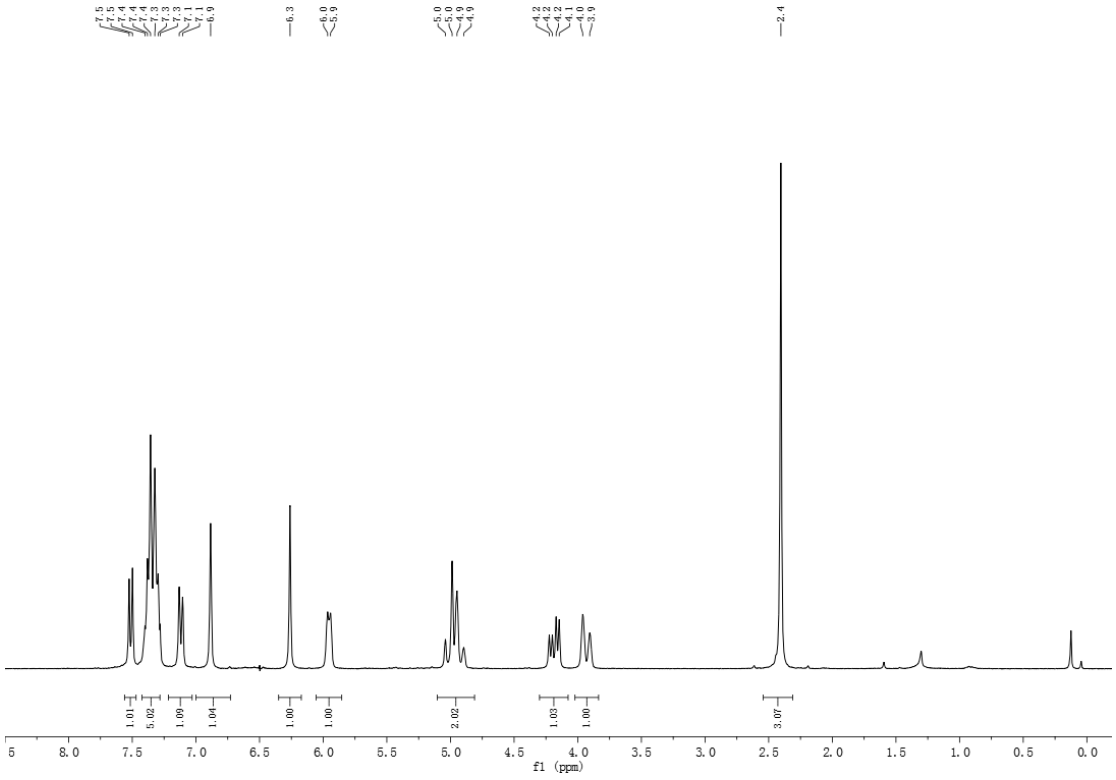
117.8
117.3
89.9
70.9
43.0
20.5
f1 (ppm)


O
SO2
N
O
Ph

3ca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5.0
5.0
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4.9
4.2
4.2
4.2
4.1
4.0
3.9
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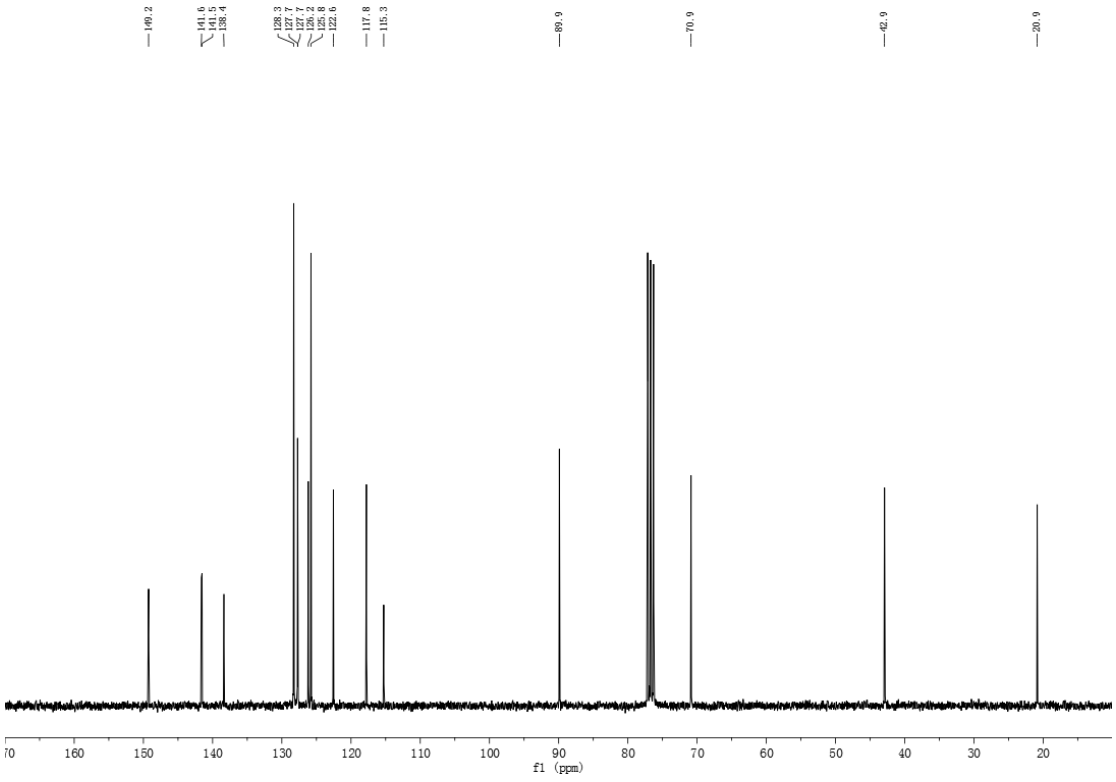
1.00
1.00
2.02
1.03
1.00
3.07
f1 (ppm)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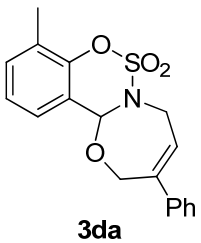
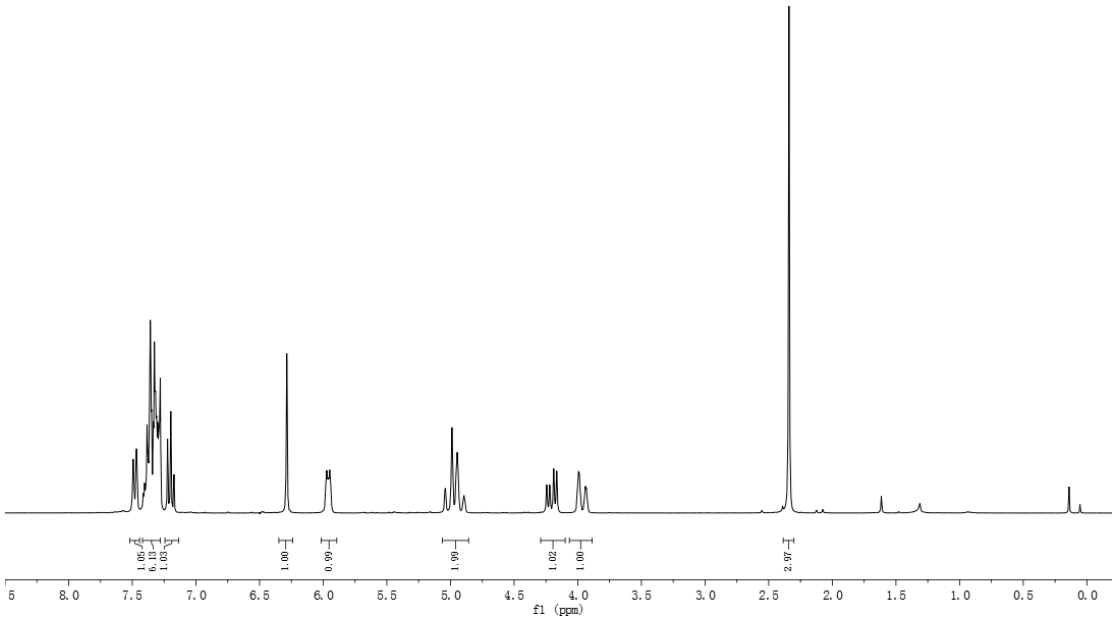
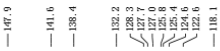
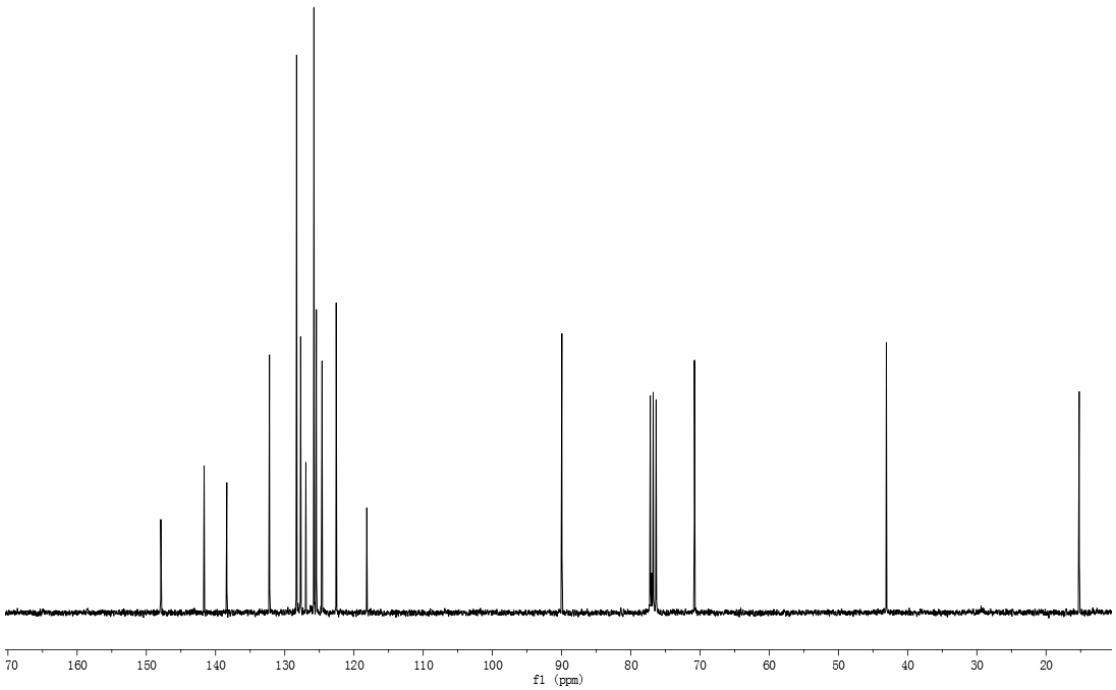
20.9
f1 (ppm)

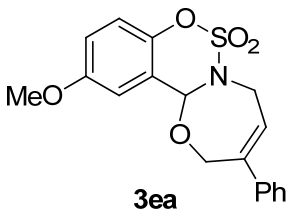


3da

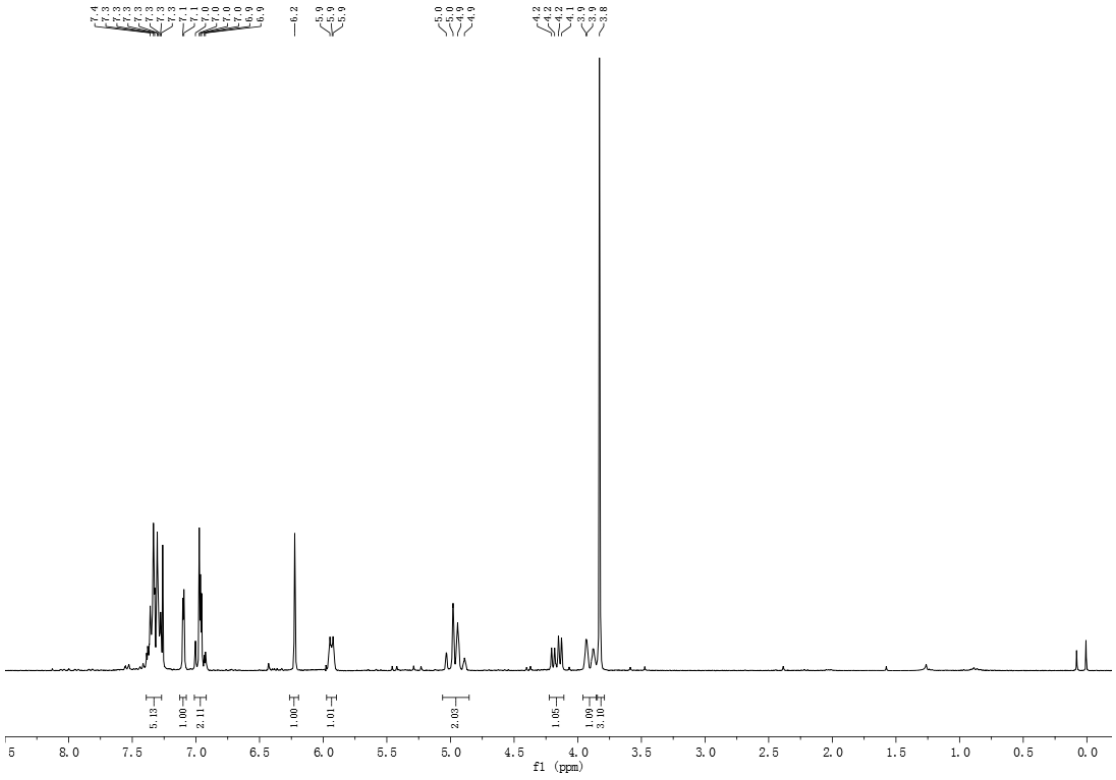


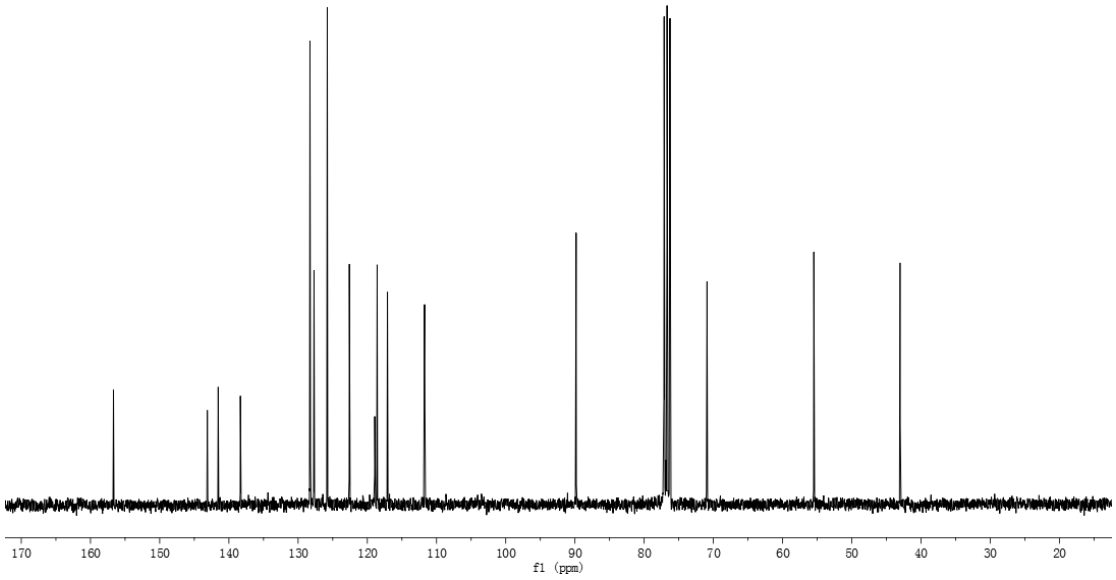


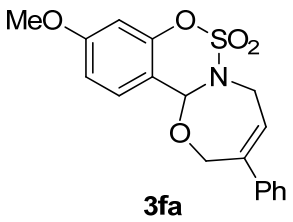




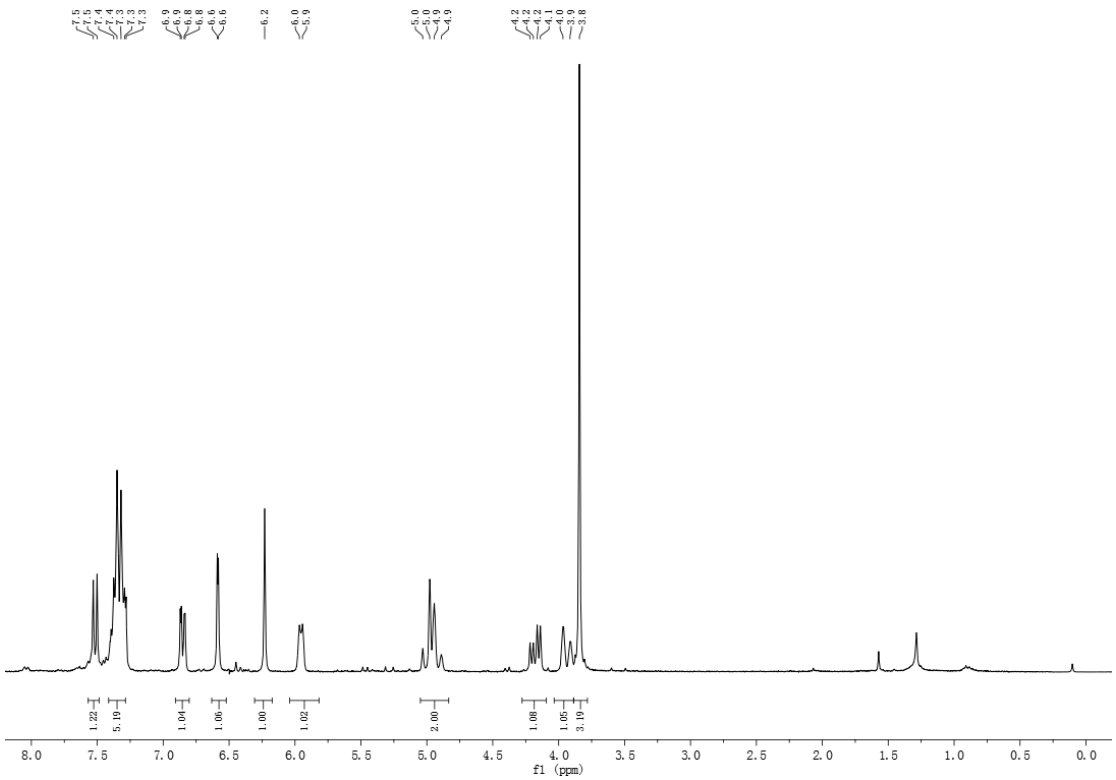
3ea






MeO
O
SO2
N
O
Ph

3fa


7.5
7.5
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7.4
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6.2
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5.9
5.0
5.0
4.9
4.9
4.2
4.2
4.2
4.1
4.0
3.9
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1.00
1.02
2.00
1.08
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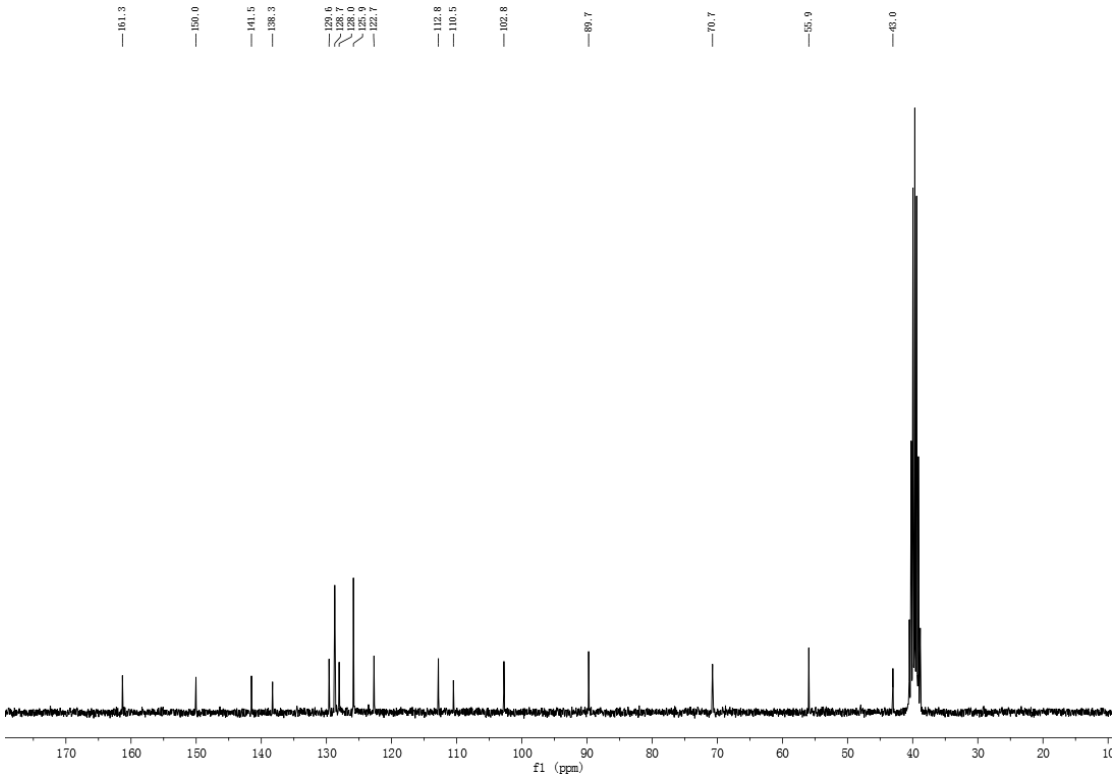
3.19
f1 (ppm)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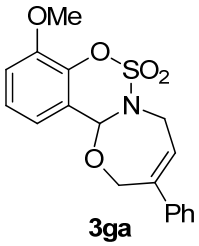
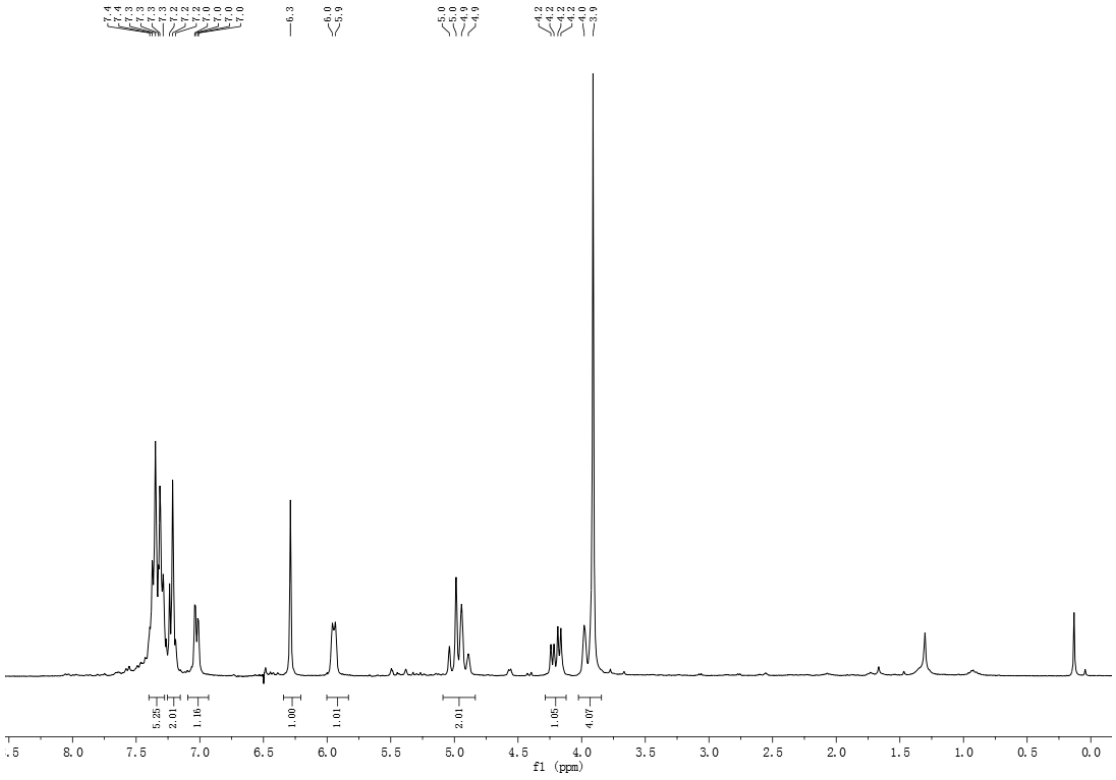
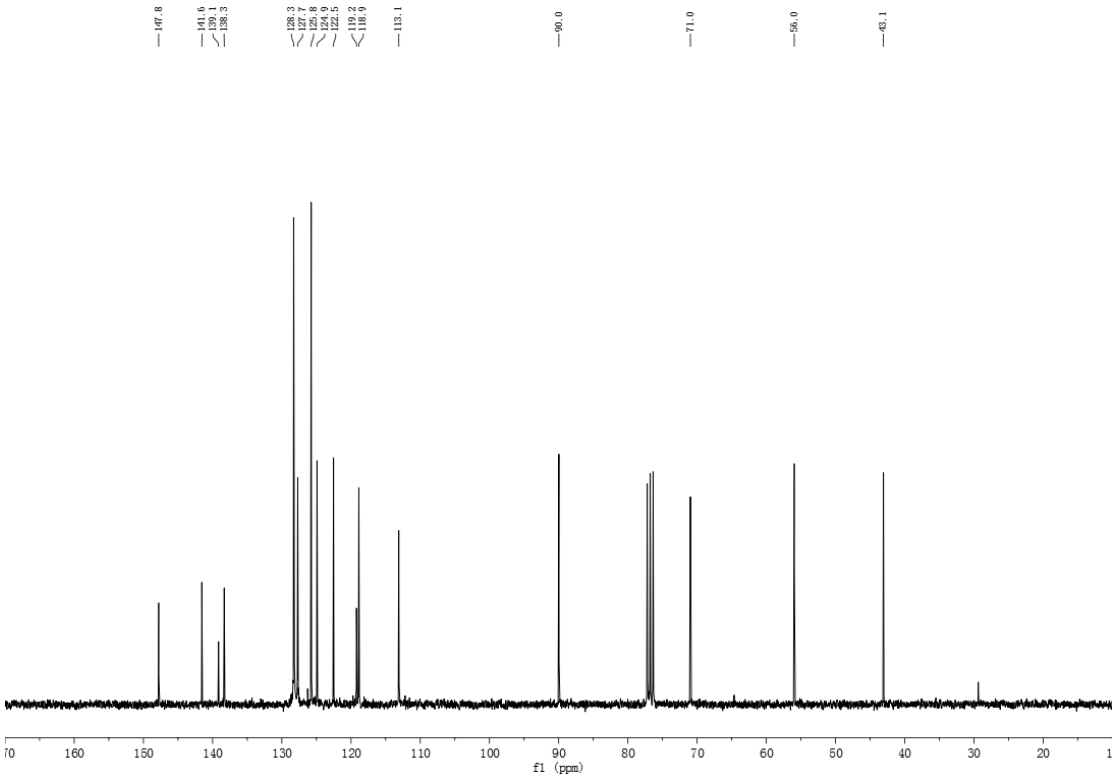
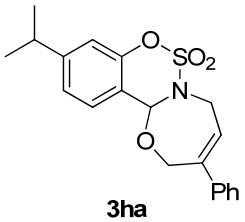
150.0
141.5
138.3
129.6
128.7
128.0
125.9
122.7
112.8
110.5
102.8
89.7
70.7
55.9
43.0
f1 (ppm)


OMe
O
SO2
N
O
Ph

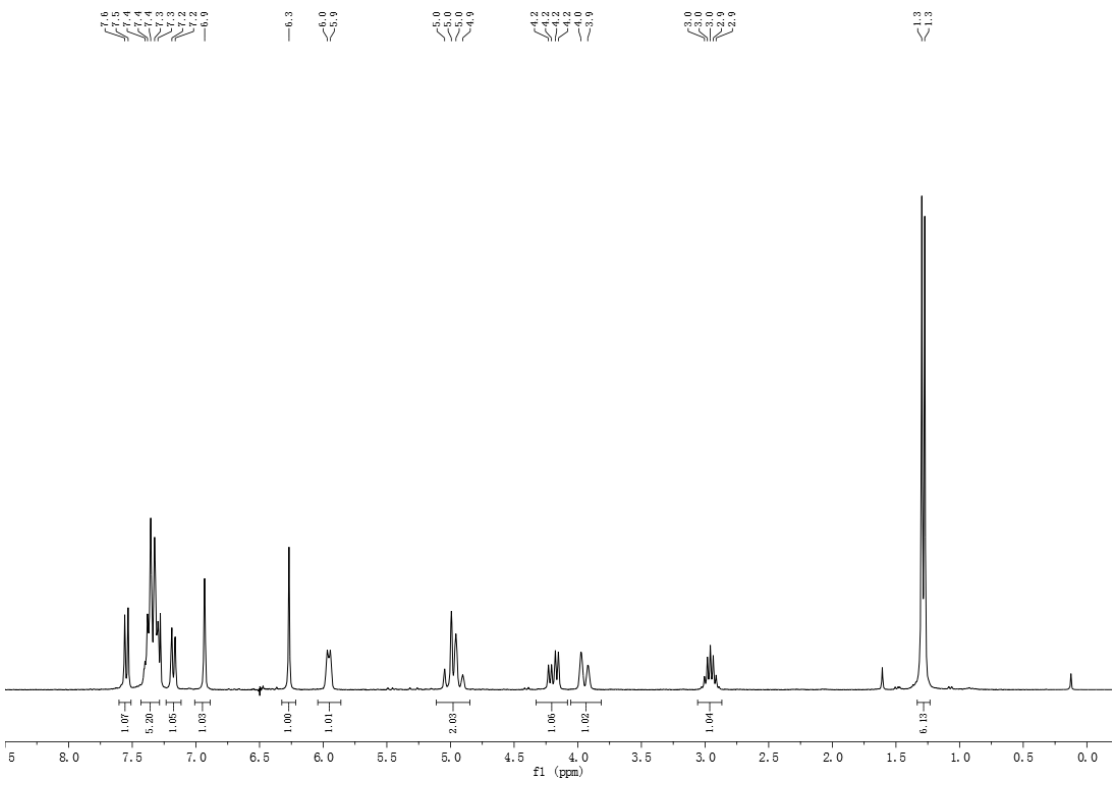
3ga

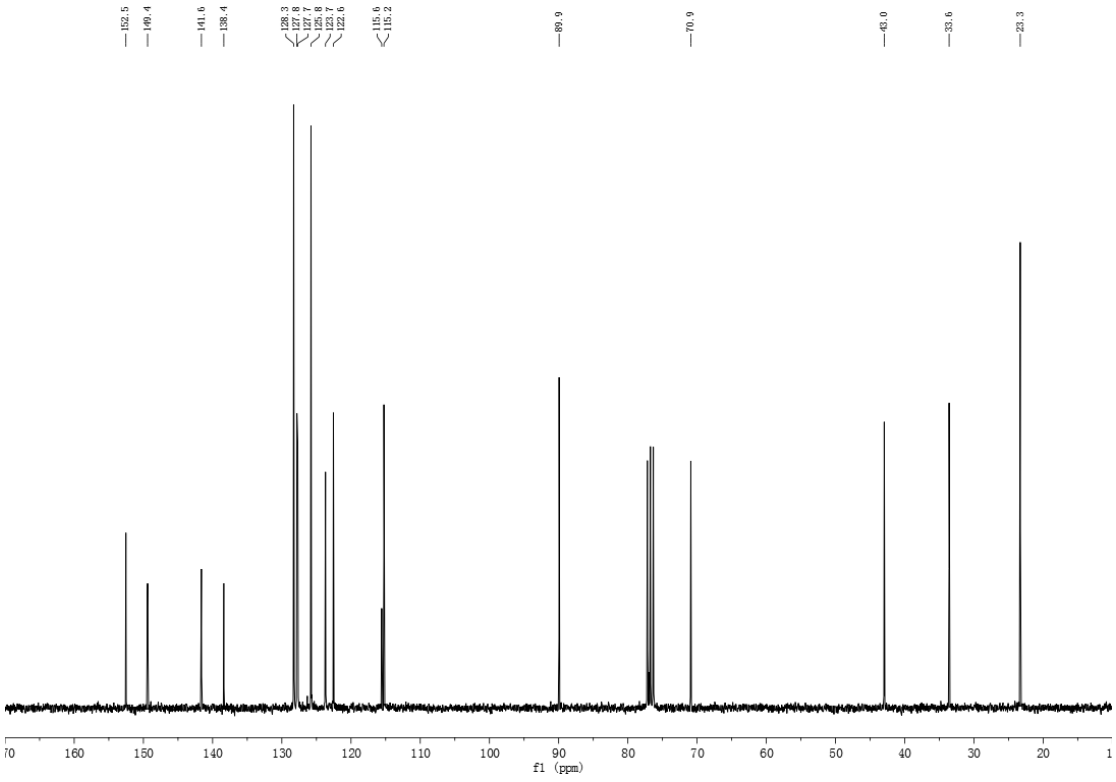

7.4
7.4
7.3
7.3
7.3
7.3
7.2
7.2
7.2
7.2
7.0
7.0
7.0
7.0
7.0
6.3
6.0
5.9
5.0
5.0
4.9
4.9
4.2
4.2
4.2
4.2
4.0
3.9
5.25
2.01
1.16
1.00
1.01
2.01
1.05
4.07
f1 (ppm)

