Electronic Supplementary Material (ESI) for Chemical Science.


# Electrochemically-promoted Synthesis of Benzo[*b*]thiophene-1,1-dioxides Via Strained Quaternary Spirocyclization

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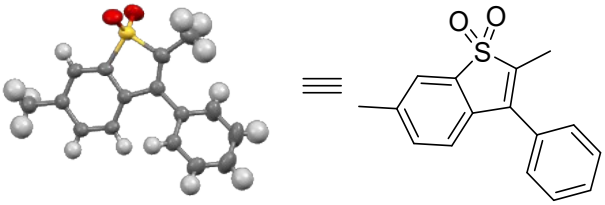
**General methods**

Unless noted, all commercial reagents and solvents were used without further purification. NMR spectra were recorded in $CDCl_3$ on 400 MHz or 500 MHz spectrometers. $^1H$ NMR chemical shifts ($\delta$) are reported in parts per million relative to tetramethylsilane (0 ppm) or residual $CHCl_3$ (7.26 ppm). $^{13}C$ NMR chemical shifts are reported relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Mass spectra were obtained on an Ultima Global spectrometer with an ESI source. The living cell imaging was measured by Nikon C2 plus. Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China). DC power supply DPS-305CF was used for all experiments.

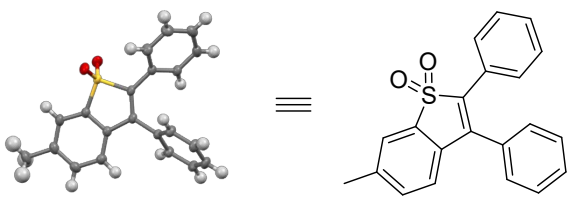

**Molecular structure and crystallographic data**



CCDC 2044891 **3aa**

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

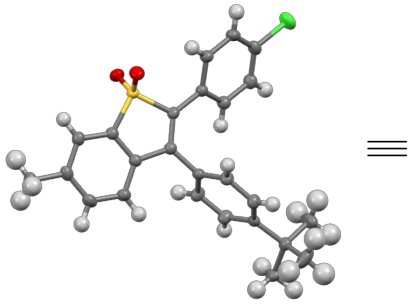
| | |
|---|---|
| Empirical formula | $C_{16}H_{14}O_2S$ |
| Formula weight | 270.33 |
| Temperature | 298(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 8.2022(8) A alpha = 75.696(2) deg. |
| | b = 10.5431(9) A beta = 88.800(3) deg. |
| | c = 18.8492(16) A gamma = 67.5160(10) deg. |
| Volume | 1454.5(2) A^3 |
| Z, Calculated density | 4, 1.235 Mg/m^3 |
| Absorption coefficient | 0.217 mm^-1 |
| F(000) | 568 |
| Crystal size | 0.45 x 0.34 x 0.30 mm |
| Theta range for data collection | 2.16 to 25.02 deg. |
| Limiting indices | -9<=h<=8, -12<=k<=12, -22<=l<=21 |
| Reflections collected / unique | 7332 / 5047 [R(int) = 0.0342] |
| Completeness to theta = 25.02 | 97.9 % |
| Absorption correction | Semi-empirical from equiv.alents |
| Max. and min. transmission | 0.9377 and 0.9086 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 5047 / 0 / 348 |
| Goodness-of-fit on F^2 | 1.030 |
| Final R indices [I>2sigma(I)] | R1 = 0.0539, wR2 = 0.1271 |
| R indices (all data) | R1 = 0.0840, wR2 = 0.1390 |
| Extinction coefficient | 0.032(2) |
| Largest diff. peak and hole | 0.260 and -0.346 e.A^-3 |



CCDC 2044867 **3Aa**

**Table 2** Crystal data and structure refinement for **3Aa**

| | |
|---|---|
| Empirical formula | $C_{21}H_{16}O_2S$ |
| Formula weight | 332.40 |
| Temperature/K | 170.01(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 8.7021(2) |
| b/Å | 10.4858(2) |
| c/Å | 18.6175(4) |
| α/° | 90 |
| β/° | 94.841(2) |
| γ/° | 90 |
| Volume/Å3 | 1692.76(6) |
| Z | 4 |
| ρcalcg/cm3 | 1.304 |
| μ/mm-1 | 0.200 |
| F(000) | 696.0 |
| Crystal size/mm3 | 0.33 × 0.31 × 0.25 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.392 to 62.1 |
| Index ranges | -9 ≤ h ≤ 12, -10 ≤ k ≤ 14, -26 ≤ l ≤ 26 |
| Reflections collected | 13579 |
| Independent reflections | 4586 [Rint = 0.0134, Rsigma = 0.0155] |
| Data/restraints/parameters | 4586/0/218 |
| Goodness-of-fit on F2 | 1.043 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0353, wR2 = 0.0988 |
| Final R indexes [all data] | R1 = 0.0385, wR2 = 0.1009 |
| Largest diff. peak/hole / e Å-3 | 0.41/-0.34 |



