Electronic Supplementary Information

Rh(III)-Catalyzed Synthesis of Sultones through C-H Activation Directed by Sulfonic Acid Group

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Contents

I. General Infromation

General. All reactions were carried out using Schlenk techniques or in an argon-filled glovebox. NMR Spectra were recorded on a Bruker 400 MHz or 500 MHz NMR spectrometer in the solvents indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Agilent 6540 Q-Tof. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

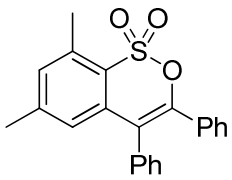
Materials. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Diphenylacetylene, 3-hexyne, 4-octyne, 1-phenyl-1-propyne, 1-phenyl-1-pentyne, and 1-phenyl-1-hexyne were obtained from commercial sources. Other diarylacetylenes[1] and 1-cyclopropyl-2-phenylethyne[2] were prepared according to literature reports and the NMR data agree with those in the literature reports.

II. Experimental Procedures and Characterizations

General procedures for the synthesis of sultones 3

Arylsulfonic acid (0.22 mmol), alkynes (0.20 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), AgOAc (2.0 equiv) and dioxane (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 16 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compounds **3**.

Characterizations.

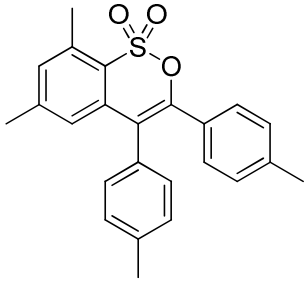


6,8-Dimethyl-3,4-diphenylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3a)

3a was obtained according to the general procedure in 86% yield, white solid, mp 182-184 ^{o}C. R_f (PE/EA = 20/1): 0.34.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 3H), 7.27 – 7.13 (m, 7H), 7.09 (s, 1H),

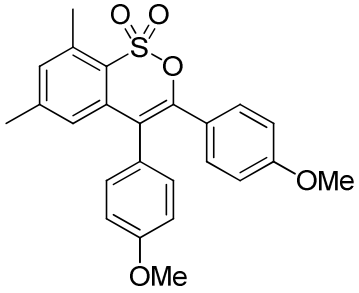
6.68 (s, 1H), 2.73 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 143.3, 135.7, 135.5, 134.9, 132.8, 132.5, 131.3, 129.4, 129.2, 128.8, 128.6, 128.0, 127.9, 126.5, 121.3, 21.7, 20.7. HRMS: $[M + H]^+$ calculated for $C_{22}H_{19}O_3S$: 363.1055, found 363.1051. IR (cm^{-1}): 3054, 2922, 1614, 1597, 1490, 1443, 1362, 1193, 1173, 1090, 1073, 1010, 901, 832, 779, 770, 746.



6,8-Dimethyl-3,4-di-*p*-tolylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3b)

3b was obtained according to the general procedure in 93% yield, white solid, mp 152-153 °C. R_f (PE/EA = 20/1): 0.32.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.17 – 7.10 (m, 4H), 7.06 (s, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.68 (s, 1H), 2.72 (s, 3H), 2.39 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 143.1, 139.5, 138.3, 135.9, 135.6, 132.5, 132.0, 131.2, 130.0, 129.8, 128.8, 128.7, 127.9, 126.5, 120.6, 21.7, 21.5, 21.4, 20.7. HRMS: $[M + H]^+$ calculated for $C_{24}H_{23}O_3S$: 391.1368, found 391.1365.

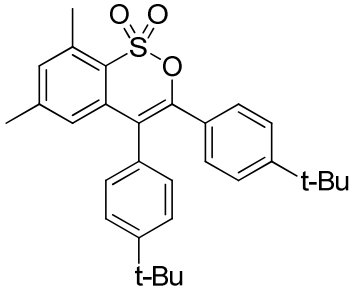


3,4-Bis(4-methoxyphenyl)-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3c)

3c was obtained according to the general procedure in 83% yield, white solid, mp 169-170 °C. R_f (PE/EA = 20/1): 0.13.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 7.17 – 7.12 (m, 2H), 7.05 (s, 1H), 6.96 – 6.91 (m, 2H), 6.72 – 6.66 (m, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 2.71 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 159.7, 148.3, 143.1, 136.1, 135.6, 132.5, 132.3, 130.4, 127.7, 127.2, 126.3, 125.0, 119.5, 114.8, 113.6, 55.4, 55.4, 21.7,

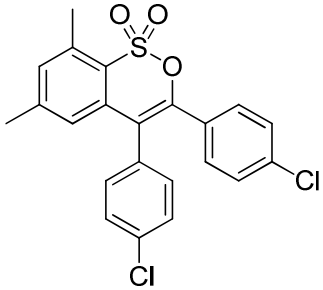
20.7. HRMS: $[M + H]^+$ calculated for $C_{24}H_{23}O_5S$: 423.1266, found 423.1259. IR (cm^{-1}): 2997, 2976, 2940, 2841, 2058, 1903, 1606, 1574, 1508, 1466, 1442, 1357, 1302, 1289, 1261, 1250, 1192, 1172, 1078, 1034, 1015, 974, 841, 804, 708, 661.



3,4-Bis(4-(*tert*-butyl)phenyl)-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3d)

3d was obtained according to the general procedure in 92% yield, white solid, mp 168-170 ^oC. R_f (PE/EA = 20/1): 0.46.

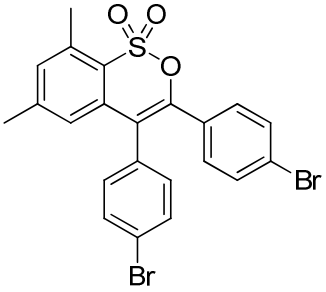
^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.20 – 7.13 (m, 6H), 7.06 (s, 1H), 6.70 (s, 1H), 2.73 (s, 3H), 2.24 (s, 3H), 1.37 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 151.7, 148.2, 143.1, 136.0, 135.6, 132.5, 132.0, 130.9, 129.7, 128.5, 127.9, 126.6, 126.2, 124.9, 120.6, 34.9, 34.8, 31.5, 31.2, 21.8, 20.7. HRMS: $[M + H]^+$ calculated for $C_{30}H_{35}O_3S$: 475.2307, found 475.2305.



3,4-Bis(4-chlorophenyl)-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3e)

3e was obtained according to the general procedure in 72% yield, white solid, mp 163-164 ^oC. R_f (PE/EA = 20/1): 0.30.

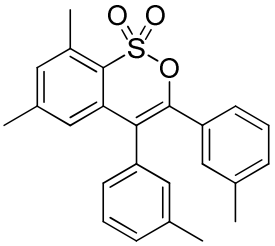
^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.22 – 7.14 (m, 6H), 7.12 (s, 1H), 6.62 (s, 1H), 2.73 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.6, 136.0, 135.8, 135.0, 134.9, 133.17, 133.15, 132.7, 130.8, 130.1, 129.8, 128.6, 127.9, 126.3, 120.7, 21.8, 20.7. HRMS: $[M + H]^+$ calculated for $C_{22}H_{17}Cl_2O_3S$: 431.0275, found 431.0273.



3,4-Bis(4-bromophenyl)-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3f)

3f was obtained according to the general procedure in 61% yield, white solid, mp 127-128 °C. R_f (PE/EA = 20/1): 0.28.

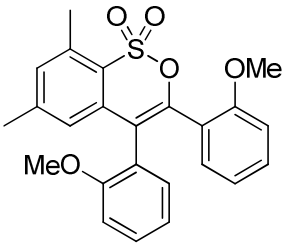
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.08 (m, 5H), 6.62 (s, 1H), 2.73 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 143.6, 136.0, 134.8, 133.6, 133.2, 132.9, 132.7, 131.5, 131.1, 130.3, 127.8, 126.3, 124.2, 123.2, 120.7, 21.8, 20.7. HRMS: $[M + H]^+$ calculated for $C_{22}H_{17}Br_2O_3S$: 518.9265, found 518.9273.



6,8-Dimethyl-3,4-di-*m*-tolylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3g)

3g was obtained according to the general procedure in 85% yield, white solid, mp 119-120 °C. R_f (PE/EA = 20/1): 0.38.

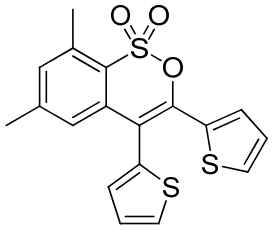
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.14 (s, 1H), 7.09 – 7.01 (m, 5H), 6.97 (dd, *J* = 6.1, 2.7 Hz, 1H), 6.69 (s, 1H), 2.73 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 143.2, 138.9, 137.7, 135.7, 135.6, 134.8, 132.6, 132.3, 131.7, 130.1, 129.3, 129.2, 129.0, 128.4, 127.79, 127.76, 126.6, 126.0, 121.2, 21.8, 21.5, 21.5, 20.7. HRMS: $[M + H]^+$ calculated for $C_{24}H_{23}O_3S$: 391.1368, found 391.1373.



3,4-Bis(2-methoxyphenyl)-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3h)

3h was obtained according to the general procedure in 59% yield, white solid, mp 163-164 °C. R_f (PE/EA = 20/1): 0.08.

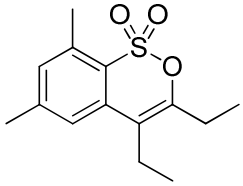
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 3H), 7.07 (dd, *J* = 7.8, 1.7 Hz, 2H), 6.84 – 6.78 (dd, *J* = 10.7, 4.3 Hz, 2H), 6.77 – 6.69 (m, 2H), 6.59 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 2.72 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.6, 147.8, 143.0, 135.5, 134.8, 132.4, 132.2, 131.2, 130.9, 129.9, 127.8, 125.7, 123.8, 122.5, 120.6, 120.1, 119.3, 111.1, 111.0, 55.7, 55.5, 21.7, 20.7. HRMS: $[M + H]^+$ calculated for $C_{24}H_{23}O_5S$: 423.1266, found 423.1267.



6,8-Dimethyl-3,4-di(thiophen-2-yl)benzo[*c*][1,2]oxathiine 1,1-dioxide (3i)

3i was obtained according to the general procedure in 79% yield, white solid, mp 181-182 °C. R_f (PE/EA = 20/1): 0.30.

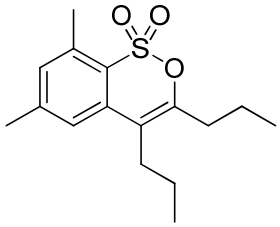
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.39 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.32 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.25 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.13 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.07 (s, 1H), 6.98 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.75 (s, 1H), 2.72 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 143.6, 135.7, 135.7, 134.5, 134.1, 132.6, 131.4, 131.1, 130.2, 129.5, 128.4, 127.4, 127.1, 126.2, 110.9, 21.8, 20.6. HRMS: $[M + H]^+$ calculated for $C_{18}H_{15}O_3S_3$: 375.0183, found 375.0175. IR (cm^{-1}): 3111, 3100, 2919, 1611, 1561, 1460, 1422, 1354, 1224, 1197, 1180, 1083, 1075, 1040, 1001, 947, 856, 834, 815, 723, 709.



3,4-Diethyl-6,8-dimethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3j)

3j was obtained according to the general procedure in 70% yield, white solid, mp 61-62 °C. R_f (PE/EA = 20/1): 0.35.

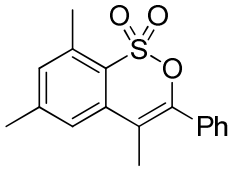
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.04 (s, 1H), 2.64 (s, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 143.2, 135.8, 134.0, 131.8, 128.3, 123.1, 117.2, 24.4, 21.8, 20.9, 20.7, 14.2, 10.9. HRMS: $[M + H]^+$ calculated for $C_{14}H_{19}O_3S$: 267.1055, found 267.1055. IR (cm^{-1}): 2972, 2939, 2877, 1652, 1597, 1570, 1463, 1379, 1354, 1196, 1163, 1128, 1048, 1015, 979, 955, 924, 859, 840, 759, 661, 572, 559.



6,8-Dimethyl-3,4-dipropylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3k)

3k was obtained according to the general procedure in 66% yield, white solid, mp 39-40 ^{o}C. R_f (PE/EA = 20/1): 0.41.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 7.04 (s, 1H), 2.65 (s, 3H), 2.51 (t, *J* = 7.8 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.39 (s, 3H), 1.78 – 1.66 (m, 2H), 1.60 – 1.49 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 143.1, 135.9, 134.2, 131.9, 128.4, 123.3, 116.5, 33.0, 29.5, 22.6, 21.9, 20.8, 19.8, 14.0, 13.8. HRMS: $[M + H]^+$ calculated for $C_{16}H_{23}O_3S$: 295.1368, found 295.1367.

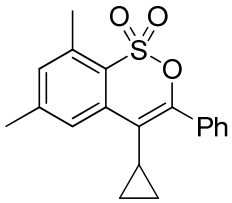


4,6,8-Trimethyl-3-phenylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3l)

3l was obtained according to the general procedure in 61% yield, white solid. R_f (PE/EA = 20/1): 0.31.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.46 – 7.38 (m, 3H), 7.19 (s, 1H), 7.09 (s, 1H), 2.69 (s, 3H), 2.40 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.5, 135.6, 135.6, 132.4, 132.3, 129.9, 129.6, 128.4, 128.1, 124.3, 113.4,

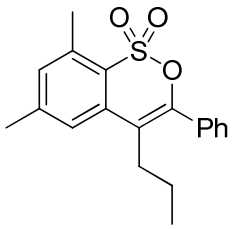
21.8, 20.6, 15.6. HRMS: $[M + H]^+$ calculated for $C_{17}H_{17}O_3S$: 301.0898, found 301.0890.



4-Cyclopropyl-6,8-dimethyl-3-phenylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3m)

3m was obtained according to the general procedure in 65% yield, white solid, mp 108-109 ^oC. R_f (PE/EA = 20/1): 0.30.

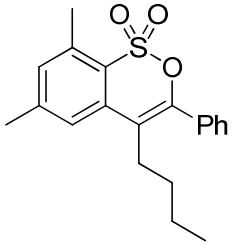
^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.61 (s, 1H), 7.47 – 7.41 (m, 3H), 7.10 (s, 1H), 2.69 (s, 3H), 2.45 (s, 3H), 1.94 (tt, *J* = 8.2, 5.5 Hz, 1H), 0.91 – 0.83 (m, 2H), 0.19 – 0.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.2, 136.8, 135.4, 132.4, 132.2, 130.0, 129.9, 128.0, 125.3, 118.6, 22.0, 20.7, 10.6, 10.4. HRMS: $[M + H]^+$ calculated for $C_{19}H_{19}O_3S$: 327.1055, found 327.1057. IR (cm^{-1}): 3087, 3062, 3013, 2978, 2924, 2861, 1618,1599,1570, 1459, 1447, 1361, 1207, 1191, 1179, 1092, 1076, 1035, 1021, 836, 762, 693, 567.



6,8-Dimethyl-3-phenyl-4-propylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3n)

3n was obtained according to the general procedure in 58% yield, white solid, mp 102-103 ^oC. R_f (PE/EA = 20/1): 0.33.

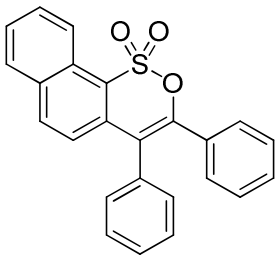
^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 4.8, 2.9 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.23 (s, 1H), 7.12 (s, 1H), 2.71 (s, 3H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.55 – 1.44 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 143.2, 136.1, 134.2, 132.8, 132.5, 129.9, 129.6, 129.1, 128.6, 124.3, 118.4, 29.7, 22.3, 21.9, 20.8, 13.5. HRMS: $[M + H]^+$ calculated for $C_{19}H_{21}O_3S$: 329.1211, found 329.1202.



4-Butyl-6,8-dimethyl-3-phenylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3o)

3o was obtained according to the general procedure in 50% yield, white solid, mp 90-91 ^{o}C. R_f (PE/EA = 20/1): 0.38.

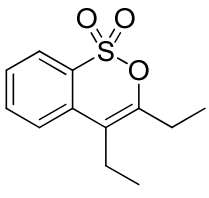
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.47 – 7.41 (m, 3H), 7.24 (s, 1H), 7.11 (s, 1H), 2.72 – 2.65 (m, 5H), 2.42 (s, 3H), 1.48 – 1.38 (m, 2H), 1.26 – 1.15 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.2, 135.9, 134.2, 132.7, 132.5, 129.9, 129.5, 129.0, 128.5, 124.3, 118.6, 31.1, 27.3, 22.0, 21.9, 20.8, 13.8. HRMS: $[M + H]^+$ calculated for $C_{20}H_{23}O_3S$: 343.1368, found 343.1376.



3,4-Diphenylnaphtho[1,2-*c*][1,2]oxathiine 1,1-dioxide (3p)

3p was obtained according to the general procedure in 62% yield, white solid, mp 170-171 ^{o}C. R_f (PE/EA = 20/1): 0.27.

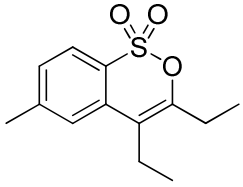
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 (dd, *J* = 11.5, 4.1 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 6.5, 3.6 Hz, 3H), 7.35 – 7.29 (m, 4H), 7.23 (dt, *J* = 14.4, 6.0 Hz, 3H), 7.13 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 134.7, 134.5, 133.6, 133.2, 132.3, 131.5, 129.7, 129.4, 129.4, 128.9, 128.8, 128.7, 128.2, 127.9, 127.2, 126.5, 124.7, 124.3, 121.4. HRMS: $[M + H]^+$ calculated for $C_{24}H_{17}O_3S$: 385.0898, found 385.0893.



3,4-Diethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3q)

3q was obtained according to the general procedure in 56% yield, white solid, mp 84-85 °C. R_f (PE/EA = 20/1): 0.25.

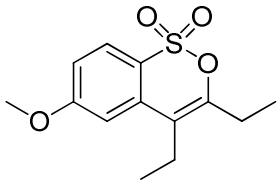
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.54 – 7.43 (m, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 133.4, 133.4, 131.6, 128.1, 124.6, 123.8, 117.2, 24.6, 20.6, 14.2, 11.0. HRMS: $[M + H]^+$ calculated for $C_{12}H_{15}O_3S$: 239.0742, found 239.0736.



3,4-Diethyl-6-methylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3r)

3r was obtained according to the general procedure in 63% yield, white solid, mp 67-68 °C. R_f (PE/EA = 20/1): 0.25.

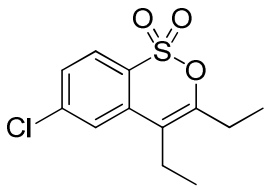
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.26 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 144.1, 133.4, 129.0, 128.8, 125.0, 123.8, 117.1, 24.6, 22.2, 20.6, 14.3, 11.0. HRMS: $[M + H]^+$ calculated for $C_{13}H_{17}O_3S$: 253.0898, found 253.0892.



3,4-Diethyl-6-methoxybenzo[*c*][1,2]oxathiine 1,1-dioxide (3s)

3s was obtained according to the general procedure in 60% yield, white solid, mp 89-90 °C. R_f (PE/EA = 20/1): 0.16.

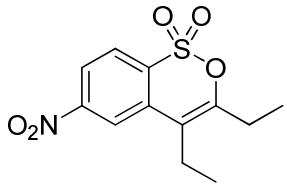
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 6.98 – 6.93 (m, 2H), 3.89 (s, 3H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 153.5, 135.4, 125.9, 124.1, 117.0, 112.8, 110.6, 55.9, 24.7, 20.7, 14.2, 11.0. HRMS: $[M + H]^+$ calculated for $C_{13}H_{17}O_4S$: 269.0848, found 269.0847.



6-Chloro-3,4-diethylbenzo[*c*][1,2]oxathiine 1,1-dioxide (3t)

3t was obtained according to the general procedure in 52% yield, white solid, mp 49-50 ^{o}C. R_f (PE/EA = 20/1): 0.35.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.48 – 7.42 (m, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.1, 135.3, 129.9, 128.2, 125.4, 124.8, 116.7, 24.7, 20.6, 14.1, 10.9. HRMS: $[M + H]^+$ calculated for $C_{12}H_{14}ClO_3S$: 273.0352, found 273.0350.