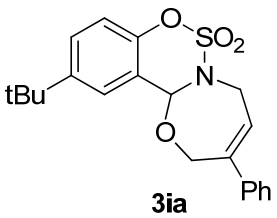

147.8
141.6
139.1
136.3
128.3
127.7
125.8
124.9
122.5
119.2
116.9
113.1
90.0
71.0
56.0
43.1
f1 (ppm)


O
SO2
N
O
Ph

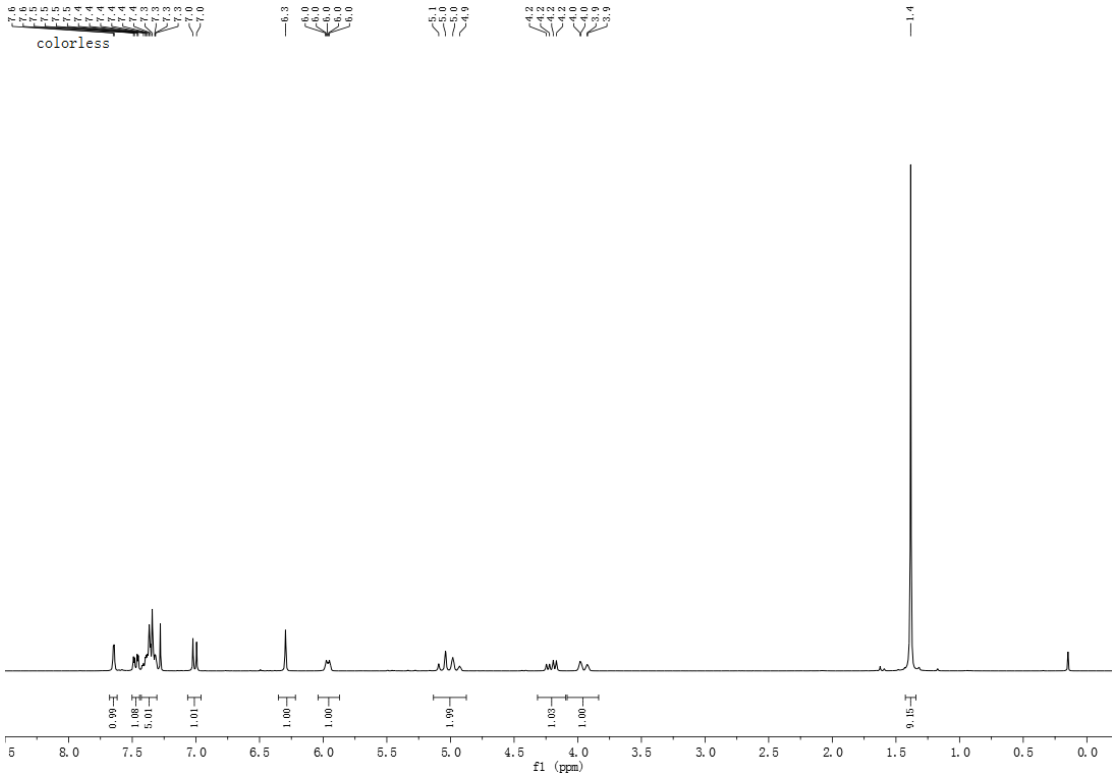
3ha

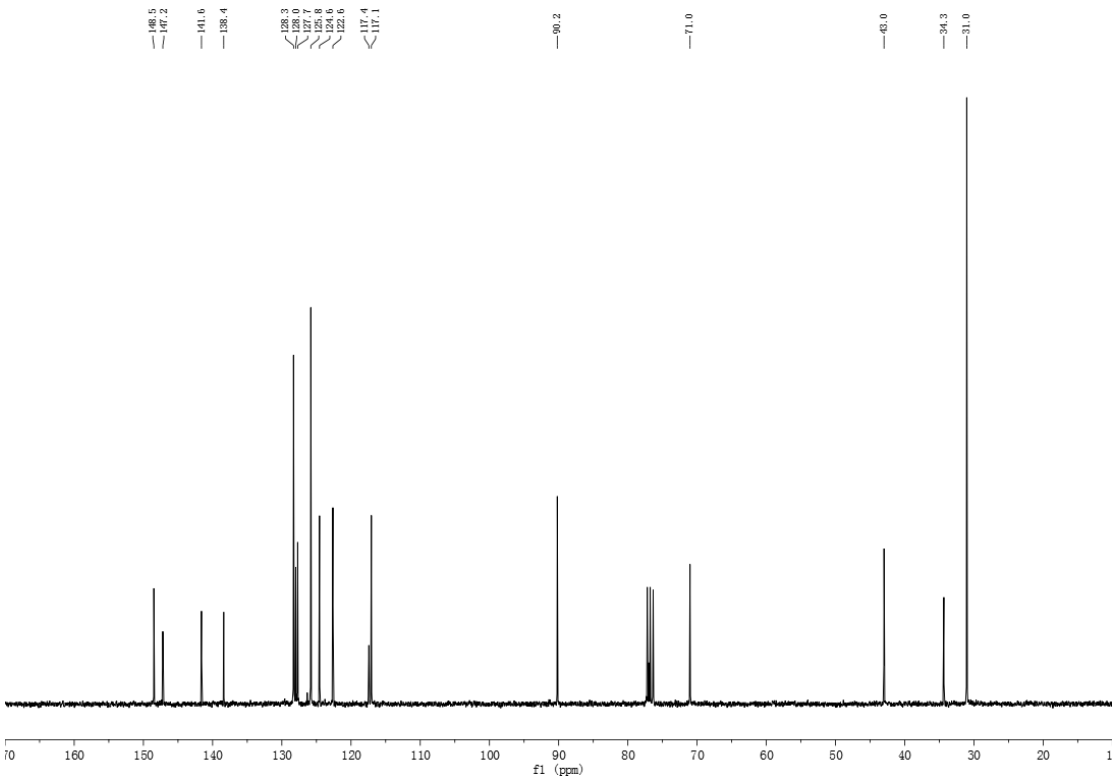

7.6
7.5
7.4
7.4
7.4
7.3
7.3
7.2
7.2
6.9
6.3
6.0
5.9
5.0
5.0
5.0
4.9
4.2
4.2
4.2
4.2
4.0
3.9
3.0
3.0
3.0
2.9
2.9
1.3
1.3
1.07
5.20
1.05
1.03
1.00
1.01
2.03
1.06
1.02
1.04
6.13
f1 (ppm)

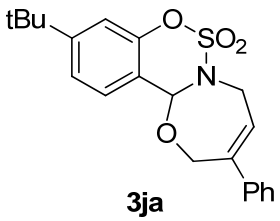

152.5
149.4
141.6
138.4
128.3
127.8
127.7
125.8
123.7
122.6
115.6
115.2
89.9
70.9
43.0
33.6
23.3
f1 (ppm)



3ia







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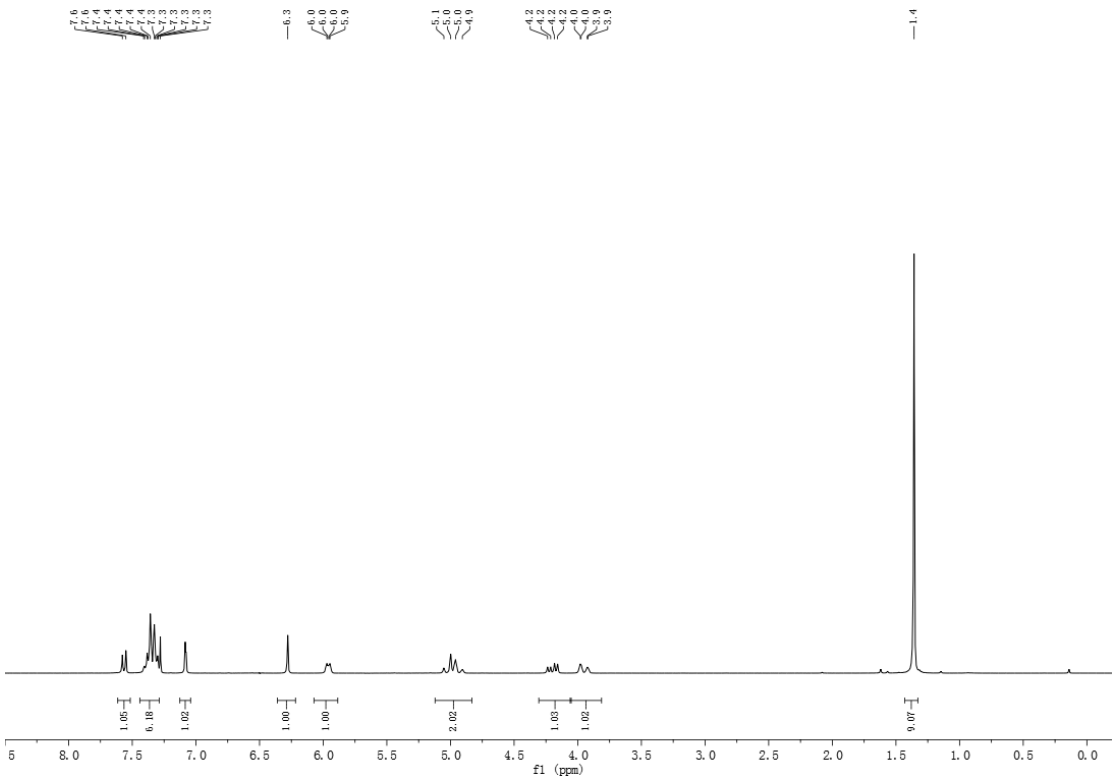
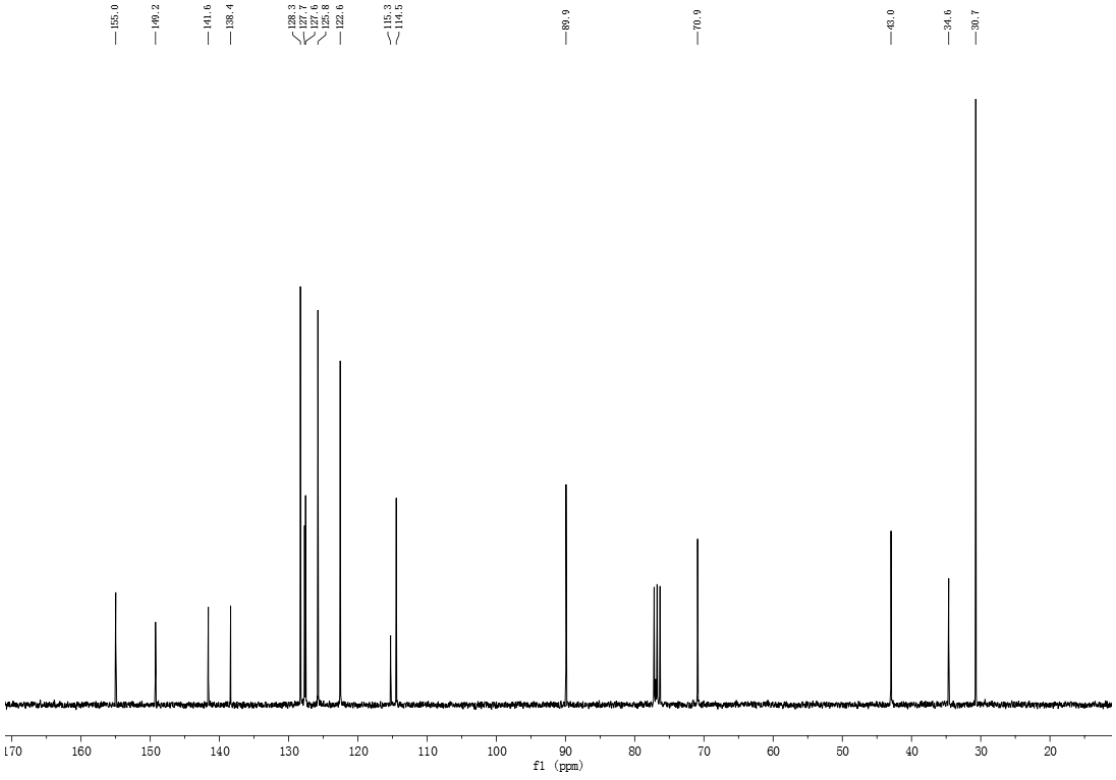
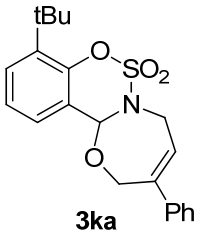
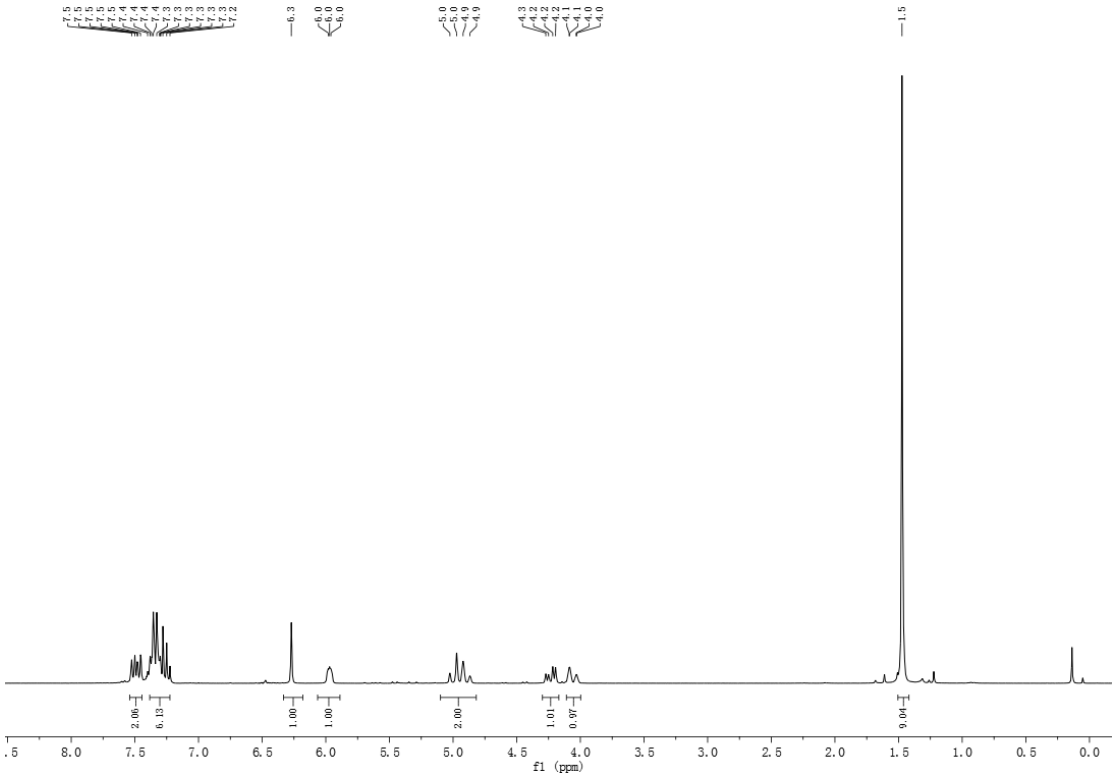
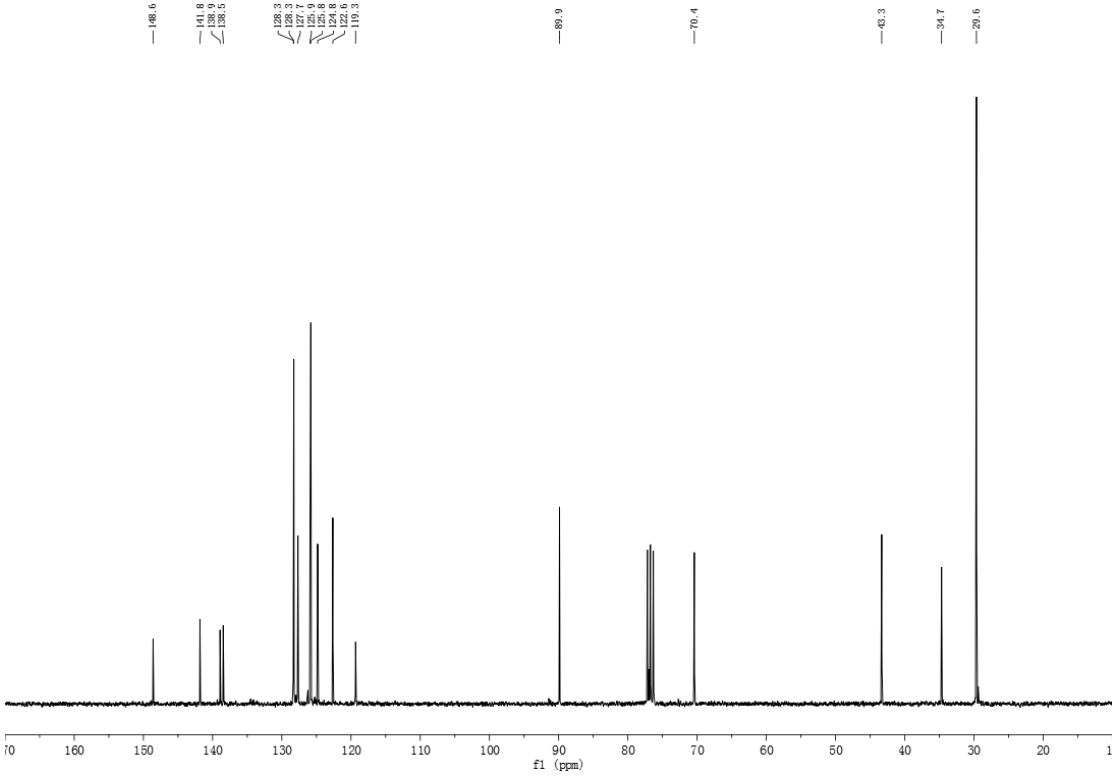