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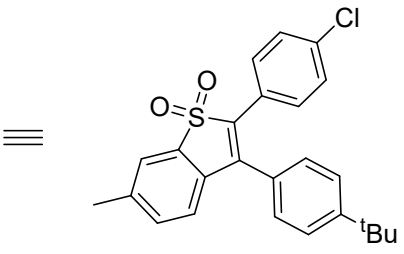



**3la'**

**Table 3** Crystal data and structure refinement for **3la'**

| | |
|---|---|
| Empirical formula | $C_{25}H_{23}ClO_2S$ |
| Formula weight | 422.94 |

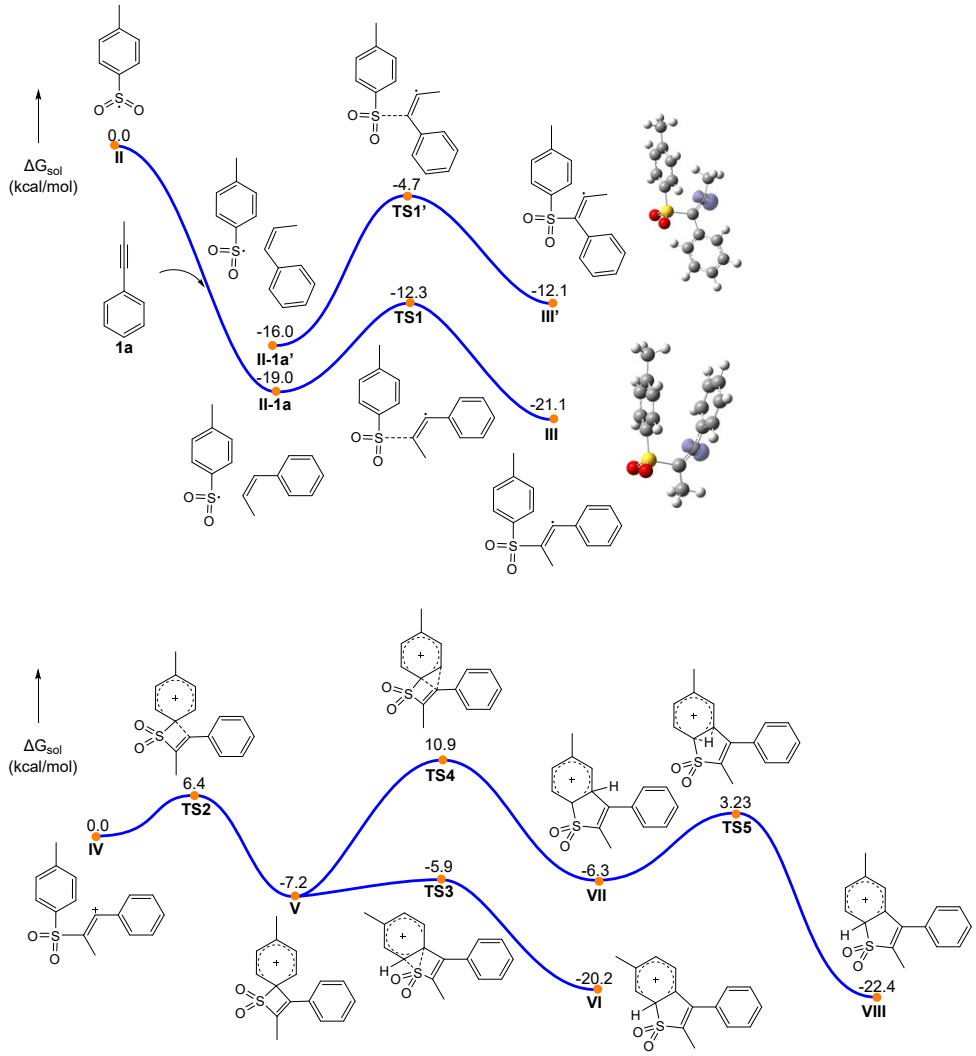
| | |
|---|---|
| Temperature/K | 170 |
| Bond precision/Å | 0.0019 |
| Wavelength | 1.54184 |
| Space group | P -1 |
| Hall group | -P 1 |
| a/Å | 9.2866(3) |
| b/Å | 10.4269(3) |
| c/Å | 11.1292(3) |
| α/° | 87.053(2) |
| β/° | 81.996(2) |
| γ/° | 86.100(2) |
| Volume/Å$^3$ | 1063.72(5) |
| Z | 2 |
| Dx,g cm$^{-3}$ | 1.321 |
| Mu (mm$^{-1}$) | 2.647 |
| F(000) | 444.0 |
| F000’ | 446.46 |
| h,k,lmax | 11,13,14 |
| Nref | 4501 |
| Tmin,Tmax | 0.652,0.728 |
| Tmin’ | 0.518 |
| Data completeness | 0.954 |
| Theta(max) | 77.034 |
| R(reflections) | 0.0343( 4146) |
| wR2(reflections) | 0.0969( 4296) |
| S | 1.077 |
| Npar | 266 |
| Correction method | # Reported T |
| AbsCorr | MULTI-SCAN |
| Limits | Tmin=0.707 Tmax=1.000 |