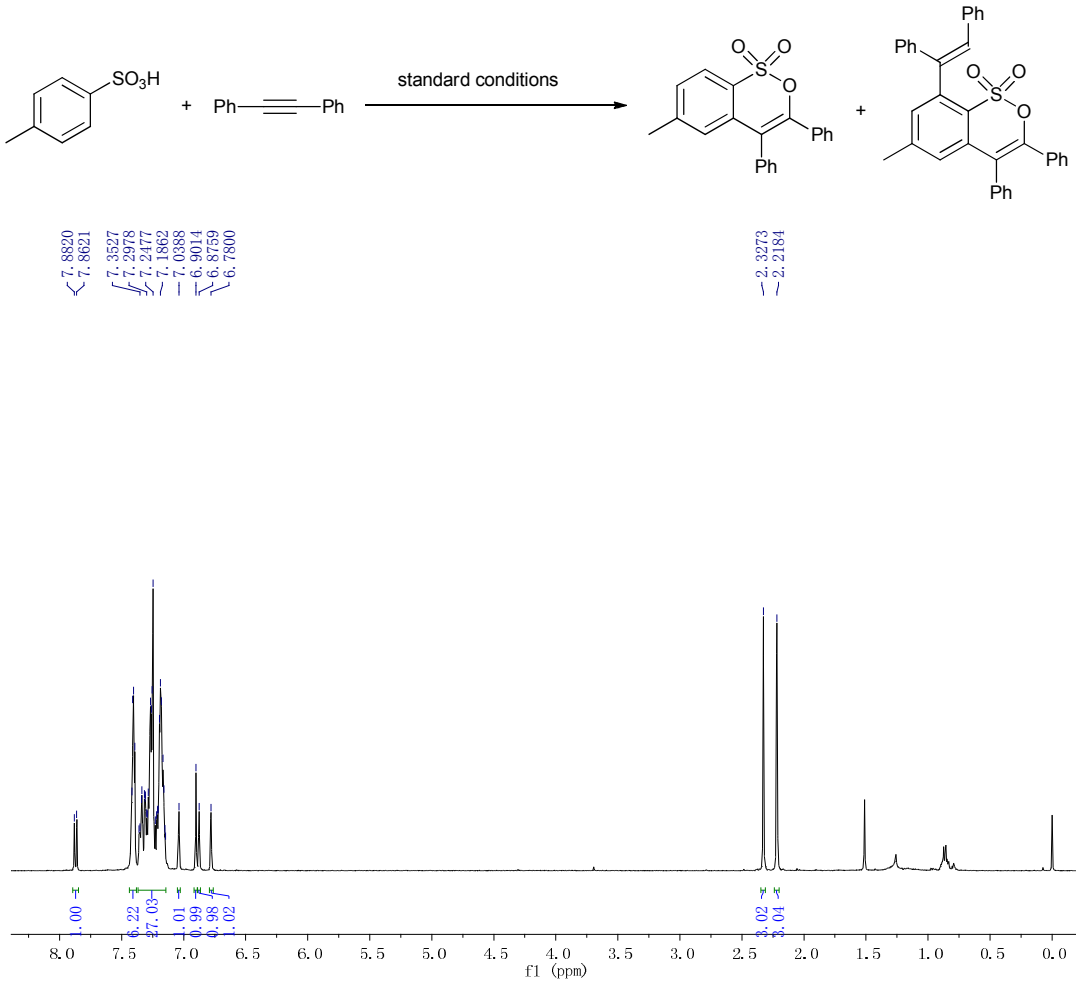


3,4-Diethyl-6-nitrobenzo[*c*][1,2]oxathiine 1,1-dioxide (3u)

3u was obtained according to the general procedure in 49% yield, white solid, mp 115-116 ^{o}C. R_f (PE/EA = 20/1): 0.25.

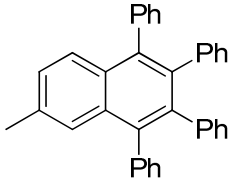
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.28 (m, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 151.0, 136.0, 135.5, 125.7, 122.8, 119.9, 117.0, 24.8, 20.7, 14.1, 10.8. HRMS: $[M + H]^+$ calculated for $C_{12}H_{14}NO_5S$: 284.0593, found 284.0582. IR (cm^{-1}): 3106, 3079, 2979, 2942, 2888, 1642, 1532, 1467, 1376, 1350, 1304, 1203, 1162, 1134, 1032, 841, 766, 746.

However, when the reactions of *para*-substituted arylsulfonic acids with diphenylacetylene were carried out under optimal reaction conditions, the sultone products were formed together with olefination of desired sultones (1:1).



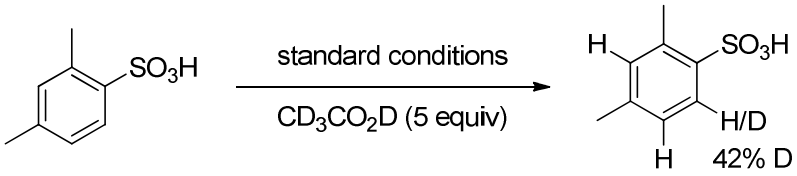
III. Synthesis of compound 4

p-Toluenesulfonic acid (0.20 mmol), diphenylacetylene (0.20 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), AgOAc (1.0 equiv), Ag_2CO_3 (1.0 equiv) and *t*-BuOH (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 80 °C for 22 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford compounds **4** in 85% yield.

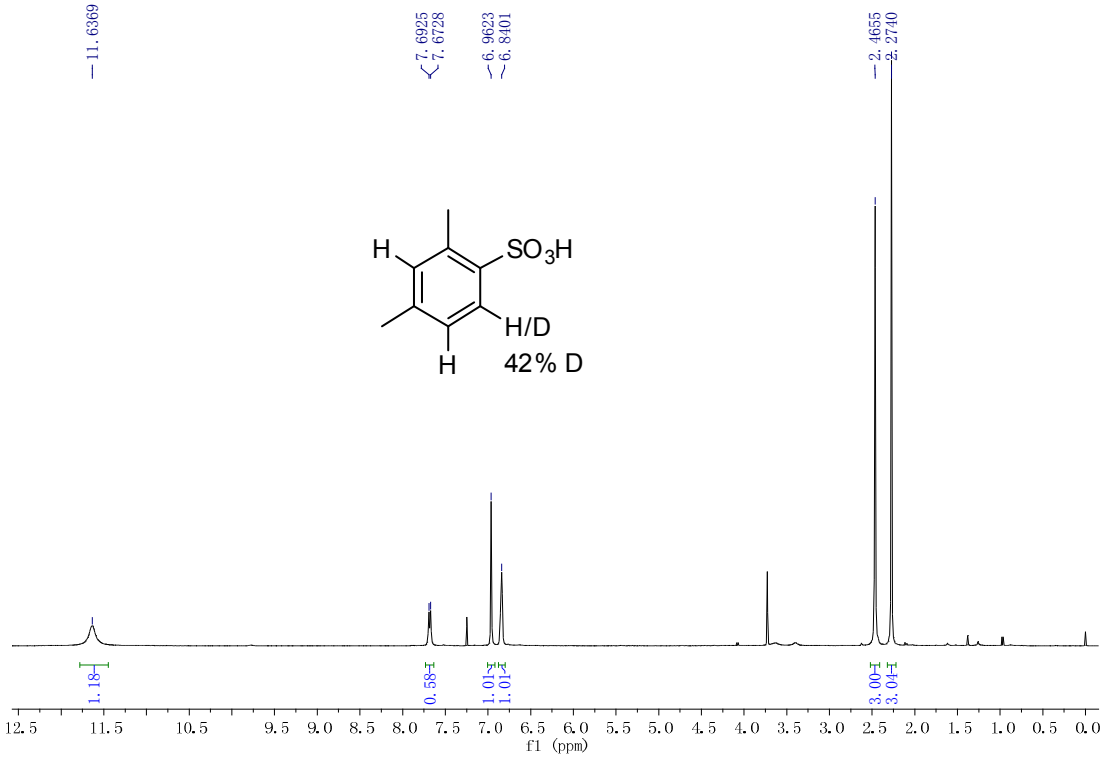


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 1H), 7.40 (s, 1H), 7.25 – 7.16 (m, 11H), 6.88 – 6.78 (m, 10H), 2.39 (s, 3H). The ^{1}H NMR data agree with those in a literature report.[3]

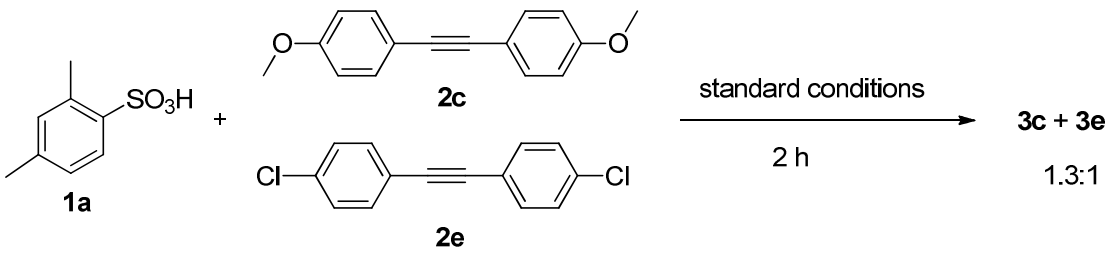
IV. Deuterium experiment



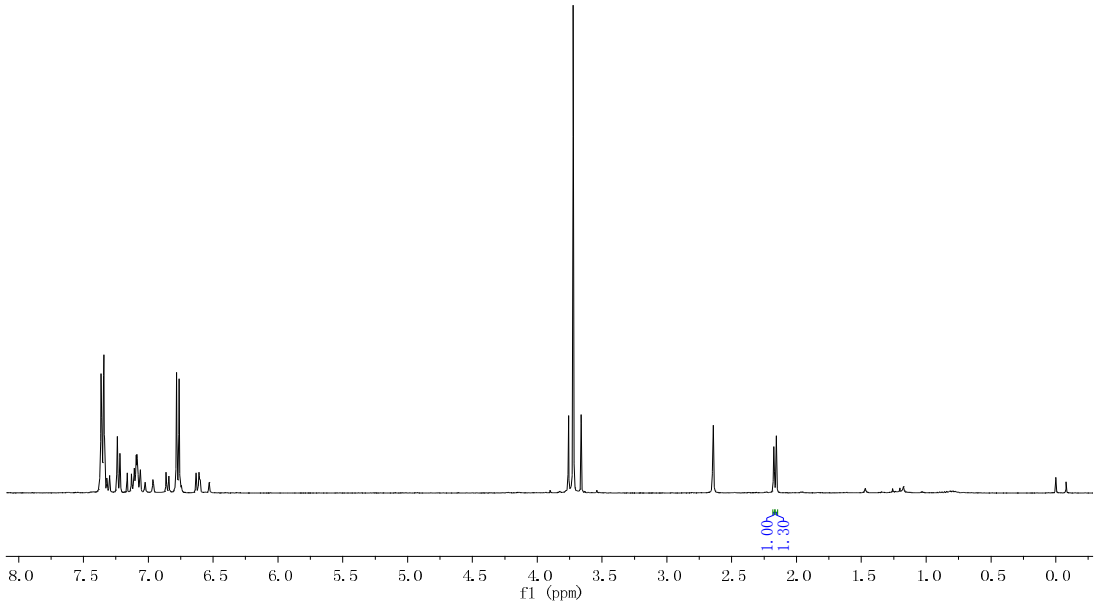
m-Xylenesulfonic acid (0.3 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), AgOAc (2.0 equiv), AcOH-d_4 (5.0 equiv) and dioxane (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 16 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was diluted with EtOAc, then washed with 2 N HCl aqueous solution (20 mL). Subsequently, the mixture was extracted with ethyl acetate (4*20 mL). The combined organic layer and then dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuo. 42% deuterium incorporation was observed at the *ortho* position of **1a** by 1H NMR analysis.

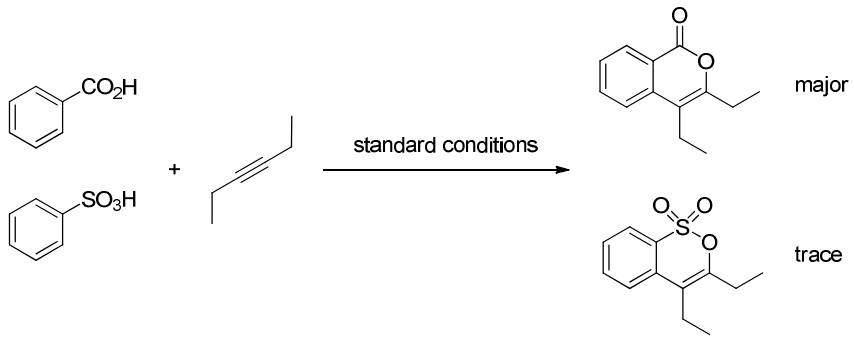


V. Competition experiment

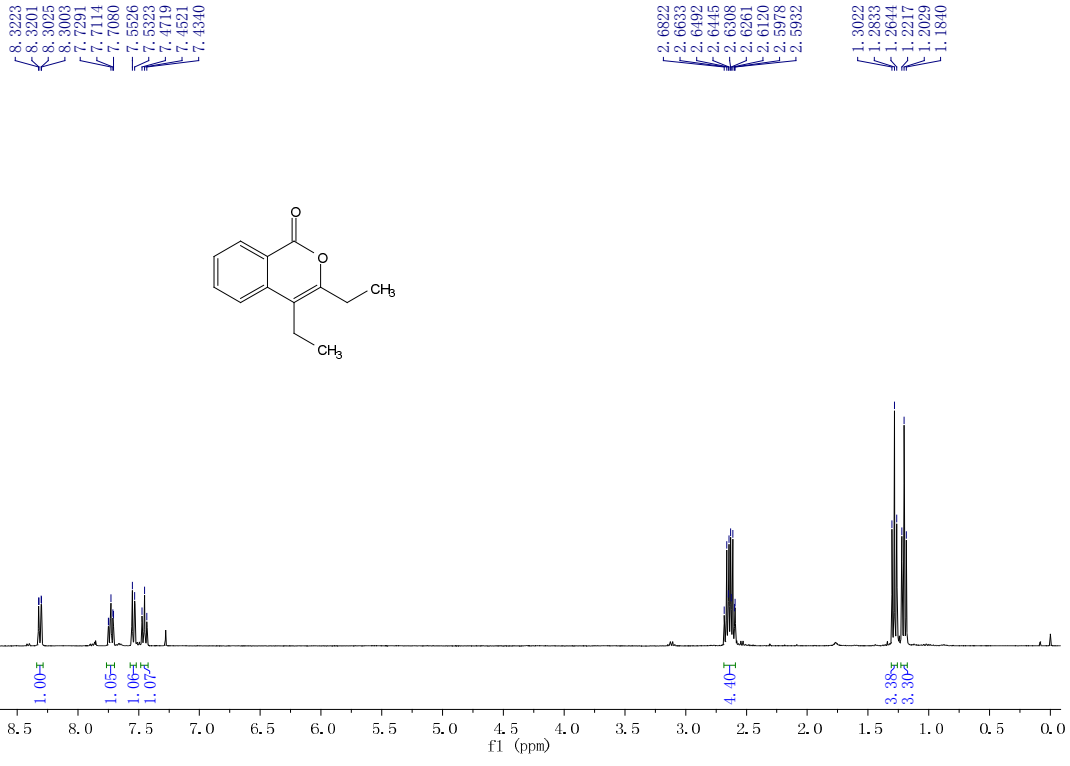


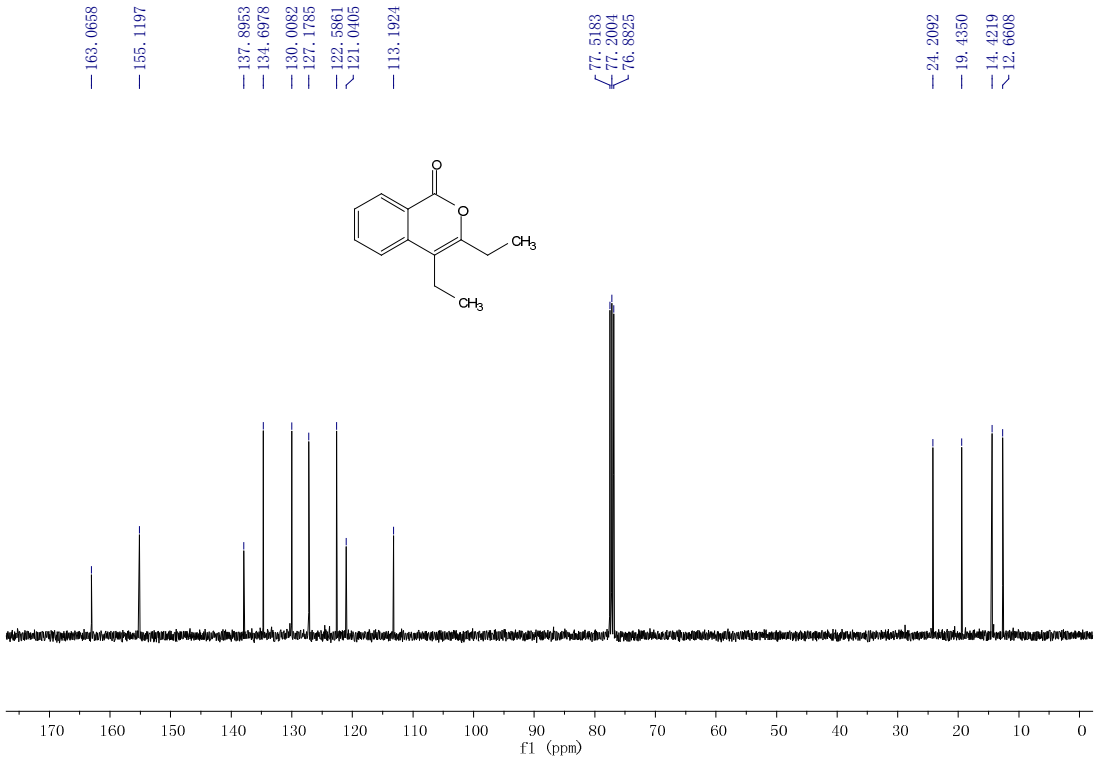
m-Xylenesulfonic acid (0.20 mmol), **2c** (0.20 mmol), **2e** (0.20 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), AgOAc (2.0 equiv) and dioxane (2 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 2 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography using PE/EA to afford mixture of **3c** and **3e**. ^{1}H NMR analysis of the product mixture obtained revealed that **3c** and **3e** were obtained in 1.3:1 ratio, suggesting that more electron-rich alkyne is kinetically favored.





Benzenesulfonic acid (0.51 mmol), benzoic acid (0.51 mmol), 3-hexyne (0.50 mmol), $[RhCp^*Cl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), AgOAc (2.0 equiv) and dioxane (5 mL) were charged into the sealed tube. The reaction mixture was stirred at 100 °C for 16 h, then cooled to room temperature. GC-MS analysis of the product mixture obtained revealed that product of benzoic acid with 3-hexyne was the major one and only trace of the other be detected. NMR of the major product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 7.9, 0.9 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 2.65 (q, J = 7.5 Hz, 2H), 2.62 (q, J = 7.5 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H), 1.20 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 155.1, 137.90, 134.7, 130.0, 127.2, 122.6, 121.0, 113.2, 24.2, 19.4, 14.4, 12.7. The NMR data agree with those in a literature report.[4]





VI. References

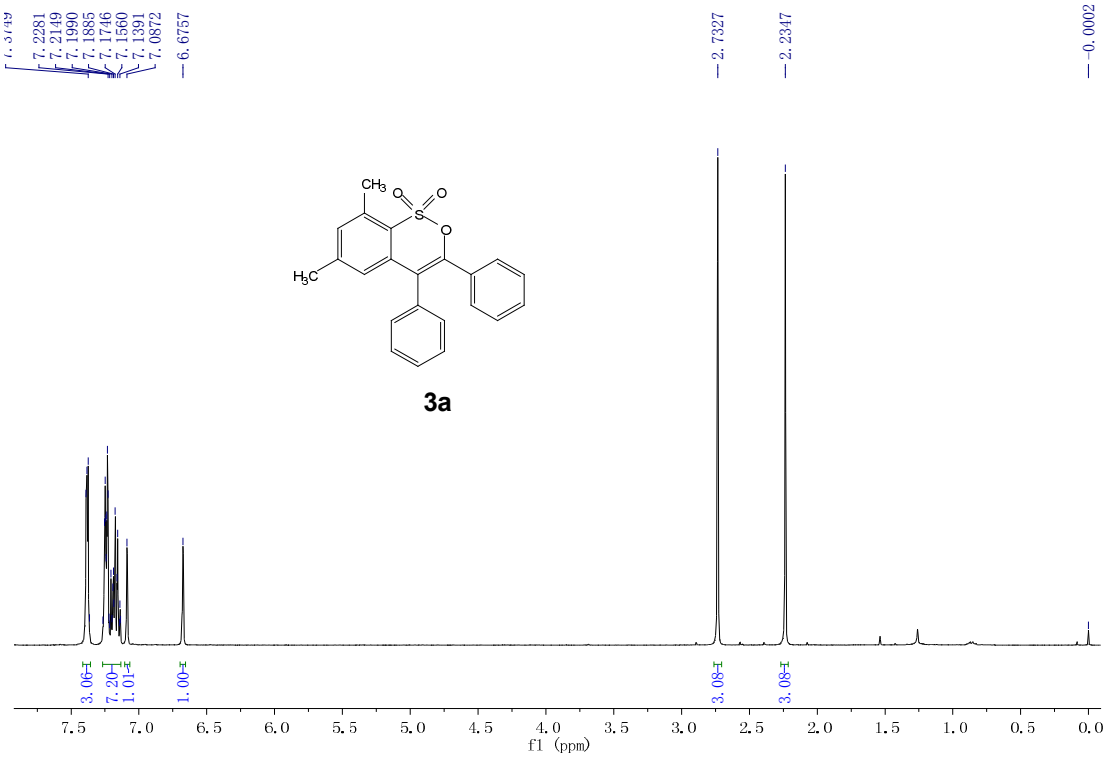
1. Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199.