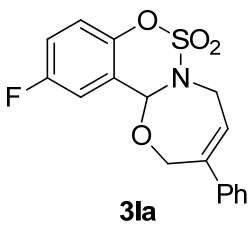




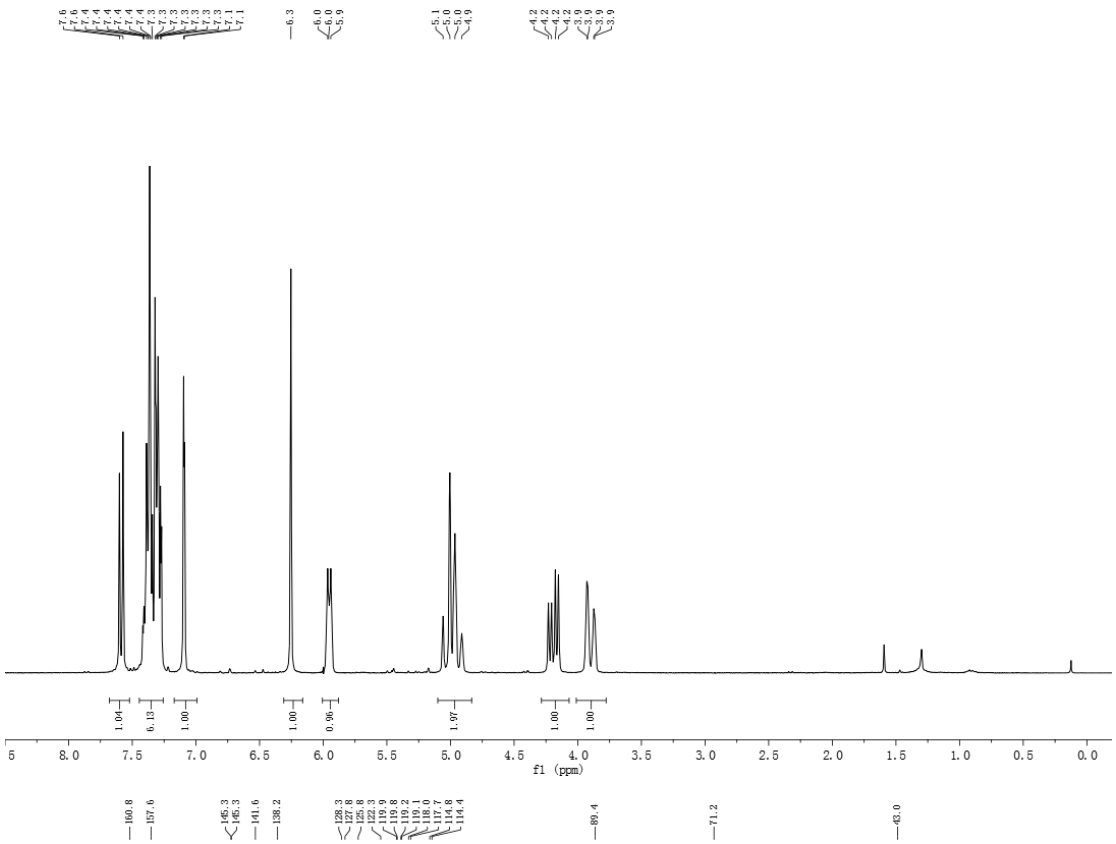
3ka

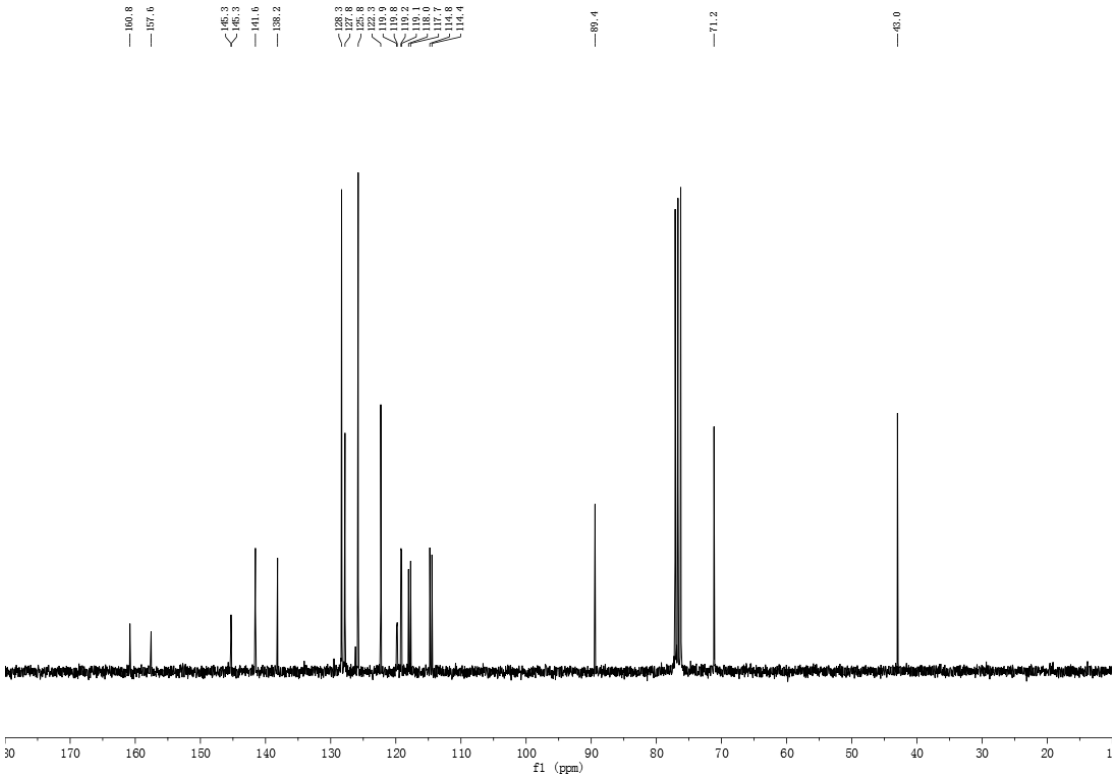


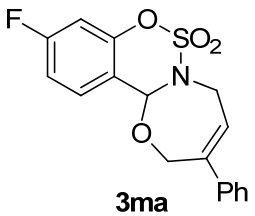




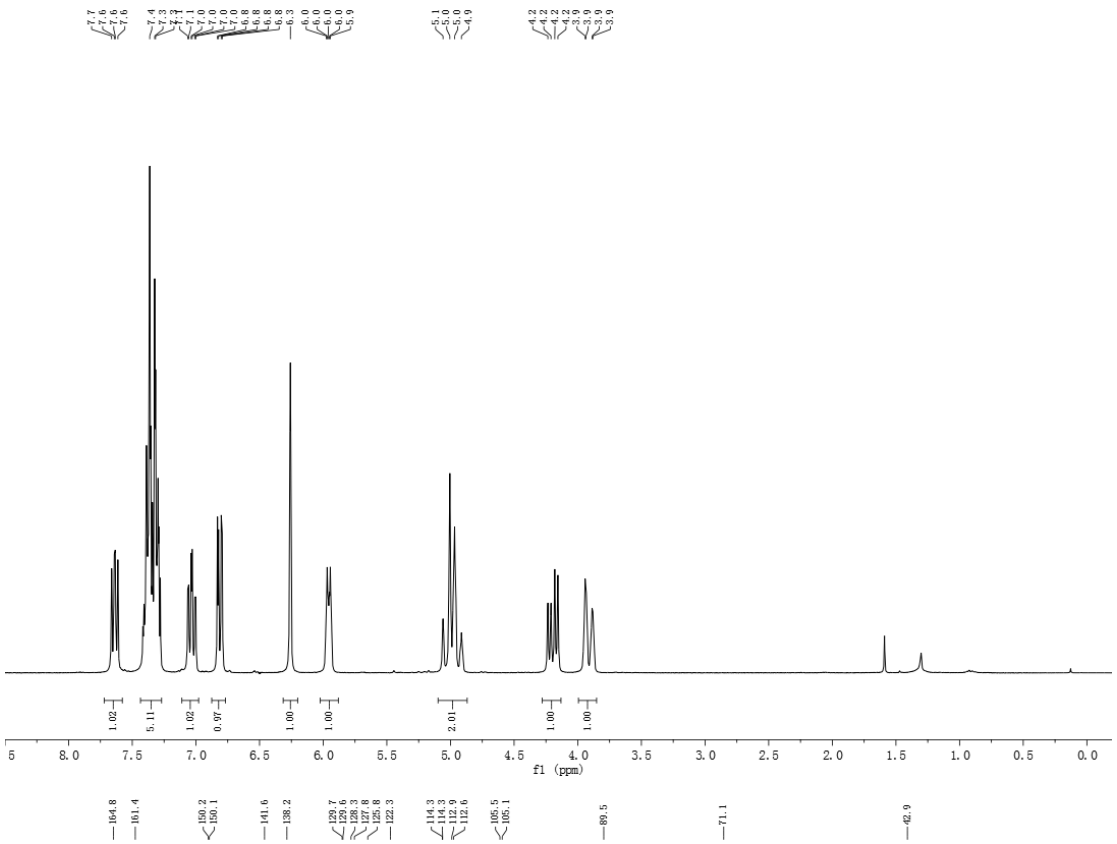
3la

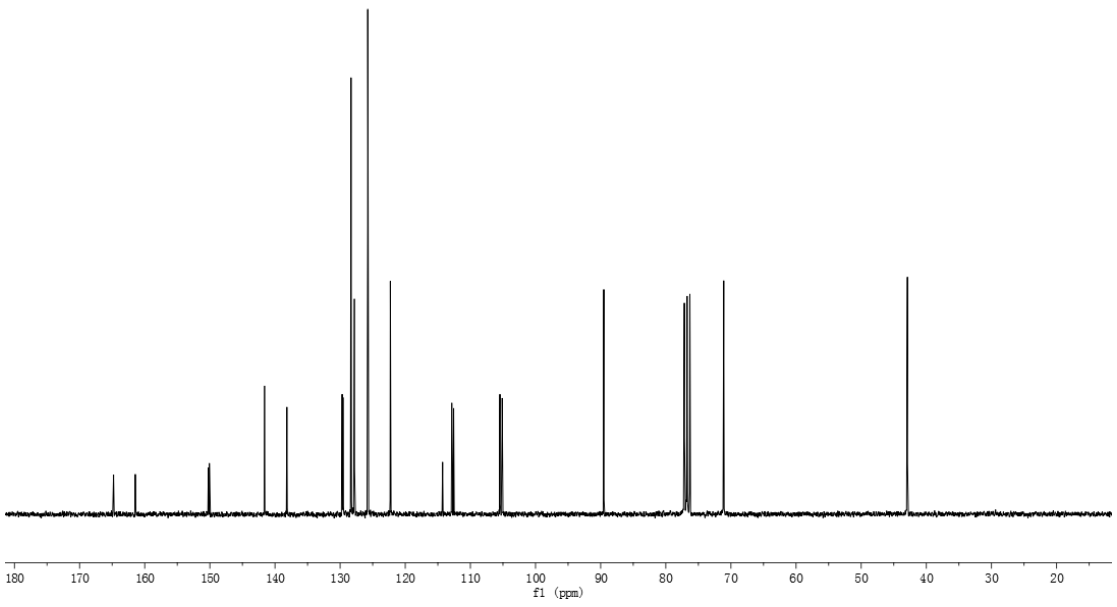


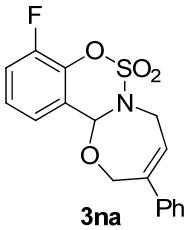




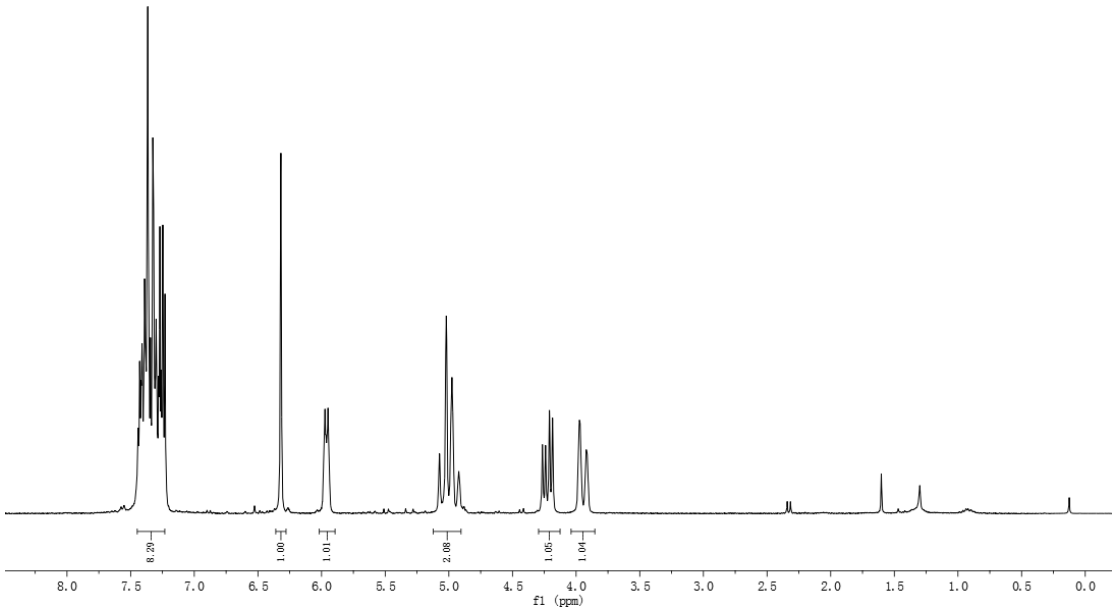
3ma

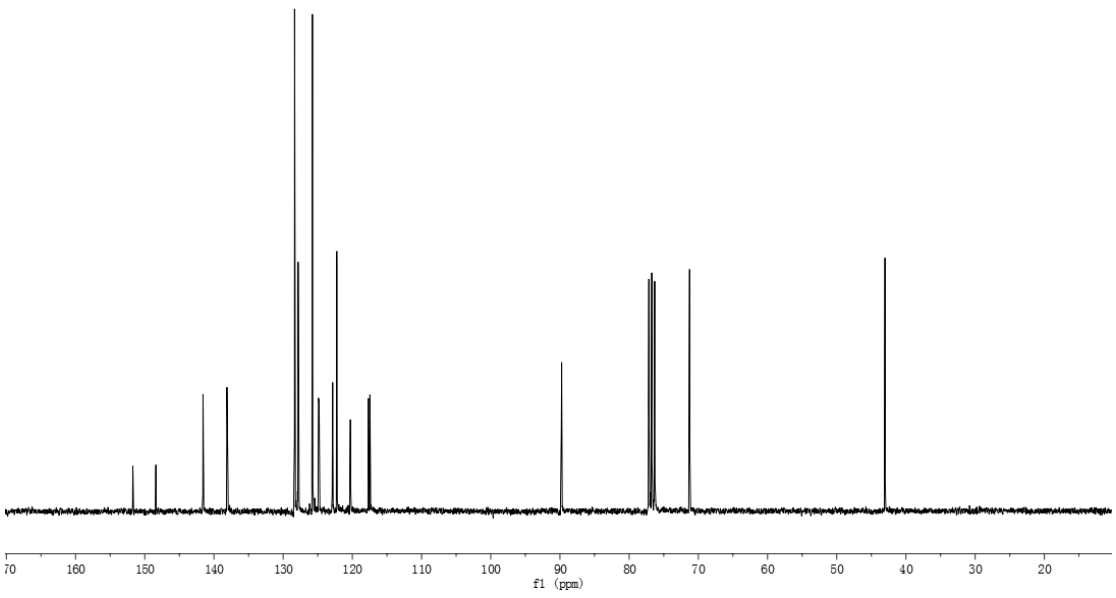


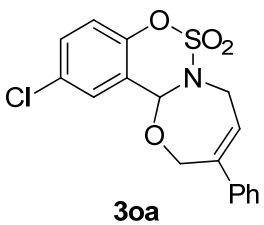




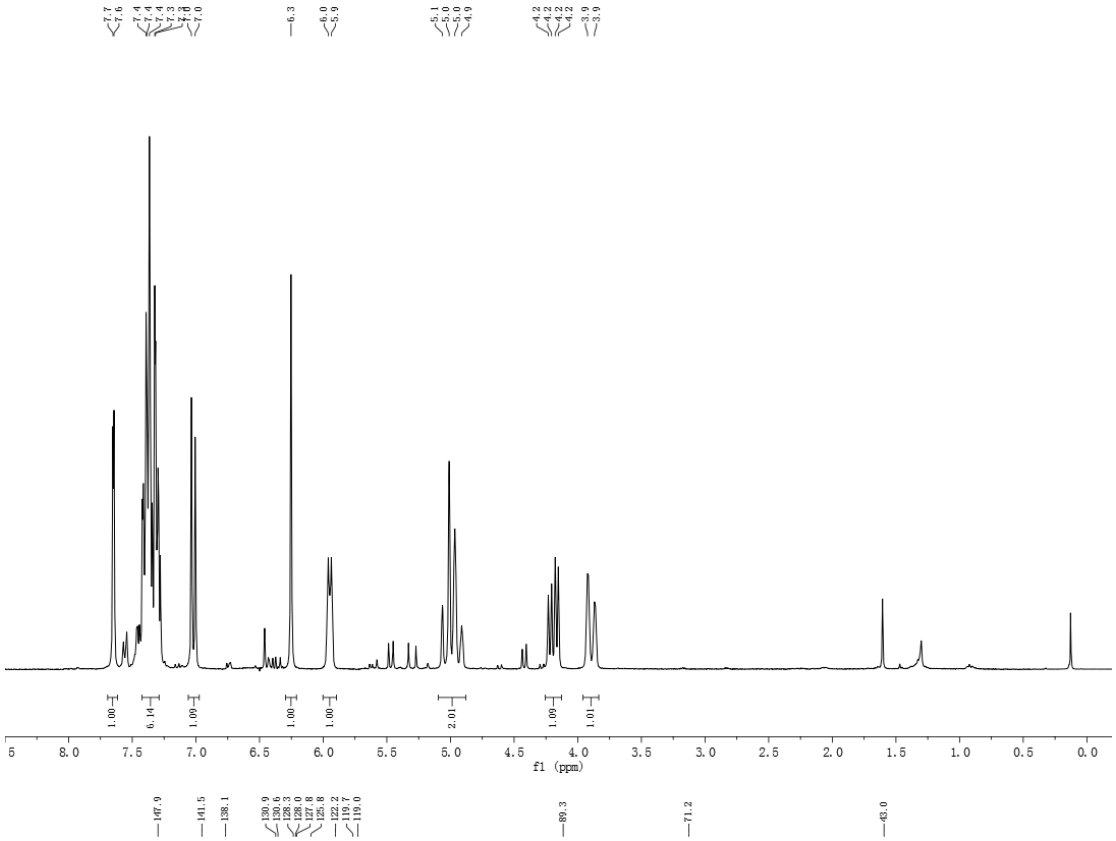
3na

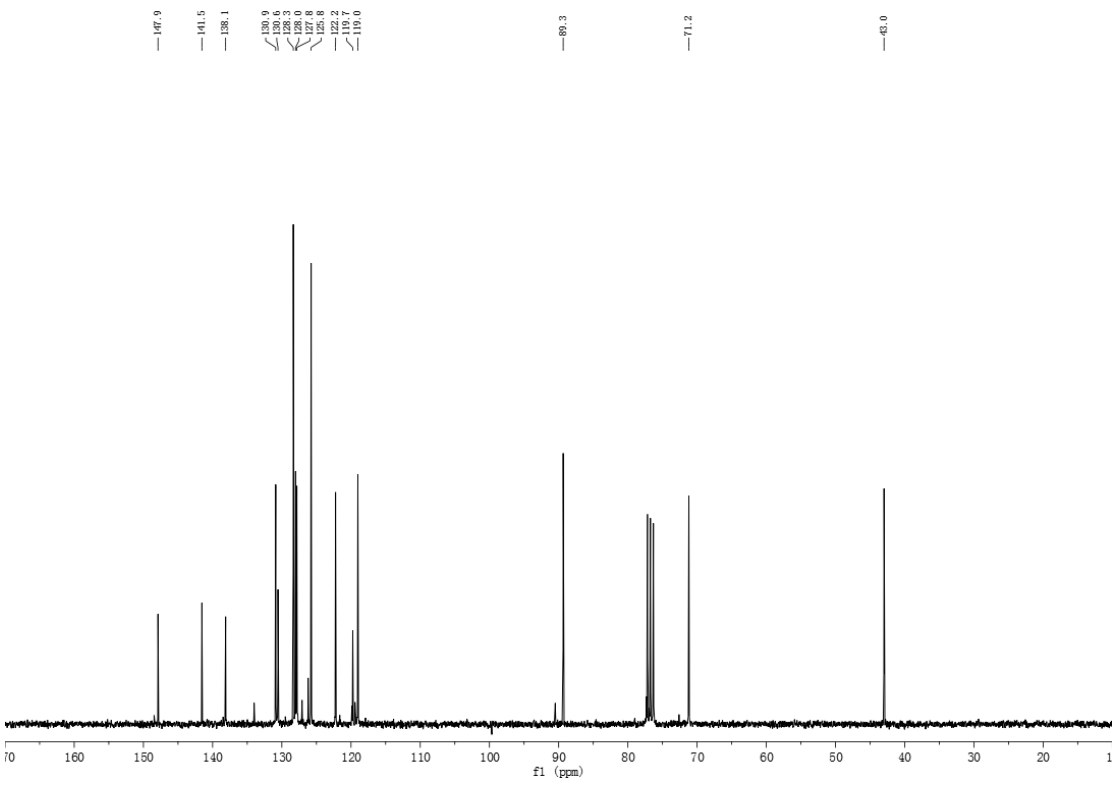


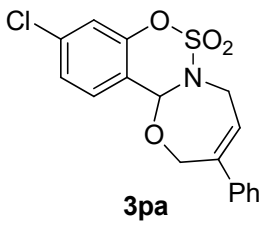



O
SO2
N
Cl
O
Ph

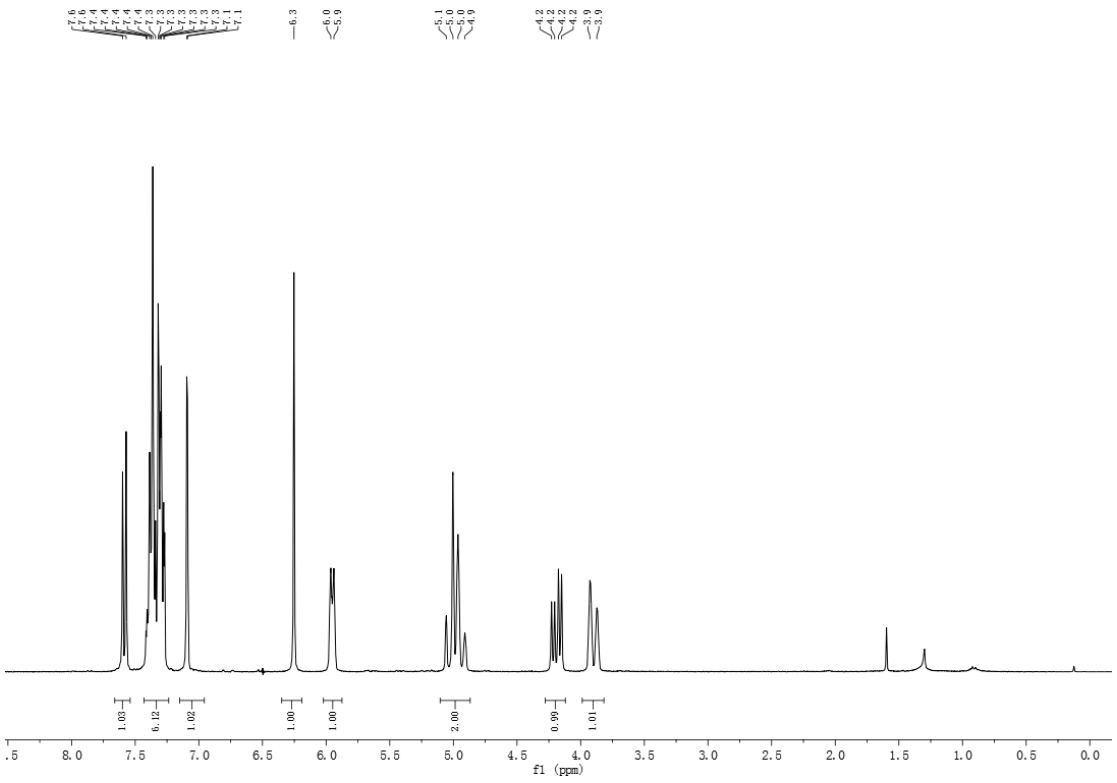
3oa

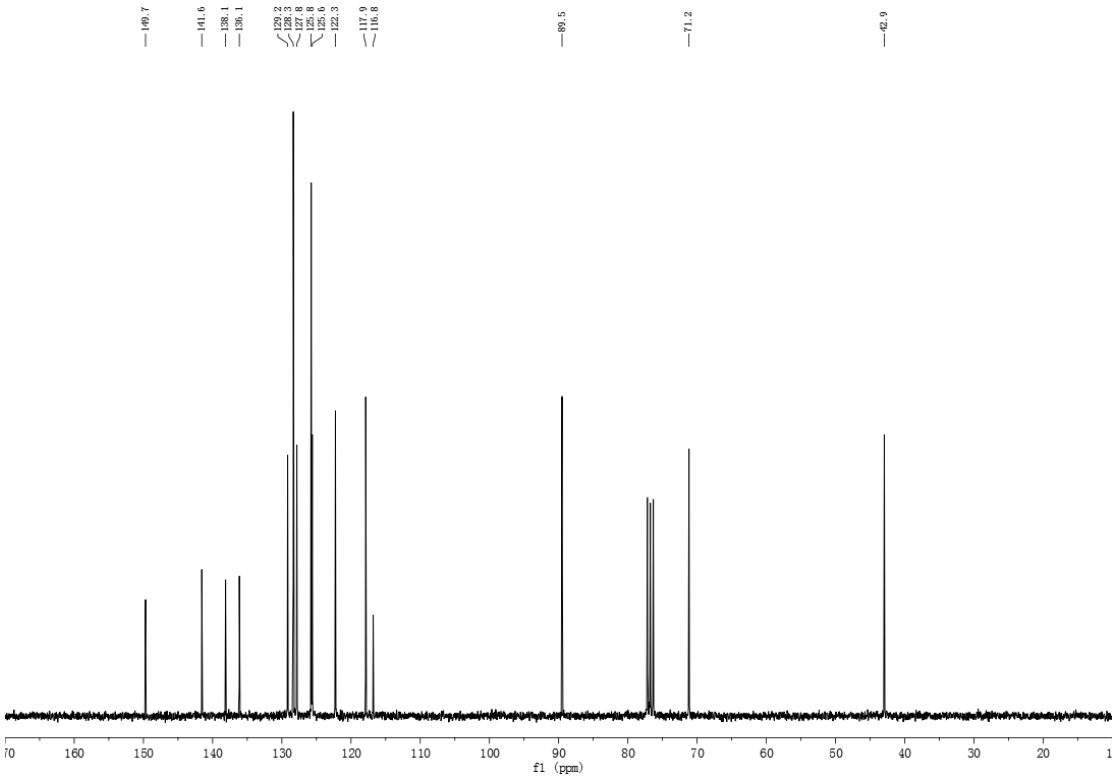

7.7
7.6
7.4
7.4
7.4
7.3
7.0
7.0
6.3
6.0
5.9
5.1
5.0
5.0
4.9
4.2
4.2
4.2
4.2
3.9
3.9
1.00
6.14
1.09
1.00
1.00
2.01
1.09
1.01
f1 (ppm)

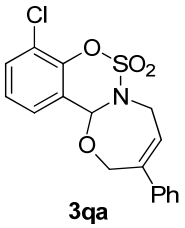

147.9
141.5
138.1
130.9
130.6
128.3
128.0
127.8
125.8
122.2
119.7
119.0
89.3
71.2
43.0
f1 (ppm)



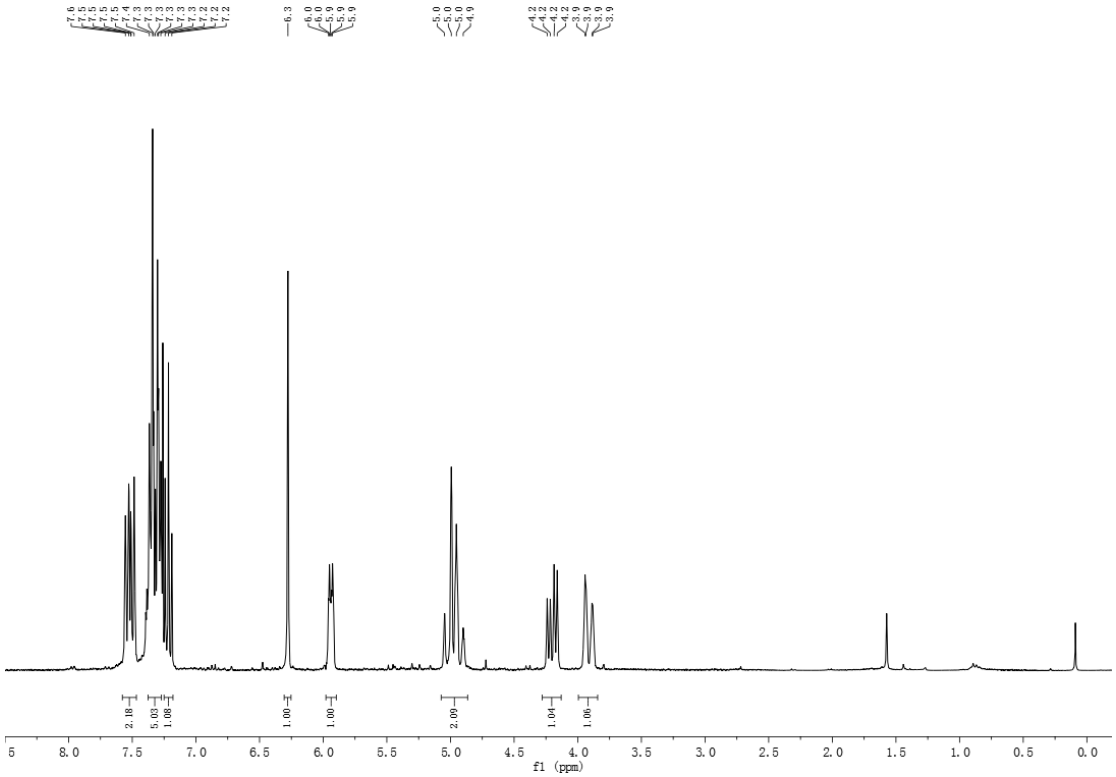
3pa

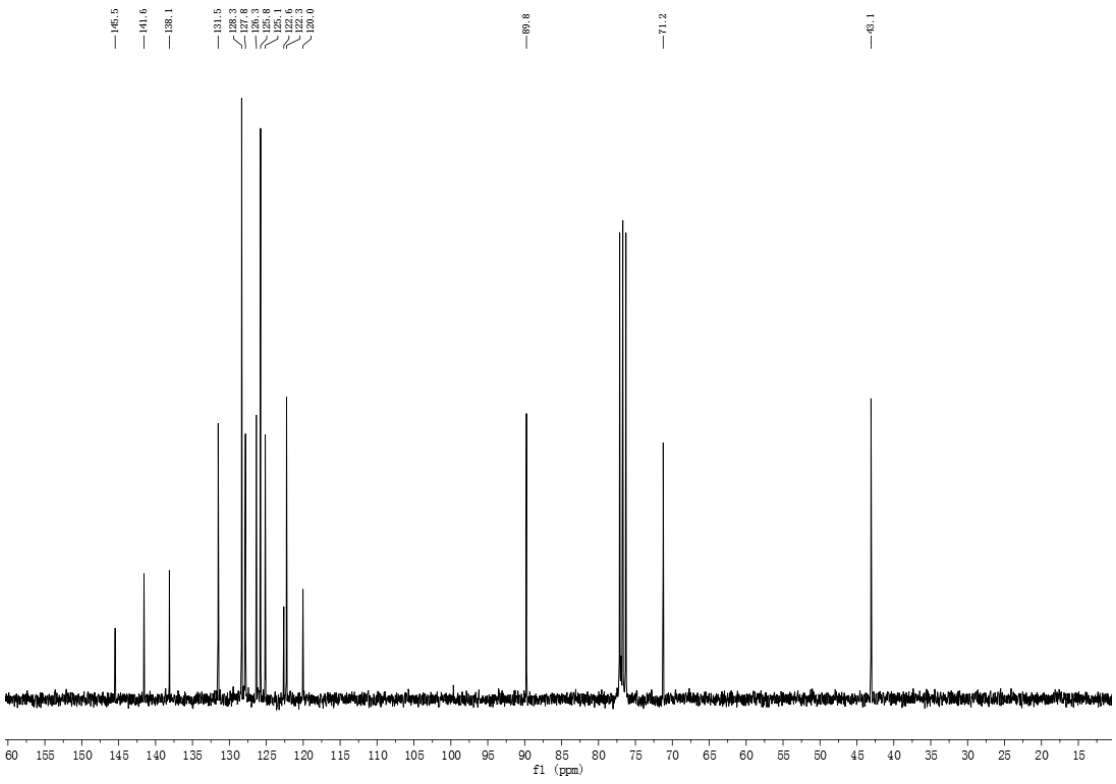


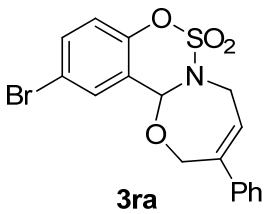




3qa

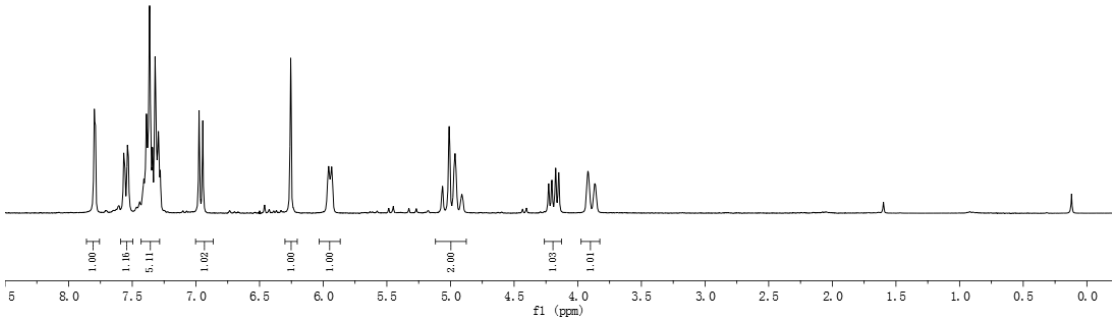




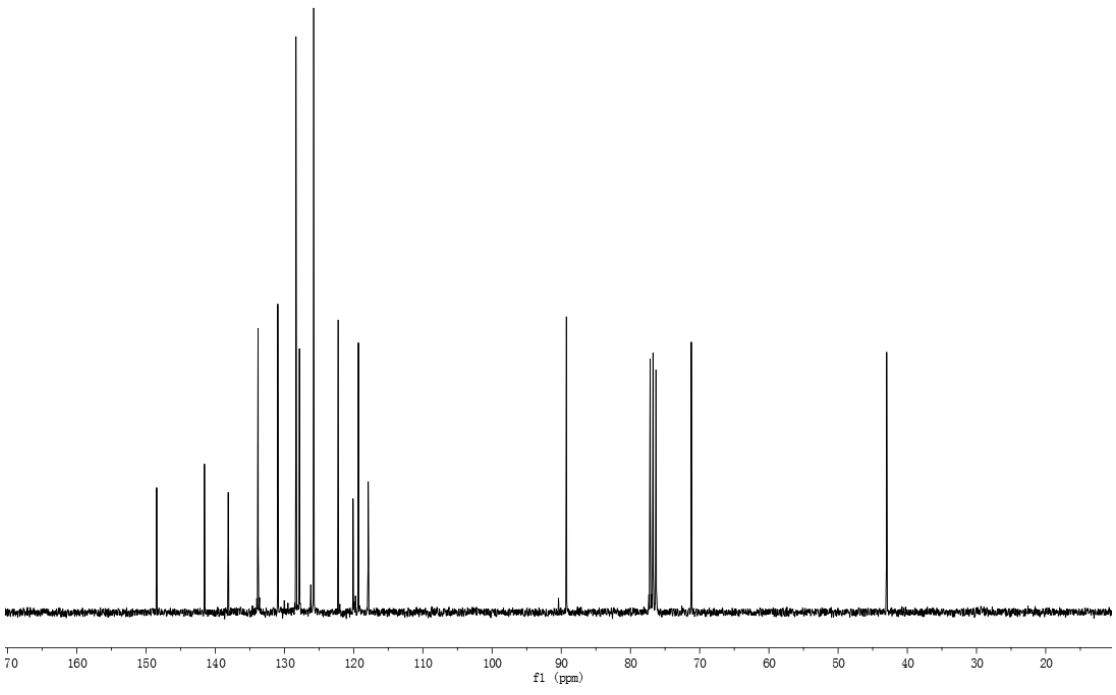

O
SO2
N
Br
O
Ph

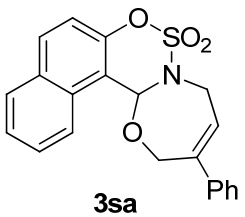
3ra


7.8
7.8
7.6
7.5
7.4
7.4
7.3
7.3
7.0
6.9
6.3
6.0
5.9
5.1
5.0
5.0
4.9
4.2
4.2
4.2
4.1
3.9
3.9

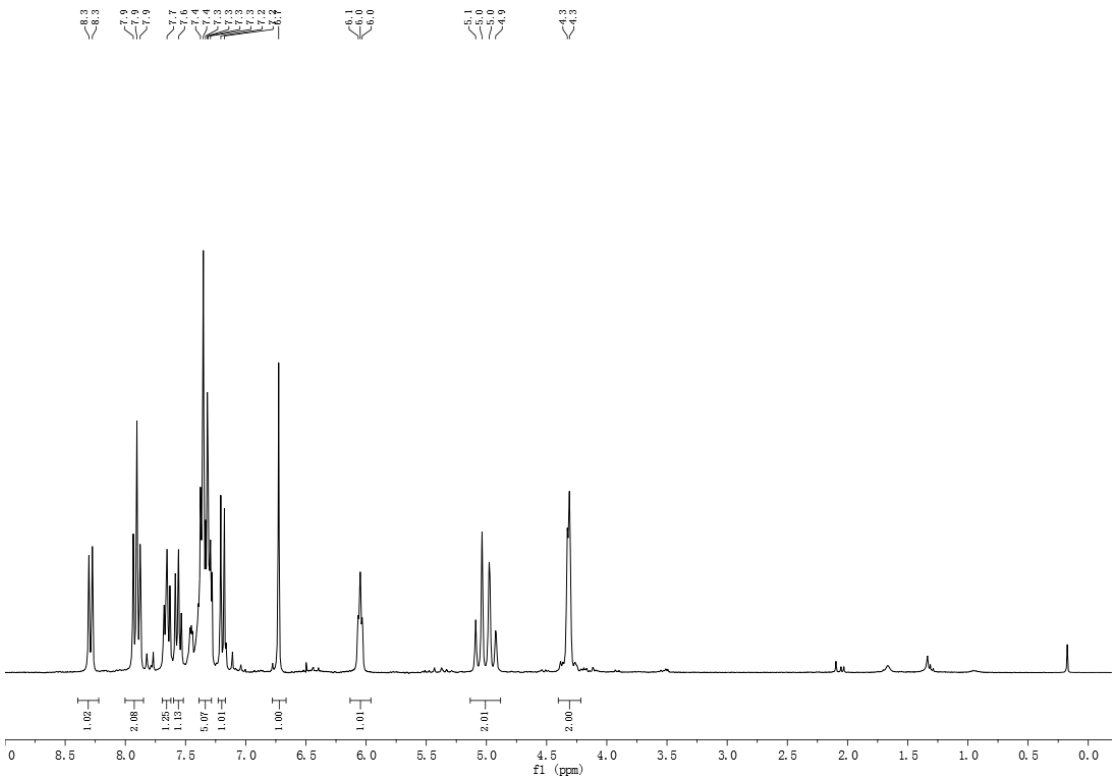

1.00
1.16
5.11
1.02
1.00
1.00
2.00
1.03
1.01
f1 (ppm)

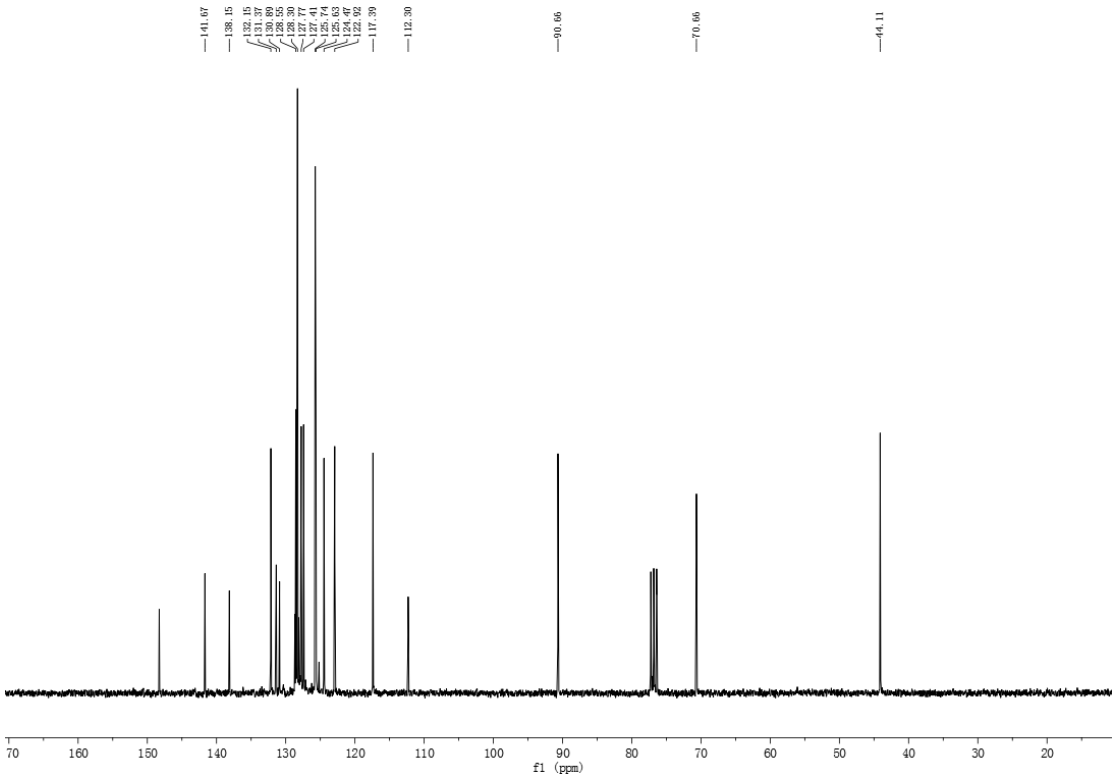

148.5
141.6
138.1
133.8
131.0
128.3
127.8
125.8
122.2
120.1
119.3
117.9
89.3
71.2
43.0