**DFT calculations**

**Computational studies Computational details:**

All calculations were performed using Gaussian 16, Revision A.03 package.[1] M06-2X density functional and 6-311G(d) basis set was employed for geometry optimizations and frequency calculations of reactants, intermediates, transition states and products. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on all the TSs. In order to evaluate the solvent effect of Dichloromethane (DCM), SMD method[2] was applied. And it was computed with M06-2X density functional and 6-311++G(d,p) basis set. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K. All the 3D molecular structures of the

species were generated by using the CYL view program.[3]




**Cartesian coordinates of the optimized structures:**

**II**

E = -819.436382 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -2.85639700 | 1.00010600 | 0.00622300 |
| C | -1.46900600 | 0.98541500 | 0.04553700 |
| C | -0.80026400 | 2.20311700 | 0.08259300 |
| C | -1.46778200 | 3.42164000 | 0.04737000 |
| C | -2.85508800 | 3.40841100 | 0.00802900 |
| C | -3.56633100 | 2.20460600 | -0.01297600 |
| H | -3.39719200 | 0.05983300 | -0.01123500 |
| H | -0.92027300 | 0.05143900 | 0.06283700 |
| H | -0.91806700 | 4.35501000 | 0.06607300 |
| H | -3.39497800 | 4.34924300 | -0.00802800 |
| S | 0.99114100 | 2.20223700 | 0.07964700 |
| O | 1.45100100 | 3.47941800 | 0.64708700 |

| | | | |
|---|---|---|---|
| O | 1.44976600 | 0.92370900 | 0.64503500 |
| C | -5.06917300 | 2.20586900 | -0.02784300 |
| H | -5.46163600 | 1.31660400 | -0.52294900 |
| H | -5.45628400 | 2.21306000 | 0.99543500 |
| H | -5.45974100 | 3.08960500 | -0.53432600 |

**1aa**

E = -347.652446 a.u.

0 1

| | | | |
|---|---|---|---|
| C | -1.42183500 | 0.69012700 | -0.00018100 |
| C | -0.02923600 | 0.69169100 | 0.00163100 |
| C | 0.66918300 | 1.89255700 | 0.00145700 |
| C | -0.02301200 | 3.11094700 | -0.00050700 |
| C | -1.42432200 | 3.10230100 | -0.00222400 |
| C | -2.11586200 | 1.89748100 | -0.00207400 |
| H | -1.96449300 | -0.24847000 | -0.00006100 |
| H | 0.51596200 | -0.24549300 | 0.00317900 |
| H | 1.75333900 | 1.89663300 | 0.00287900 |
| H | -1.96216400 | 4.04360400 | -0.00368100 |
| H | -3.20015400 | 1.90153100 | -0.00344300 |
| C | 0.69512200 | 4.35427400 | -0.00091200 |
| C | 1.29665800 | 5.39885600 | -0.00143200 |
| C | 2.02649900 | 6.66308600 | -0.00192500 |
| H | 2.49075900 | 6.84186200 | 0.97018800 |
| H | 2.81395200 | 6.65380200 | -0.75823700 |
| H | 1.35488600 | 7.49601700 | -0.21770900 |