2. Li, C.-W.; Pati, K.; Lin, G.-Y.; Sohel, S. M. A.; Hung, H.-H.; Liu, R.-S. *Angew. Chem. Int. Ed.* **2010**, *49*, 9891.

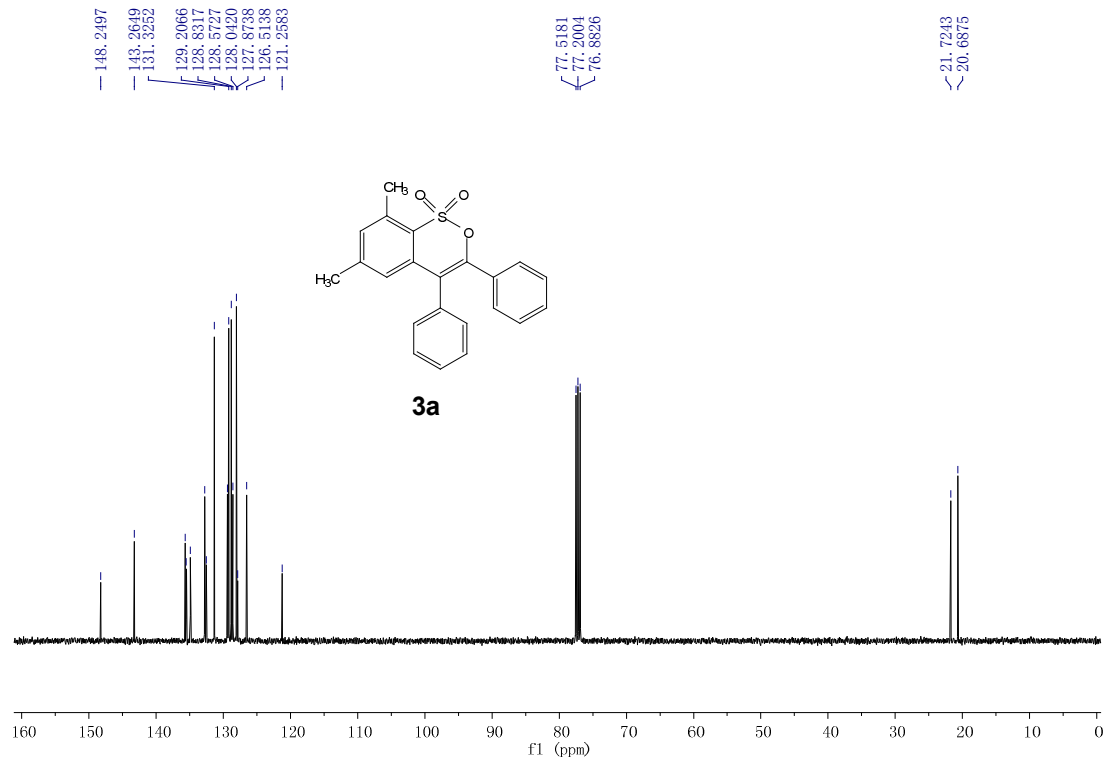
3. Fukutani, T.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 5198.

4. Ackermann, L.; Pospech, J.; Graczyk, K.; Rauch, K. *Org. Lett.* **2012**, *14*, 930.

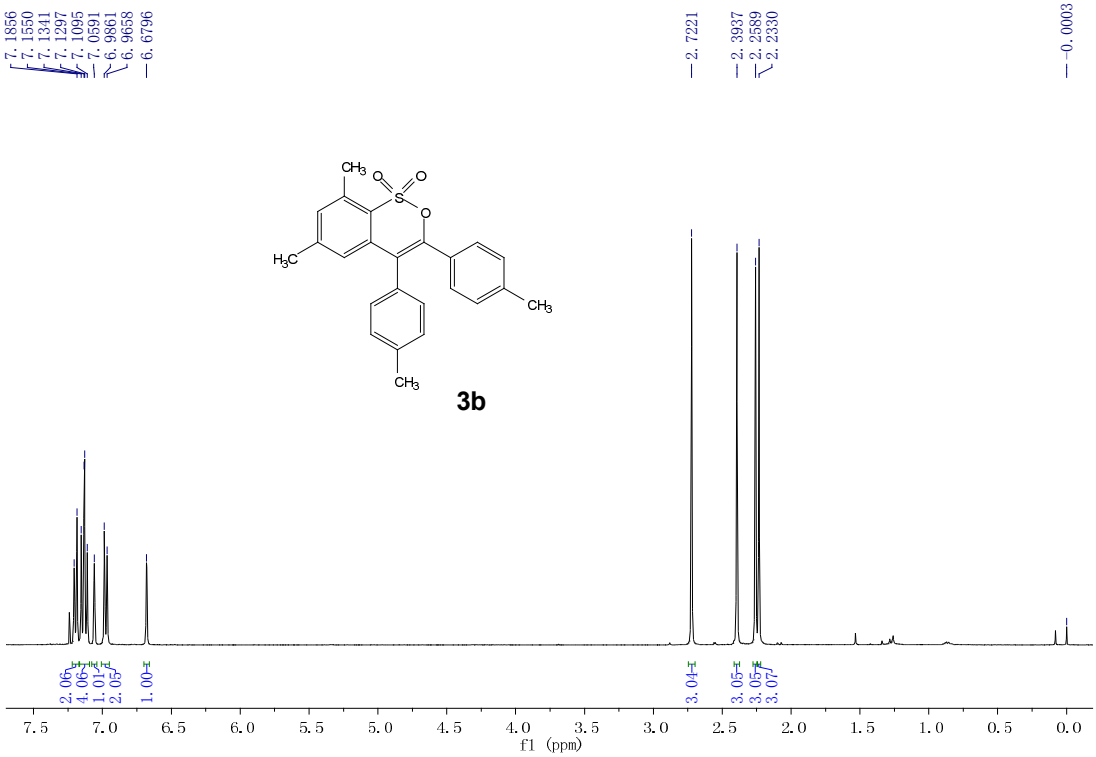
VII. ^{1}H NMR and ^{13}C NMR spectra (NOESY for 3o)