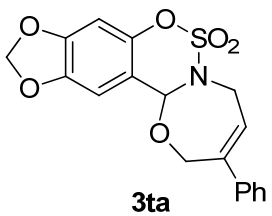

f1 (ppm)


O
SO2
N
O
Ph

3sa

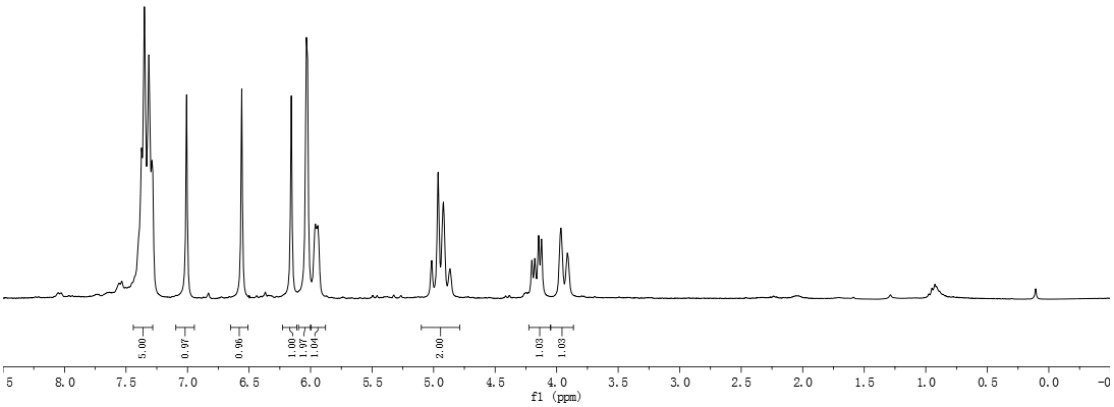

8.3
8.3
7.9
7.9
7.9
7.7
7.6
7.4
7.4
7.3
7.3
7.3
7.2
7.2
6.1
6.0
6.0
5.1
5.0
5.0
4.9
4.3
4.3
1.02
2.08
1.25
1.13
5.07
1.01
1.00
1.01
2.01
2.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.67
138.15
132.15
131.37
130.89
128.55
128.39
127.77
127.41
125.74
125.63
124.47
122.92
117.39
112.30
90.66
70.66
44.11
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

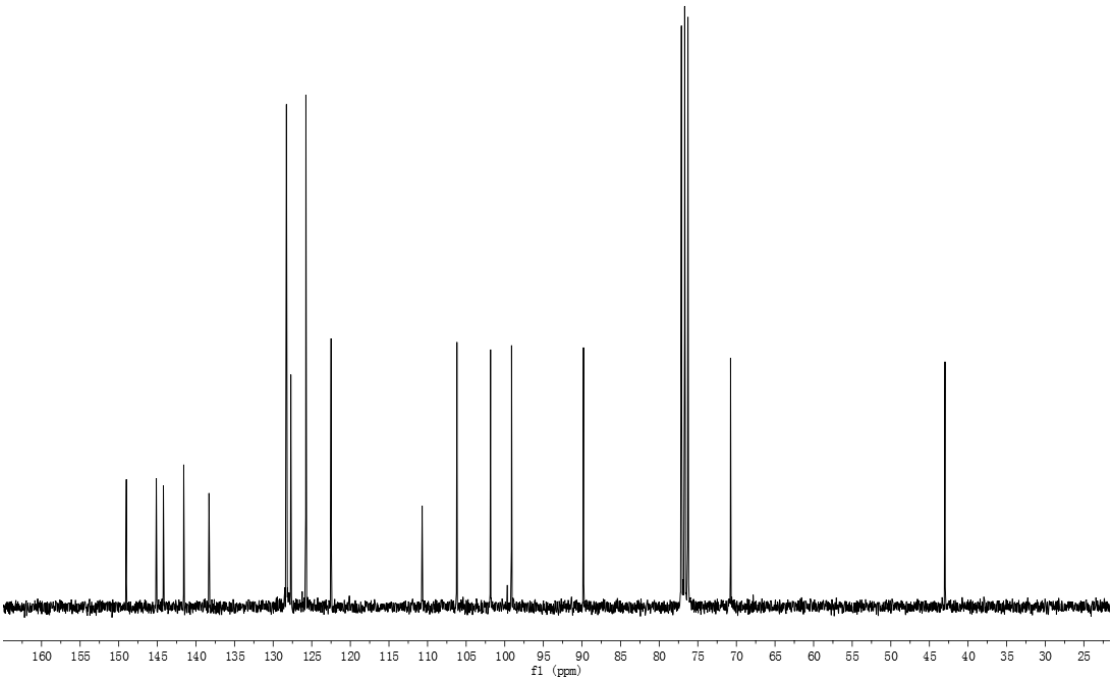

O
O
O
SO2
N
O
Ph

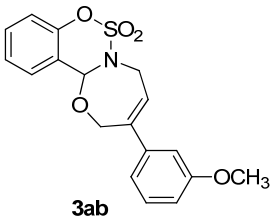
3ta


7.4
7.4
7.3
7.3
7.0
6.6
6.2
6.0
6.0
6.0
5.9
5.0
5.0
4.9
4.9
4.2
4.2
4.1
4.1
4.0
3.9

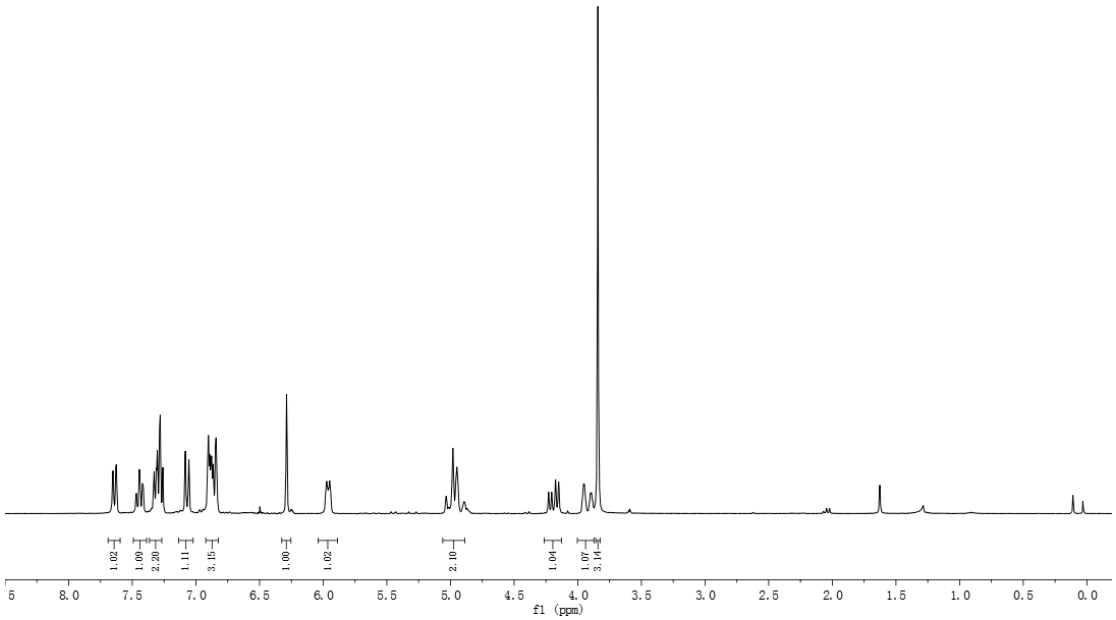

5.00
0.97
0.96
1.00
1.97
1.04
2.00
1.03
1.03
f1 (ppm)

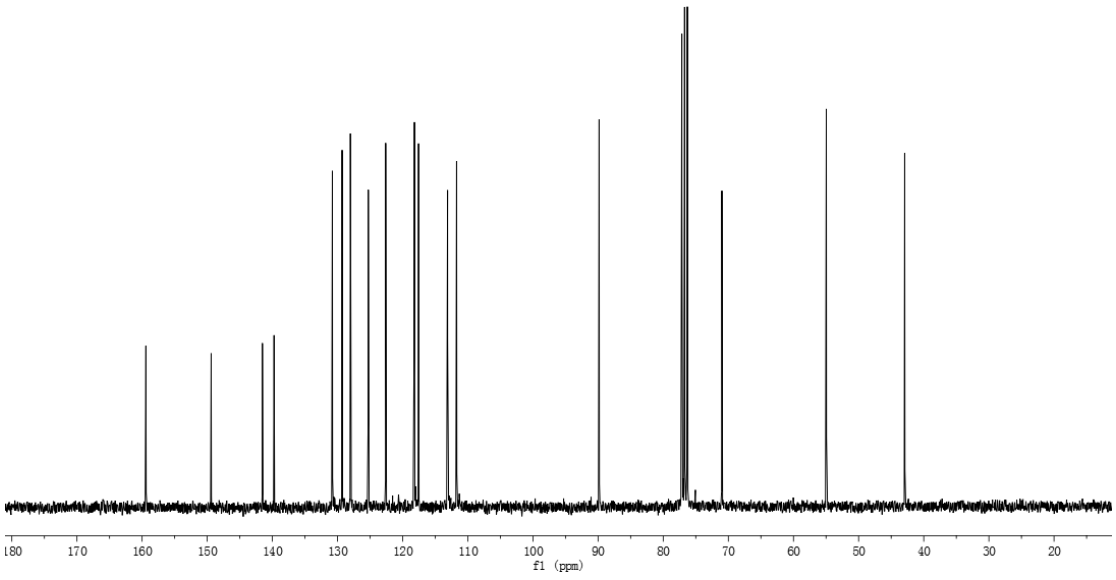

149.0
145.1
144.2
141.6
138.3
128.3
127.7
125.8
122.5
110.7
106.2
101.8
99.1
89.8
70.8
43.0

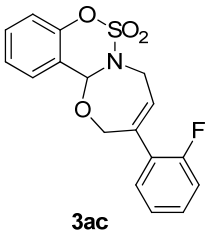

f1 (ppm)



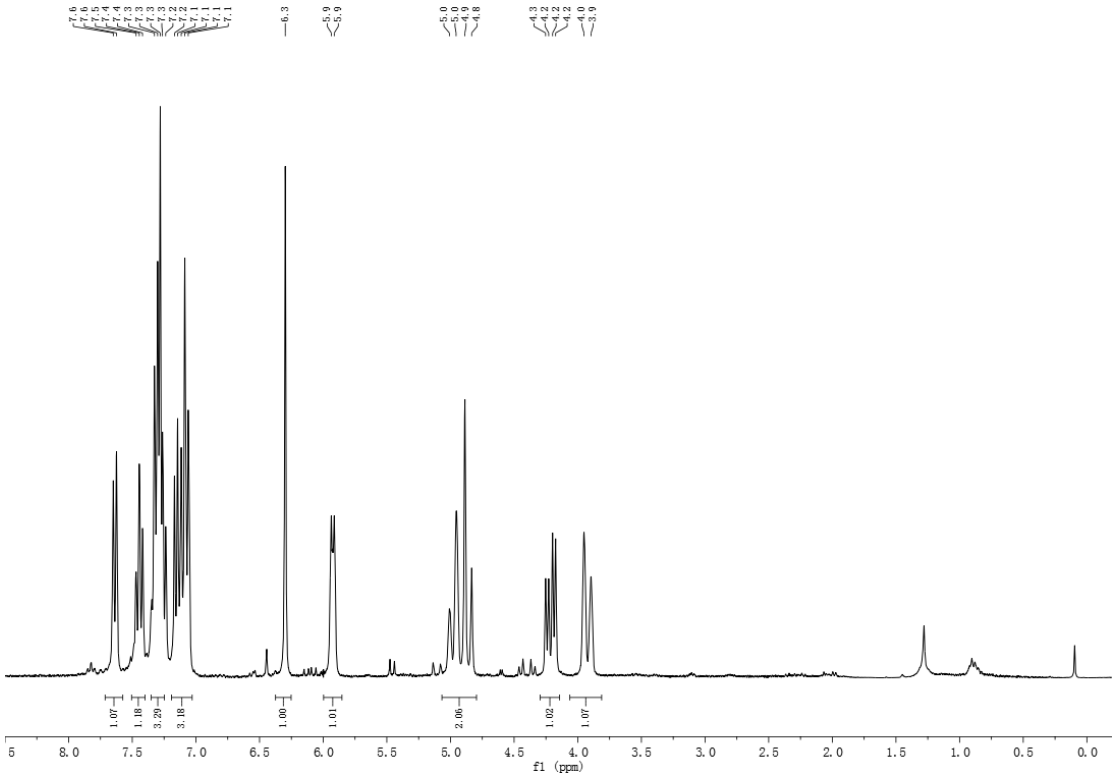
3ab

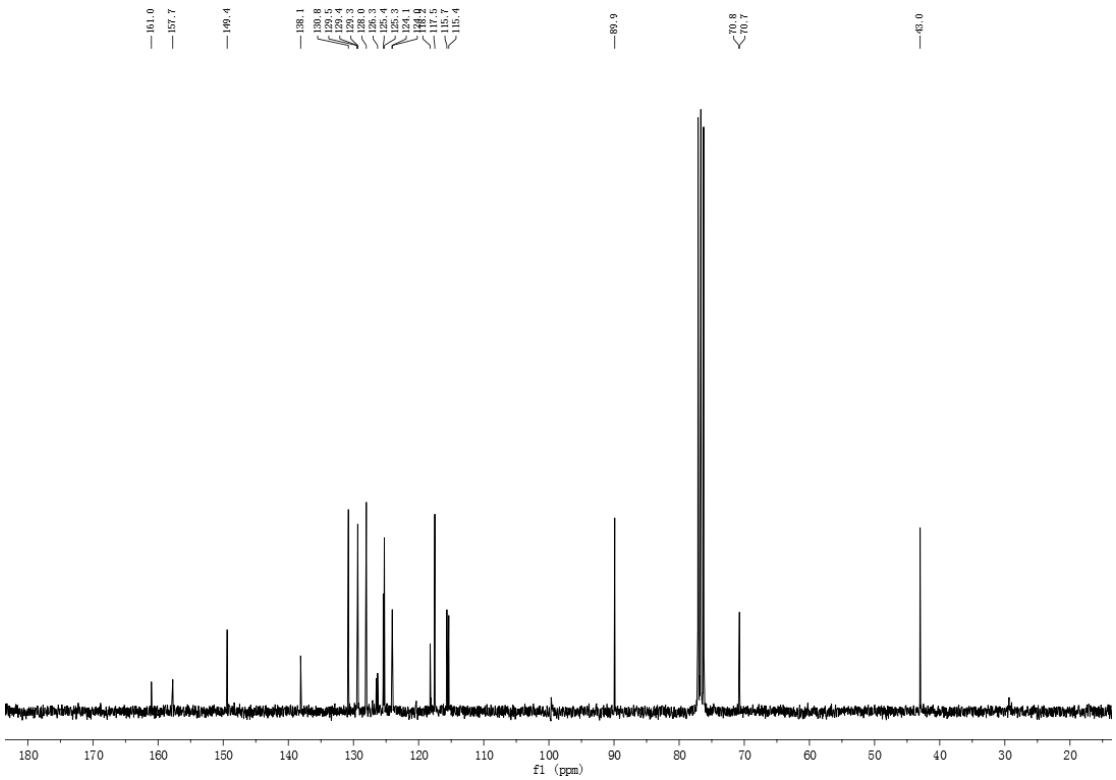


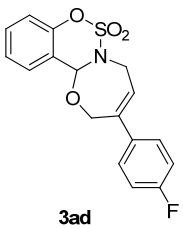



O
SO2
N
O
F

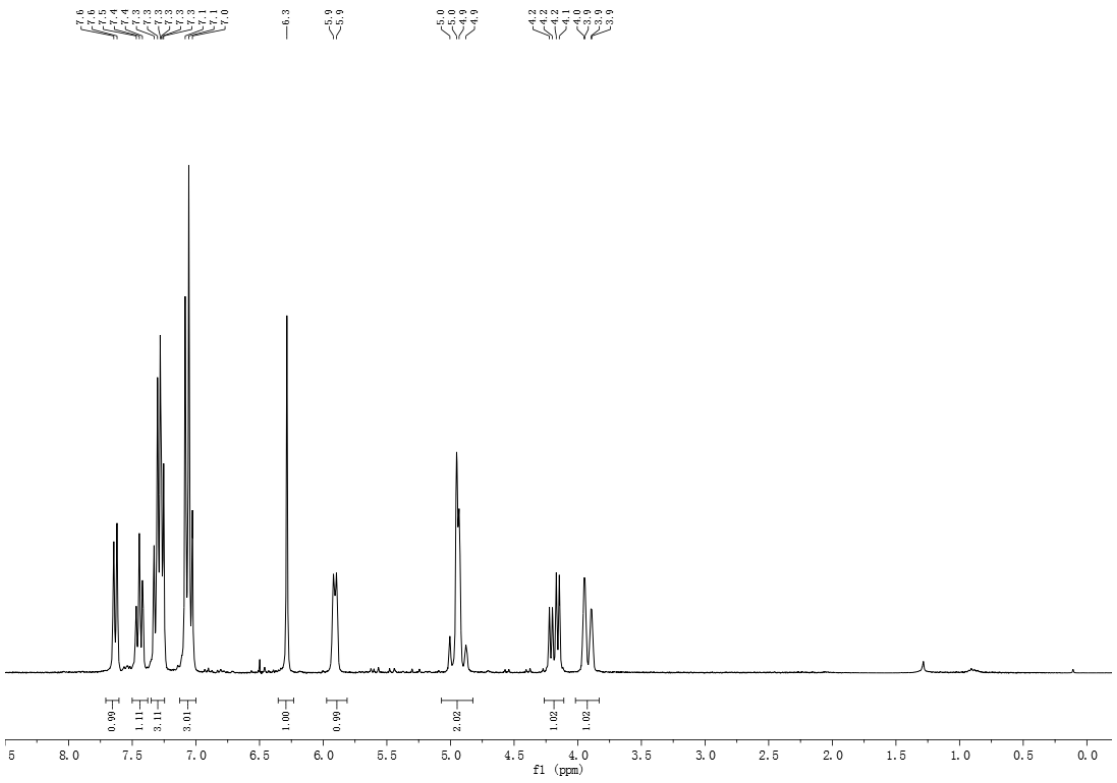
3ac


7.6
7.6
7.5
7.4
7.4
7.3
7.3
7.3
7.2
7.2
7.1
7.1
7.1
6.3
5.9
5.9
5.0
5.0
4.9
4.8
4.3
4.2
4.2
4.2
4.0
3.9
1.07
1.18
3.29
3.18
1.00
1.01
2.00
1.02
1.07
f1 (ppm)


161.0
157.7
149.4
138.1
130.8
129.5
129.4
129.3
128.0
126.3
125.4
125.3
124.1
89.9
70.8
70.7
43.0
f1 (ppm)


O
SO2
N
O
F

3ad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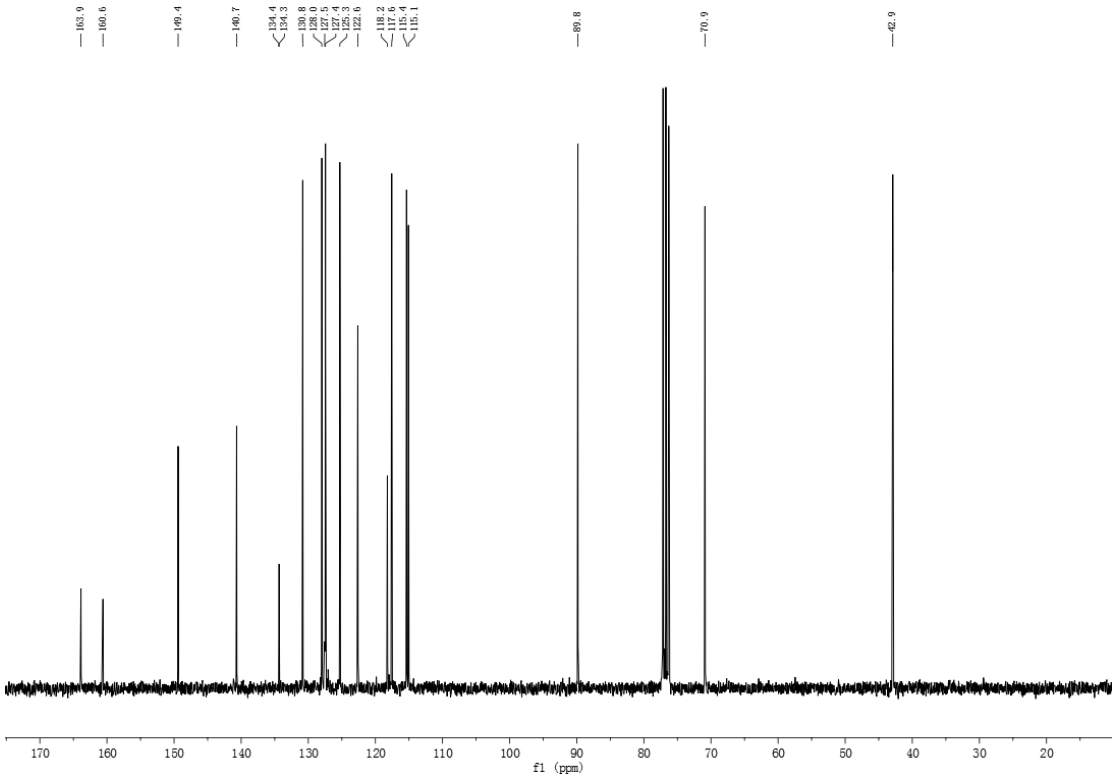
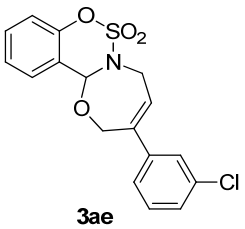
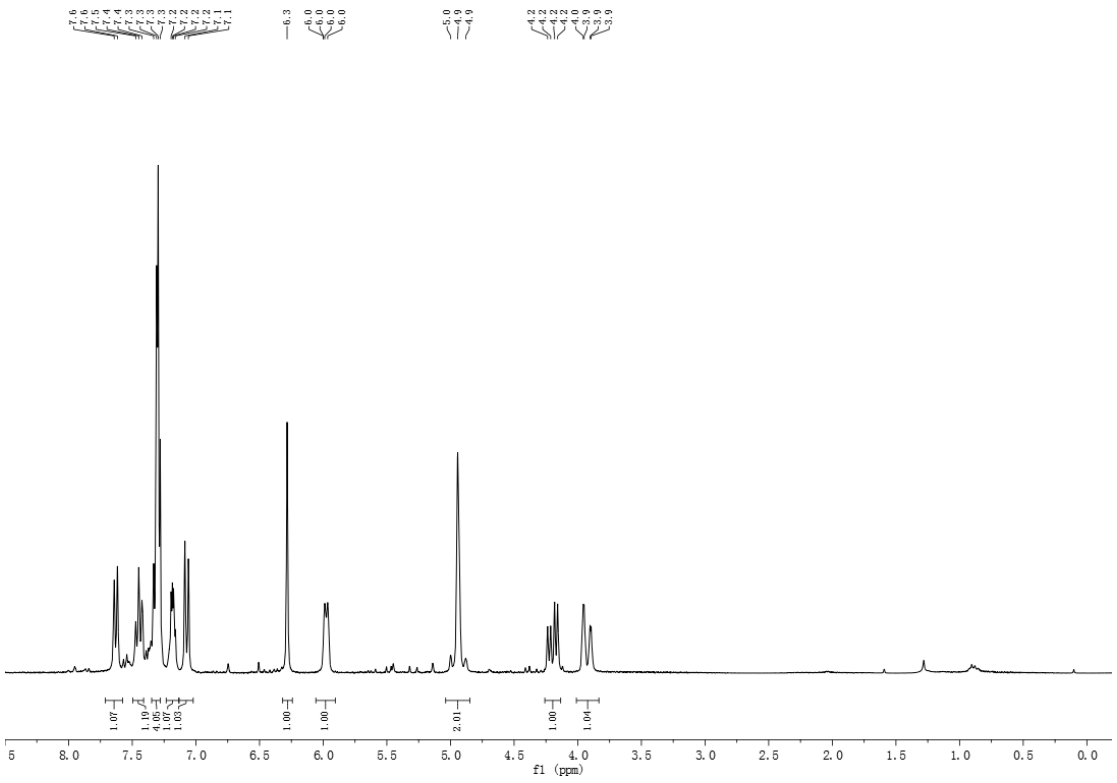
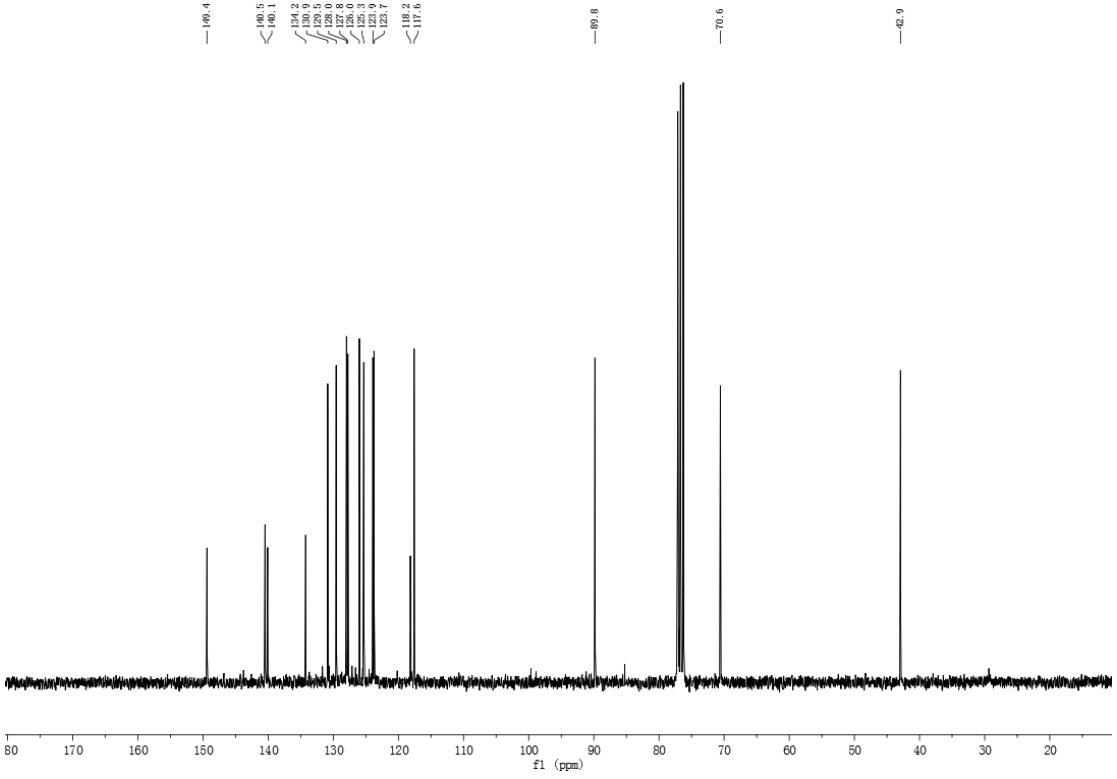
7.6
7.5
7.4
7.4
7.3
7.3
7.3
7.3
7.3
7.3
7.1
7.1
7.0
6.3
5.9
5.9
5.0
5.0
4.9
4.9
4.2
4.2
4.2
4.1
4.0
3.9
3.9
3.9
0.99
1.11
3.11
3.01
1.00
0.99
2.02
1.02
1.02
f1 (ppm)

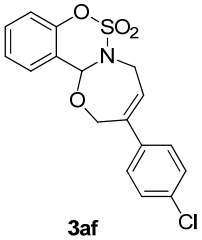

163.9
160.6
149.4
140.7
134.4
134.3
130.8
128.0
127.5
127.4
125.3
122.6
118.2
117.6
115.4
115.1
89.8
70.9
42.9
f1 (ppm)



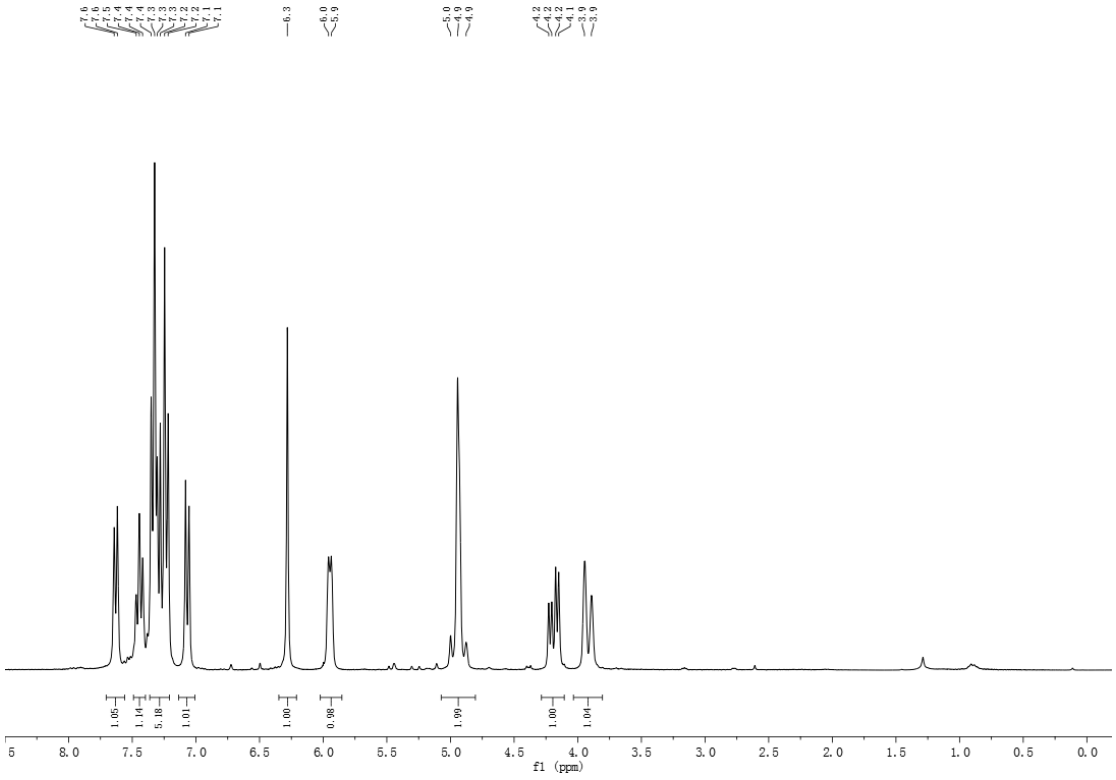
3ae






O
SO2
N
O
Cl

3af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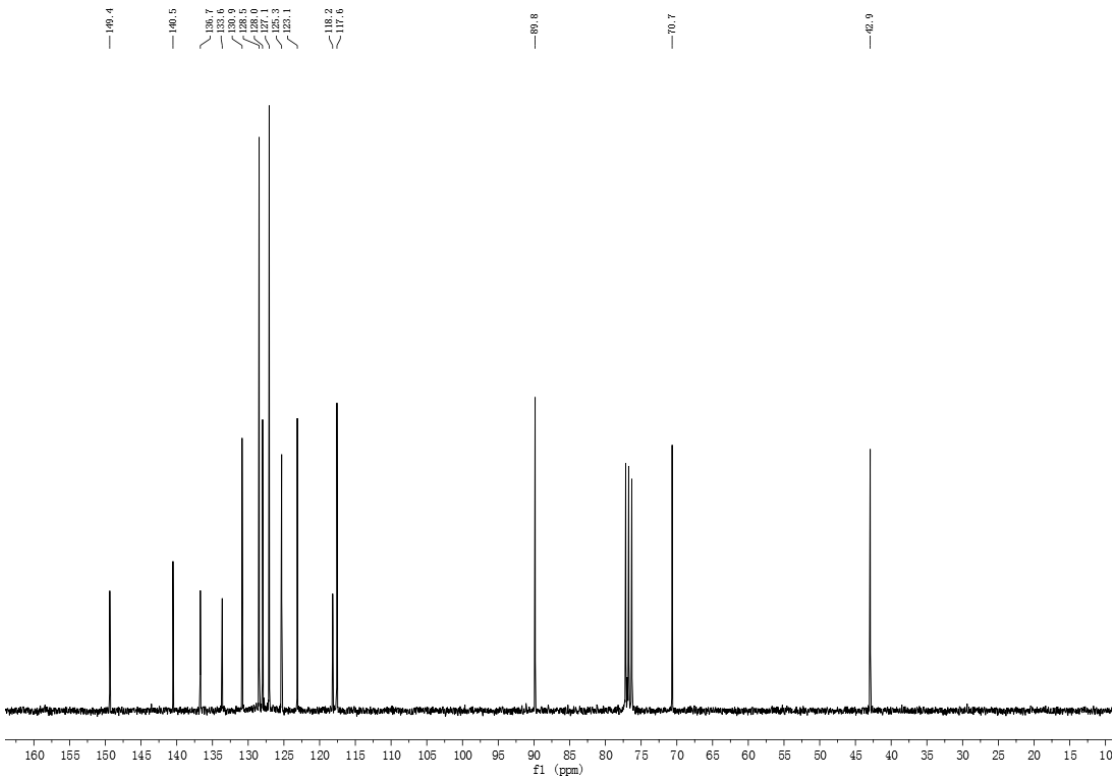
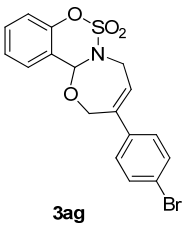
7.6
7.5
7.4
7.4
7.4
7.3
7.3
7.2
7.2
7.1
7.1
6.3
6.0
5.9
5.0
4.9
4.9
4.2
4.2
4.2
4.1
3.9
3.9
1.05
1.14
5.18
1.01
1.00
0.98
1.99
1.00
1.04
f1 (ppm)