**II-1aa**

E = -1167.101686 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -1.26249900 | 0.81994200 | 2.79614600 |
| C | -0.96622700 | 2.16543300 | 2.63702300 |
| C | -1.95712900 | 3.00186200 | 2.13505900 |
| C | -3.20837000 | 2.53060900 | 1.76133700 |
| C | -3.47898600 | 1.17761200 | 1.92519400 |
| C | -2.51348100 | 0.30700200 | 2.43472600 |
| H | -0.50441200 | 0.15127900 | 3.19113900 |
| H | 0.00767500 | 2.56005100 | 2.90169200 |
| H | -3.95426400 | 3.20209600 | 1.35218800 |
| H | -4.45031500 | 0.79115700 | 1.63472200 |
| S | -1.55181200 | 4.71106700 | 1.80243500 |
| O | -2.79626100 | 5.49905900 | 1.85432100 |

| | | | |
|---|---|---|---|
| O | -0.40469100 | 5.08542300 | 2.64643200 |
| C | -2.80516500 | -1.15933700 | 2.58732000 |
| H | -1.92650000 | -1.76142700 | 2.34771200 |
| H | -3.08708600 | -1.38831600 | 3.61942200 |
| H | -3.62729300 | -1.46913200 | 1.94041600 |
| C | -3.14547400 | -0.22809900 | -1.44894400 |
| C | -3.46089000 | 1.08856900 | -1.77894000 |
| C | -2.53952800 | 2.10377200 | -1.55811300 |
| C | -1.28647700 | 1.81003100 | -1.00137600 |
| C | -0.97418800 | 0.48412900 | -0.67487400 |
| C | -1.90092100 | -0.52702100 | -0.90014900 |
| H | -3.86663600 | -1.01920000 | -1.62212900 |
| H | -4.42787300 | 1.32519600 | -2.20868100 |
| H | -2.78190900 | 3.13090900 | -1.80814300 |
| H | -0.00664000 | 0.25669200 | -0.24154200 |
| H | -1.65132600 | -1.55088300 | -0.64396200 |
| C | -0.34673100 | 2.86332700 | -0.74460600 |
| C | 0.42470800 | 3.75875100 | -0.50095500 |
| C | 1.35053600 | 4.84630600 | -0.19944500 |
| H | 1.70945800 | 4.77175300 | 0.82882600 |
| H | 2.21201700 | 4.81688300 | -0.86971900 |
| H | 0.85779800 | 5.81369900 | -0.31849500 |

**TS1**

E = -1167.090770 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -1.42475700 | 0.59806400 | 2.95193700 |
| C | -0.87876700 | 1.86659800 | 2.78995700 |
| C | -1.65010100 | 2.85073400 | 2.18601800 |
| C | -2.93618900 | 2.59262200 | 1.72162800 |
| C | -3.45977300 | 1.31870900 | 1.88621800 |
| C | -2.71163300 | 0.30497200 | 2.49534200 |
| H | -0.83623800 | -0.17862800 | 3.42900900 |
| H | 0.12509900 | 2.09038600 | 3.13250700 |
| H | -3.51204700 | 3.37453400 | 1.23926000 |
| H | -4.46051800 | 1.10153000 | 1.52568300 |
| S | -0.90512400 | 4.42497600 | 1.81097800 |
| O | -1.97332100 | 5.43419400 | 1.72698800 |
| O | 0.20970200 | 4.64690400 | 2.74708900 |
| C | -3.29194900 | -1.07469400 | 2.63492200 |
| H | -2.56414700 | -1.77481000 | 3.04636200 |
| H | -4.16432800 | -1.06341600 | 3.29373400 |
| H | -3.62392100 | -1.45200500 | 1.66393700 |