3a



3a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7.1297
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6.9861
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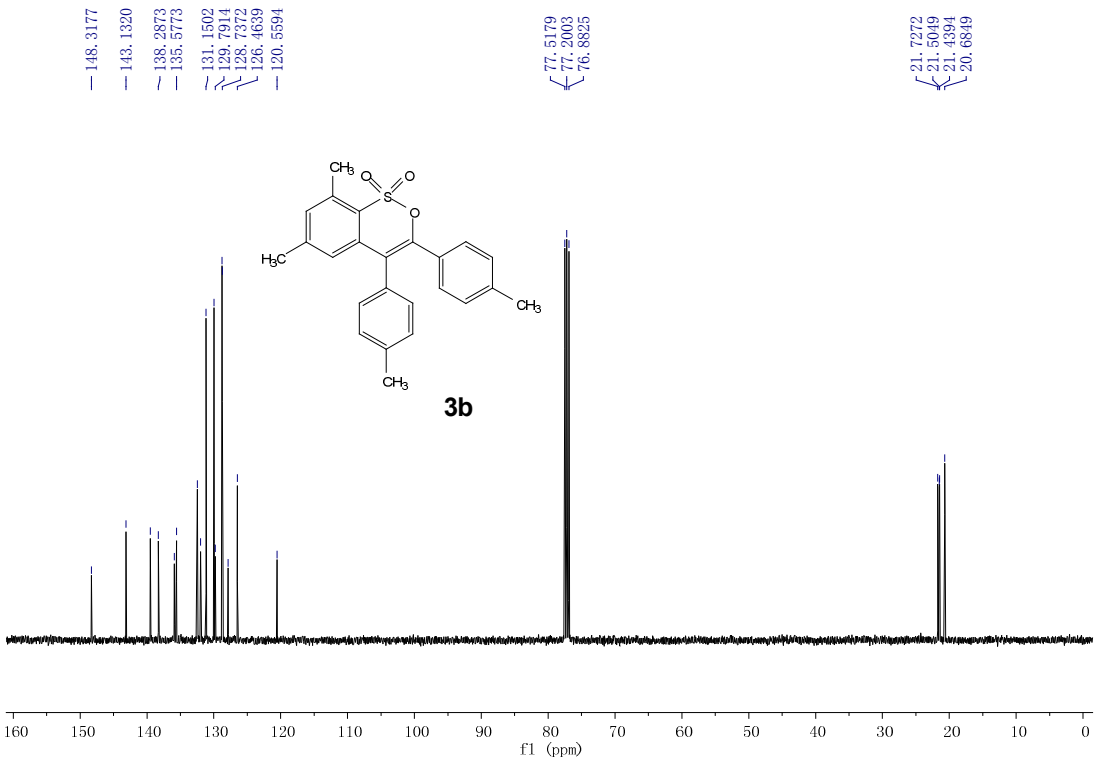
6.6796
2.7221
2.3937
2.2589
2.2330
-0.0003
3b
2.06
4.06
1.01
2.05
1.00
3.04
3.05
3.05
3.07
f1 (ppm)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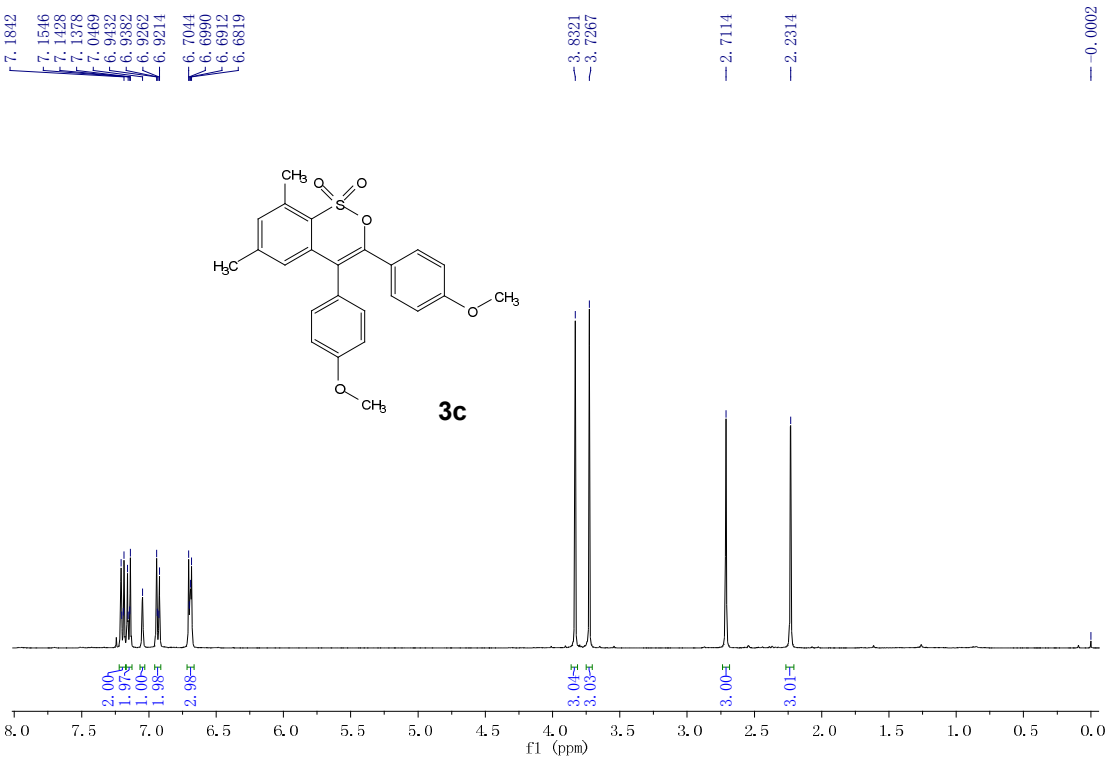
21.5049
21.4394
20.6849
3b
f1 (ppm)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6.9382
6.9262
6.9214
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6.6990
6.6912
6.6819
3.8321
3.7267
2.7114
2.2314
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3c
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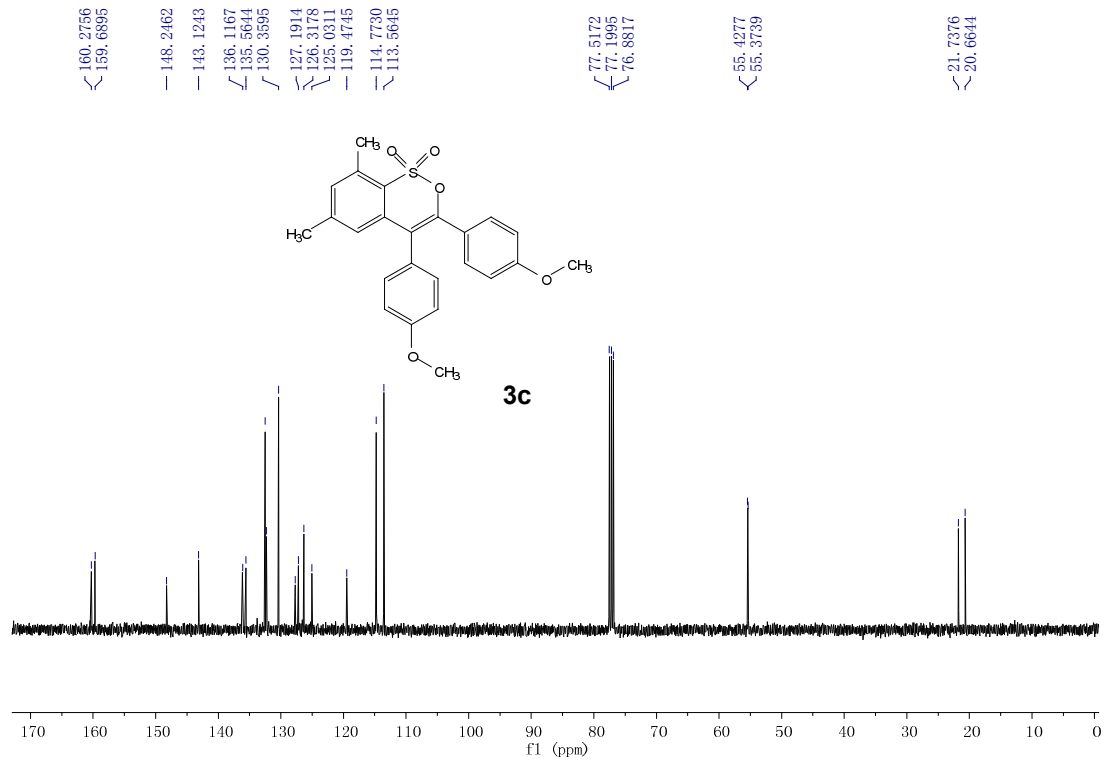
1.97
1.00
1.98
2.98
3.04
3.03
3.00
3.01
f1 (ppm)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114.7730
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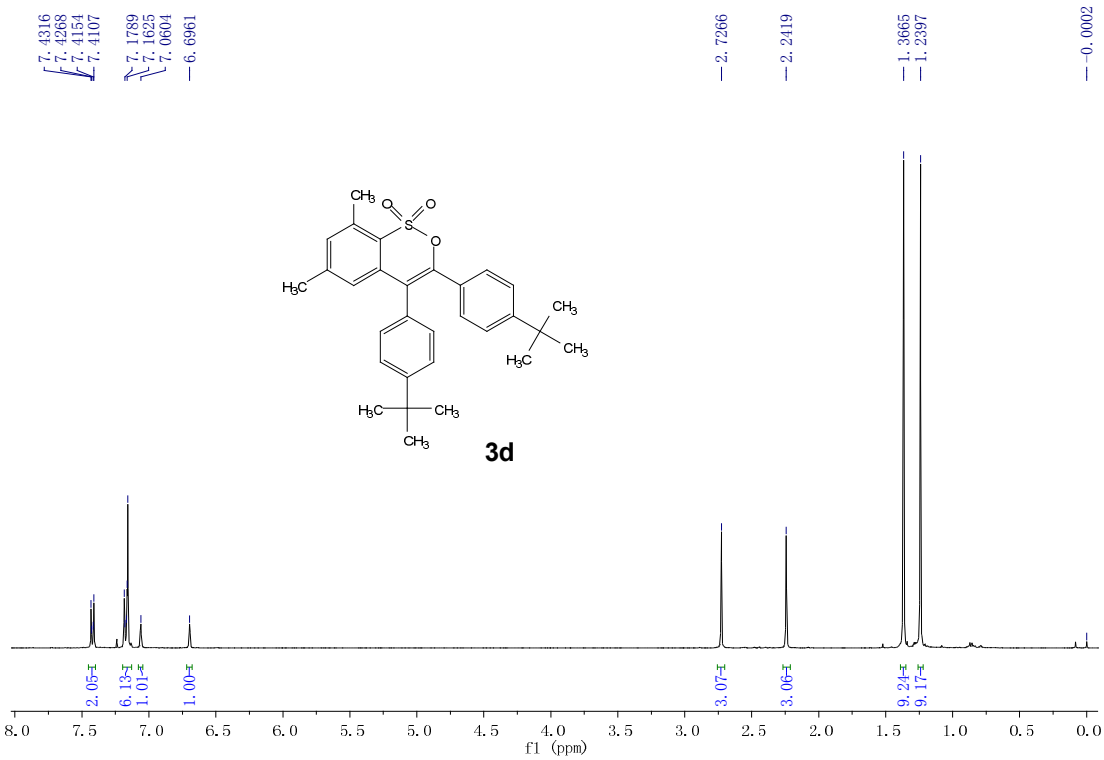
20.6644
3c
f1 (ppm)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7.4268
7.4154
7.4107
7.1789
7.1625
7.0604
6.6961
2.7266
2.2419
1.3665
1.2397
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3d
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6.13
1.01
1.00
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3.06
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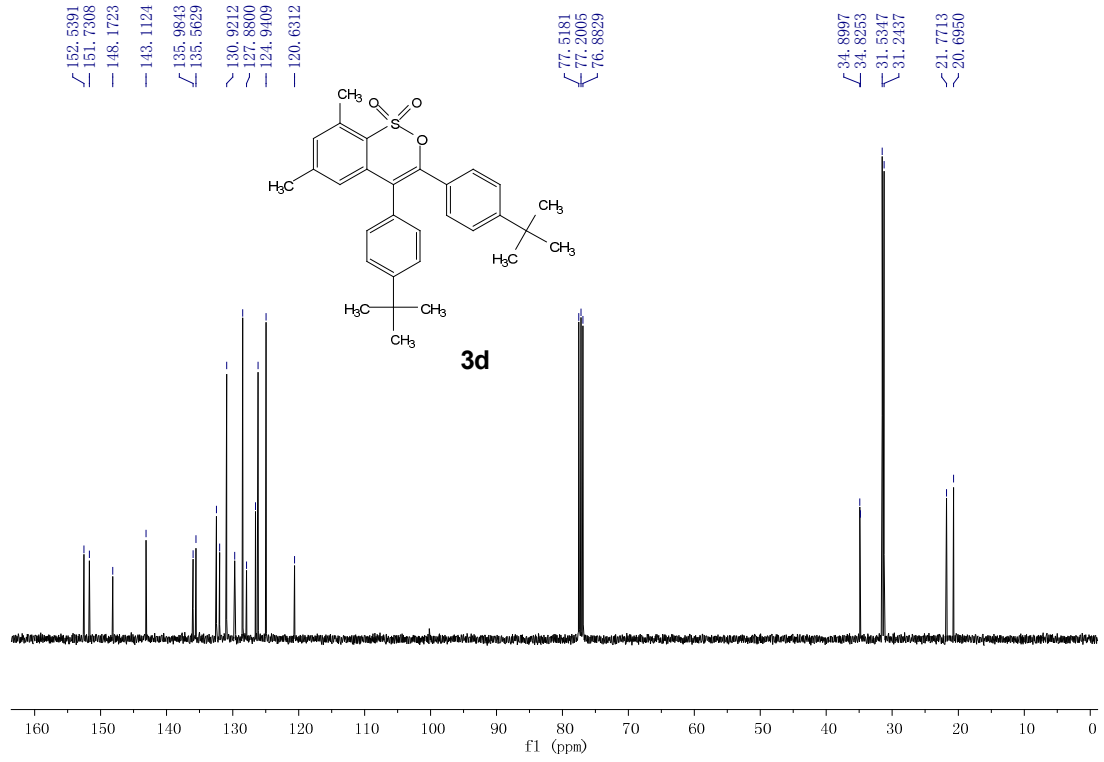
9.17
f1 (ppm)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21.7713
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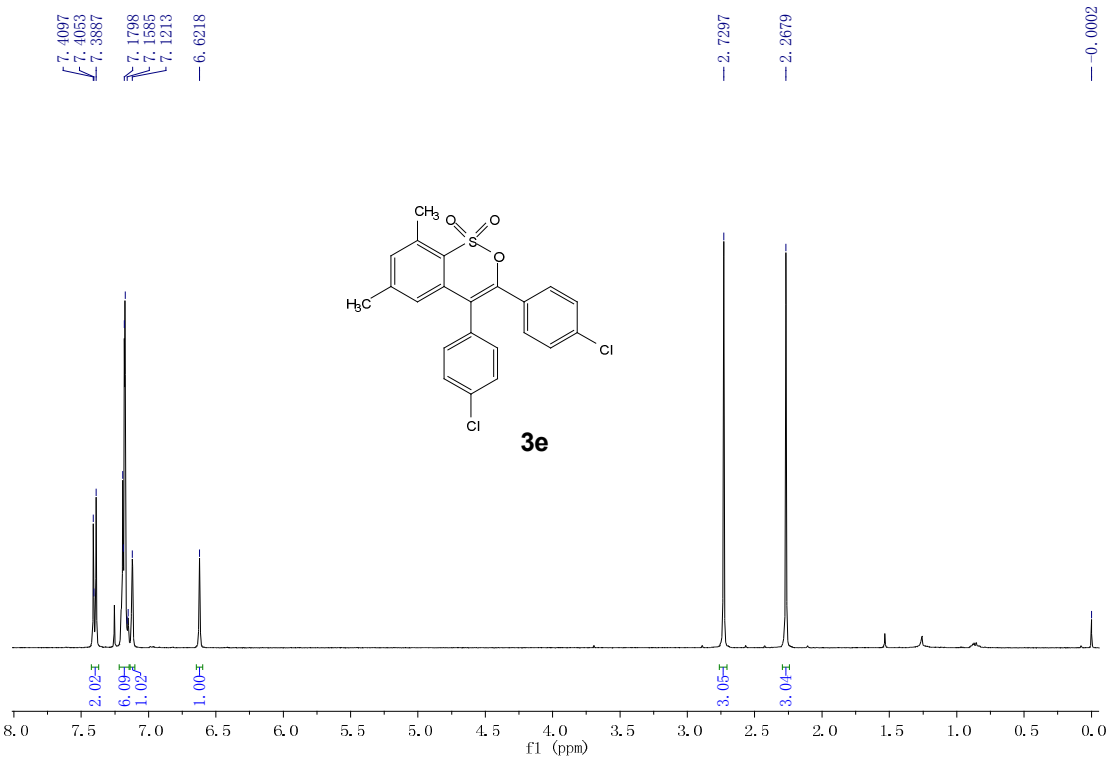
3d
f1 (ppm)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CH3
O
O
S
O
H3C
Cl
Cl
3e
2.02
6.09
1.02
1.00
3.05
3.04
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.0
1.5
1.0
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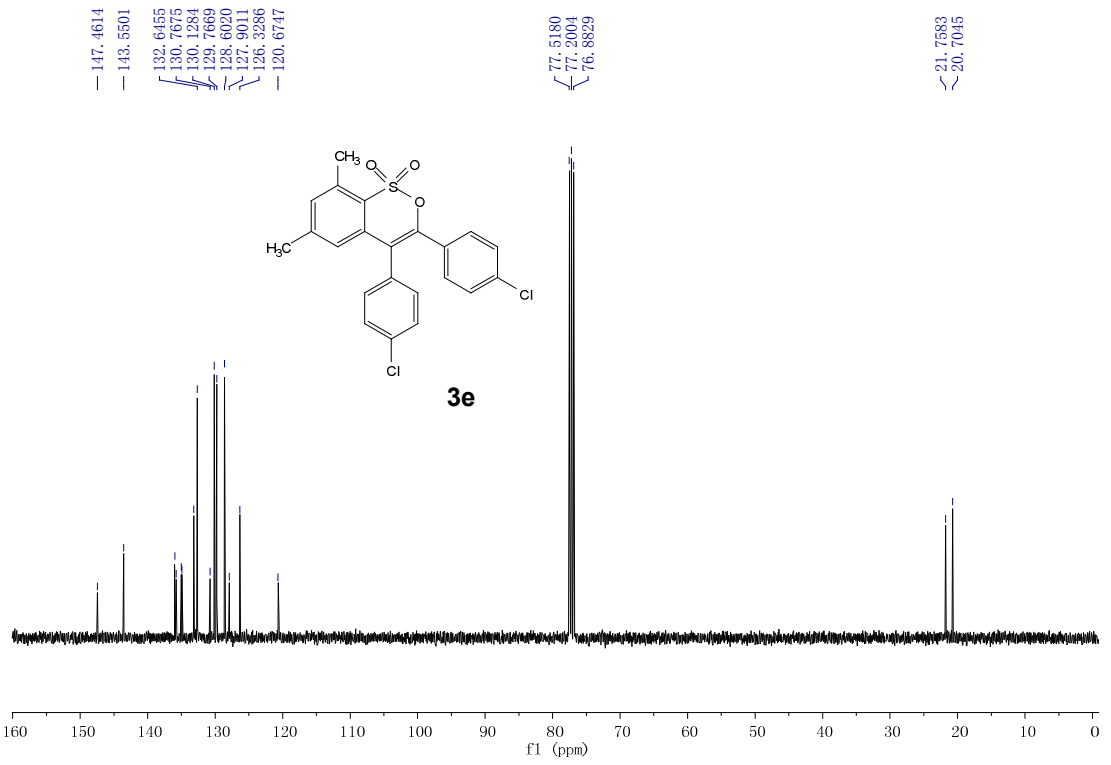
0.0
f1 (ppm)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O
S
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H3C
Cl
Cl
3e
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90
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70
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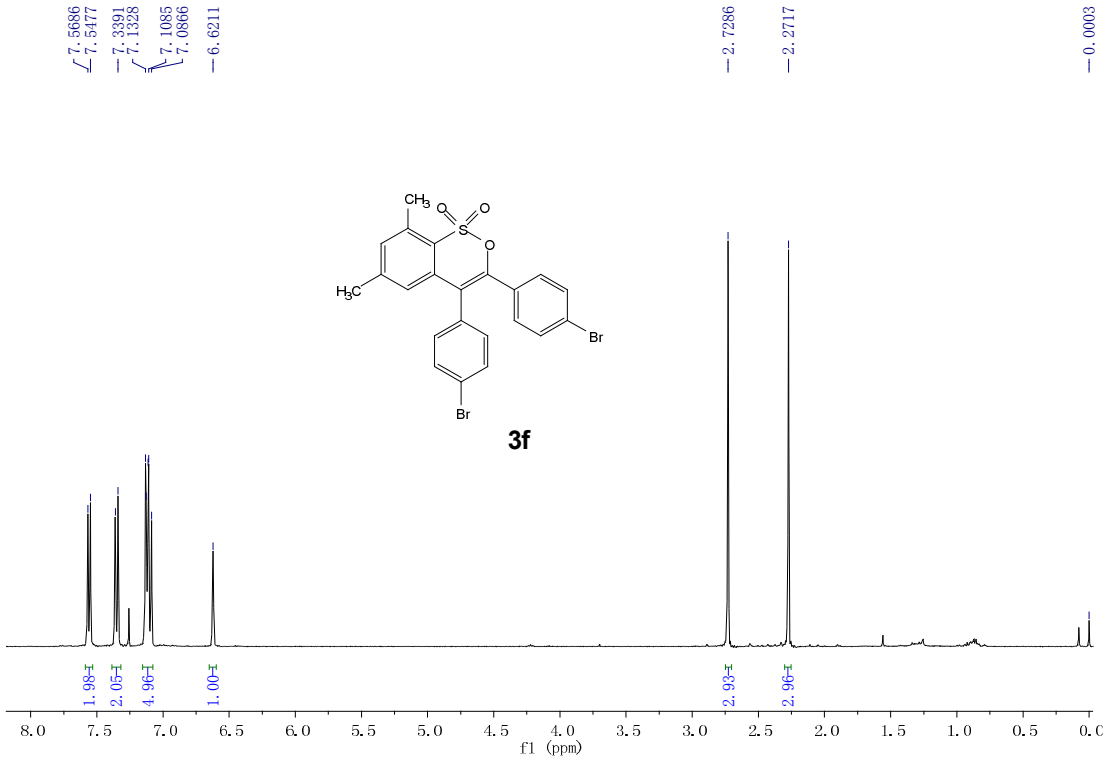
50
40
30
20
10
0
f1 (ppm)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S
O
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H3C
Br
Br
3f
1.98
2.05
4.96
1.00
2.93
2.96
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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1.5
1.0
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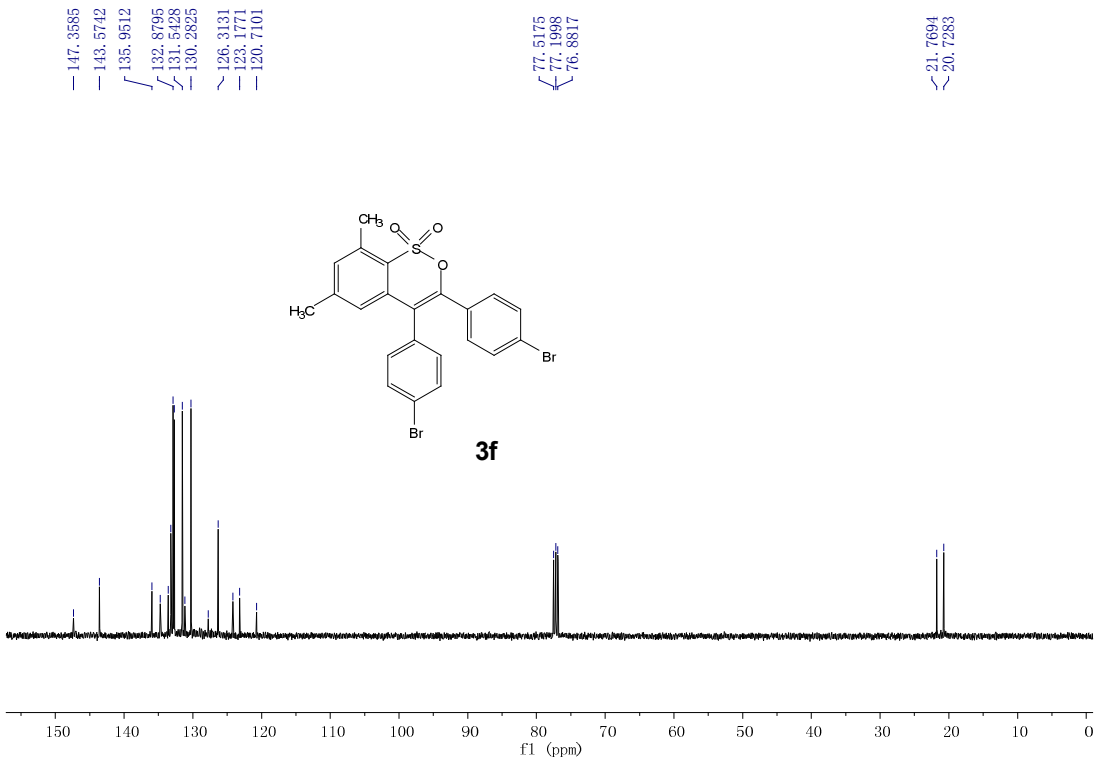
0.0
f1 (ppm)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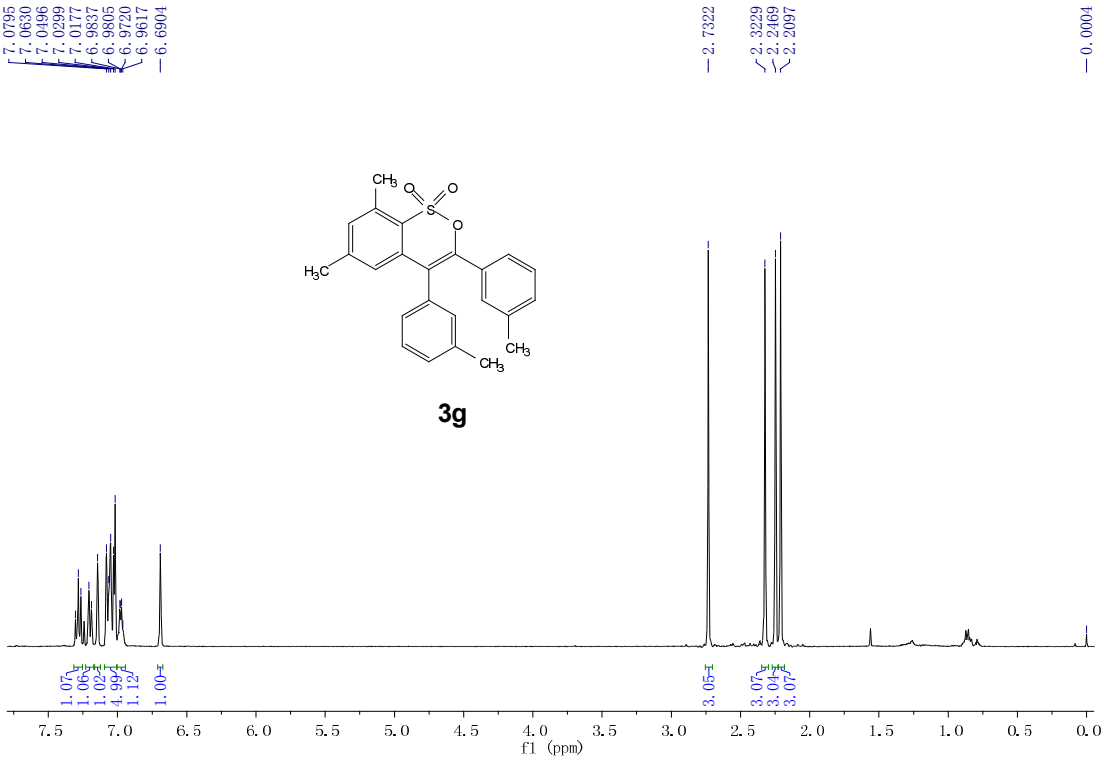
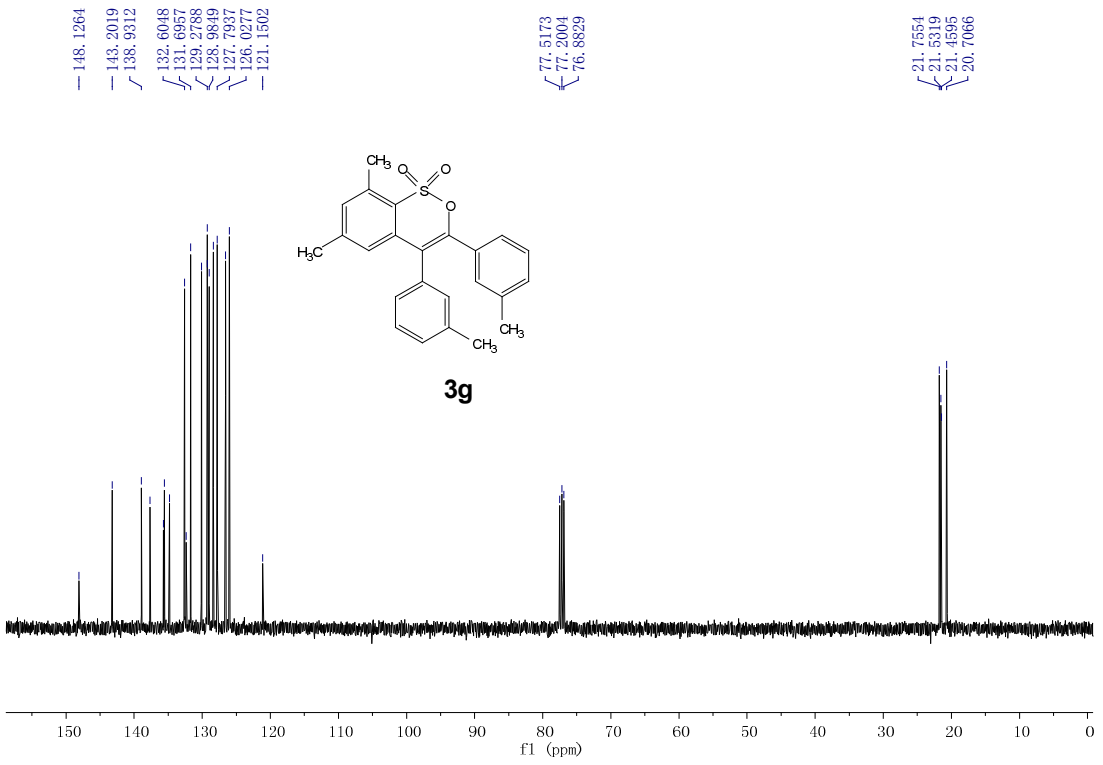
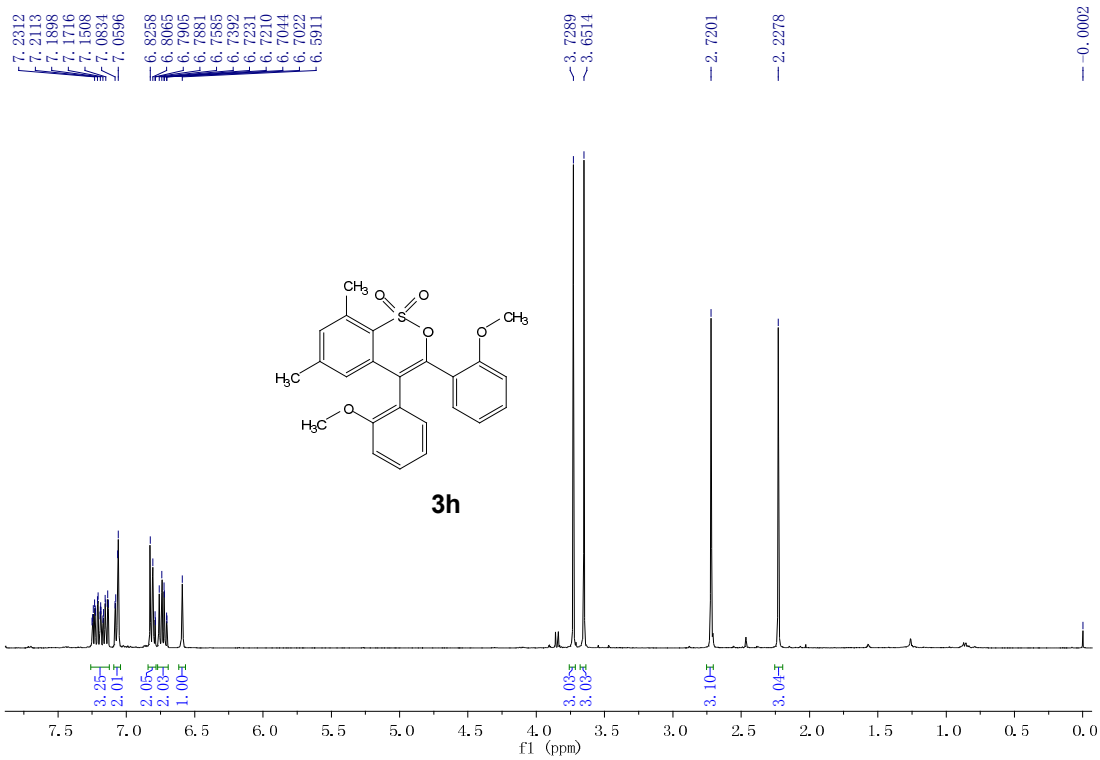
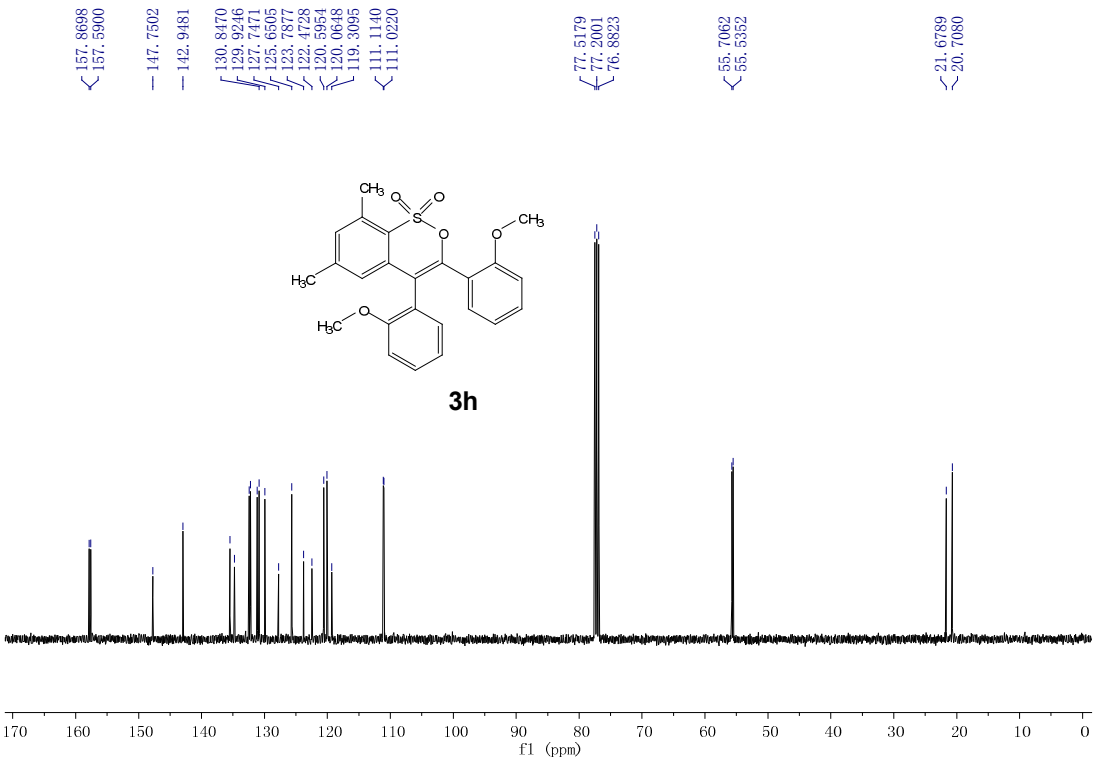
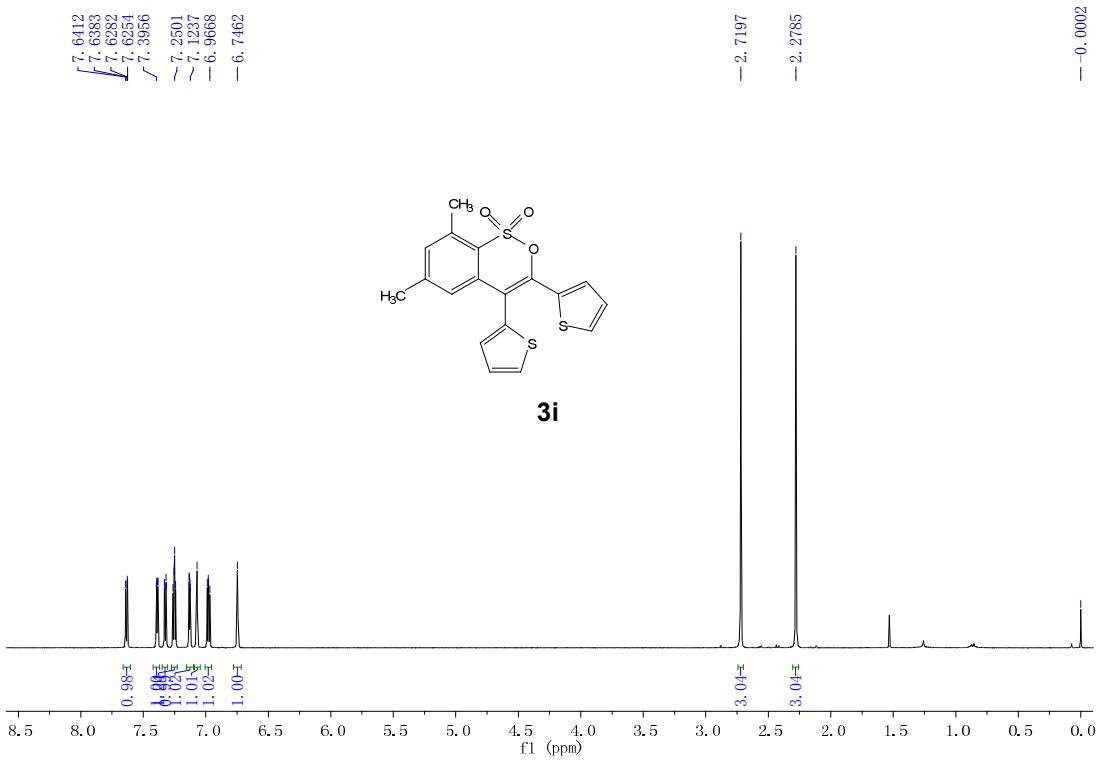
130.2825
126.3131
123.1771
120.7101
77.5175
77.1998
76.8817
21.7694
20.7283
CH3
O
S
O
O
H3C
Br
Br
3f
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.0795
7.0630
7.0496
7.0299
7.0177
6.9837
6.9805
6.9720
6.9617
6.6904
2.7322
2.3229
2.2469
2.2097
0.0004
3g
1.07
1.06
1.02
4.99
1.12
1.00
3.05
3.07
3.04
3.07
f1 (ppm)