149.4
140.5
136.7
133.6
130.9
128.5
128.0
127.1
125.3
123.1
118.2
117.6
89.8
70.7
42.9
f1 (ppm)



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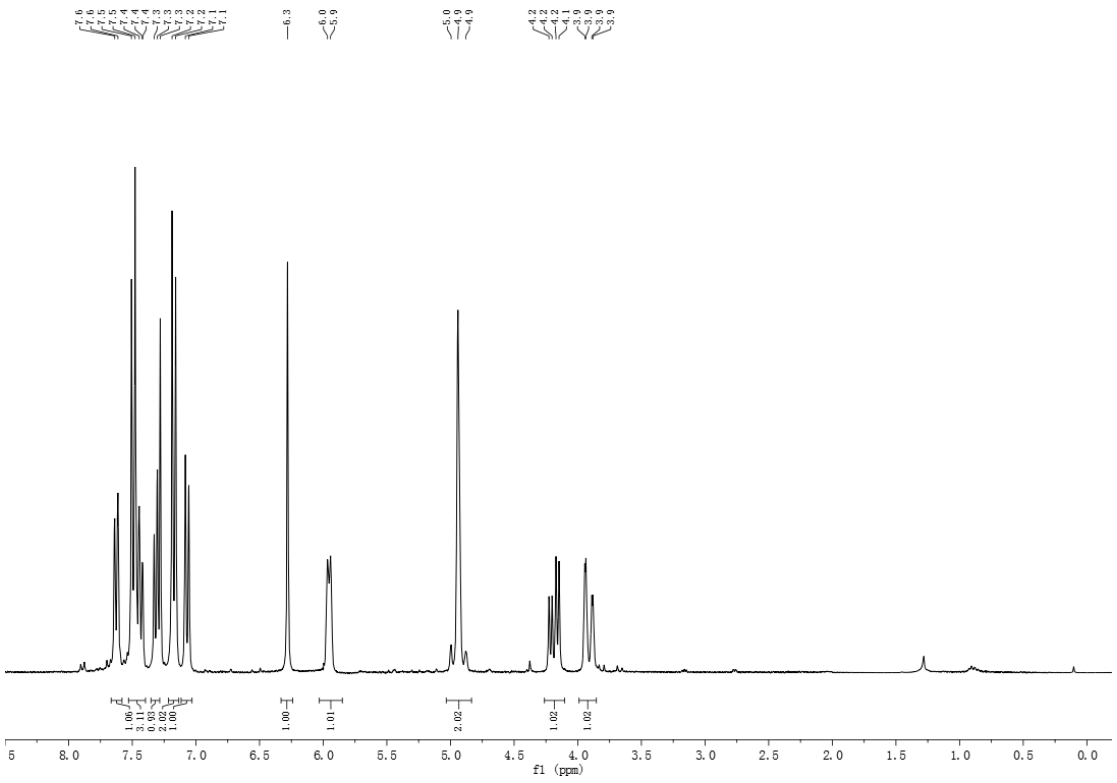
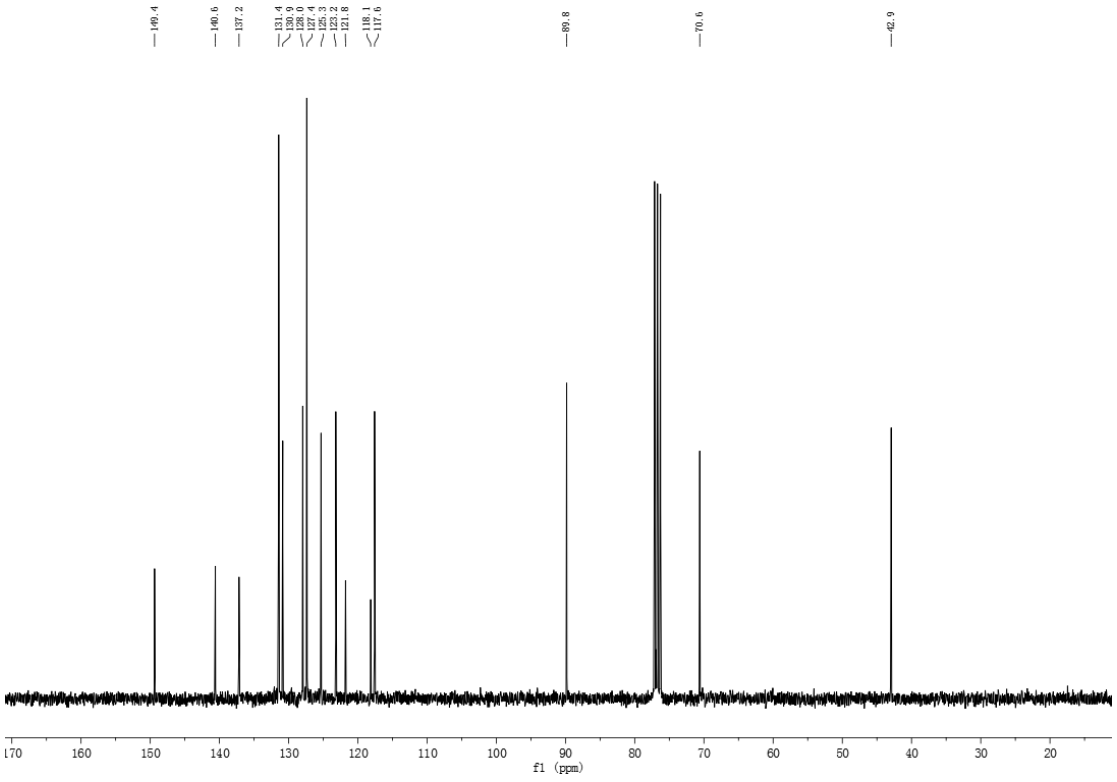
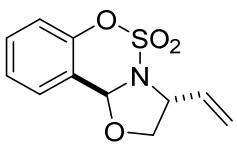
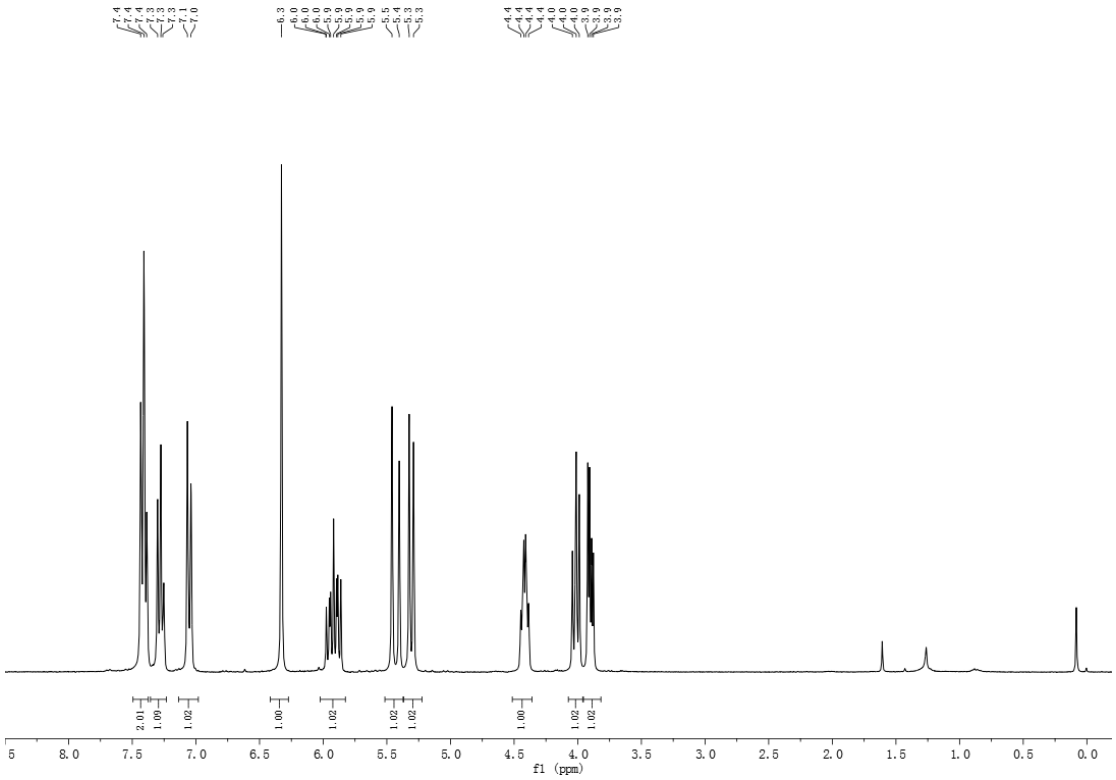
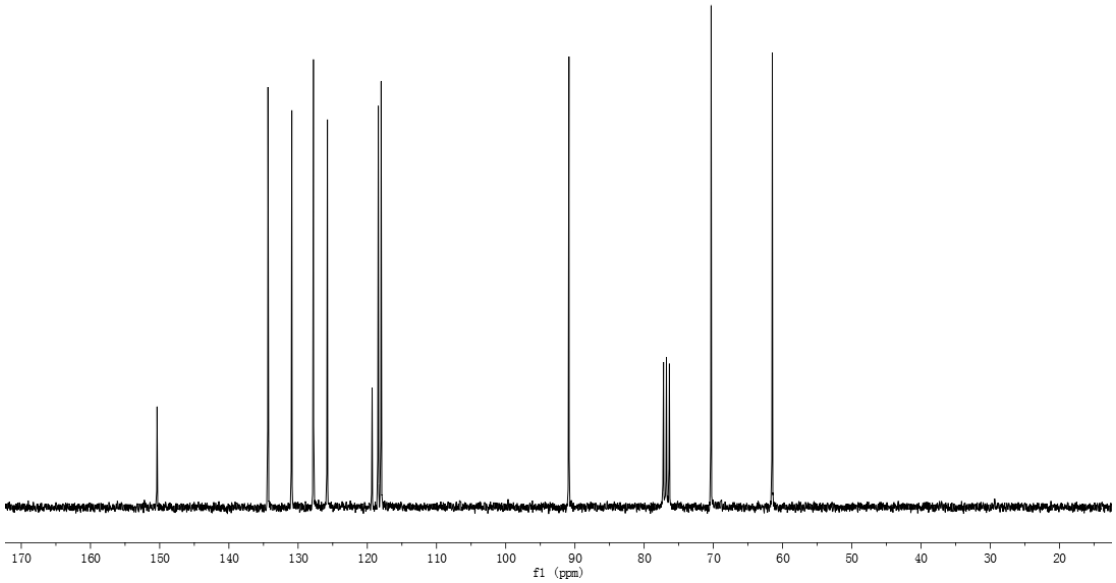


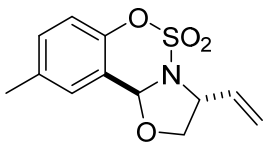




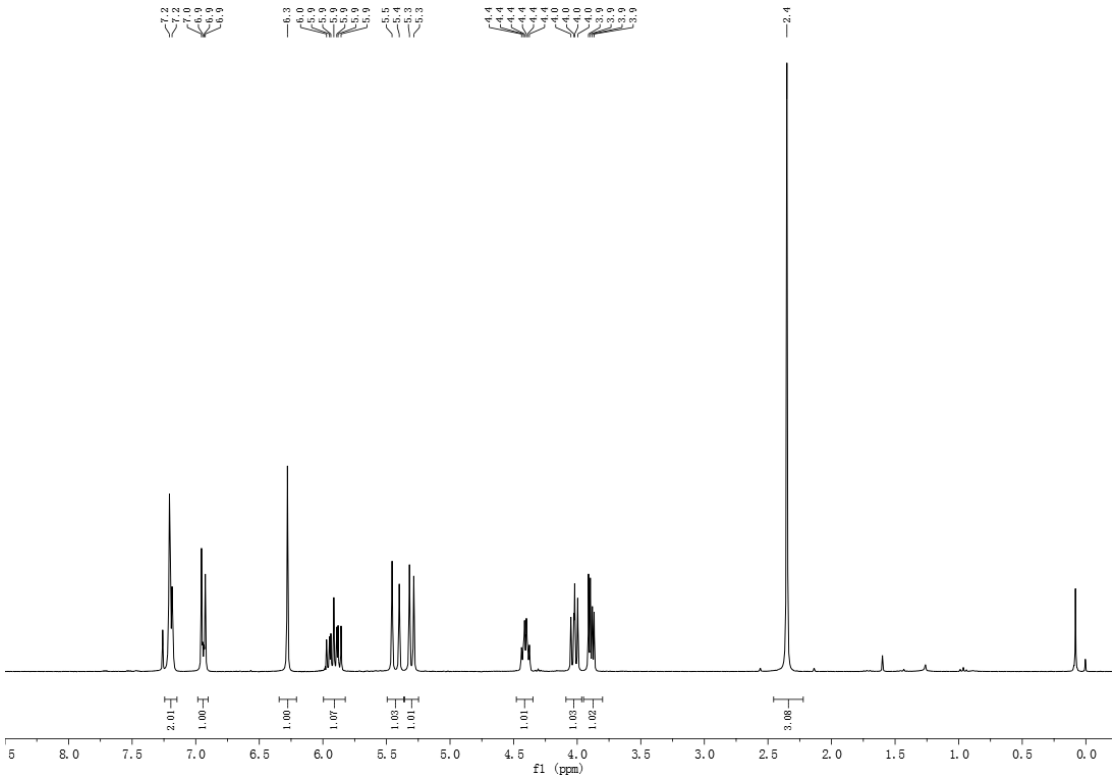
7a

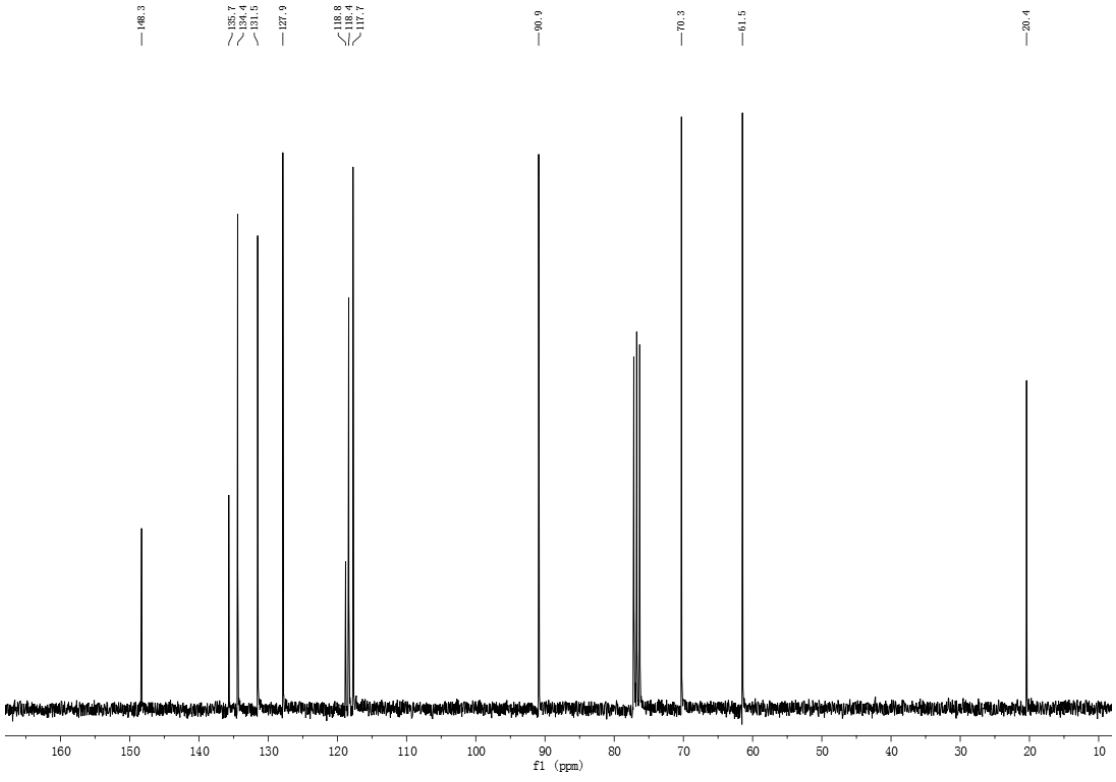


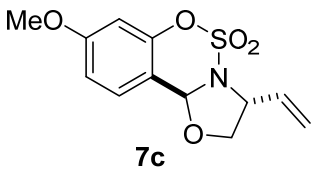



O
SO2
N
O

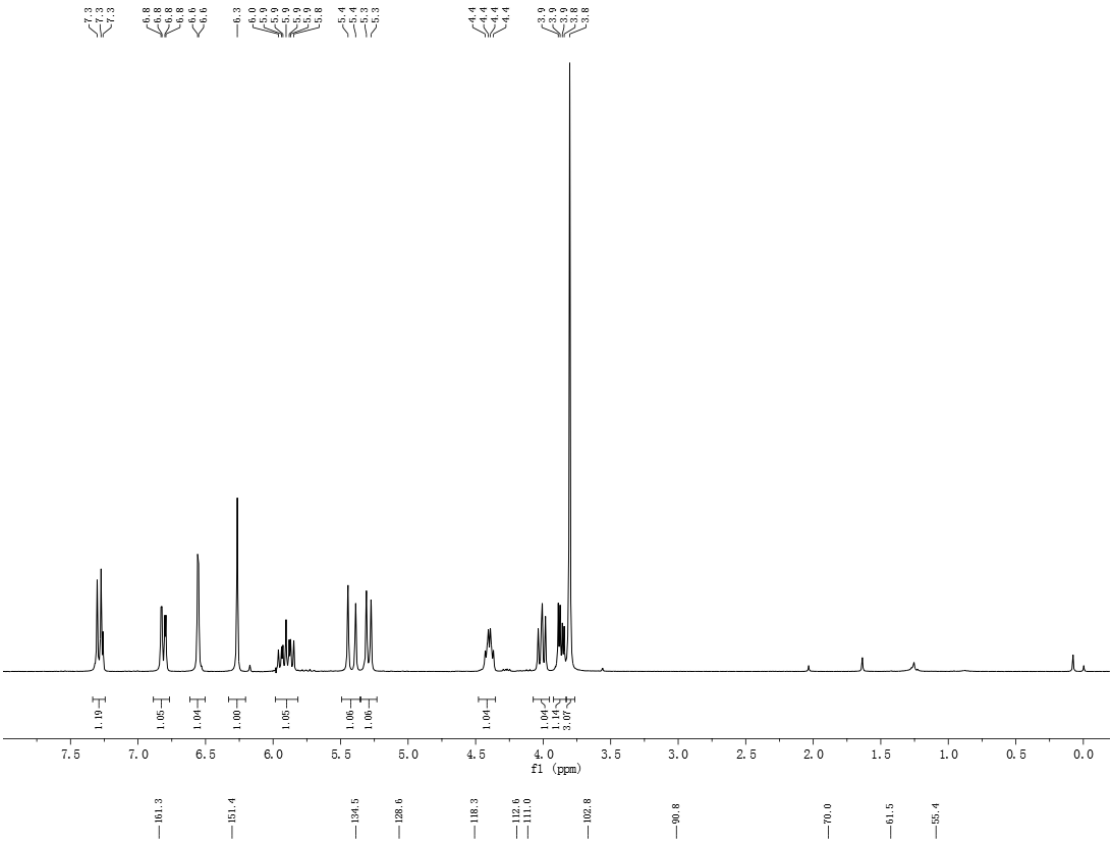
7b

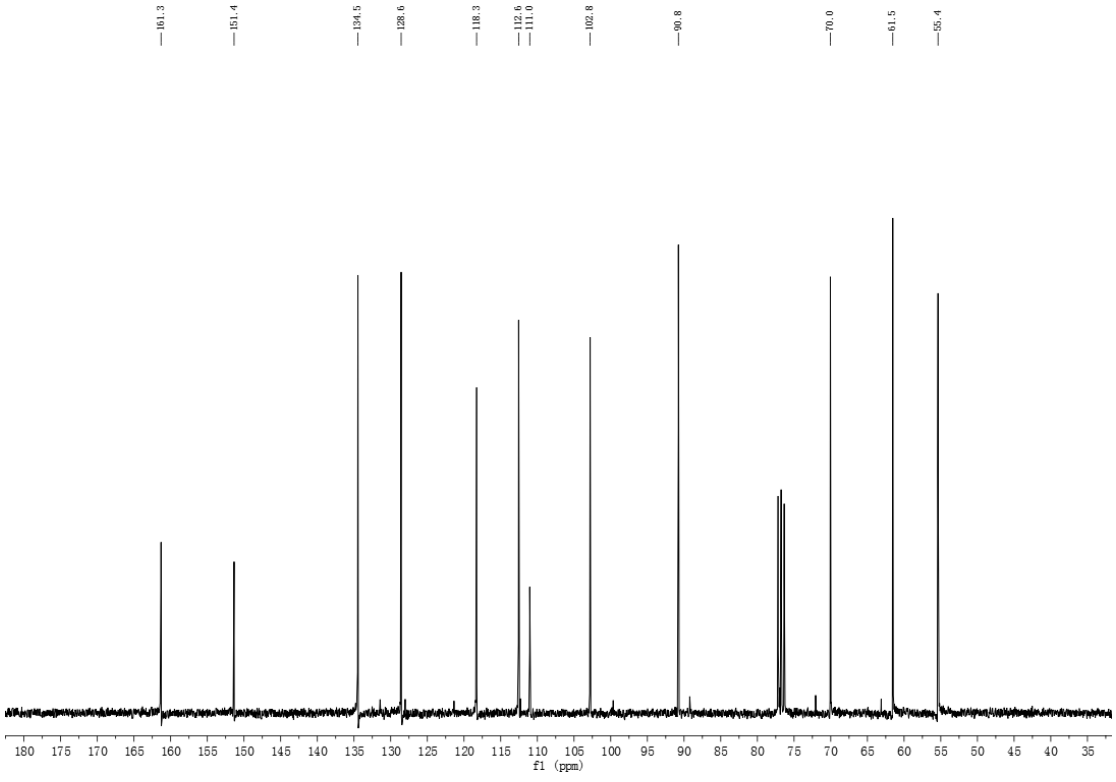

7.2
7.2
7.0
6.9
6.9
6.9
6.3
6.0
5.9
5.9
5.9
5.9
5.9
5.5
5.4
5.3
5.3
4.4
4.4
4.4
4.4
4.4
4.4
4.0
4.0
4.0
4.0
3.9
3.9
3.9
3.9
2.4
2.01
1.00
1.00
1.07
1.03
1.01
1.01
1.03
1.02
3.08
f1 (ppm)


148.3
135.7
134.4
131.5
127.9
118.8
118.4
117.7
90.9
70.3
61.5
20.4
f1 (ppm)


MeO
O
SO2
N
O

7c


7.3
7.3
7.3
6.8
6.8
6.8
6.8
6.6
6.6
6.3
6.0
5.9
5.9
5.9
5.9
5.9
5.8
5.4
5.4
5.3
5.3
4.4
4.4
4.4
4.4
3.9
3.9
3.9
3.8
3.8
1.19
1.05
1.04
1.00
1.05
1.06
1.06
1.04
1.04
1.47
3.07
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
0.0
f1 (ppm)


161.3
151.4
134.5
128.6
118.3
112.6
111.0
102.8
90.8
70.0
61.5
55.4
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
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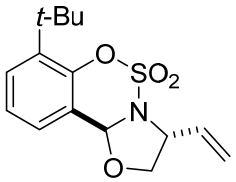
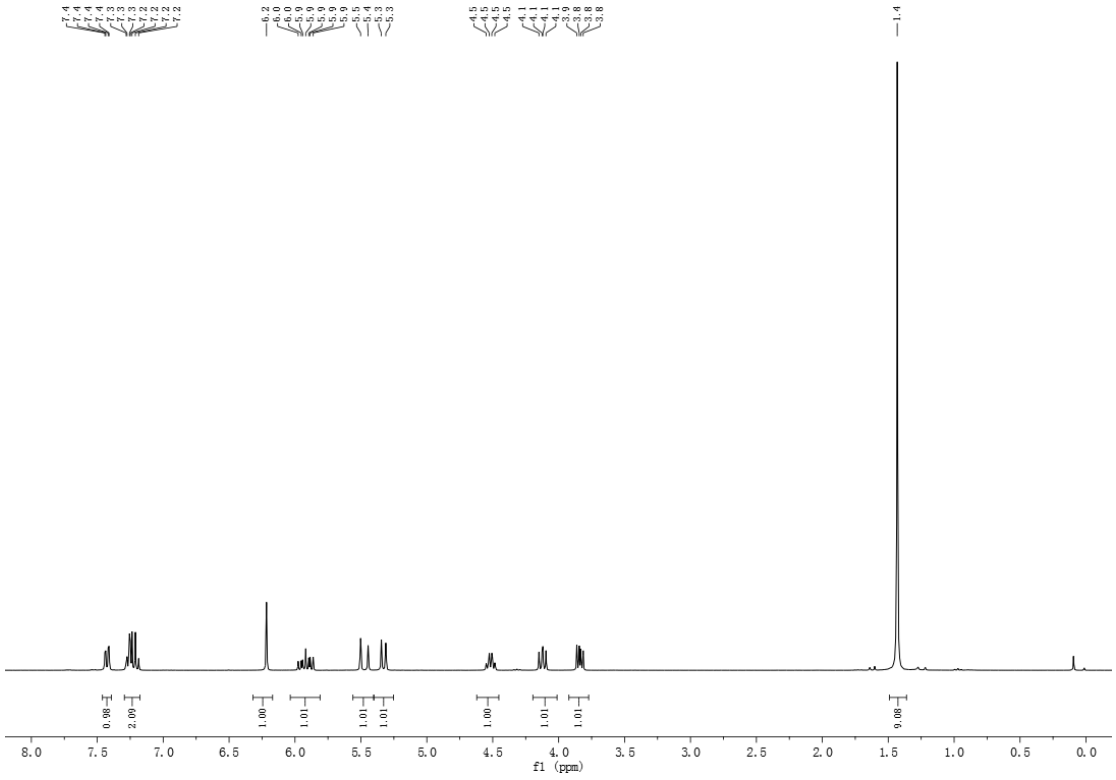
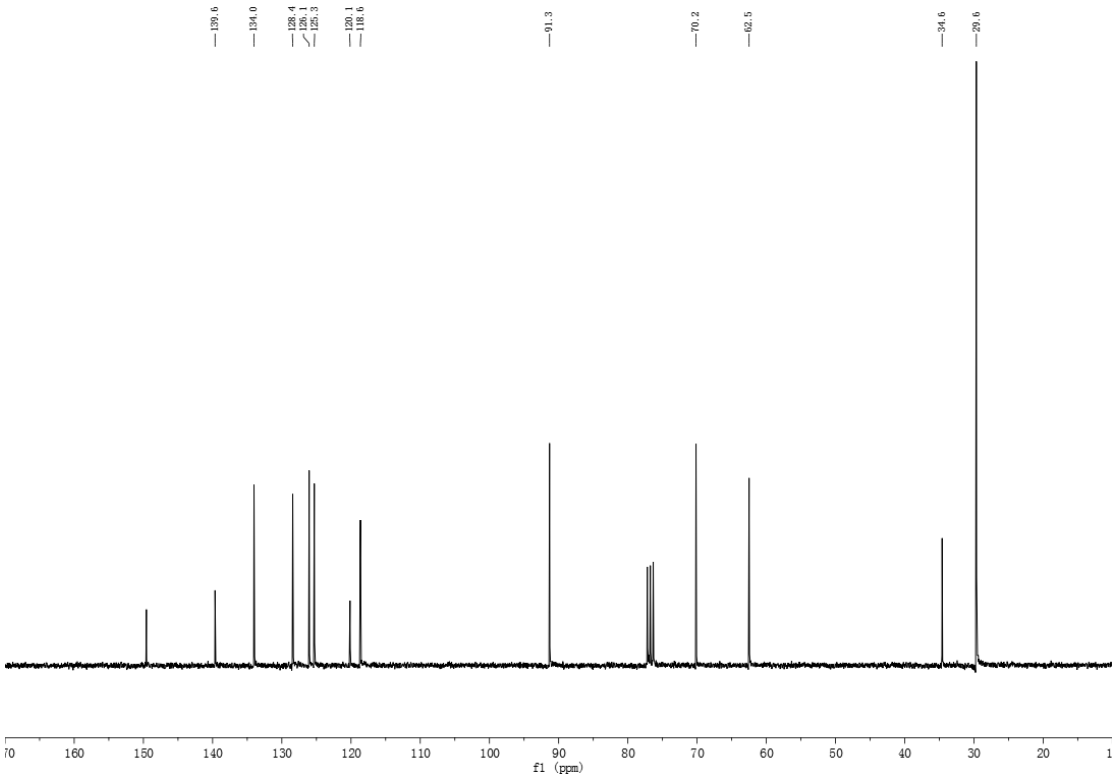
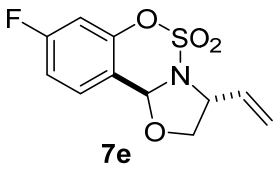
65
60
55
50
45
40
35
f1 (ppm)