| | | | |
|---|---|---|---|
| C | -2.83777200 | -0.41456500 | -1.43933300 |
| C | -3.29820300 | 0.82498400 | -1.88563900 |
| C | -2.54287800 | 1.96706800 | -1.67518600 |
| C | -1.30473900 | 1.87952500 | -1.00851500 |
| C | -0.83873700 | 0.62324300 | -0.57676900 |
| C | -1.60757400 | -0.51076600 | -0.78922100 |
| H | -3.43498900 | -1.30471600 | -1.60217800 |
| H | -4.25230300 | 0.89849700 | -2.39498500 |
| H | -2.89896600 | 2.93551300 | -2.00761100 |
| H | 0.11408400 | 0.55745400 | -0.06417500 |
| H | -1.25025000 | -1.47399600 | -0.44213500 |
| C | -0.55966100 | 3.04740800 | -0.73092600 |
| C | -0.02488500 | 4.06370400 | -0.26900100 |
| C | 0.91027100 | 5.20341800 | -0.35739900 |
| H | 1.64630700 | 5.15697500 | 0.44716800 |
| H | 1.42859500 | 5.17990800 | -1.31638500 |
| H | 0.36982200 | 6.14886600 | -0.27224100 |

**III**

E = -1167.102856 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -2.31041700 | 0.68297500 | 3.74894300 |
| C | -1.11388500 | 1.22744800 | 3.29672600 |
| C | -1.12409500 | 2.51085900 | 2.76659400 |
| C | -2.29516000 | 3.25663300 | 2.67384200 |
| C | -3.48036100 | 2.69176400 | 3.11948200 |
| C | -3.50593200 | 1.39879600 | 3.65548400 |
| H | -2.31619600 | -0.31692200 | 4.16980600 |
| H | -0.18810200 | 0.66651000 | 3.35677900 |
| H | -2.27680500 | 4.25538100 | 2.25231100 |
| H | -4.40401800 | 3.25698300 | 3.04370400 |
| S | 0.37119700 | 3.16230700 | 2.06963000 |
| O | 0.30416300 | 4.62304600 | 2.08668200 |
| O | 1.51440900 | 2.50671200 | 2.70418900 |
| C | -4.80934700 | 0.79952800 | 4.10442300 |
| H | -4.67280900 | -0.21043500 | 4.49179800 |
| H | -5.26810300 | 1.40882800 | 4.88715000 |
| H | -5.51640000 | 0.75589900 | 3.27139300 |
| C | -4.88732500 | 1.33847400 | -0.22568200 |
| C | -4.44080100 | 2.60082300 | -0.62521500 |
| C | -3.09033700 | 2.89711100 | -0.63090900 |
| C | -2.14687700 | 1.92030600 | -0.22485300 |
| C | -2.60917400 | 0.63674900 | 0.15618800 |

| | | | |
|---|---|---|---|
| C | -3.96537600 | 0.36263700 | 0.15987600 |
| H | -5.94793300 | 1.11484500 | -0.21980400 |
| H | -5.15580400 | 3.35718300 | -0.92873000 |
| H | -2.73882800 | 3.87834200 | -0.92912100 |
| H | -1.89062300 | -0.11501100 | 0.46186200 |
| H | -4.31172100 | -0.61717200 | 0.47005500 |
| C | -0.78725100 | 2.22647900 | -0.18268000 |
| C | 0.34279100 | 2.61136000 | 0.32001700 |
| C | 1.69980600 | 2.72042600 | -0.31969000 |
| H | 2.40795200 | 2.05460300 | 0.17641000 |
| H | 1.63039500 | 2.45259200 | -1.37290900 |
| H | 2.07854500 | 3.74241900 | -0.23956700 |

**II-1aa'**

E = -1167.098468 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -1.38187800 | 0.19937200 | 2.63425700 |
| C | -0.51354400 | 1.28437300 | 2.67966000 |
| C | -1.04622100 | 2.55910000 | 2.54282300 |
| C | -2.40186700 | 2.77911400 | 2.32502300 |
| C | -3.24777400 | 1.68025800 | 2.28500400 |
| C | -2.75351600 | 0.37985200 | 2.43910000 |
| H | -0.98501600 | -0.80339700 | 2.75212100 |
| H | 0.54970800 | 1.14241000 | 2.83328400 |
| H | -2.78568000 | 3.78515200 | 2.20193500 |
| H | -4.31062900 | 1.83316600 | 2.12789600 |
| S | 0.06314400 | 3.96541300 | 2.52836100 |
| O | -0.69804700 | 5.15137500 | 2.94965500 |
| O | 1.29353600 | 3.58134100 | 3.24062200 |
| C | -3.69019100 | -0.79571000 | 2.41571200 |
| H | -4.47541900 | -0.65950400 | 1.66990000 |
| H | -3.15918300 | -1.72310700 | 2.19812100 |
| H | -4.17840800 | -0.91043900 | 3.38791400 |
| C | -0.89504900 | 3.24971400 | -0.74458800 |
| C | -0.31164200 | 4.29653600 | -0.60515000 |
| C | -1.59582900 | 1.98065800 | -0.90931700 |
| H | -2.67677100 | 2.13294900 | -0.90110700 |
| H | -1.32240800 | 1.50990700 | -1.85611200 |
| H | -1.34016900 | 1.29373600 | -0.09838800 |
| C | 0.38724400 | 5.53394700 | -0.40141100 |
| C | -0.27338300 | 6.75885400 | -0.55714200 |
| C | 1.73182600 | 5.52279200 | -0.00453300 |
| C | 0.40172200 | 7.94943500 | -0.31963700 |