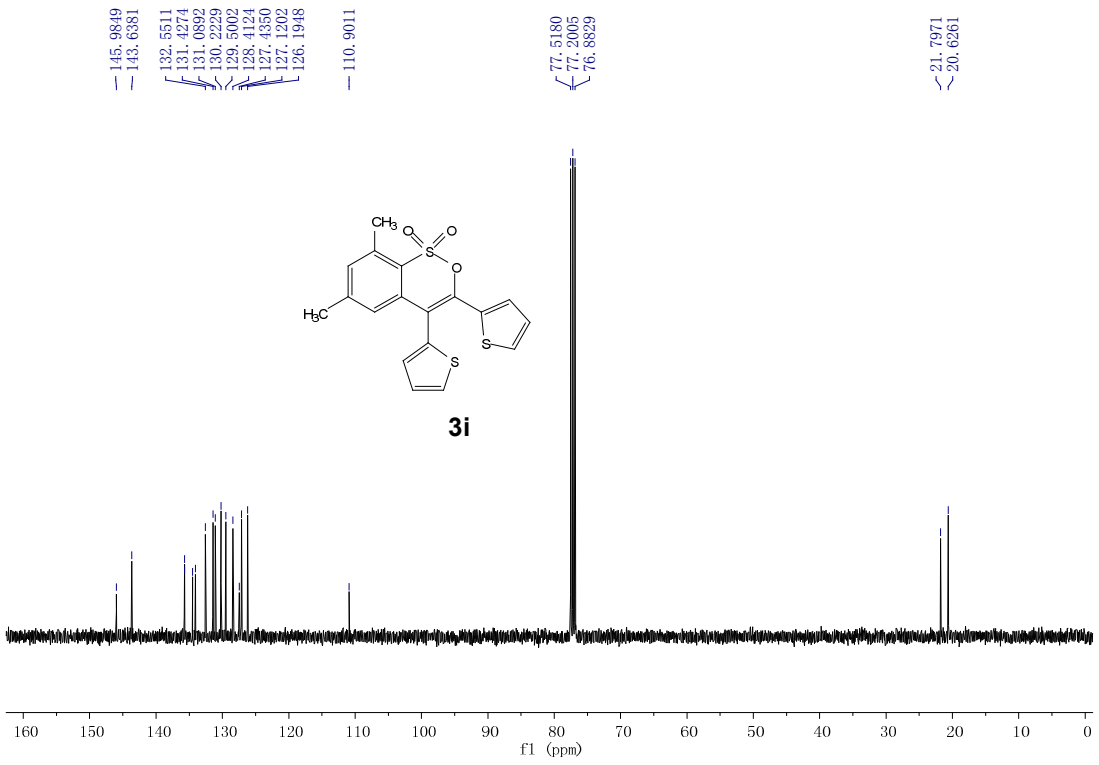

148.1264
143.2019
138.9312
132.6048
131.6957
129.2788
128.9849
127.7937
126.0277
121.1502
77.5173
77.2004
76.8829
21.7554
21.5319
21.4595
20.7066
3g
f1 (ppm)


7.2312
7.2113
7.1898
7.1716
7.1508
7.0834
7.0596
6.8258
6.8065
6.7905
6.7881
6.7585
6.7392
6.7231
6.7210
6.7044
6.7022
6.5911
3.7289
3.6514
2.7201
2.2278
-0.0002
3h
3.25
2.01
2.05
2.03
1.00
3.03
3.03
3.10
3.04
f1 (ppm)

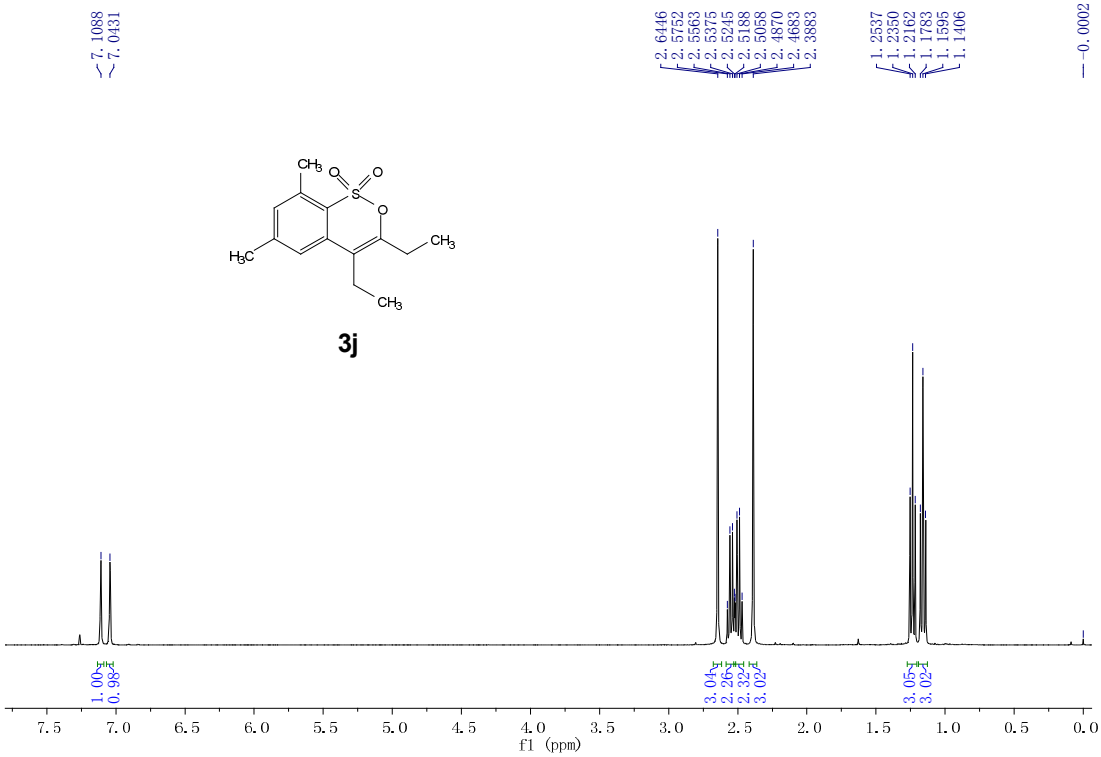

157.8698
157.5900
147.7502
142.9481
130.8470
129.9246
127.7471
125.6505
123.7877
122.4728
120.5954
120.0648
119.3095
111.1140
111.0220
77.5179
77.2001
76.8823
55.7062
55.5352
21.6789
20.7080
3h
f1 (ppm)

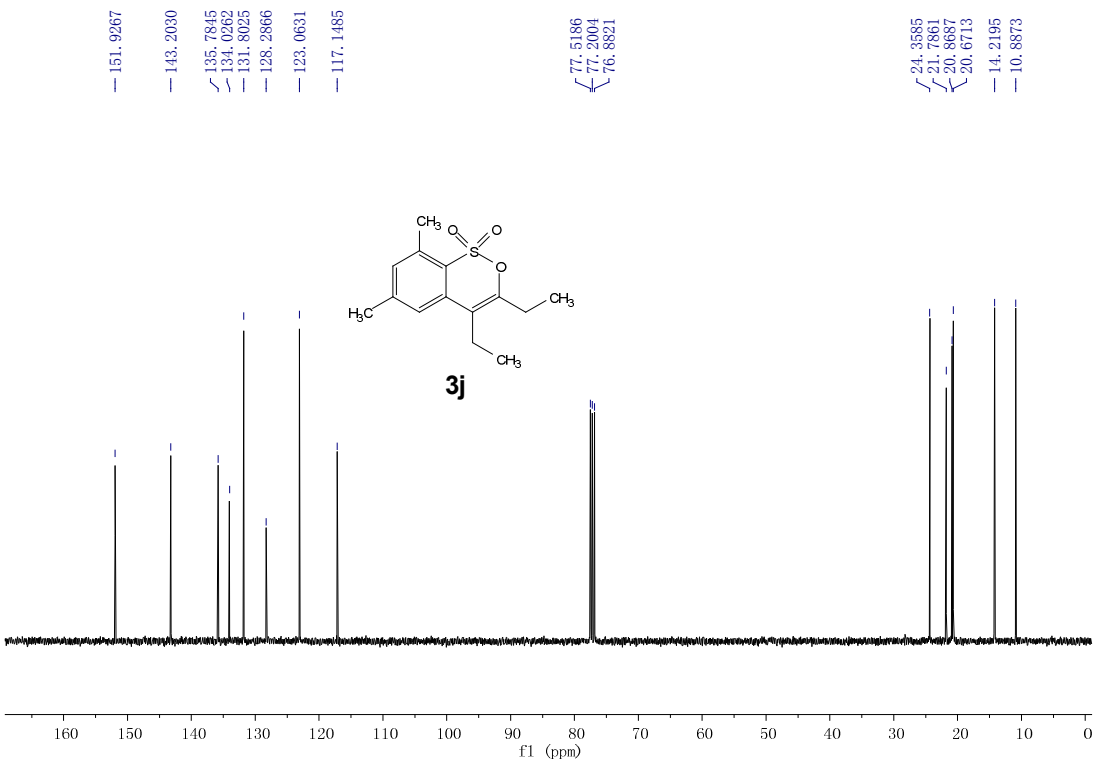

7.6412
7.6383
7.6282
7.6254
7.3956
7.2501
7.1237
6.9668
6.7462
2.7197
2.2785
-0.0002
0.98
1.02
1.01
1.02
1.00
3.04
3.04
f1 (ppm)

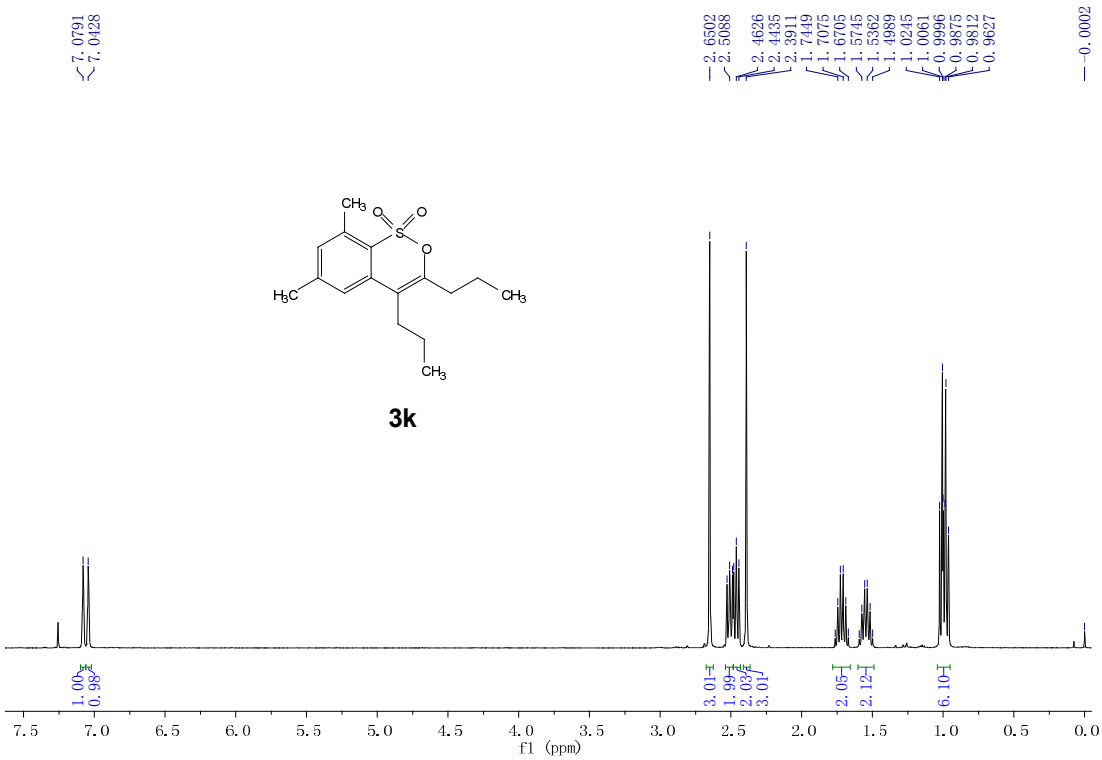
3i


145.9849
143.6381
132.5511
131.4274
131.0892
130.2229
129.5002
128.4124
127.4350
127.1202
126.1948
110.9011
77.5180
77.2005
76.8829
21.7971
20.6261
f1 (ppm)

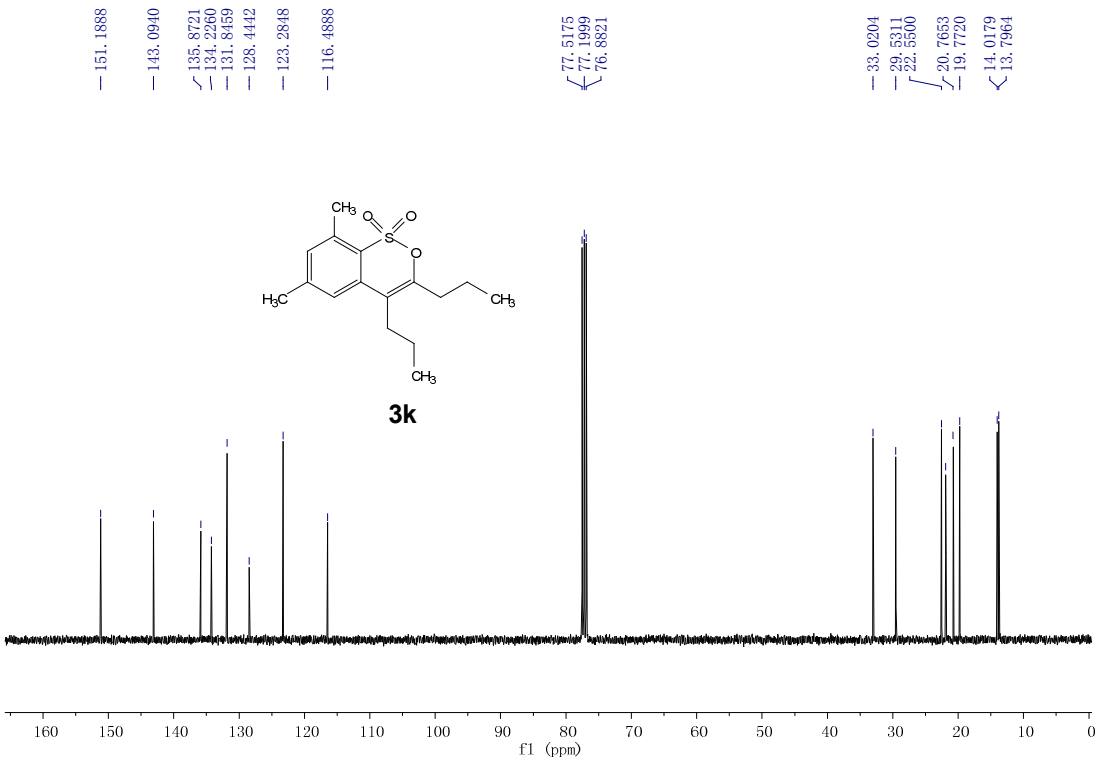
3i


7.1088
7.0431
2.6446
2.5752
2.5563
2.5375
2.5245
2.5188
2.5058
2.4870
2.4683
2.3883
1.2537
1.2350
1.2162
1.1783
1.1595
1.1406
-0.0002
3j
1.00
0.98
3.04
2.26
2.32
3.02
3.05
3.02
f1 (ppm)

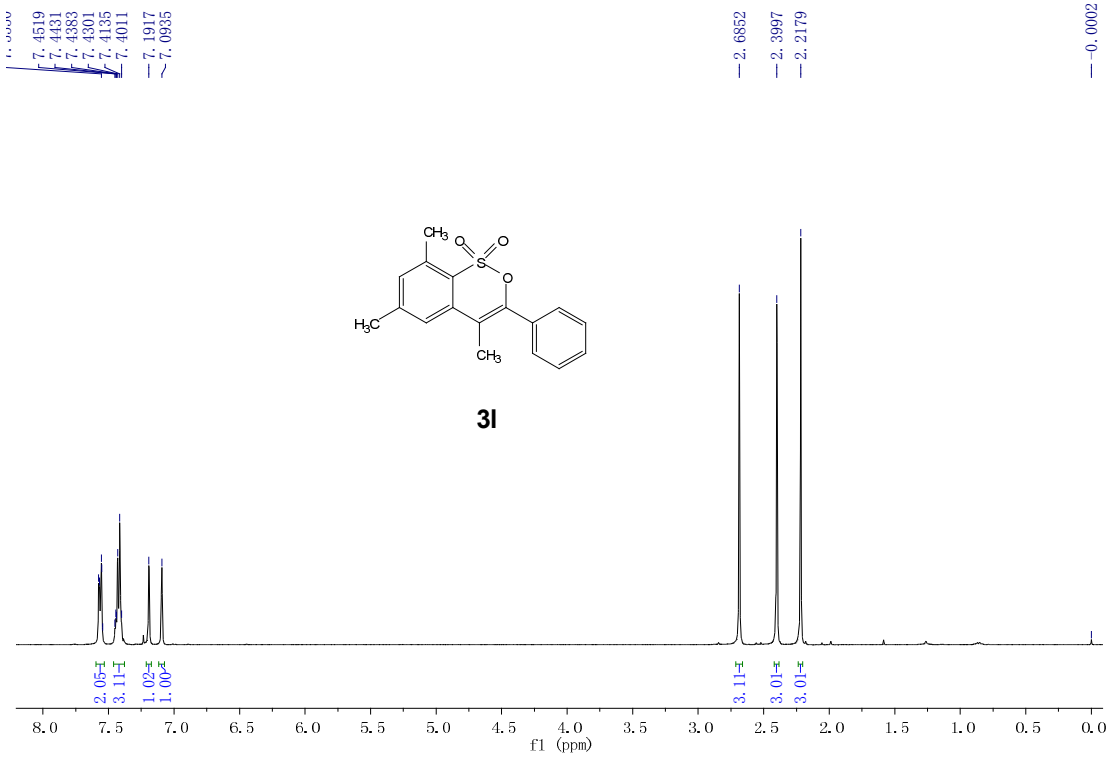

151.9267
143.2030
135.7845
134.0262
131.8025
128.2866
123.0631
117.1485
77.5186
77.2004
76.8821
24.3585
21.7861
20.8687
20.6713
14.2195
10.8873
3j
f1 (ppm)