7d







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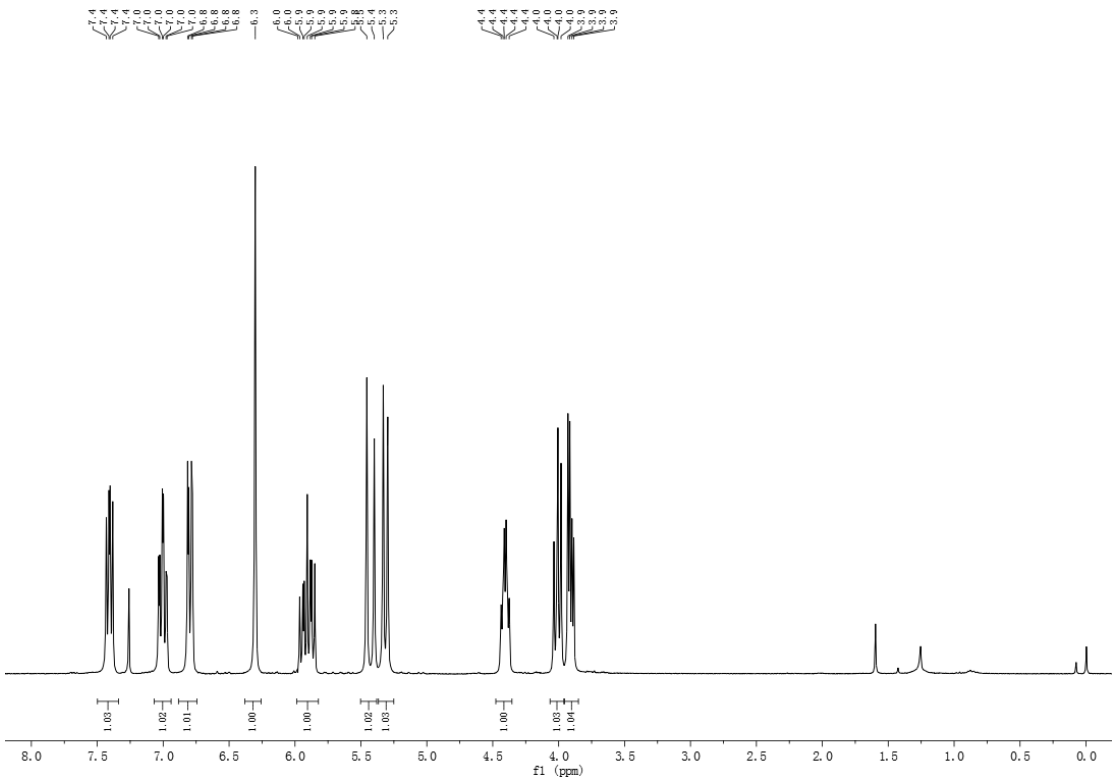

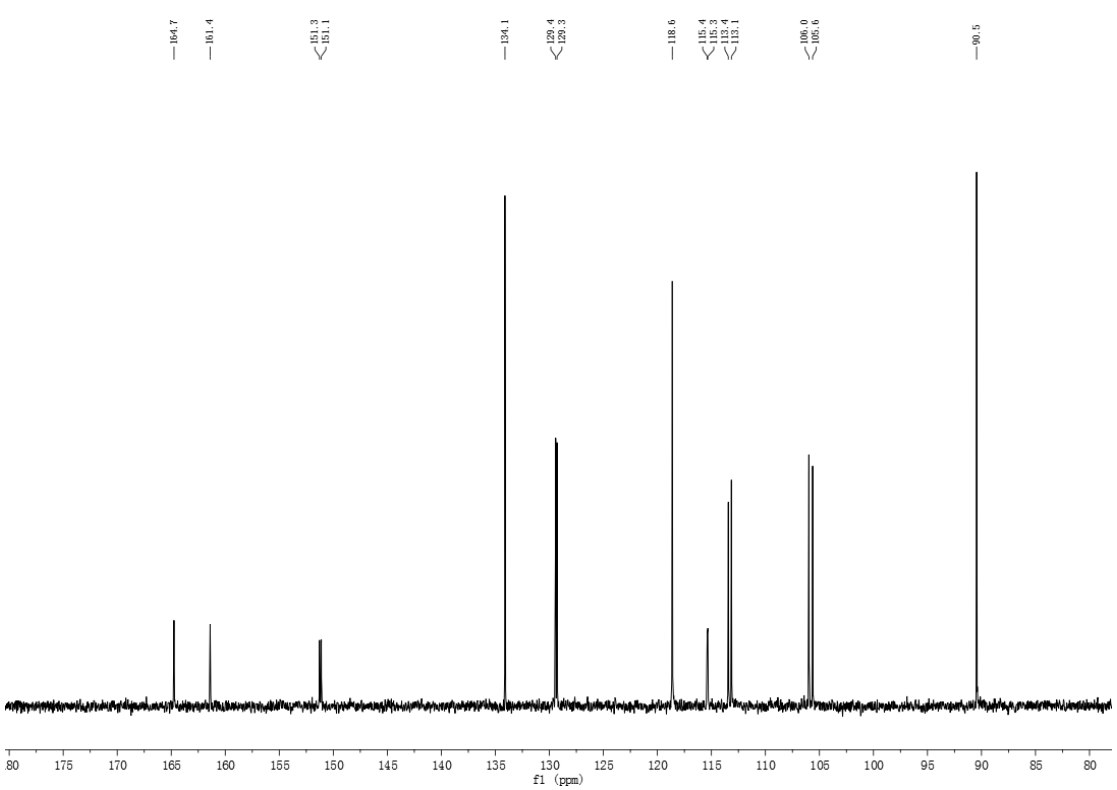

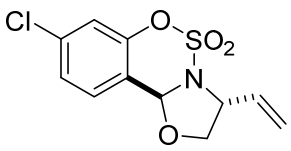

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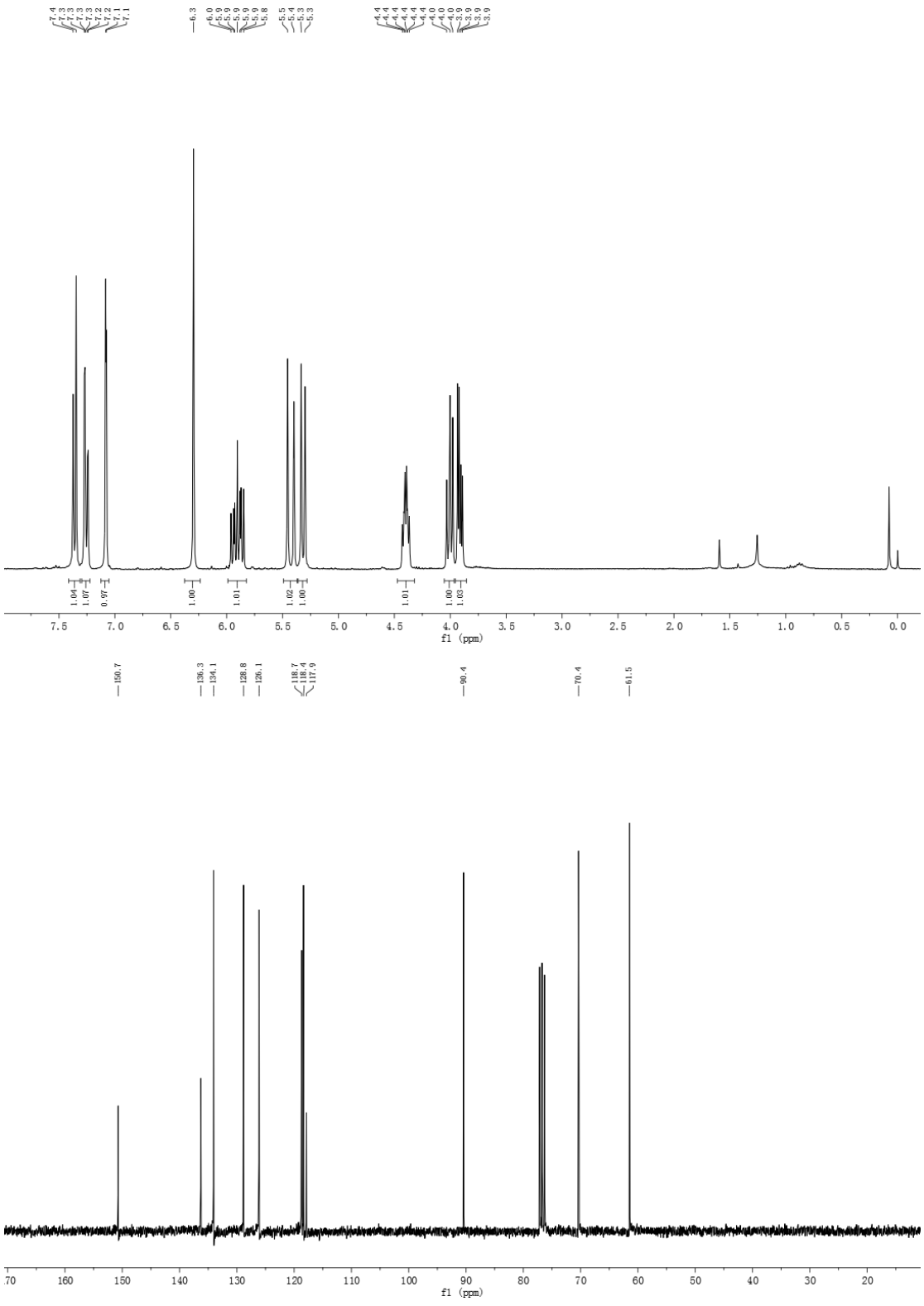
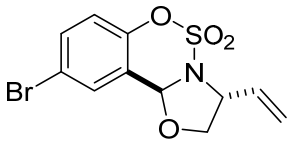
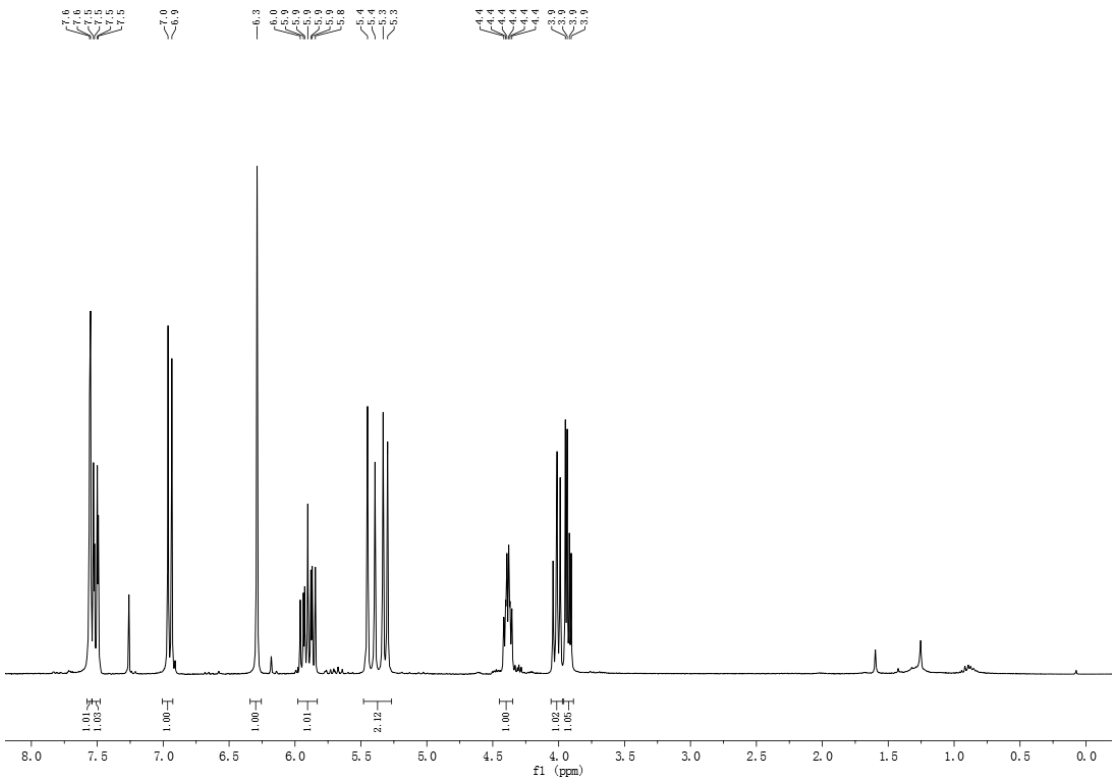



O
SO2
N
Br
O

7g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7.6
7.5
7.5
7.5
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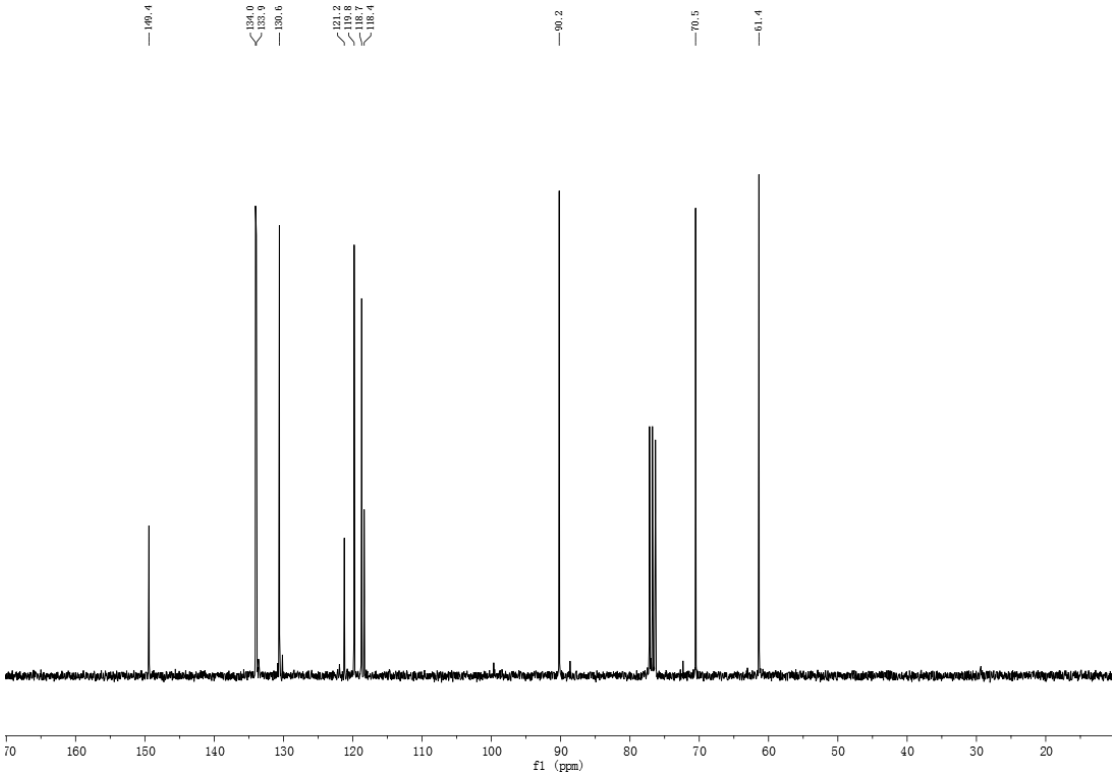
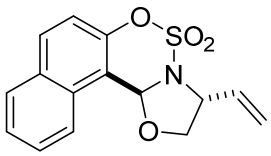
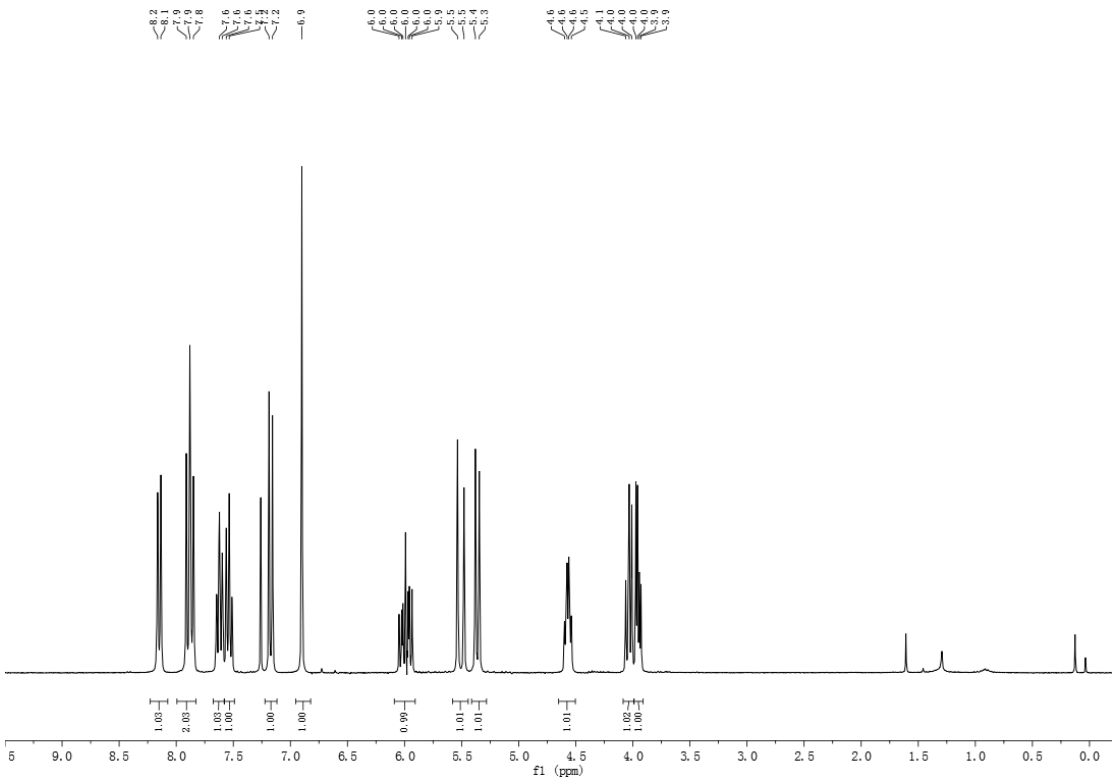
6.9
6.3
6.0
5.9
5.9
5.9
5.9
5.8
5.4
5.4
5.3
5.3
4.4
4.4
4.4
4.4
4.4
4.4
3.9
3.9
3.9
3.9
3.9
1.01
1.03
1.00
1.00
1.01
2.12
1.00
1.02
1.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.4
134.0
133.9
130.6
121.2
119.8
118.7
118.4
90.2
70.5
61.4
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


O
SO2
N
O

7h


8.2
8.1
7.9
7.8
7.6
7.6
7.6
7.5
7.2
6.9
6.0
6.0
6.0
6.0
6.0
5.9
5.5
5.5
5.4
5.3
4.6
4.6
4.5
4.5
4.1
4.0
4.0
4.0
4.0
3.9
3.9
1.03
2.03
1.03
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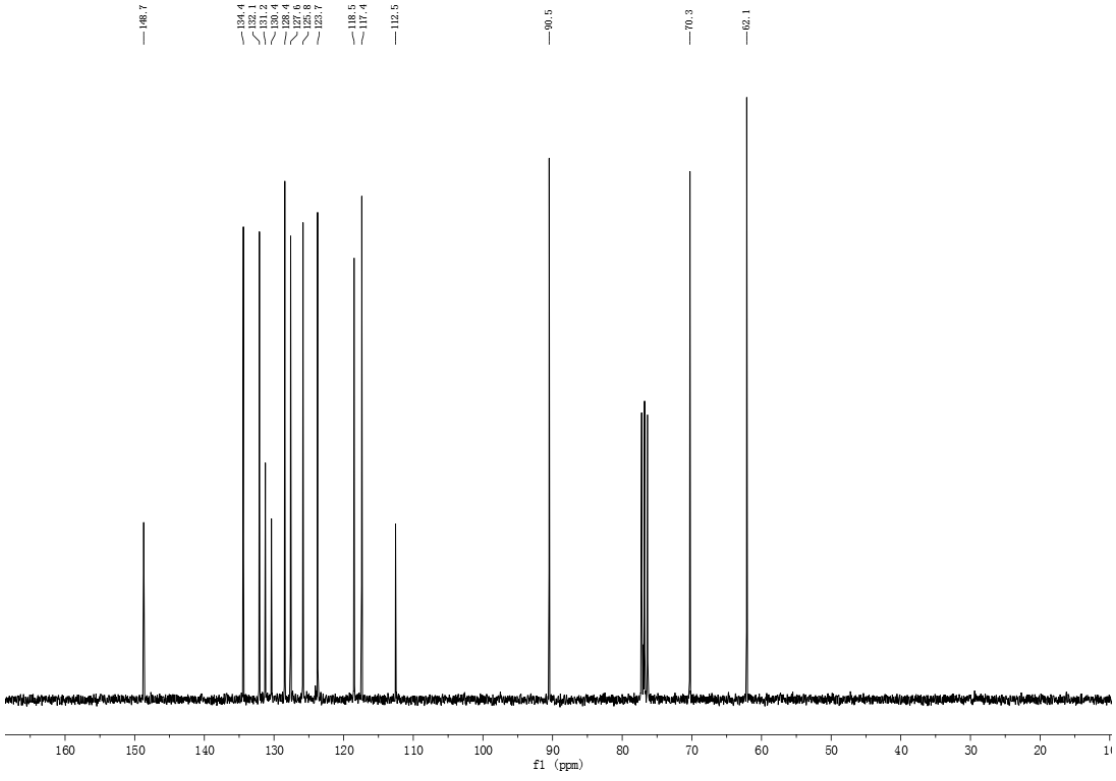
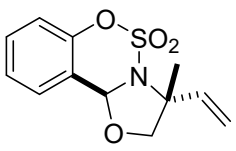
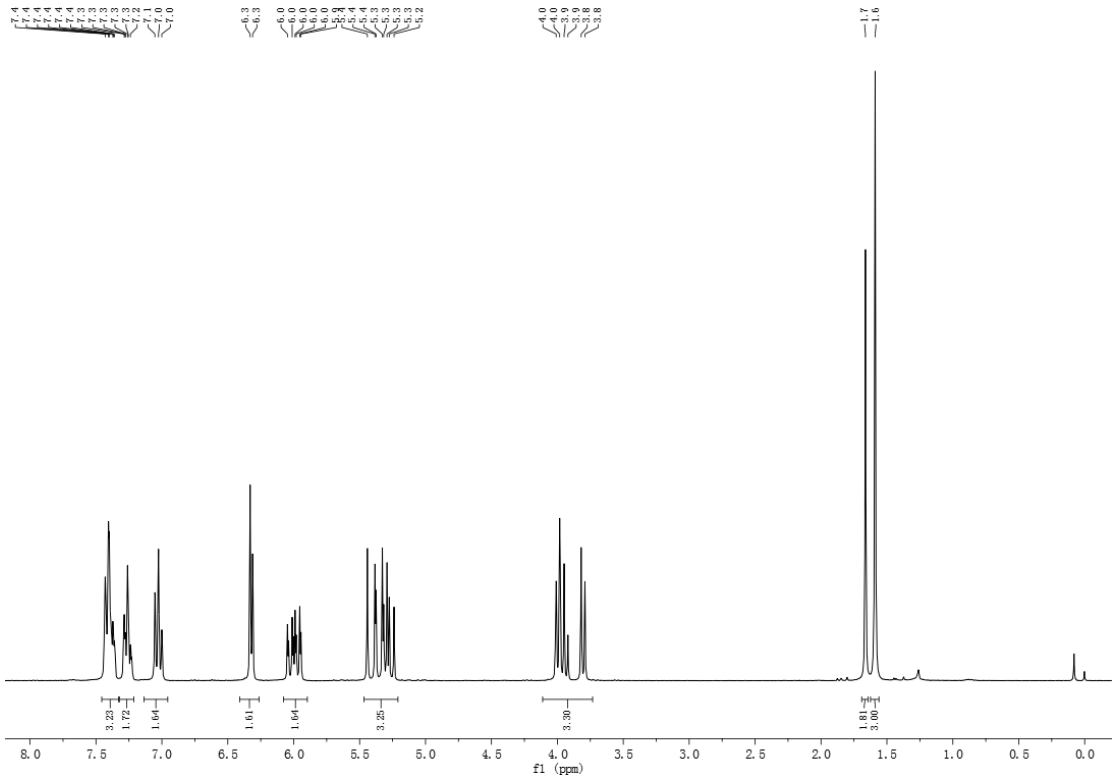
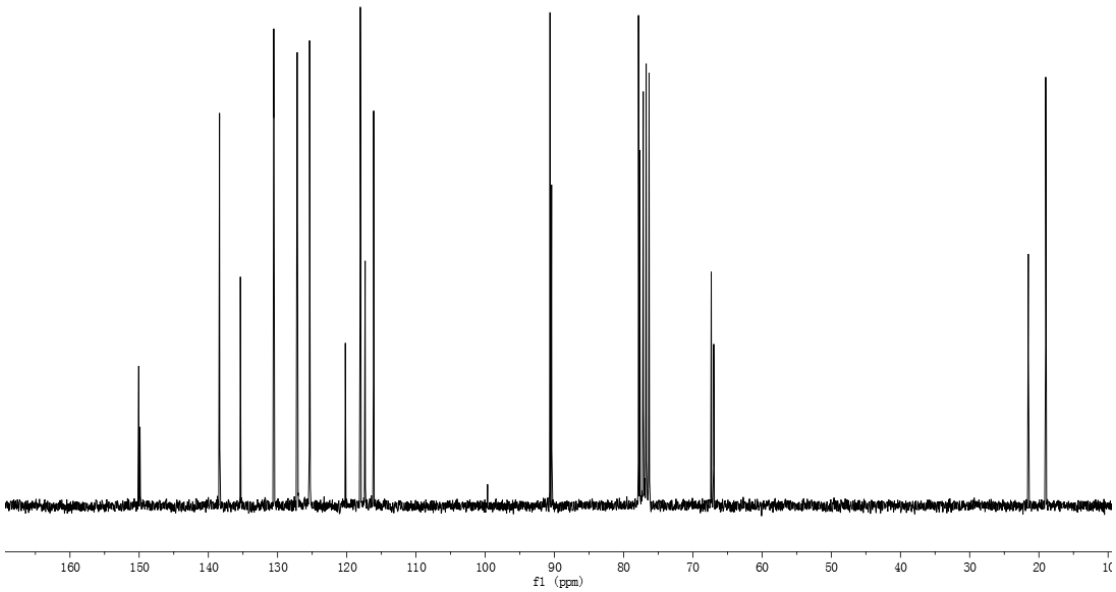
1.00
1.00
0.99
1.01
1.01
1.01
1.02
1.00
f1 (ppm)

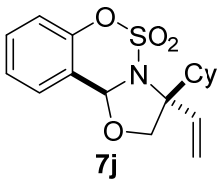

148.7
134.4
132.1
131.2
130.4
128.4
127.6
126.8
125.7
118.5
117.4
112.5
90.5
70.3
62.1
f1 (ppm)