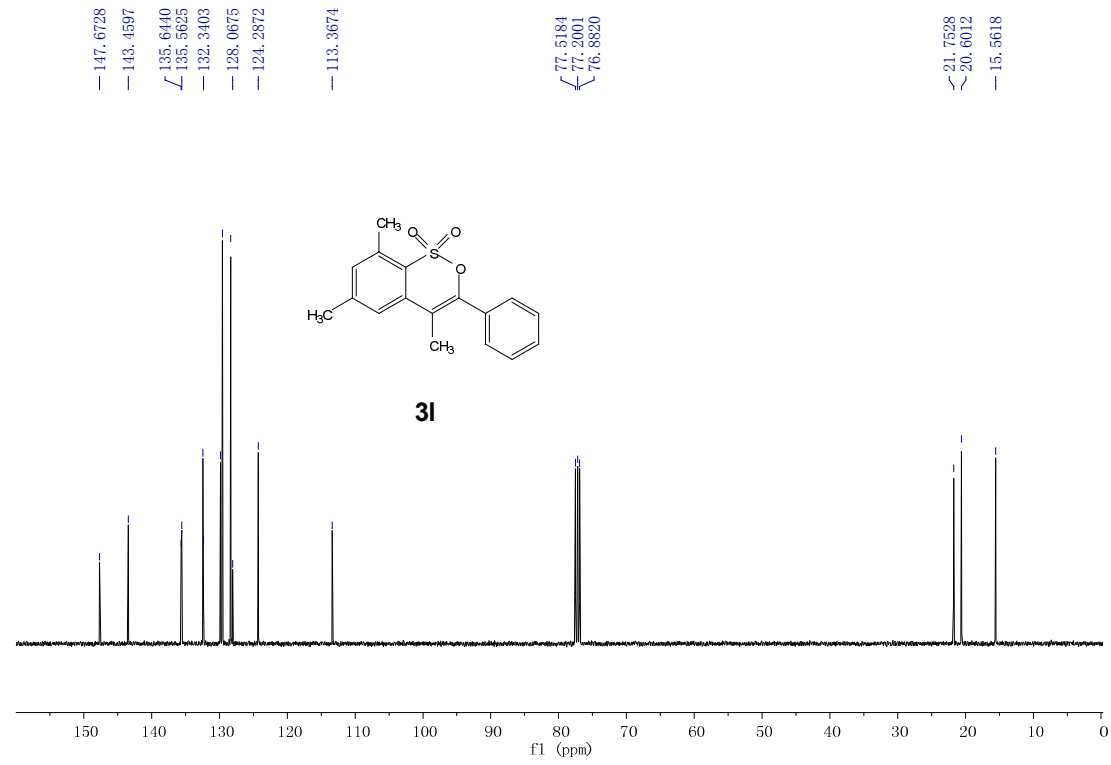

7.0791
7.0428
2.6502
2.5088
2.4626
2.4435
2.3911
1.7449
1.7075
1.6705
1.5745
1.5362
1.4989
1.0245
1.0061
0.9996
0.9875
0.9812
0.9627
-0.0002
1.00
0.98
3.01
1.99
2.03
3.01
2.05
2.12
6.10
f1 (ppm)

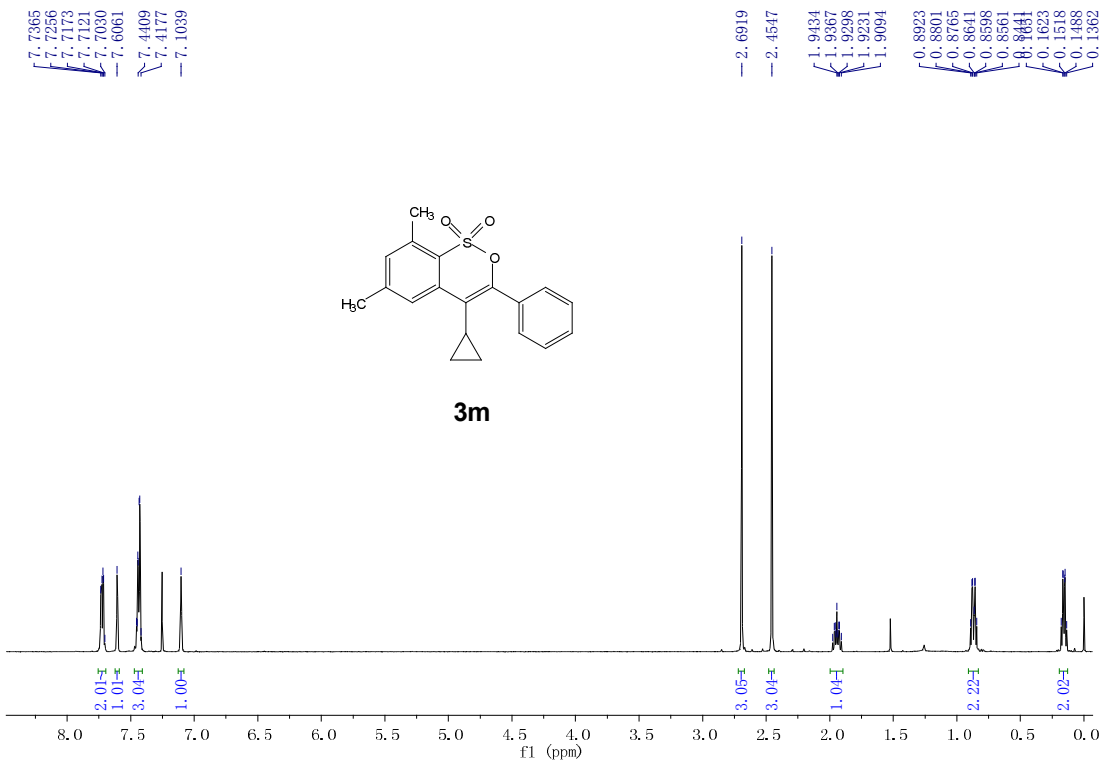
3k

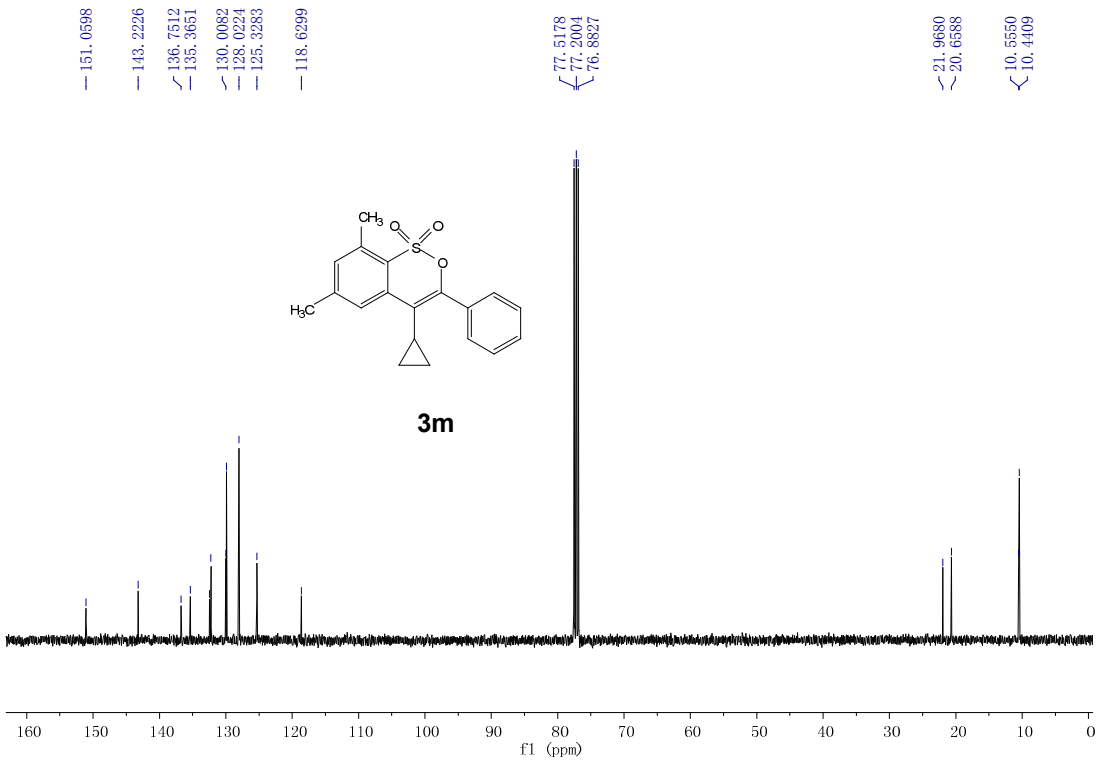

151.1888
143.0940
135.8721
134.2260
131.8459
128.4442
123.2848
116.4888
77.5175
77.1999
76.8821
33.0204
29.5311
22.5500
20.7653
19.7720
14.0179
13.7964
f1 (ppm)

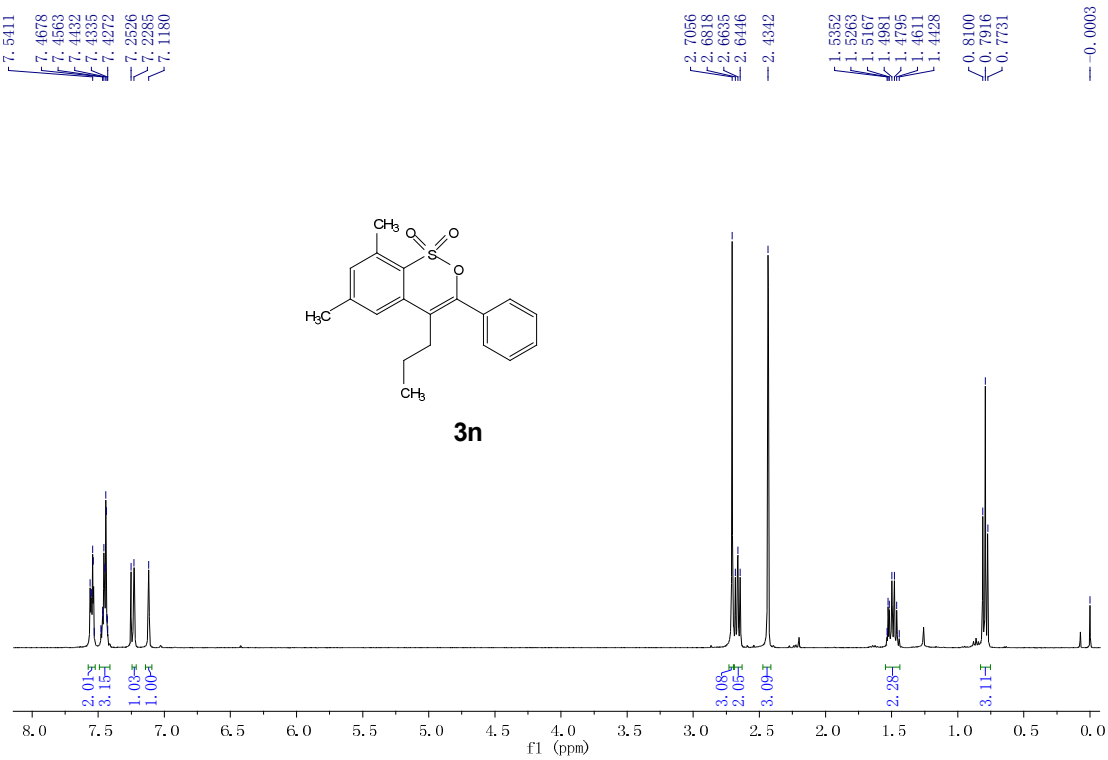
3k

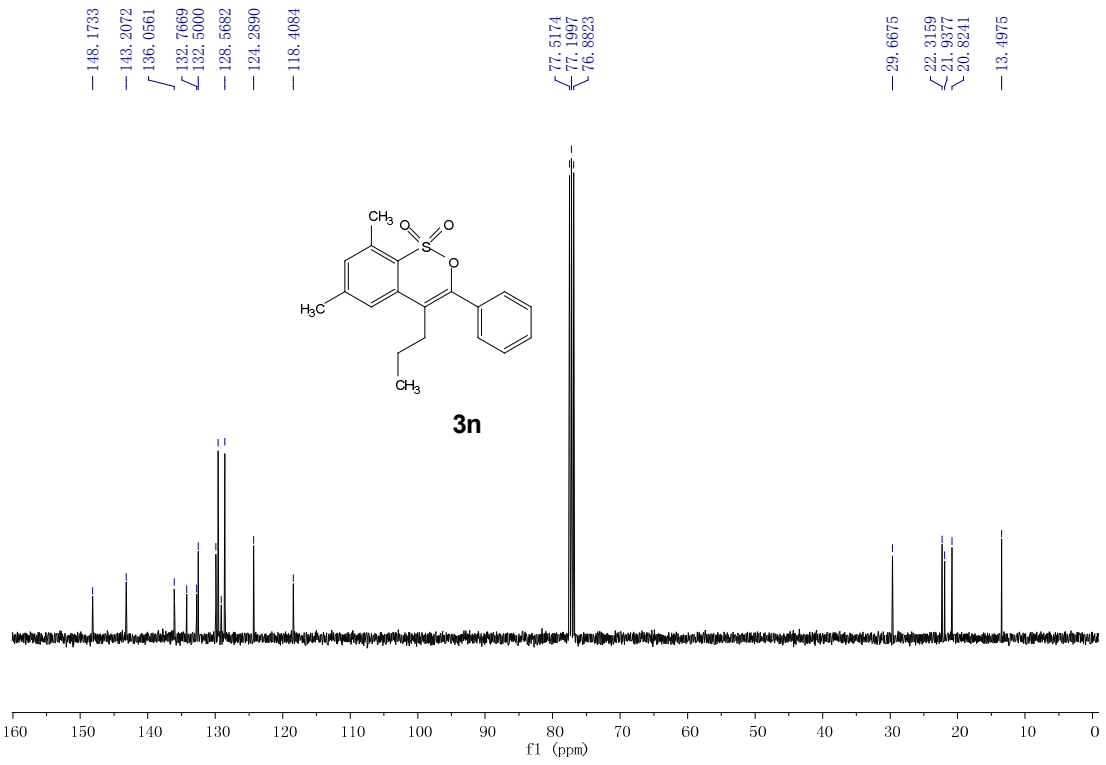

7.4519
7.4431
7.4383
7.4301
7.4135
7.4011
7.1917
7.0935
2.6852
2.3997
2.2179
-0.0002
CH3
O
O
S
O
H3C
CH3
3I
2.05
3.11
1.02
1.00
3.11
3.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

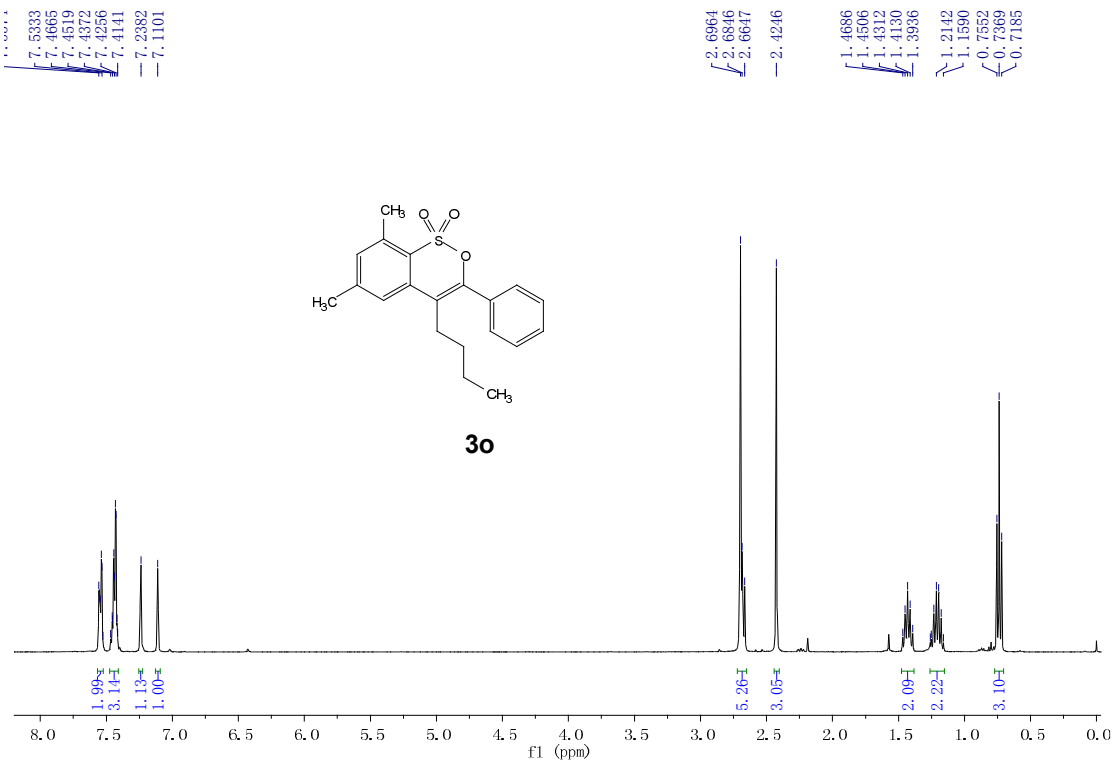

147.6728
143.4597
135.6440
135.5625
132.3403
128.0675
124.2872
113.3674
77.5184
77.2001
76.8820
21.7528
20.6012
15.5618
CH3
O
O
S
O
H3C
CH3
3I
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7365
7.7256
7.7173
7.7121
7.7030
7.6061
7.4409
7.4177
7.1039
2.6919
2.4547
1.9434
1.9367
1.9298
1.9231
1.9094
0.8923
0.8801
0.8765
0.8641
0.8598
0.8561
0.1623
0.1518
0.1488
0.1362
CH3
O
S
O
O
H3C
3m
2.01
1.01
3.04
1.00
3.05
3.04
1.04
2.22
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)

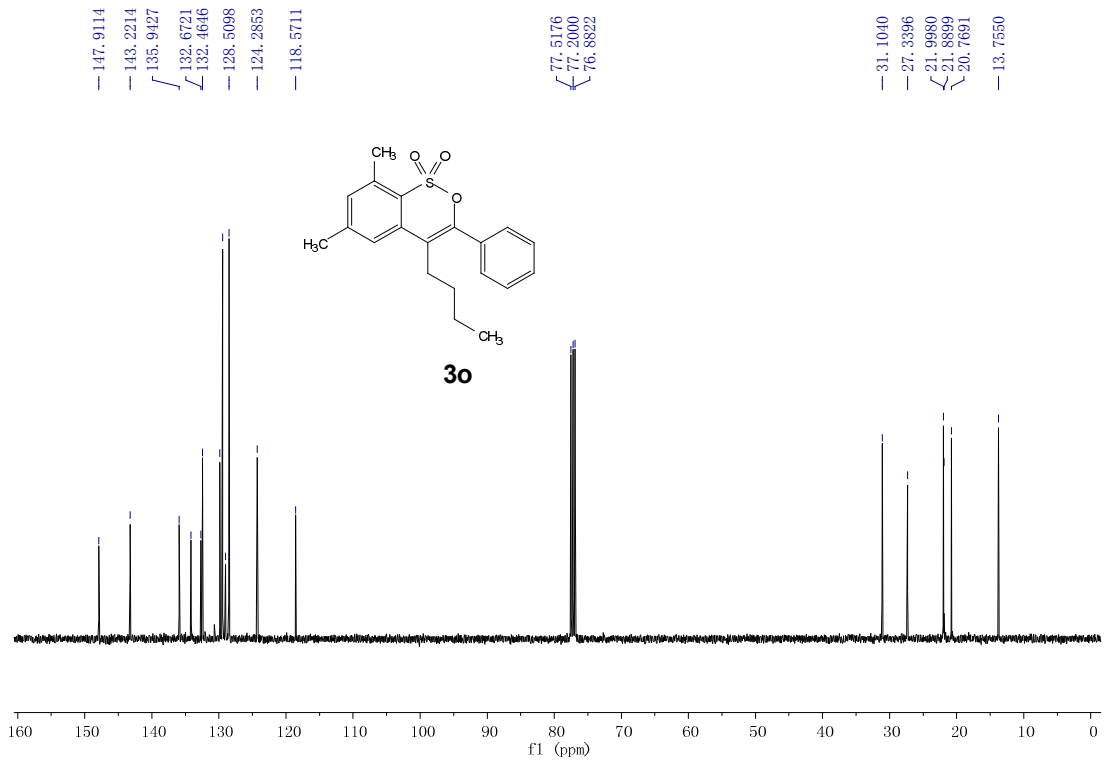

151.0598
143.2226
136.7512
135.3651
130.0082
128.0224
125.3283
118.6299
77.5178
77.2004
76.8827
21.9680
20.6588
10.5550
10.4409
CH3
O
S
O
O
H3C
3m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.5411
7.4678
7.4563
7.4432
7.4335
7.4272
7.2526
7.2285
7.1180
2.7056
2.6818
2.6635
2.6446
2.4342
1.5352
1.5263
1.5167
1.4981
1.4795
1.4611
1.4428
0.8100
0.7916
0.7731
-0.0003
CH3
O
S
O
O
H3C
CH3
3n
2.01
3.15
1.03
1.00
3.08
2.05
3.09
2.28
3.11
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)

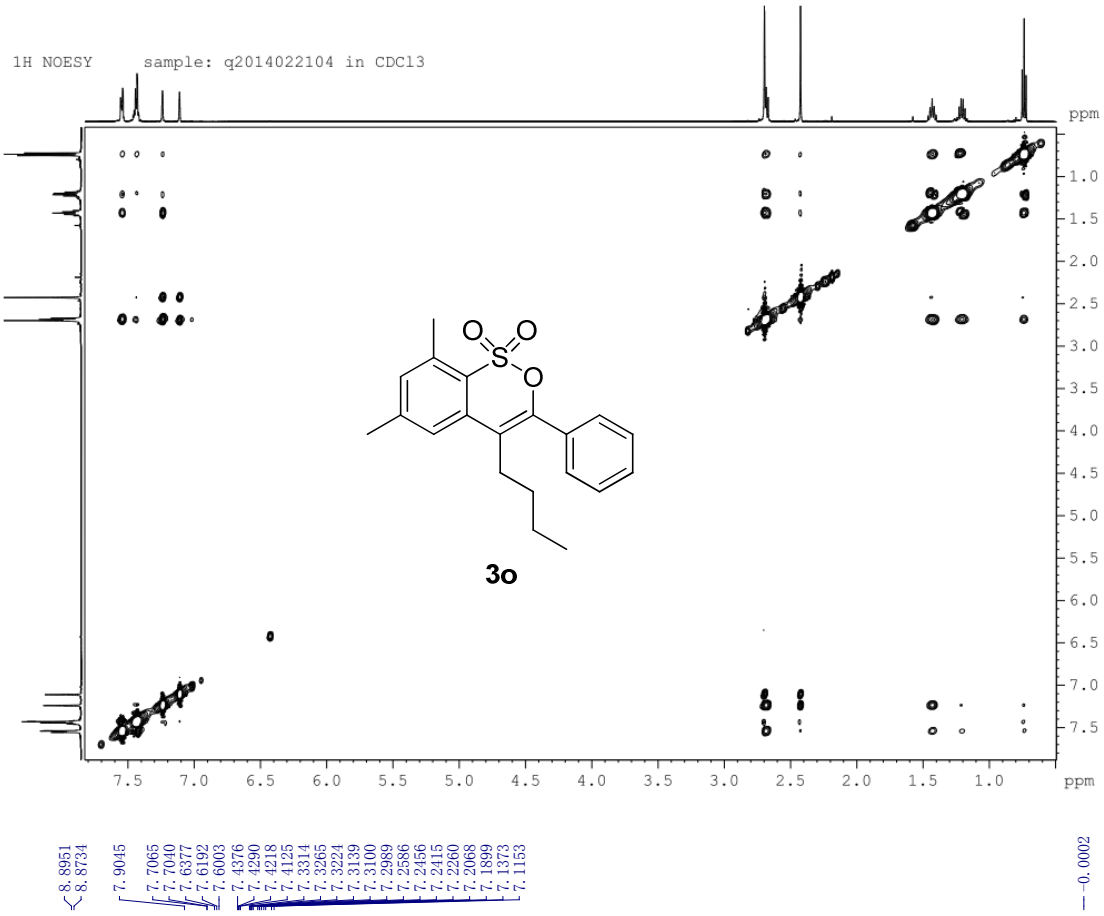

148.1733
143.2072
136.0561
132.7669
132.5000
128.5682
124.2890
118.4084
77.5174
77.1997
76.8823
29.6675
22.3159
21.9377
20.8241
13.4975
CH3
O
S
O
O
H3C
CH3
3n
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.5333
7.4665
7.4519
7.4372
7.4256
7.4141
7.2382
7.1101
2.6964
2.6846
2.6647
2.4246
1.4686
1.4506
1.4312
1.4130
1.3936
1.2142
1.1590
0.7552
0.7369
0.7185
CH3
O
O
S
O
H3C
CH3
1.99
3.14
1.13
1.00
5.26
3.05
2.09
2.22
3.10
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)

3o


147.9114
143.2214
135.9427
132.6721
132.4646
128.5098
124.2853
118.5711
77.5176
77.2000
76.8822
31.1040
27.3396
21.9980
21.8899
20.7691
13.7550
CH3
O
O
S
O
H3C
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3o


1H NOESY
sample: q2014022104 in CDCl3
ppm
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 ppm

3o

8.8951
8.8734
7.9045
7.7065
7.7040
7.6377
7.6192
7.6003
7.4376
7.4290
7.4218
7.4125
7.3314
7.3265
7.3224
7.3139
7.3100
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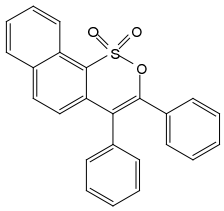
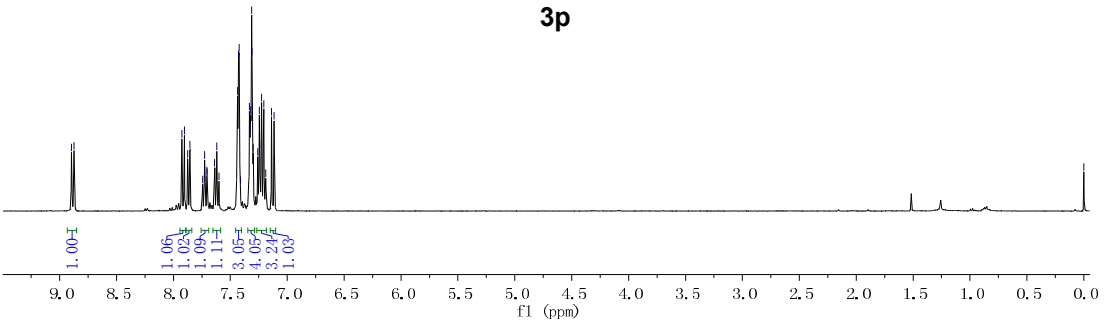
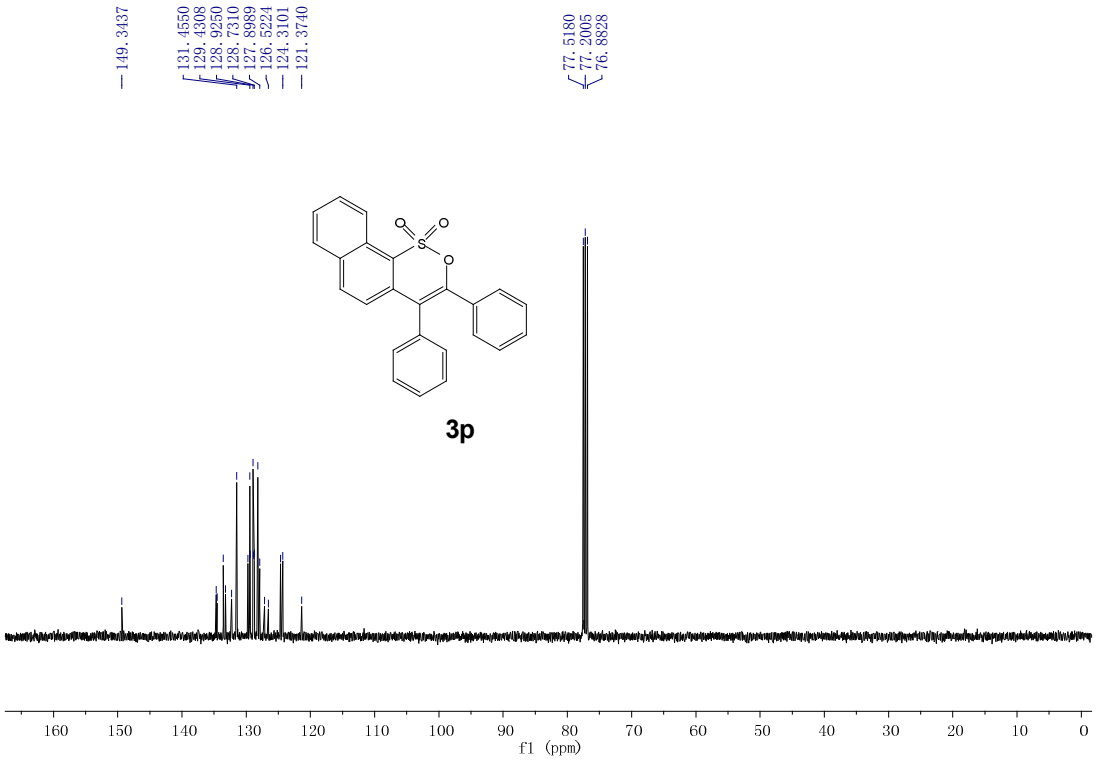
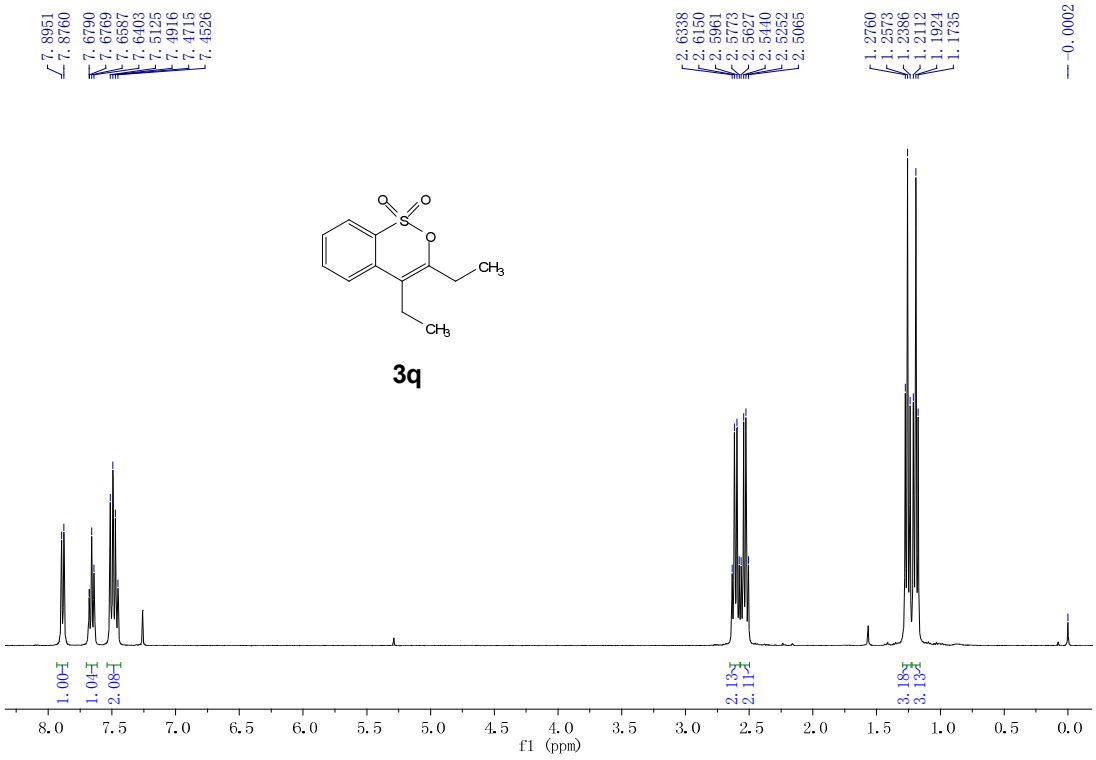
7.2586
7.2456
7.2415
7.2260
7.2068
7.1899
7.1373
7.1153
0.0002

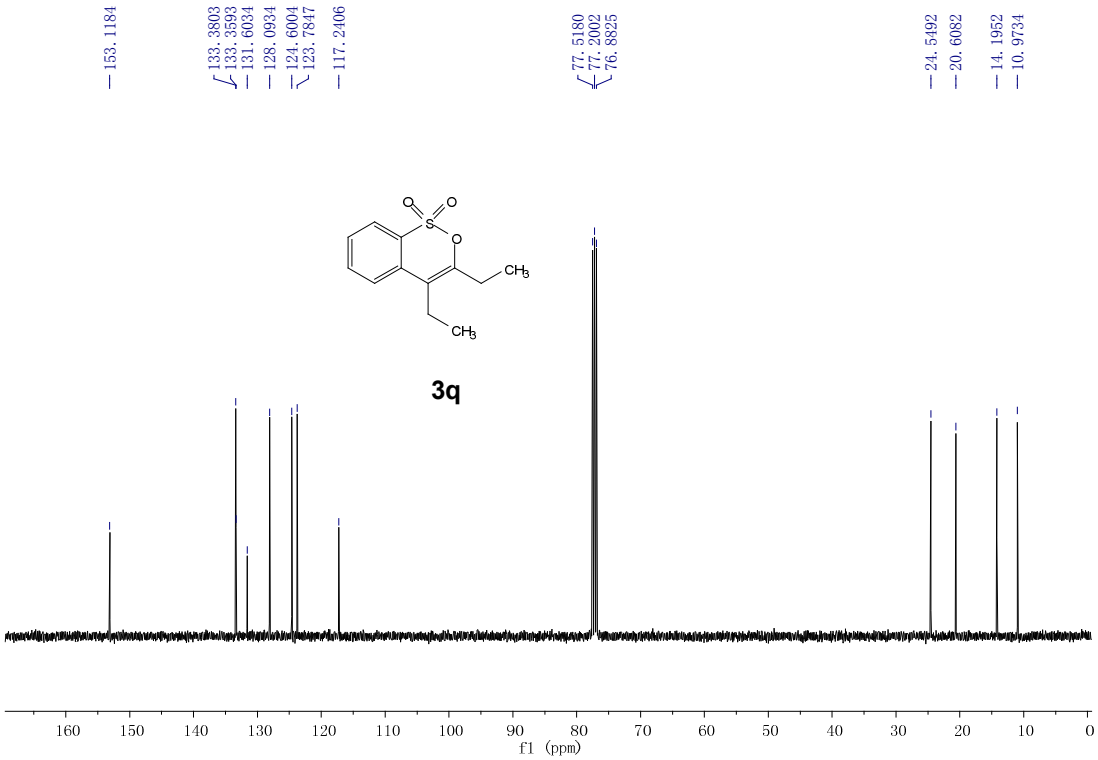


3p


1.00
1.06
1.02
1.09
1.11
3.05
4.05
3.24
1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.3437
131.4550
129.4308
128.9250
128.7310
127.8989
126.5224
124.3101
121.3740
77.5180
77.2005
76.8828
3p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.8951
7.8760
7.6790
7.6769
7.6587
7.6403
7.5125
7.4916
7.4715
7.4526
2.6338
2.6150
2.5961
2.5773
2.5627
2.5440
2.5252
2.5065
1.2760
1.2573
1.2386
1.2112
1.1924
1.1735
0.0002
CH3
CH3
3q
1.00
1.04
2.08
2.13
2.11
3.18
3.13
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)


153.1184
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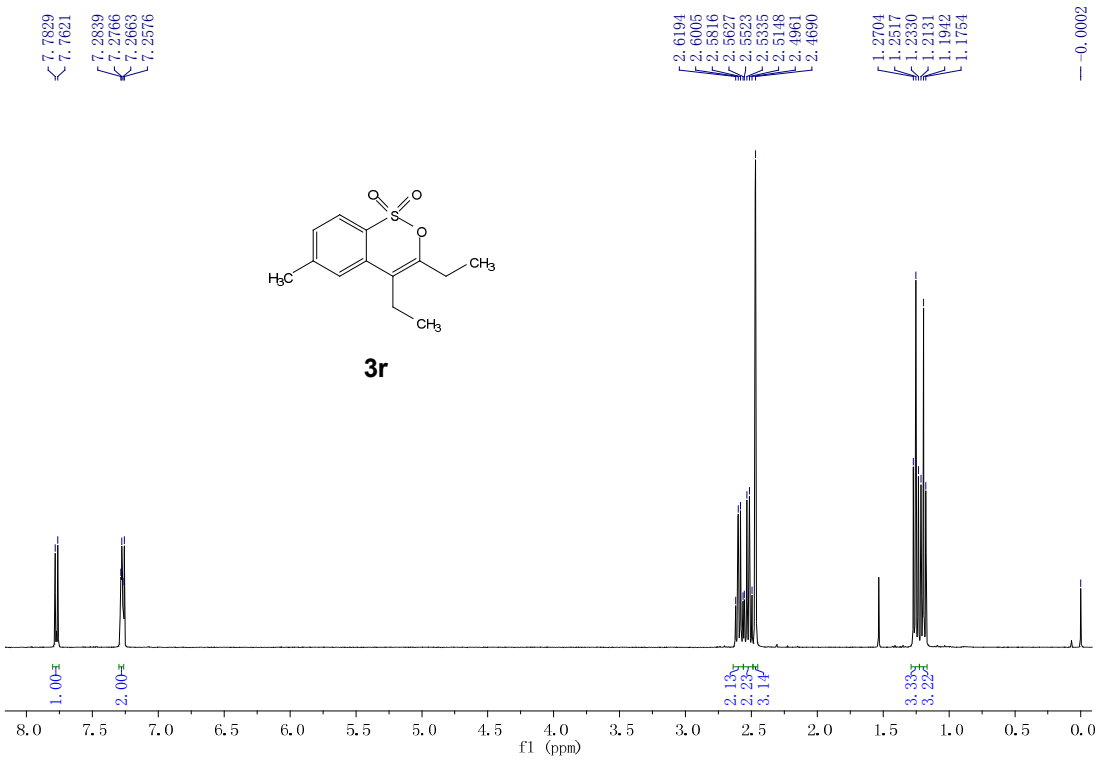
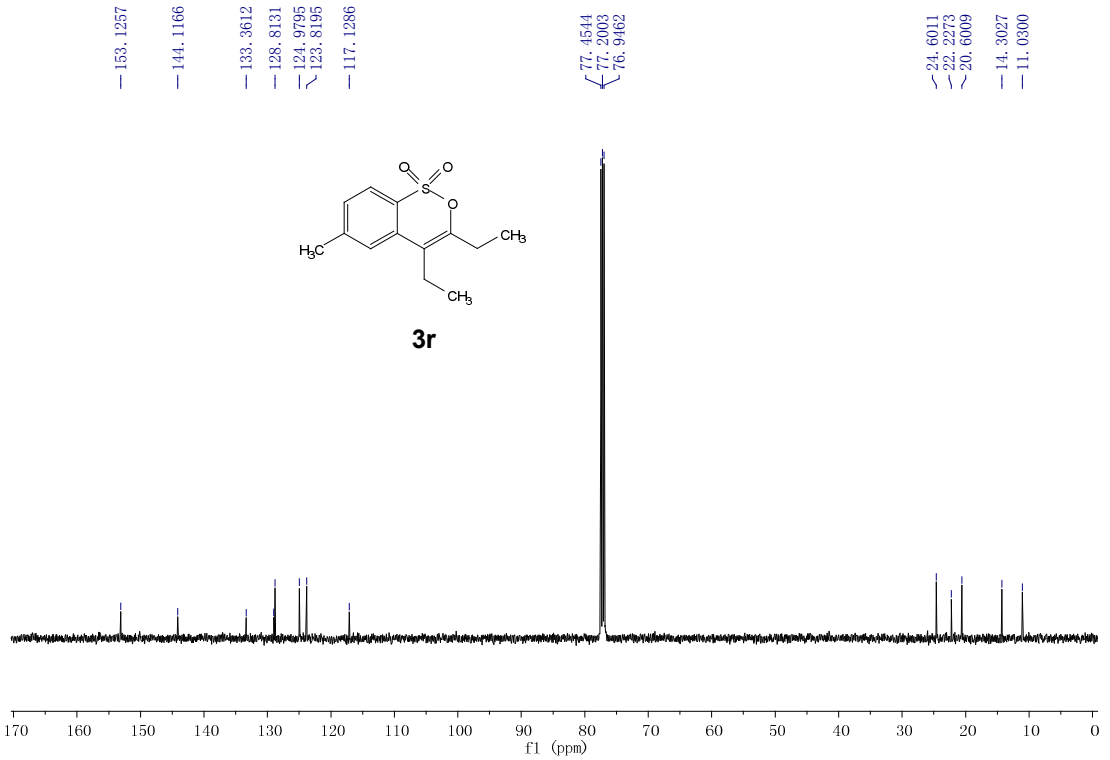
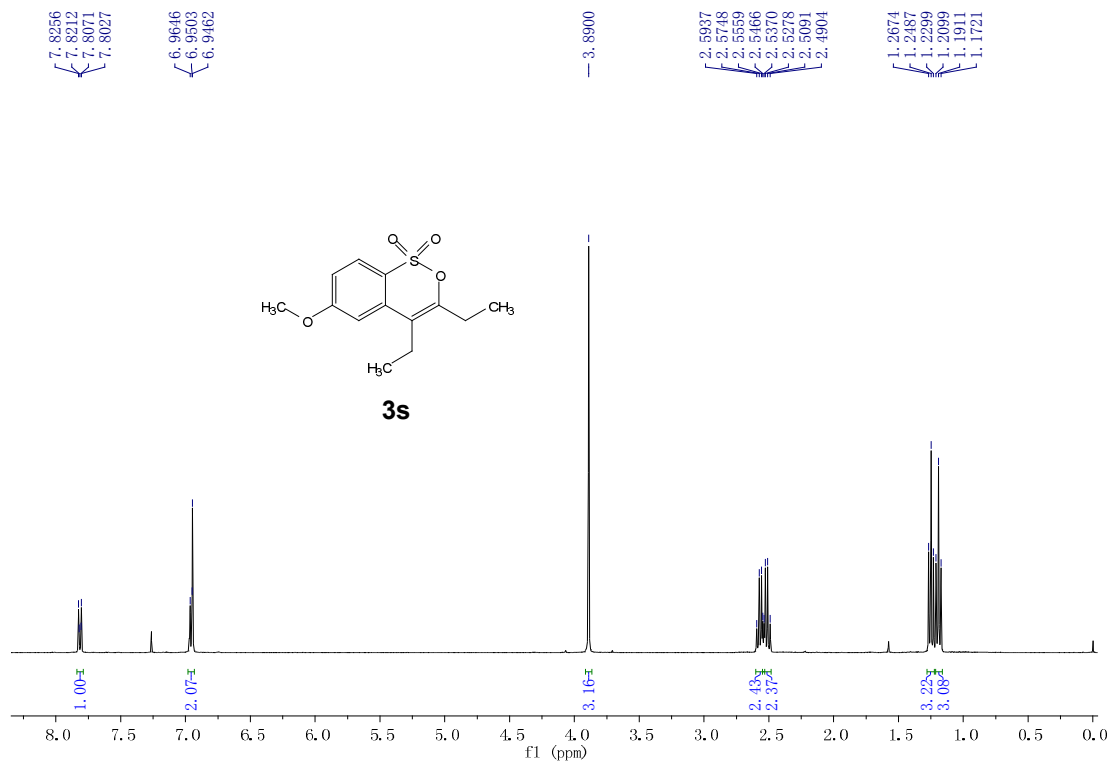
133.3593
131.6034
128.0934
124.6004
123.7847
117.2406
77.5180
77.2002
76.8825
24.5492
20.6082
14.1952
10.9734
3q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7829
7.7621
7.2839
7.2766
7.2663
7.2576
2.6194
2.6005
2.5816
2.5627
2.5523
2.5335
2.5148
2.4961
2.4690
1.2704
1.2517
1.2330
1.2131
1.1942
1.1754
-0.0002
3r
1.00
2.00
2.13
2.23
3.14
3.33
3.22
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)