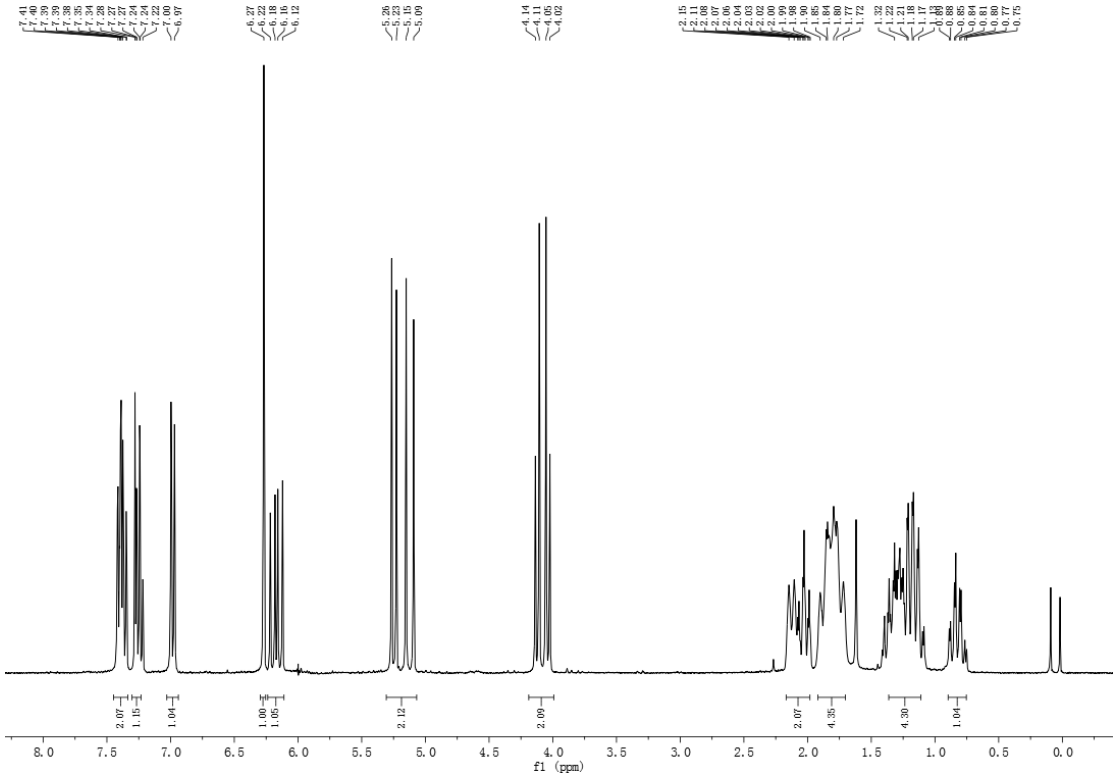
7i

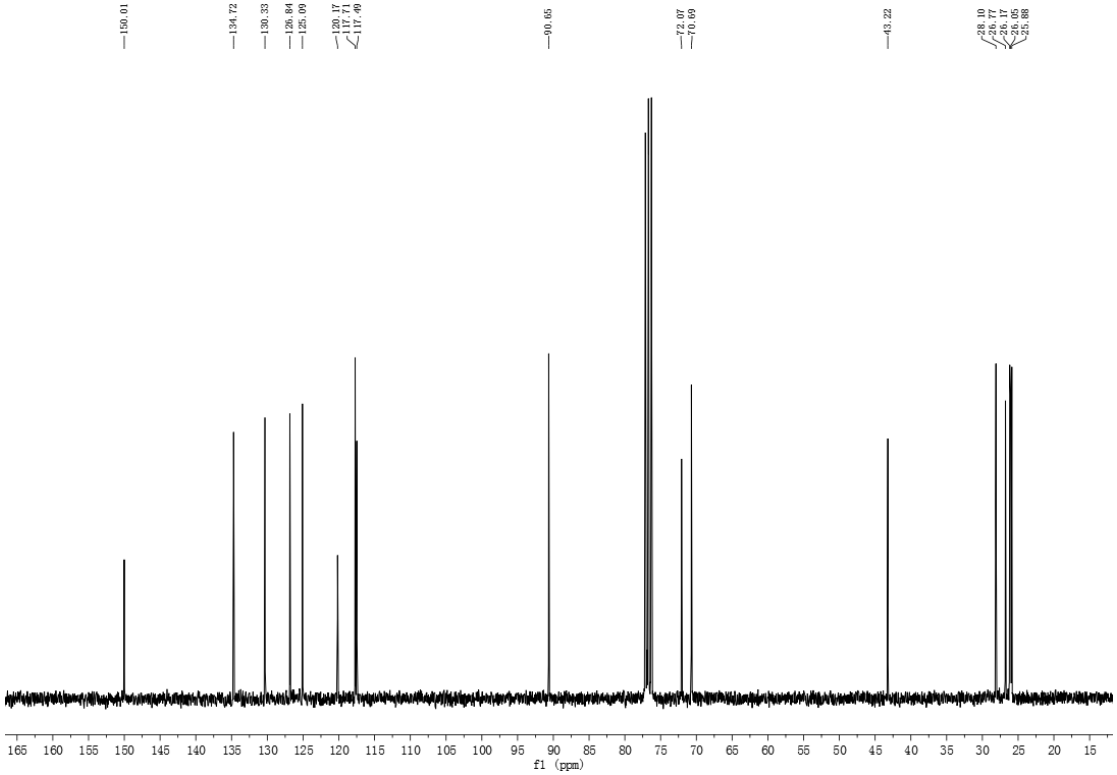


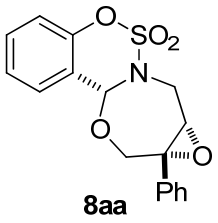




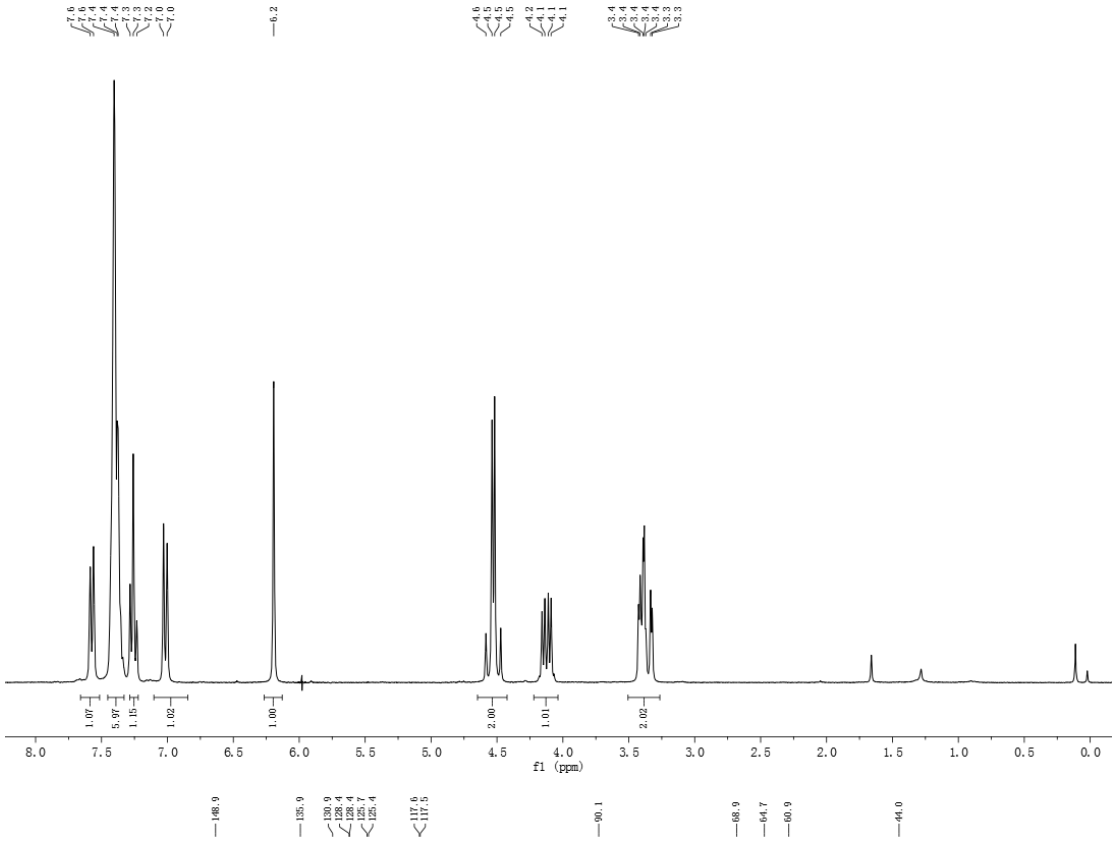
7j






O
SO2
N
O
O
Ph

8aa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7.3
7.3
7.2
7.0
7.0
6.2
4.6
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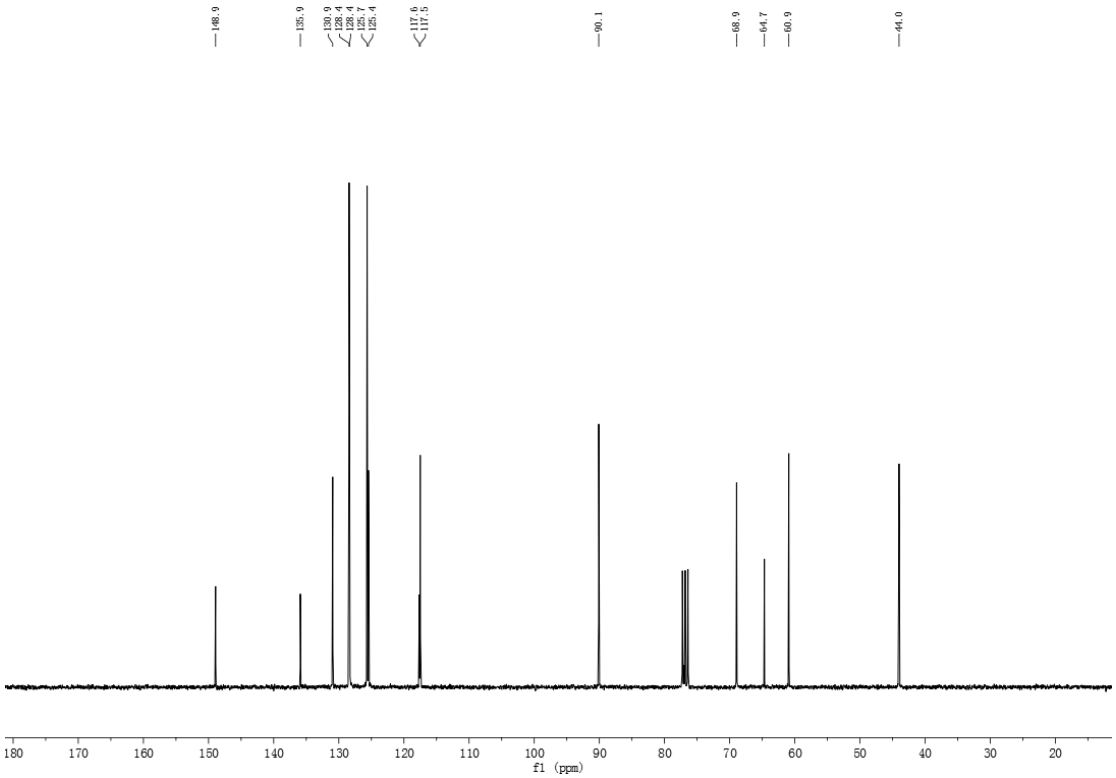
4.5
4.5
4.2
4.1
4.1
4.1
3.4
3.4
3.4
3.4
3.4
3.3
3.3
1.07
5.97
1.15
1.02
1.00
2.00
1.01
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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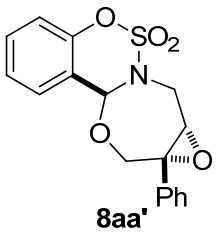
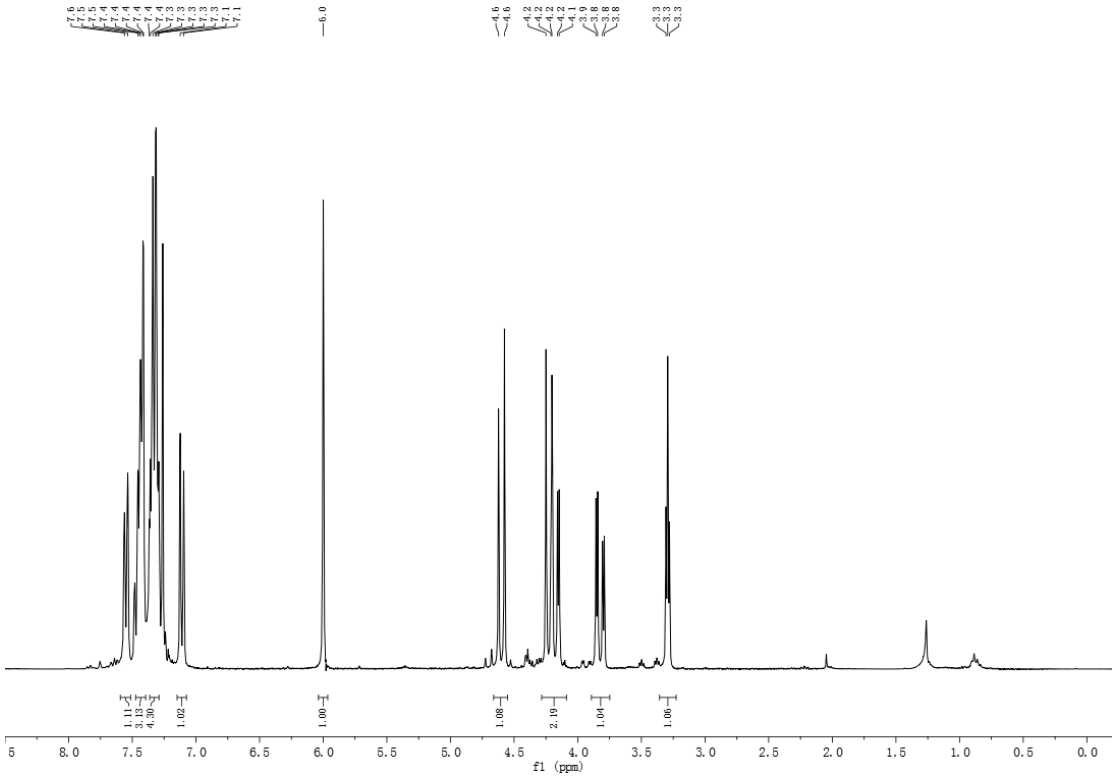
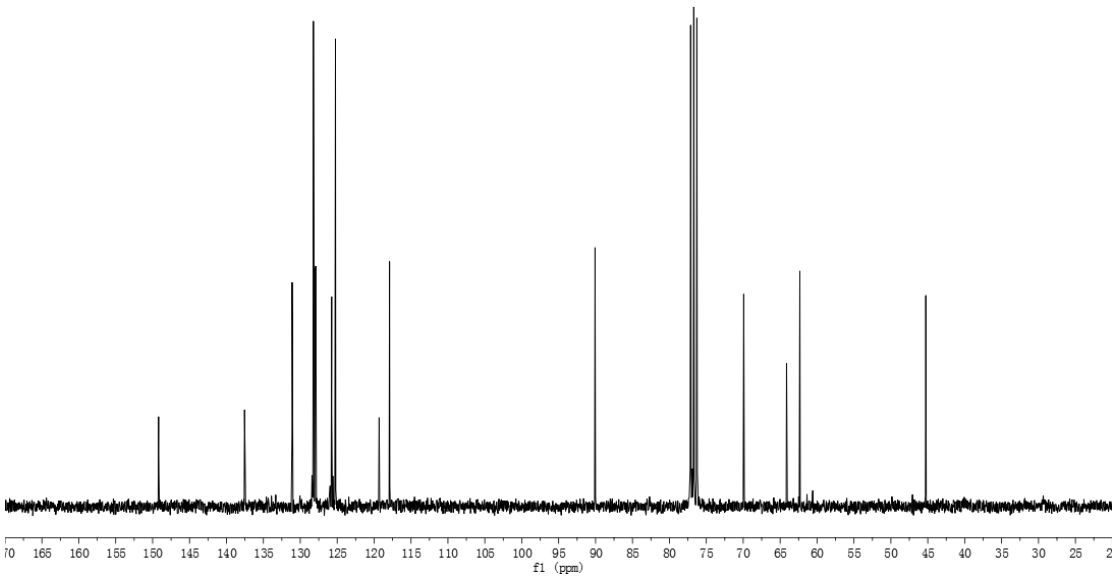
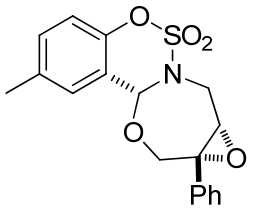
125.4
117.6
117.5
90.1
68.9
64.7
60.9
44.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



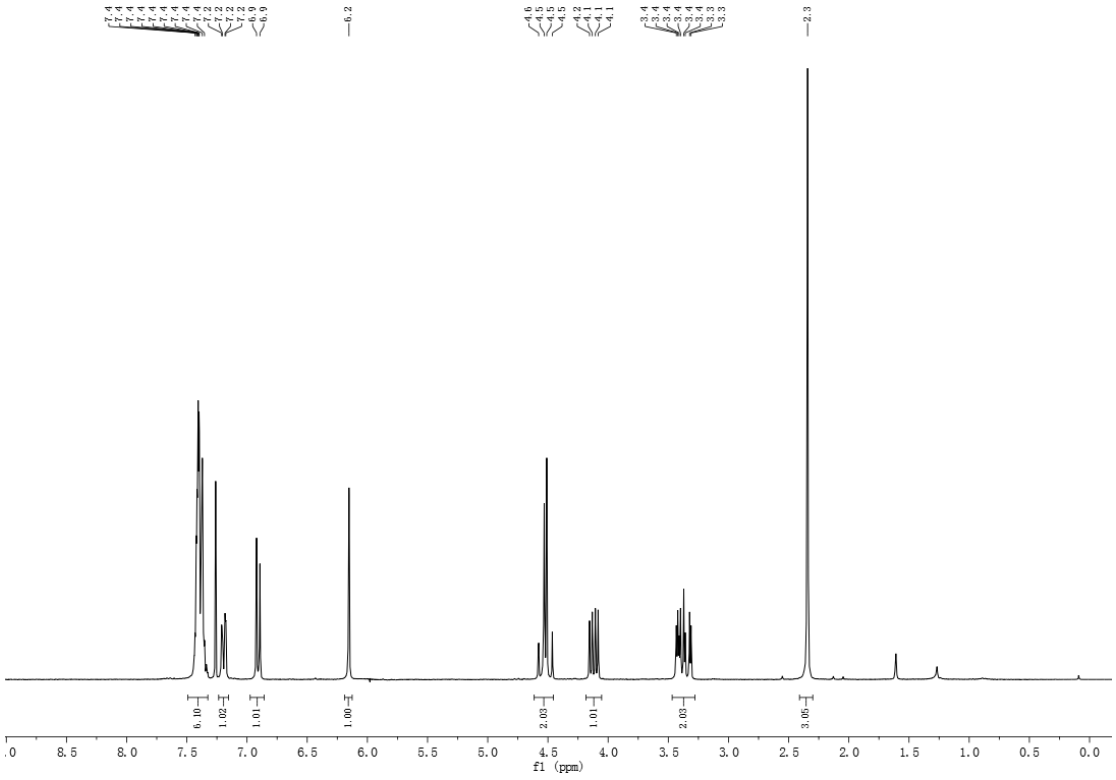
8aa'






O
SO2
N
O
O
Ph

8ba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7.2
6.9
6.2
4.6
4.5
4.2
4.1
3.4
3.3
2.3
6.10
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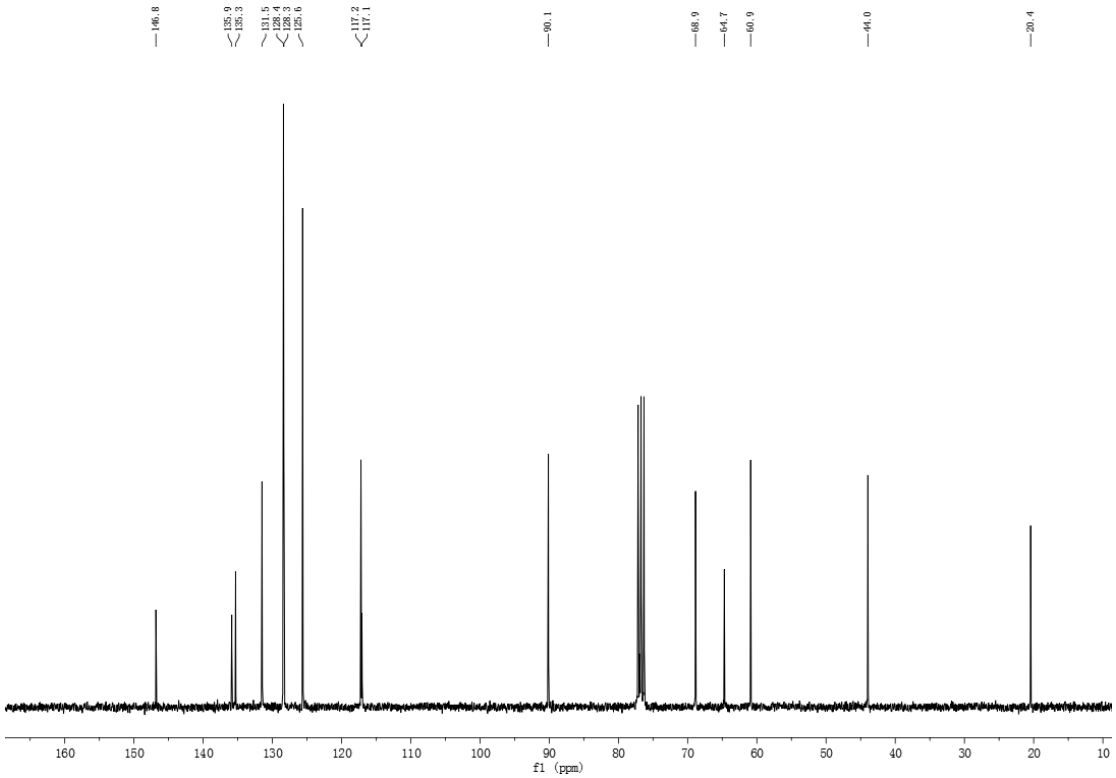
2.03
1.01
2.03
3.05
f1 (ppm)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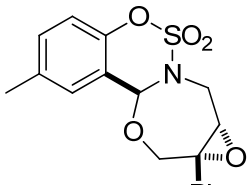
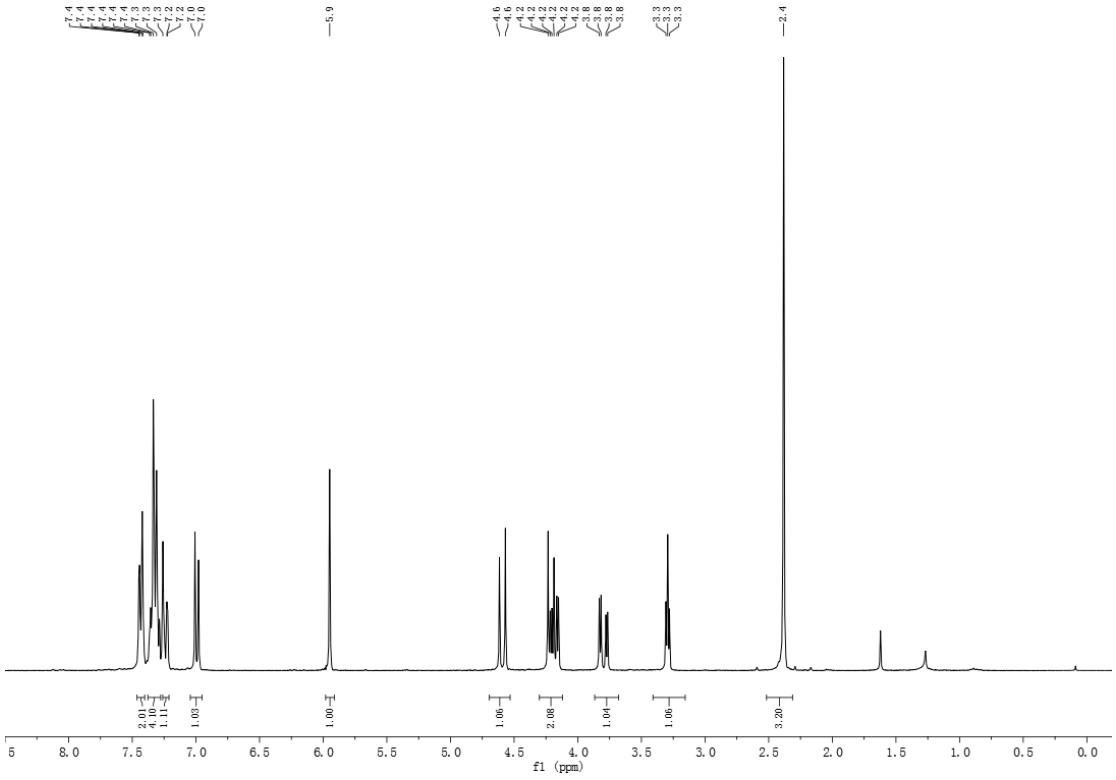
135.9
135.3
131.5
128.4
128.3
125.6
117.2
117.1
90.1
68.9
64.7
60.9
44.0
20.4
f1 (ppm)


O
SO2
N
O
O
Ph

8ba'


7.4
7.4
7.4
7.4
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7.4
7.3
7.3
7.2
7.2
7.0
7.0
5.9
4.6
4.6
4.2
4.2
4.2
4.2
4.2
4.2
3.8
3.8
3.8
3.3
3.3
3.3
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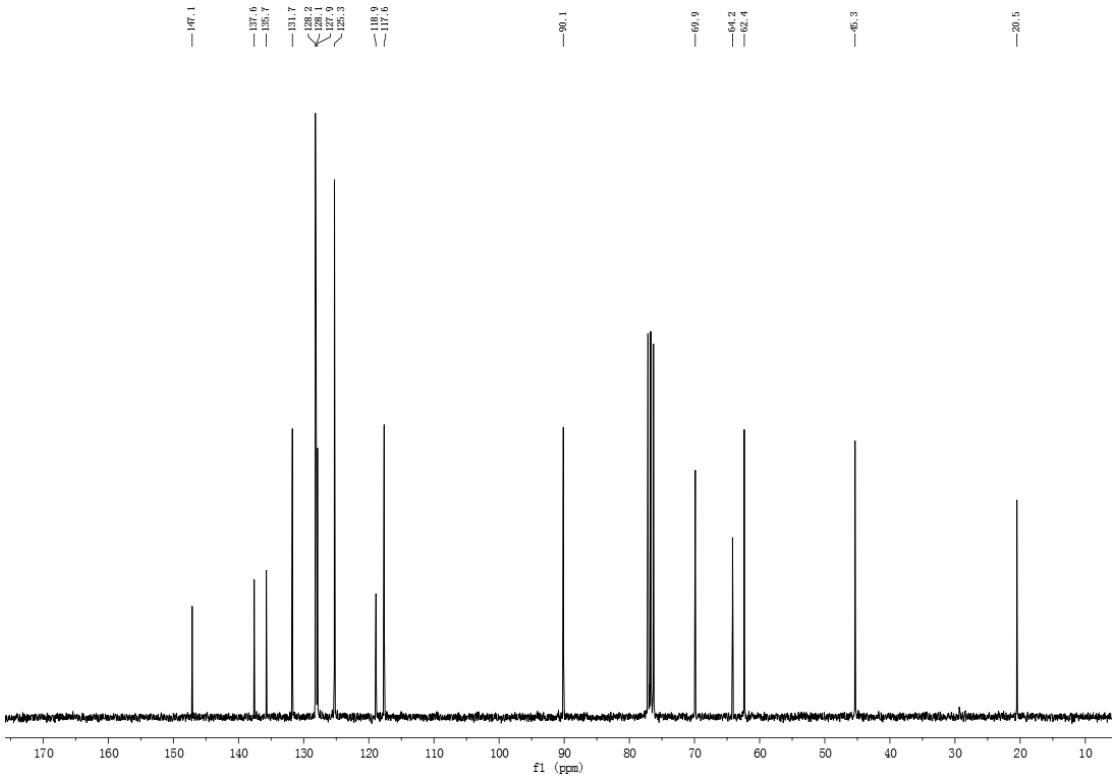
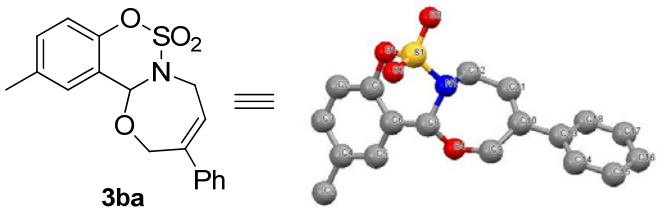
1.06
2.08
1.04
1.06
3.20
f1 (ppm)


147.1
137.6
135.7
131.7
128.2
128.1
127.9
125.3
118.9
117.6
90.1
69.9
64.2
62.4
45.3
20.5
f1 (ppm)

X-Ray Crystallographic Data

Crystallographic data for **3ba**, **7b**, **8ba** and **8ba′** have been deposited with the Cambridge Crystallographic Data Centre as deposition numbers CCDC 1569469, 1569468, 1569470 and 1569472, respectively. 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.



3ba

Table S3. Crystal data and structure refinement for **3ba**.

Identification code	**3ba**	
Empirical formula	$C_{18}H_{17}NO_4S$	
Formula weight	343.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 13.726(3) Å	a= 90°.
	b = 15.964(3) Å	b= 111.03(3)°.
	c = 7.7194(15) Å	g = 90°.
Volume	1578.8(6) $Å^3$	
Z	4	
Density (calculated)	1.445 Mg/m^3	
Absorption coefficient	0.228 mm^{-1}	
F(000)	720	
Crystal size	0.428 x 0.256 x 0.183 mm^3	
Theta range for data collection	2.038 to 27.471°.	
Index ranges	-17<=h<=17, -20<=k<=19, -9<=l<=10	
Reflections collected	9017	
Independent reflections	3518 [R(int) = 0.0468]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	None	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3518 / 2 / 218
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0872
R indices (all data)	R1 = 0.0367, wR2 = 0.0878
Absolute structure parameter	0.01(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.193 and -0.305 e.Å^{-3}

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3ba**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	5912(1)	2629(1)	9675(1)	26(1)
O1	7108(2)	2844(1)	10062(3)	30(1)
O2	5642(2)	2958(2)	11155(3)	34(1)
O3	5819(2)	1760(1)	9266(3)	34(1)
O4	5064(1)	4546(1)	6626(2)	27(1)
N1	5306(2)	3180(1)	7829(3)	23(1)
C1	7338(2)	3710(2)	10122(4)	27(1)
C2	8376(2)	3923(2)	11081(4)	34(1)
C3	8658(2)	4755(2)	11206(4)	38(1)
C4	7937(2)	5382(2)	10370(4)	34(1)
C5	6911(2)	5152(2)	9381(4)	29(1)
C6	6591(2)	4316(2)	9249(4)	26(1)
C7	8244(3)	6295(2)	10573(5)	43(1)
C8	5451(2)	4095(2)	8282(4)	24(1)
C9	3996(2)	4360(2)	5524(4)	27(1)
C10	3934(2)	3700(2)	4079(4)	23(1)
C11	4638(2)	3091(2)	4397(4)	26(1)
C12	5551(2)	2945(2)	6165(4)	25(1)
C13	3064(2)	3782(2)	2257(4)	23(1)
C14	2127(2)	4171(2)	2119(4)	28(1)
C15	1318(2)	4246(2)	404(4)	33(1)
C16	1429(2)	3934(2)	-1188(4)	32(1)
C17	2358(2)	3554(2)	-1067(4)	30(1)
C18	3165(2)	3478(2)	631(4)	27(1)

Table S5. Bond lengths [Å] and angles [°] for **3ba**.