153.1257
144.1166
133.3612
128.8131
124.9795
123.8195
117.1286
77.4544
77.2003
76.9462
24.6011
22.2273
20.6009
14.3027
11.0300
3r
f1 (ppm)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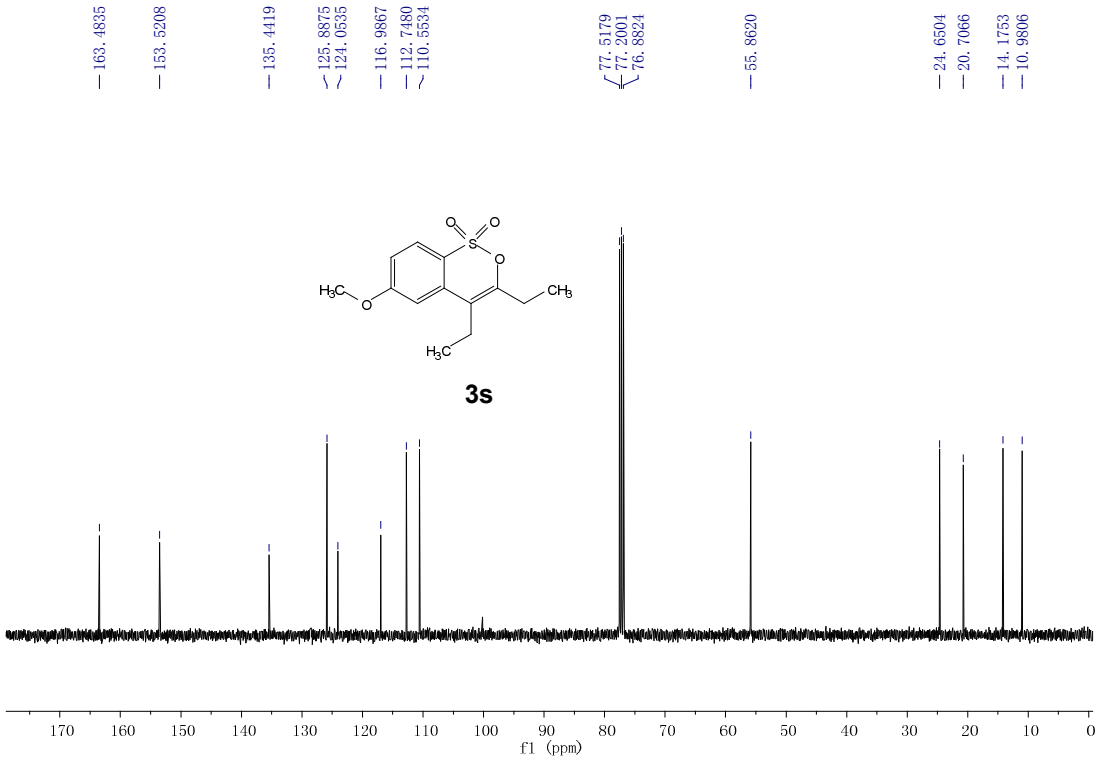
7.8071
7.8027
6.9646
6.9503
6.9462
3.8900
2.5937
2.5748
2.5559
2.5466
2.5370
2.5278
2.5091
2.4904
1.2674
1.2487
1.2299
1.2099
1.1911
1.1721
3s
1.00
2.07
3.16
2.43
2.37
3.22
3.08
f1 (ppm)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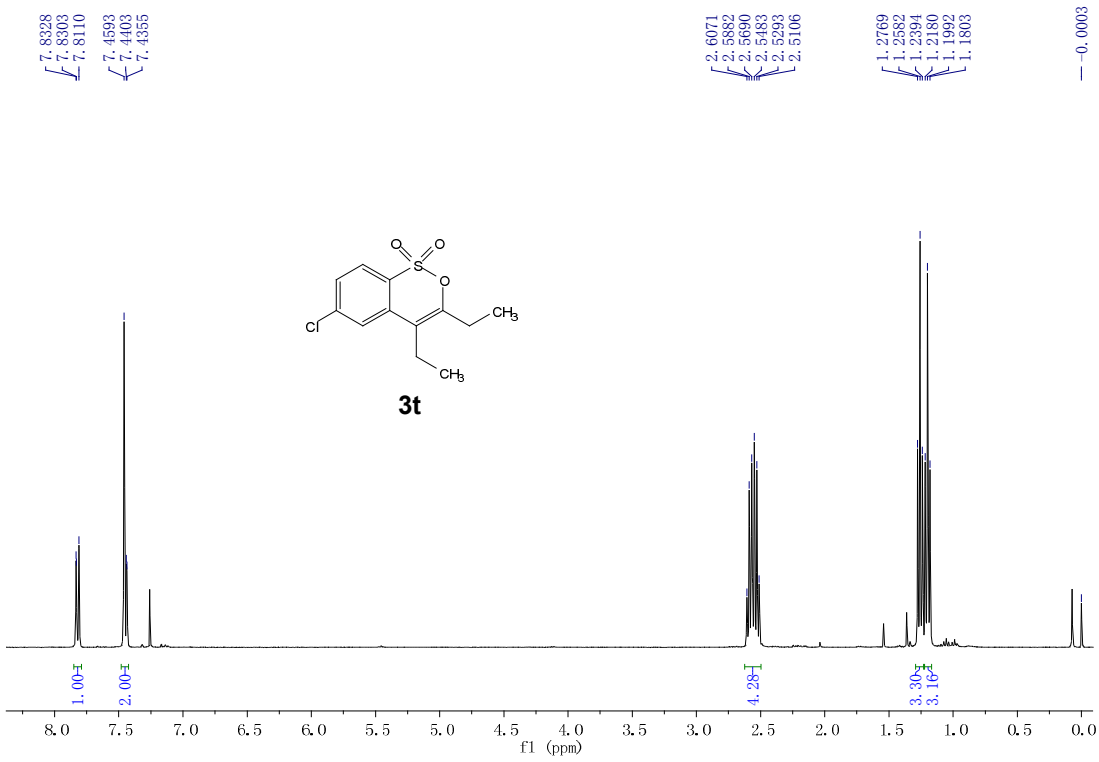
153.5208
135.4419
125.8875
124.0535
116.9867
112.7480
110.5534
77.5179
77.2001
76.8824
55.8620
24.6504
20.7066
14.1753
10.9806
3s
f1 (ppm)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7.8110
7.4593
7.4403
7.4355
2.6071
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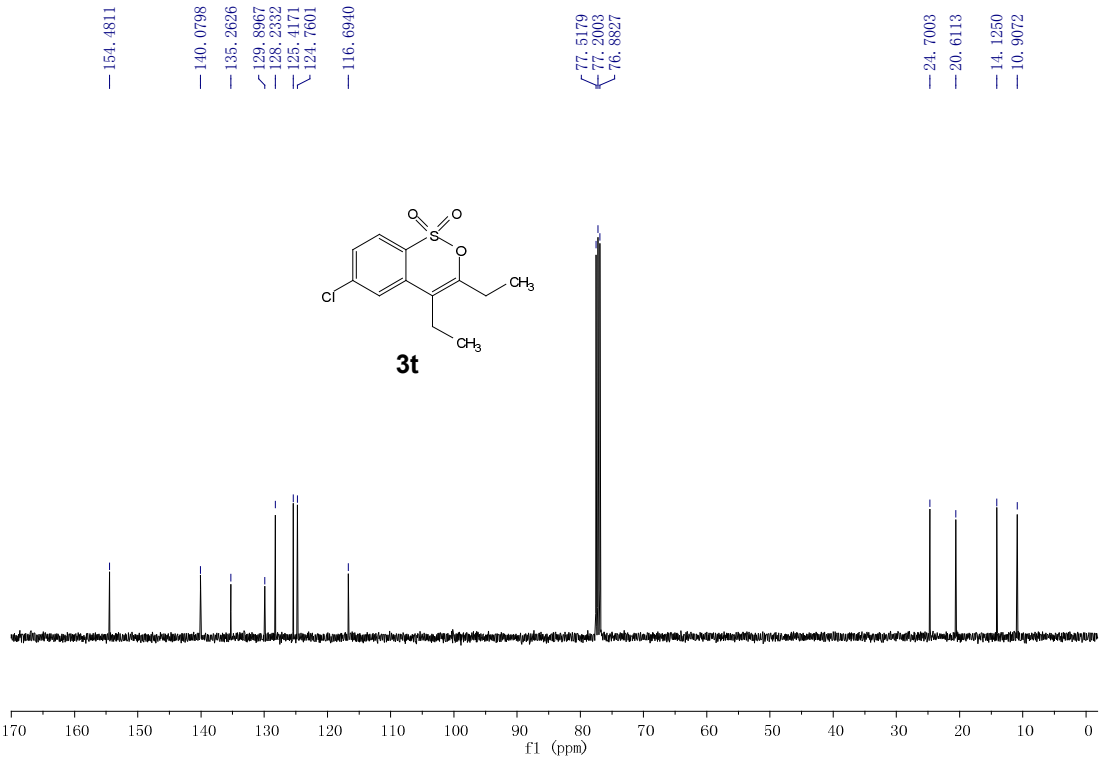
2.5690
2.5483
2.5293
2.5106
1.2769
1.2582
1.2394
1.2180
1.1992
1.1803
0.0003
1.00
2.00
4.28
3.30
3.16
3t
f1 (ppm)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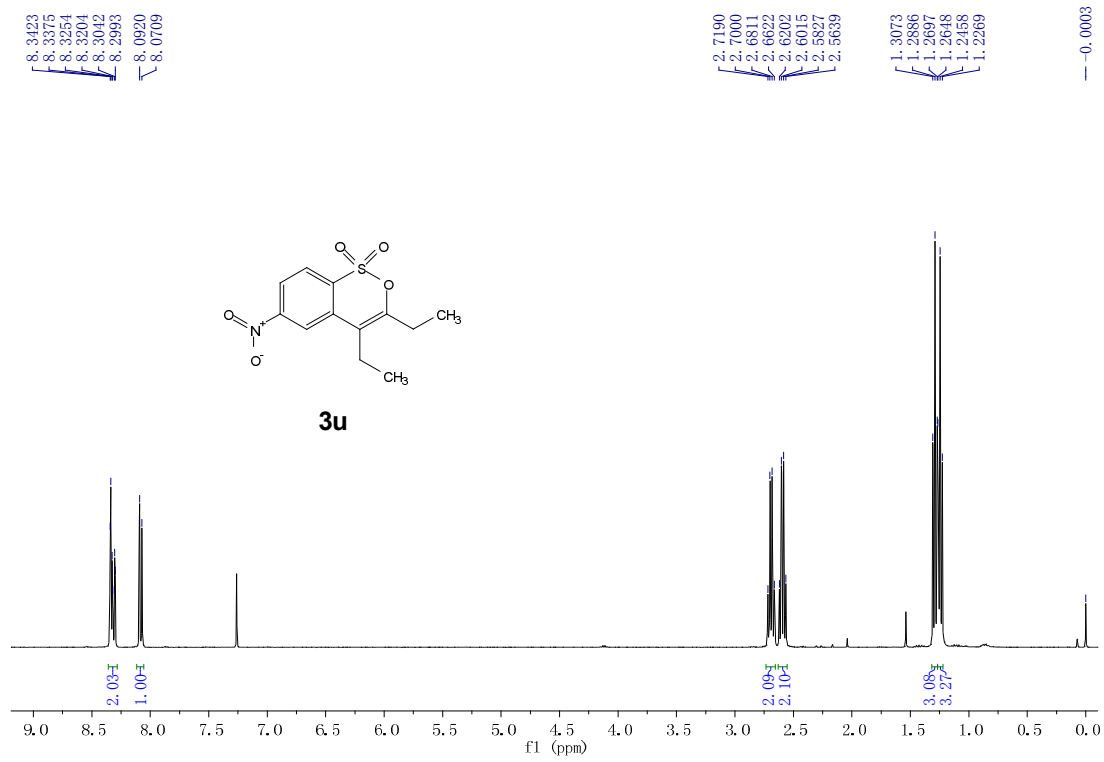
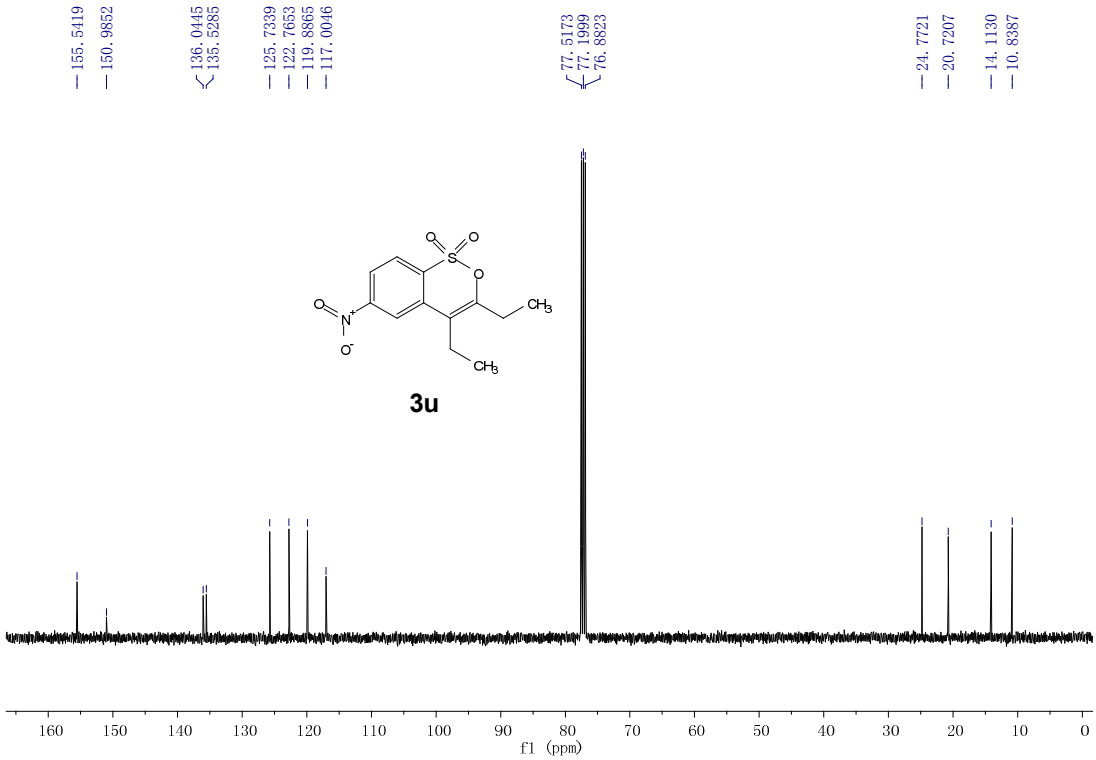
140.0798
135.2626
129.8967
128.2332
125.4171
124.7601
116.6940
77.5179
77.2003
76.8827
24.7003
20.6113
14.1250
10.9072
Cl
CH3
CH3
3t
f1 (ppm)


8.3423
8.3375
8.3254
8.3204
8.3042
8.2993
8.0920
8.0709
2.7190
2.7000
2.6811
2.6622
2.6202
2.6015
2.5827
2.5639
1.3073
1.2886
1.2697
1.2648
1.2458
1.2269
-0.0003
O
N+
O-
CH3
CH3
3u
2.03
1.00
2.09
2.10
3.08
3.27
f1 (ppm)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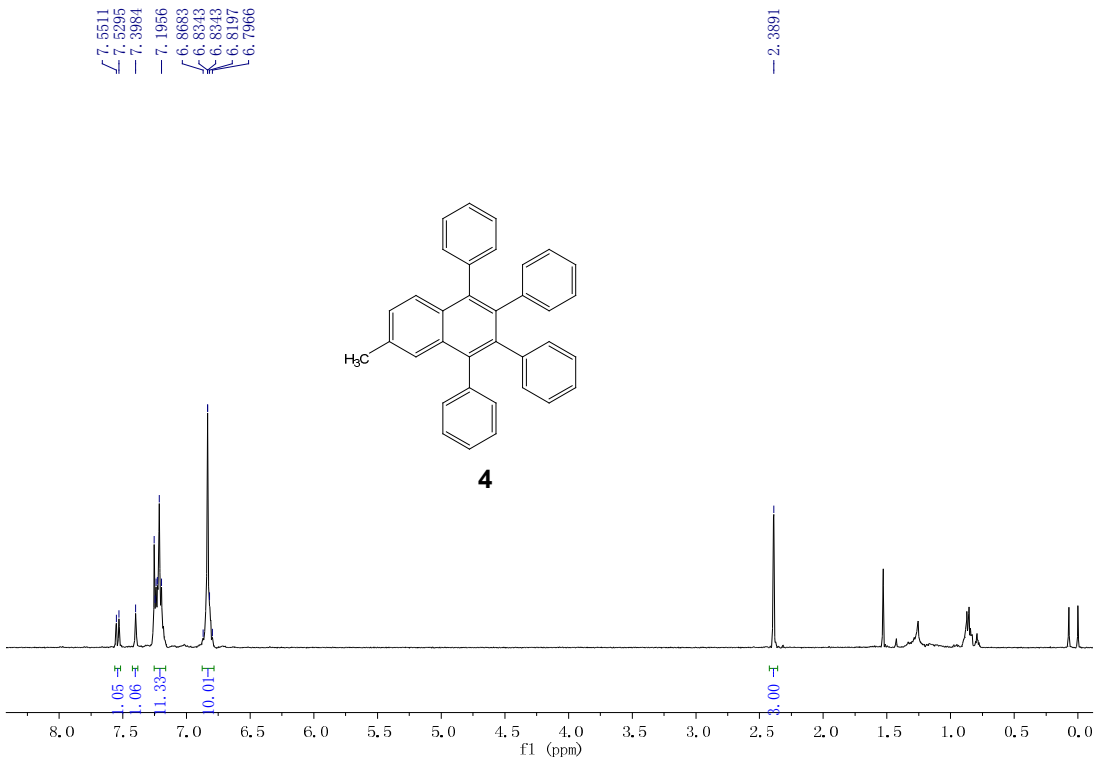
150.9852
136.0445
135.5285
125.7339
122.7653
119.8865
117.0046
77.5173
77.1999
76.8823
24.7721
20.7207
14.1130
10.8387
3u
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.3984
7.1956
6.8683
6.8343
6.8343
6.8197
6.7966
2.3891
4
1.05
1.06
11.33
10.01
3.00
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)