S1-O1	1.596(2)
S1-O2	1.423(2)
S1-O3	1.418(2)
S1-N1	1.626(2)
O1-C1	1.416(4)
O4-C8	1.396(3)
O4-C9	1.437(3)
N1-C8	1.499(3)
N1-C12	1.488(4)
C1-C2	1.391(4)
C1-C6	1.394(4)
C2-H2	0.9300
C2-C3	1.377(5)
C3-H3	0.9300
C3-C4	1.393(5)
C4-C5	1.389(4)
C4-C7	1.510(5)
C5-H5	0.9300
C5-C6	1.397(4)
C6-C8	1.513(4)
C7-H7A	0.9600
C7-H7B	0.9600
C7-H7C	0.9600
C8-H8	0.9800
C9-H9A	0.9700
C9-H9B	0.9700
C9-C10	1.514(4)
C10-C11	1.331(4)
C10-C13	1.488(4)
C11-H11	0.9300
C11-C12	1.503(4)
C12-H12A	0.9700
C12-H12B	0.9700
C13-C14	1.397(4)
C13-C18	1.398(4)
C14-H14	0.9300

C14-C15	1.395(4)
C15-H15	0.9300
C15-C16	1.384(5)
C16-H16	0.9300
C16-C17	1.384(4)
C17-H17	0.9300
C17-C18	1.385(4)
C18-H18	0.9300
O1-S1-N1	102.46(12)
O2-S1-O1	108.46(13)
O2-S1-N1	107.75(12)
O3-S1-O1	104.87(13)
O3-S1-O2	120.80(14)
O3-S1-N1	110.92(12)
C1-O1-S1	114.79(17)
C8-O4-C9	114.0(2)
C8-N1-S1	109.84(17)
C12-N1-S1	114.66(17)
C12-N1-C8	113.2(2)
C2-C1-O1	115.5(2)
C2-C1-C6	121.6(3)
C6-C1-O1	122.9(2)
C1-C2-H2	120.6
C3-C2-C1	118.8(3)
C3-C2-H2	120.6
C2-C3-H3	119.2
C2-C3-C4	121.7(3)
C4-C3-H3	119.2
C3-C4-C7	121.3(3)
C5-C4-C3	118.4(3)
C5-C4-C7	120.2(3)
C4-C5-H5	119.2
C4-C5-C6	121.6(3)
C6-C5-H5	119.2
C1-C6-C5	117.9(2)
C1-C6-C8	121.9(2)
C5-C6-C8	120.0(2)
C4-C7-H7A	109.5

C4-C7-H7B	109.5
C4-C7-H7C	109.5
H7A-C7-H7B	109.5
H7A-C7-H7C	109.5
H7B-C7-H7C	109.5
O4-C8-N1	108.3(2)
O4-C8-C6	108.5(2)
O4-C8-H8	109.4
N1-C8-C6	111.6(2)
N1-C8-H8	109.4
C6-C8-H8	109.4
O4-C9-H9A	109.5
O4-C9-H9B	109.5
O4-C9-C10	110.9(2)
H9A-C9-H9B	108.1
C10-C9-H9A	109.5
C10-C9-H9B	109.5
C11-C10-C9	121.8(2)
C11-C10-C13	121.4(2)
C13-C10-C9	116.7(2)
C10-C11-H11	116.8
C10-C11-C12	126.5(3)
C12-C11-H11	116.8
N1-C12-C11	111.8(2)
N1-C12-H12A	109.3
N1-C12-H12B	109.3
C11-C12-H12A	109.3
C11-C12-H12B	109.3
H12A-C12-H12B	107.9
C14-C13-C10	121.0(3)
C14-C13-C18	118.0(2)
C18-C13-C10	120.9(2)
C13-C14-H14	119.7
C15-C14-C13	120.6(3)
C15-C14-H14	119.7
C14-C15-H15	119.7
C16-C15-C14	120.5(3)
C16-C15-H15	119.7

C15-C16-H16	120.3
C17-C16-C15	119.3(3)
C17-C16-H16	120.3
C16-C17-H17	119.8
C16-C17-C18	120.4(3)
C18-C17-H17	119.8
C13-C18-H18	119.4
C17-C18-C13	121.1(3)
C17-C18-H18	119.4

Symmetry transformations used to generate equivalent atoms:

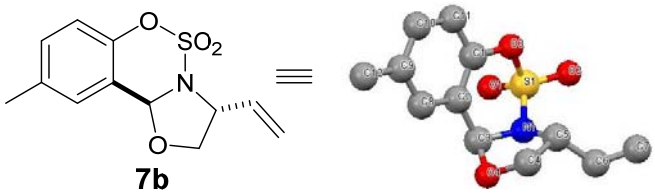
Table S6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3ba**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	24(1)	29(1)	24(1)	5(1)	7(1)	3(1)
O1	23(1)	30(1)	33(1)	3(1)	7(1)	3(1)
O2	33(1)	44(1)	27(1)	6(1)	13(1)	6(1)
O3	35(1)	28(1)	35(1)	8(1)	9(1)	2(1)
O4	27(1)	23(1)	24(1)	2(1)	1(1)	-2(1)
N1	24(1)	22(1)	21(1)	2(1)	5(1)	2(1)
C1	24(1)	32(1)	25(1)	0(1)	9(1)	0(1)
C2	25(1)	46(2)	30(1)	1(1)	7(1)	1(1)
C3	28(1)	52(2)	32(2)	-10(1)	10(1)	-12(1)
C4	35(2)	41(2)	28(1)	-7(1)	13(1)	-9(1)
C5	32(1)	29(1)	26(1)	-6(1)	10(1)	-4(1)
C6	23(1)	30(2)	22(1)	-3(1)	6(1)	-2(1)
C7	45(2)	42(2)	45(2)	-13(2)	18(2)	-18(2)
C8	24(1)	22(1)	23(1)	-1(1)	5(1)	0(1)
C9	26(1)	24(1)	25(1)	-2(1)	4(1)	4(1)
C10	25(1)	22(1)	21(1)	1(1)	8(1)	-1(1)
C11	32(1)	22(1)	22(1)	0(1)	9(1)	1(1)
C12	26(1)	26(1)	23(1)	1(1)	8(1)	4(1)

C13	24(1)	20(1)	23(1)	1(1)	5(1)	-3(1)
C14	27(1)	27(1)	28(1)	1(1)	10(1)	2(1)
C15	26(1)	32(2)	36(2)	1(1)	5(1)	4(1)
C16	28(1)	32(2)	29(1)	2(1)	1(1)	-2(1)
C17	34(1)	29(1)	25(1)	-3(1)	7(1)	-2(1)
C18	25(1)	26(1)	28(1)	-2(1)	7(1)	0(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3ba**.

	x	y	z	U(eq)
H2	8869	3511	11628	41
H3	9348	4902	11866	45
H5	6426	5563	8793	35
H7A	8326	6483	11799	65
H7B	7711	6620	9674	65
H7C	8892	6364	10376	65
H8	5062	4248	9079	29
H9A	3649	4866	4914	32
H9B	3639	4160	6324	32
H11	4557	2718	3429	31
H12A	5747	2358	6247	30
H12B	6142	3273	6141	30
H14	2043	4381	3179	33
H15	699	4508	329	40
H16	885	3979	-2328	39
H17	2441	3349	-2133	36
H18	3784	3221	691	32



7b

Table S8. Crystal data and structure refinement for **7b**.

Identification code	**7b**	
Empirical formula	$C_{12}H_{13}NO_4S$	
Formula weight	267.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.7561(12) Å	a= 90°.
	b = 10.135(2) Å	b= 90°.
	c = 20.636(4) Å	g = 90°.
Volume	1203.9(4) $Å^3$	
Z	4	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	0.275 mm^{-1}	
F(000)	560	
Crystal size	0.416 x 0.192 x 0.036 mm^3	
Theta range for data collection	3.580 to 27.478°.	
Index ranges	-6<=h<=7, -13<=k<=13, -26<=l<=26	
Reflections collected	8693	
Independent reflections	2747 [R(int) = 0.1069]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2747 / 0 / 164	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1004	
R indices (all data)	R1 = 0.0799, wR2 = 0.1081	
Absolute structure parameter	0.23(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.312 and -0.340 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	1678(2)	1031(1)	3525(1)	28(1)
O1	3260(5)	284(3)	3908(1)	34(1)
O2	-266(5)	439(3)	3224(1)	36(1)
O3	571(5)	2155(3)	3974(1)	29(1)
O4	5837(5)	3430(3)	2798(1)	29(1)
N1	3201(6)	1845(3)	3006(2)	25(1)
C1	2130(7)	3137(4)	4198(2)	26(1)
C2	4215(7)	3408(4)	3890(2)	24(1)
C3	5099(7)	2631(4)	3311(2)	24(1)
C4	3752(7)	3876(4)	2481(2)	32(1)
C5	2010(7)	2731(4)	2527(2)	26(1)
C6	1622(9)	2011(4)	1905(2)	33(1)
C7	-411(9)	1860(5)	1633(2)	41(1)
C8	5544(7)	4442(4)	4133(2)	24(1)
C9	4833(7)	5199(4)	4661(2)	29(1)
C10	2762(7)	4858(4)	4963(2)	30(1)
C11	1397(7)	3837(4)	4739(2)	29(1)
C12	6264(8)	6360(4)	4885(2)	37(1)

Table S10. Bond lengths [Å] and angles [°] for **7b**.

S1-O1	1.424(3)
S1-O2	1.414(3)
S1-O3	1.601(3)
S1-N1	1.611(3)
O3-C1	1.417(5)
O4-C3	1.399(4)
O4-C4	1.440(5)
N1-C3	1.492(5)
N1-C5	1.501(5)

C1-C2	1.385(5)
C1-C11	1.390(5)
C2-C3	1.518(5)
C2-C8	1.391(5)
C3-H3	0.9800
C4-H4A	0.9700
C4-H4B	0.9700
C4-C5	1.536(6)
C5-H5	0.9800
C5-C6	1.494(5)
C6-H6	0.9300
C6-C7	1.307(6)
C7-H7A	0.9300
C7-H7B	0.9300
C8-H8	0.9300
C8-C9	1.394(5)
C9-C10	1.389(6)
C9-C12	1.509(5)
C10-H10	0.9300
C10-C11	1.378(6)
C11-H11	0.9300
C12-H12A	0.9600
C12-H12B	0.9600
C12-H12C	0.9600
O1-S1-O3	108.11(16)
O1-S1-N1	107.07(18)
O2-S1-O1	121.68(18)
O2-S1-O3	103.98(17)
O2-S1-N1	110.83(18)
O3-S1-N1	103.70(16)
C1-O3-S1	115.9(2)
C3-O4-C4	105.9(3)
C3-N1-S1	113.0(2)

C3-N1-C5	107.0(3)
C5-N1-S1	119.7(3)
C2-C1-O3	122.6(4)
C2-C1-C11	122.1(4)
C11-C1-O3	115.3(3)
C1-C2-C3	123.3(4)
C1-C2-C8	117.4(4)
C8-C2-C3	119.4(3)
O4-C3-N1	102.2(3)
O4-C3-C2	113.4(3)
O4-C3-H3	109.9
N1-C3-C2	111.3(3)
N1-C3-H3	109.9
C2-C3-H3	109.9
O4-C4-H4A	110.5
O4-C4-H4B	110.5
O4-C4-C5	106.2(3)
H4A-C4-H4B	108.7
C5-C4-H4A	110.5
C5-C4-H4B	110.5
N1-C5-C4	101.2(3)
N1-C5-H5	110.3
C4-C5-H5	110.3
C6-C5-N1	110.0(3)
C6-C5-C4	114.4(3)
C6-C5-H5	110.3
C5-C6-H6	118.0
C7-C6-C5	124.1(4)
C7-C6-H6	118.0
C6-C7-H7A	120.0
C6-C7-H7B	120.0
H7A-C7-H7B	120.0
C2-C8-H8	118.8

C2-C8-C9	122.4(4)
C9-C8-H8	118.8
C8-C9-C12	120.6(4)
C10-C9-C8	117.8(4)
C10-C9-C12	121.7(4)
C9-C10-H10	119.2
C11-C10-C9	121.7(4)
C11-C10-H10	119.2
C1-C11-H11	120.7
C10-C11-C1	118.7(4)
C10-C11-H11	120.7
C9-C12-H12A	109.5
C9-C12-H12B	109.5
C9-C12-H12C	109.5
H12A-C12-H12B	109.5
H12A-C12-H12C	109.5
H12B-C12-H12C	109.5

Symmetry transformations used to generate equivalent atoms:

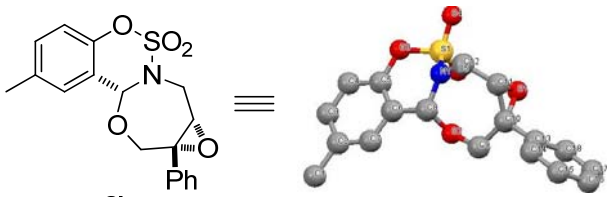
Table S11. Anisotropic displacement parameters ($Å^2$ x 10^3) for **7b**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	27(1)	26(1)	30(1)	2(1)	-2(1)	-2(1)
O1	34(2)	32(2)	37(2)	9(1)	-4(2)	2(1)
O2	32(2)	34(2)	41(2)	-3(1)	-5(2)	-8(1)
O3	23(1)	35(2)	30(2)	-2(1)	4(1)	-4(1)
O4	24(2)	37(2)	27(2)	2(1)	4(1)	-3(1)
N1	22(2)	28(2)	24(2)	-1(1)	-3(2)	2(2)
C1	22(2)	28(2)	27(2)	1(2)	-6(2)	-1(2)

C2	22(2)	27(2)	25(2)	6(2)	1(2)	2(2)
C3	23(2)	25(2)	26(2)	0(2)	0(2)	2(2)
C4	31(2)	35(2)	29(2)	2(2)	-4(2)	2(2)
C5	26(2)	30(2)	23(2)	-1(2)	1(2)	5(2)
C6	36(2)	35(2)	28(2)	-4(2)	0(2)	4(2)
C7	42(3)	48(3)	32(2)	-3(2)	-6(2)	1(2)
C8	21(2)	26(2)	26(2)	3(2)	0(2)	-2(2)
C9	32(2)	26(2)	29(2)	1(2)	-5(2)	1(2)
C10	36(2)	30(2)	24(2)	-3(2)	2(2)	7(2)
C11	26(2)	36(2)	24(2)	0(2)	5(2)	4(2)
C12	41(3)	31(2)	38(3)	-6(2)	-2(2)	-1(2)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **7b**.

	x	y	z	U(eq)
H3	6364	2045	3446	29
H4A	4067	4090	2031	38
H4B	3143	4655	2694	38
H5	528	3044	2703	31
H6	2907	1648	1698	40
H7A	-1729	2211	1829	49
H7B	-540	1400	1245	49
H8	6957	4635	3936	29
H10	2283	5331	5326	36
H11	14	3622	4947	34
H12A	7884	6139	4862	55
H12B	5862	6573	5325	55
H12C	5958	7106	4612	55



8ba

Table S13. Crystal data and structure refinement for **8ba**.

Identification code	**8ba**	
Empirical formula	$C_{18}H_{17}NO_5S$	
Formula weight	359.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.3553(13) Å	a= 90°.
	b = 14.813(3) Å	b= 95.70(3)°.
	c = 17.085(3) Å	g = 90°.
Volume	1600.5(6) $Å^3$	
Z	4	
Density (calculated)	1.491 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	752	
Crystal size	0.247 x 0.176 x 0.138 mm^3	
Theta range for data collection	2.750 to 27.469°.	
Index ranges	-8<=h<=8, -19<=k<=18, -21<=l<=22	
Reflections collected	12513	
Independent reflections	3659 [R(int) = 0.0595]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3659 / 0 / 227	
Goodness-of-fit on F^2	1.230	
Final R indices [I>2sigma(I)]	R1 = 0.0699, wR2 = 0.1207	
R indices (all data)	R1 = 0.0792, wR2 = 0.1248	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.253 and -0.327 $e.Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **8ba**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	1731(1)	8068(1)	5376(1)	31(1)
O1	3895(3)	5962(1)	5878(1)	32(1)
O2	5680(3)	7674(1)	6623(1)	27(1)
O3	1832(3)	9135(1)	5301(1)	34(1)
O4	435(3)	7770(2)	4701(1)	41(1)
O5	1112(3)	7874(2)	6135(1)	38(1)
N1	4174(3)	7817(2)	5287(1)	26(1)
C1	8312(5)	11104(2)	7107(2)	44(1)
C2	6606(5)	10564(2)	6642(2)	31(1)
C3	4707(5)	10964(2)	6346(2)	35(1)
C4	3130(5)	10483(2)	5917(2)	34(1)
C5	3466(4)	9579(2)	5778(2)	29(1)
C6	5312(4)	9145(2)	6062(2)	26(1)
C7	6861(4)	9654(2)	6492(2)	29(1)
C8	5711(4)	8157(2)	5908(2)	25(1)
C9	6832(4)	6848(2)	6663(2)	28(1)
C10	6140(4)	6095(2)	6094(2)	26(1)
C11	5229(4)	6193(2)	5271(2)	28(1)
C12	4750(4)	7048(2)	4823(2)	29(1)
C13	7325(4)	5242(2)	6321(2)	26(1)
C14	9280(5)	5073(2)	6049(2)	33(1)
C15	10401(5)	4305(2)	6302(2)	39(1)
C16	9617(5)	3714(2)	6822(2)	37(1)
C17	7678(5)	3877(2)	7097(2)	35(1)
C18	6538(5)	4640(2)	6849(2)	31(1)

Table S15. Bond lengths [Å] and angles [°] for **8ba**.

S1-O3	1.587(2)
S1-O4	1.421(2)
S1-O5	1.421(2)
S1-N1	1.618(2)

O1-C10	1.451(3)
O1-C11	1.444(3)
O2-C8	1.418(3)
O2-C9	1.423(3)
O3-C5	1.417(3)
N1-C8	1.458(3)
N1-C12	1.455(3)
C1-H1A	0.9600
C1-H1B	0.9600
C1-H1C	0.9600
C1-C2	1.508(4)
C2-C3	1.393(4)
C2-C7	1.385(4)
C3-H3	0.9300
C3-C4	1.380(4)
C4-H4	0.9300
C4-C5	1.380(4)
C5-C6	1.383(4)
C6-C7	1.390(4)
C6-C8	1.514(4)
C7-H7	0.9300
C8-H8	0.9800
C9-H9A	0.9700
C9-H9B	0.9700
C9-C10	1.515(4)
C10-C11	1.475(4)
C10-C13	1.503(4)
C11-H11	0.9800
C11-C12	1.496(4)
C12-H12A	0.9700
C12-H12B	0.9700
C13-C14	1.391(4)
C13-C18	1.395(4)
C14-H14	0.9300
C14-C15	1.388(4)
C15-H15	0.9300
C15-C16	1.377(4)
C16-H16	0.9300

C16-C17	1.383(4)
C17-H17	0.9300
C17-C18	1.386(4)
C18-H18	0.9300
O3-S1-N1	100.03(11)
O4-S1-O3	105.59(12)
O4-S1-O5	119.21(13)
O4-S1-N1	109.64(13)
O5-S1-O3	107.01(12)
O5-S1-N1	113.22(12)
C11-O1-C10	61.24(16)
C8-O2-C9	115.0(2)
C5-O3-S1	116.71(17)
C8-N1-S1	115.61(18)
C12-N1-S1	121.79(18)
C12-N1-C8	118.6(2)
H1A-C1-H1B	109.5
H1A-C1-H1C	109.5
H1B-C1-H1C	109.5
C2-C1-H1A	109.5
C2-C1-H1B	109.5
C2-C1-H1C	109.5
C3-C2-C1	121.1(3)
C7-C2-C1	121.5(3)
C7-C2-C3	117.4(3)
C2-C3-H3	119.0
C4-C3-C2	122.0(3)
C4-C3-H3	119.0
C3-C4-H4	120.8
C5-C4-C3	118.4(3)
C5-C4-H4	120.8
C4-C5-O3	115.7(2)
C4-C5-C6	122.1(3)
C6-C5-O3	122.2(2)
C5-C6-C7	117.7(3)
C5-C6-C8	122.7(2)
C7-C6-C8	119.6(2)
C2-C7-C6	122.4(3)

C2-C7-H7	118.8
C6-C7-H7	118.8
O2-C8-N1	112.8(2)
O2-C8-C6	108.7(2)
O2-C8-H8	108.3
N1-C8-C6	110.4(2)
N1-C8-H8	108.3
C6-C8-H8	108.3
O2-C9-H9A	107.5
O2-C9-H9B	107.5
O2-C9-C10	119.1(2)
H9A-C9-H9B	107.0
C10-C9-H9A	107.5
C10-C9-H9B	107.5
O1-C10-C9	118.6(2)
O1-C10-C11	59.13(17)
O1-C10-C13	114.0(2)
C11-C10-C9	126.9(2)
C11-C10-C13	117.9(2)
C13-C10-C9	110.4(2)
O1-C11-C10	59.63(16)
O1-C11-H11	113.5
O1-C11-C12	117.6(2)
C10-C11-H11	113.5
C10-C11-C12	127.7(2)
C12-C11-H11	113.5
N1-C12-C11	115.7(2)
N1-C12-H12A	108.4
N1-C12-H12B	108.4
C11-C12-H12A	108.4
C11-C12-H12B	108.4
H12A-C12-H12B	107.4
C14-C13-C10	120.4(2)
C14-C13-C18	119.4(3)
C18-C13-C10	120.1(2)
C13-C14-H14	120.3
C15-C14-C13	119.4(3)

C15-C14-H14	120.3
C14-C15-H15	119.5
C16-C15-C14	121.0(3)
C16-C15-H15	119.5
C15-C16-H16	120.0
C15-C16-C17	120.0(3)
C17-C16-H16	120.0
C16-C17-H17	120.2
C16-C17-C18	119.7(3)
C18-C17-H17	120.2
C13-C18-H18	119.7
C17-C18-C13	120.6(3)
C17-C18-H18	119.7

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3) for **8ba**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	22(1)	37(1)	32(1)	-1(1)	-3(1)	1(1)
O1	24(1)	35(1)	35(1)	4(1)	-1(1)	-5(1)
O2	29(1)	26(1)	25(1)	2(1)	0(1)	3(1)
O3	28(1)	33(1)	38(1)	-2(1)	-6(1)	7(1)
O4	29(1)	48(1)	43(1)	-7(1)	-14(1)	2(1)
O5	27(1)	52(1)	37(1)	2(1)	6(1)	-3(1)
N1	22(1)	29(1)	26(1)	-2(1)	-2(1)	3(1)
C1	50(2)	34(2)	46(2)	-2(1)	-3(2)	-8(2)
C2	38(2)	28(2)	28(1)	2(1)	4(1)	-2(1)
C3	52(2)	25(1)	28(2)	4(1)	6(1)	4(1)
C4	39(2)	31(2)	31(2)	6(1)	1(1)	10(1)
C5	28(1)	30(2)	28(1)	4(1)	0(1)	1(1)
C6	28(1)	26(1)	25(1)	4(1)	3(1)	1(1)
C7	29(1)	31(2)	28(1)	3(1)	1(1)	0(1)
C8	20(1)	27(1)	26(1)	2(1)	-2(1)	0(1)
C9	28(1)	28(1)	28(1)	4(1)	-2(1)	2(1)

C10	23(1)	27(1)	27(1)	3(1)	2(1)	-3(1)
C11	31(1)	26(1)	26(1)	-1(1)	-2(1)	-2(1)
C12	32(1)	30(2)	24(1)	-2(1)	-1(1)	2(1)
C13	30(1)	25(1)	23(1)	0(1)	1(1)	-2(1)
C14	30(2)	34(2)	36(2)	2(1)	4(1)	-2(1)
C15	33(2)	35(2)	49(2)	-1(1)	3(1)	4(1)
C16	44(2)	27(2)	37(2)	-2(1)	-9(1)	4(1)
C17	49(2)	29(2)	27(2)	3(1)	1(1)	-4(1)
C18	36(2)	29(2)	29(2)	2(1)	3(1)	-2(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **8ba**.

	x	y	z	U(eq)
H1A	8808	11569	6779	65
H1B	9465	10713	7285	65
H1C	7748	11374	7552	65
H3	4495	11574	6442	41
H4	1872	10761	5726	40
H7	8113	9373	6687	35
H8	7125	8098	5731	30
H9A	6815	6612	7192	34
H9B	8292	6991	6593	34
H11	5532	5681	4936	34
H12A	5981	7212	4561	35
H12B	3601	6932	4418	35
H14	9830	5471	5701	40
H15	11701	4189	6116	47
H16	10392	3205	6989	44
H17	7141	3477	7447	42
H18	5237	4752	7035	38

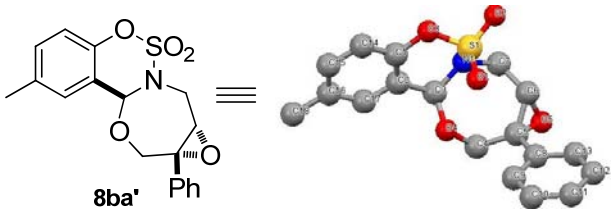


Table S18. Crystal data and structure refinement for **8ba′**.

Identification code	**8ba′**	
Empirical formula	$C_{18}H_{17}NO_5S$	
Formula weight	359.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.1967(2) Å	a= 110.691(2)°.
	b = 11.1950(3) Å	b= 92.738(2)°.
	c = 12.7835(3) Å	g = 93.838(2)°.
Volume	825.33(4) $Å^3$	
Z	2	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	0.226 mm^{-1}	
F(000)	376	
Crystal size	0.426 x 0.155x 0.107 mm^3	
Theta range for data collection	3.020 to 27.492°.	
Index ranges	-7<=h<=8, -14<=k<=14, -16<=l<=16	
Reflections collected	11406	
Independent reflections	3766 [R(int) = 0.0374]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3766 / 0 / 227	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1101	
R indices (all data)	R1 = 0.0587, wR2 = 0.1207	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.321 and -0.453 $e.Å^{-3}$	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **8ba′**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	1667(1)	3169(1)	7766(1)	27(1)
O1	404(2)	3560(2)	6998(1)	35(1)
O2	871(3)	2073(1)	7992(1)	38(1)
O3	1950(2)	4316(1)	8935(1)	32(1)
O4	4686(2)	4379(1)	6320(1)	23(1)
O5	4746(2)	1037(1)	4574(1)	30(1)
N1	4191(3)	3047(2)	7469(1)	24(1)
C1	3316(3)	5425(2)	9024(2)	26(1)
C2	4939(3)	5378(2)	8308(2)	24(1)
C3	5303(3)	4181(2)	7332(2)	23(1)
C4	5356(3)	3424(2)	5329(2)	25(1)
C5	3729(3)	2239(2)	4877(2)	23(1)
C6	3512(3)	1401(2)	5543(2)	26(1)
C7	4708(3)	1774(2)	6692(2)	27(1)
C8	1844(3)	2251(2)	4106(2)	24(1)
C9	1104(3)	3405(2)	4111(2)	27(1)
C10	-704(3)	3409(2)	3426(2)	31(1)
C11	-1813(4)	2260(2)	2738(2)	36(1)
C12	-1097(4)	1111(2)	2730(2)	38(1)
C13	721(4)	1097(2)	3401(2)	31(1)
C14	2993(4)	6531(2)	9909(2)	32(1)
C15	4377(4)	7623(2)	10093(2)	32(1)
C16	6066(3)	7625(2)	9408(2)	31(1)
C17	6302(3)	6493(2)	8518(2)	28(1)
C18	7594(4)	8805(2)	9618(2)	45(1)

Table S20. Bond lengths [Å] and angles [°] for **8ba′**.

S1-O1	1.4295(15)
S1-O2	1.4204(15)
S1-O3	1.5815(14)
S1-N1	1.6302(16)

O3-C1	1.421(2)
O4-C3	1.427(2)
O4-C4	1.440(2)
O5-C5	1.458(2)
O5-C6	1.436(2)
N1-C3	1.472(2)
N1-C7	1.487(2)
C1-C2	1.383(3)
C1-C14	1.385(3)
C2-C3	1.513(3)
C2-C17	1.394(3)
C3-H3	0.9800
C4-H4A	0.9700
C4-H4B	0.9700
C4-C5	1.528(3)
C5-C6	1.477(3)
C5-C8	1.496(3)
C6-H6	0.9800
C6-C7	1.517(3)
C7-H7A	0.9700
C7-H7B	0.9700
C8-C9	1.398(3)
C8-C13	1.400(3)
C9-H9	0.9300
C9-C10	1.390(3)
C10-H10	0.9300
C10-C11	1.387(3)
C11-H11	0.9300
C11-C12	1.386(3)
C12-H12	0.9300
C12-C13	1.387(3)
C13-H13	0.9300
C14-H14	0.9300
C14-C15	1.386(3)
C15-H15	0.9300
C15-C16	1.397(3)
C16-C17	1.394(3)
C16-C18	1.507(3)

C17-H17	0.9300
C18-H18A	0.9600
C18-H18B	0.9600
C18-H18C	0.9600
O1-S1-O3	108.08(9)
O1-S1-N1	112.55(9)
O2-S1-O1	118.45(10)
O2-S1-O3	106.14(8)
O2-S1-N1	109.45(9)
O3-S1-N1	100.40(8)
C1-O3-S1	118.04(12)
C3-O4-C4	113.60(14)
C6-O5-C5	61.38(12)
C3-N1-S1	115.47(12)
C3-N1-C7	116.70(15)
C7-N1-S1	116.08(13)
C2-C1-O3	121.83(17)
C2-C1-C14	122.40(18)
C14-C1-O3	115.68(17)
C1-C2-C3	123.10(17)
C1-C2-C17	117.50(18)
C17-C2-C3	119.40(17)
O4-C3-N1	115.33(14)
O4-C3-C2	108.05(15)
O4-C3-H3	107.7
N1-C3-C2	110.10(15)
N1-C3-H3	107.7
C2-C3-H3	107.7
O4-C4-H4A	109.1
O4-C4-H4B	109.1
O4-C4-C5	112.30(15)
H4A-C4-H4B	107.9
C5-C4-H4A	109.1
C5-C4-H4B	109.1
O5-C5-C4	113.30(15)
O5-C5-C6	58.58(11)
O5-C5-C8	115.44(15)
C6-C5-C4	117.95(16)

C6-C5-C8	118.55(17)
C8-C5-C4	118.45(16)
O5-C6-C5	60.04(12)
O5-C6-H6	115.4
O5-C6-C7	118.50(16)
C5-C6-H6	115.4
C5-C6-C7	120.87(17)
C7-C6-H6	115.4
N1-C7-C6	112.27(15)
N1-C7-H7A	109.1
N1-C7-H7B	109.1
C6-C7-H7A	109.1
C6-C7-H7B	109.1
H7A-C7-H7B	107.9
C9-C8-C5	120.98(17)
C9-C8-C13	118.69(18)
C13-C8-C5	120.26(17)
C8-C9-H9	119.7
C10-C9-C8	120.68(18)
C10-C9-H9	119.7
C9-C10-H10	120.0
C11-C10-C9	120.1(2)
C11-C10-H10	120.0
C10-C11-H11	120.2
C12-C11-C10	119.69(19)
C12-C11-H11	120.2
C11-C12-H12	119.7
C11-C12-C13	120.6(2)
C13-C12-H12	119.7
C8-C13-H13	119.9
C12-C13-C8	120.2(2)
C12-C13-H13	119.9
C1-C14-H14	120.7
C1-C14-C15	118.57(19)
C15-C14-H14	120.7
C14-C15-H15	119.3
C14-C15-C16	121.47(18)
C16-C15-H15	119.3

C15-C16-C18	121.54(19)
C17-C16-C15	117.75(19)
C17-C16-C18	120.71(19)
C2-C17-C16	122.29(19)
C2-C17-H17	118.9
C16-C17-H17	118.9
C16-C18-H18A	109.5
C16-C18-H18B	109.5
C16-C18-H18C	109.5
H18A-C18-H18B	109.5
H18A-C18-H18C	109.5
H18B-C18-H18C	109.5

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2$ x 10^3) for **8ba′**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S1	23(1)	26(1)	30(1)	9(1)	6(1)	2(1)
O1	21(1)	43(1)	43(1)	18(1)	3(1)	7(1)
O2	42(1)	29(1)	42(1)	13(1)	13(1)	-2(1)
O3	34(1)	28(1)	33(1)	7(1)	15(1)	-1(1)
O4	24(1)	22(1)	22(1)	7(1)	4(1)	2(1)
O5	37(1)	24(1)	28(1)	7(1)	7(1)	11(1)
N1	24(1)	24(1)	25(1)	9(1)	4(1)	6(1)
C1	25(1)	25(1)	27(1)	9(1)	4(1)	0(1)
C2	21(1)	27(1)	23(1)	8(1)	0(1)	4(1)
C3	17(1)	26(1)	24(1)	8(1)	2(1)	2(1)
C4	25(1)	26(1)	22(1)	5(1)	7(1)	3(1)
C5	27(1)	20(1)	23(1)	6(1)	7(1)	7(1)
C6	28(1)	21(1)	27(1)	7(1)	5(1)	7(1)
C7	29(1)	26(1)	28(1)	10(1)	5(1)	11(1)
C8	28(1)	24(1)	22(1)	9(1)	4(1)	3(1)
C9	31(1)	24(1)	26(1)	9(1)	6(1)	3(1)
C10	35(1)	34(1)	31(1)	17(1)	7(1)	12(1)

C11	31(1)	50(1)	30(1)	18(1)	-3(1)	4(1)
C12	42(1)	36(1)	29(1)	7(1)	-6(1)	-6(1)
C13	38(1)	24(1)	29(1)	9(1)	-1(1)	1(1)
C14	36(1)	32(1)	26(1)	8(1)	10(1)	5(1)
C15	43(1)	28(1)	23(1)	4(1)	4(1)	5(1)
C16	36(1)	30(1)	24(1)	9(1)	-2(1)	-2(1)
C17	25(1)	32(1)	24(1)	8(1)	1(1)	-1(1)
C18	56(2)	34(1)	37(1)	4(1)	4(1)	-11(1)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **8ba′**.

	x	y	z	U(eq)
H3	6863	4082	7345	28
H4A	6755	3170	5503	30
H4B	5527	3794	4754	30
H6	2092	919	5450	31
H7A	4323	1130	7013	32
H7B	6258	1793	6612	32
H9	1828	4179	4578	32
H10	-1171	4182	3428	38
H11	-3032	2262	2285	44
H12	-1841	340	2269	45
H13	1195	320	3383	37
H14	1872	6542	10370	39
H15	4177	8370	10686	39
H17	7408	6481	8048	34
H18A	6949	9547	10084	68
H18B	7874	8895	8916	68
H18C	8932	8725	9988	68