| | | | |
|---|---|---|---|
| H | -1.31478000 | 6.76778800 | -0.85787100 |
| C | 2.39951200 | 6.71794200 | 0.23188900 |
| H | 2.24532700 | 4.57469300 | 0.11377600 |
| C | 1.73680800 | 7.93271300 | 0.07630300 |
| H | -0.11773100 | 8.89345600 | -0.43991500 |
| H | 3.43846000 | 6.69964600 | 0.54091100 |
| H | 2.25893200 | 8.86401400 | 0.26470200 |

**TS1'**

E = -1167.080517 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -1.38146000 | 0.14566100 | 2.50504900 |
| C | -0.60364400 | 1.29695000 | 2.52279300 |
| C | -1.24095000 | 2.53149400 | 2.49488900 |
| C | -2.62514500 | 2.64018600 | 2.42481500 |
| C | -3.38455900 | 1.47754500 | 2.40607700 |
| C | -2.77657400 | 0.21860700 | 2.44514300 |
| H | -0.89789600 | -0.82524500 | 2.53610500 |
| H | 0.47795000 | 1.24018200 | 2.56456600 |
| H | -3.09807700 | 3.61542000 | 2.39267500 |
| H | -4.46643400 | 1.54733900 | 2.35902900 |
| S | -0.25680400 | 4.01153700 | 2.36561500 |
| O | -1.01426500 | 5.12456900 | 2.95500000 |
| O | 1.08347100 | 3.71077600 | 2.89164700 |
| C | -3.60908500 | -1.03347500 | 2.45547200 |
| H | -4.55506400 | -0.88548800 | 1.93254300 |
| H | -3.07915500 | -1.86609300 | 1.99055300 |
| H | -3.84220900 | -1.32357600 | 3.48426800 |
| C | -0.88082200 | 3.43821000 | -0.39759700 |
| C | -0.22041700 | 4.31630200 | 0.19116400 |
| C | -1.67555900 | 2.31203600 | -0.85300900 |
| H | -2.73205200 | 2.58426500 | -0.89886000 |
| H | -1.35697600 | 1.99553900 | -1.85024700 |
| H | -1.56408800 | 1.45747600 | -0.17647300 |
| C | 0.52802600 | 5.56353400 | 0.03065100 |
| C | -0.10733000 | 6.68371600 | -0.51419600 |
| C | 1.86645800 | 5.64561900 | 0.42616300 |
| C | 0.59717900 | 7.87069300 | -0.67319500 |
| H | -1.14859500 | 6.61597300 | -0.80813400 |
| C | 2.56452100 | 6.83662400 | 0.26129500 |
| H | 2.35488300 | 4.77810500 | 0.85420500 |
| C | 1.93281500 | 7.94927900 | -0.28668700 |
| H | 0.10121900 | 8.73644100 | -1.09735700 |

| | | | |
|---|---|---|---|
| H | 3.60418100 | 6.89412000 | 0.56289100 |
| H | 2.47953800 | 8.87722900 | -0.41105300 |

**III'**

E = -1167.089402 a.u.

0 2

| | | | |
|---|---|---|---|
| C | -1.47895100 | 0.02635300 | 2.42969600 |
| C | -0.59904700 | 1.10172200 | 2.38968500 |
| C | -1.12148400 | 2.38831900 | 2.37228200 |
| C | -2.49251500 | 2.62471100 | 2.39170100 |
| C | -3.35394500 | 1.53804000 | 2.42583800 |
| C | -2.86144500 | 0.22773500 | 2.44440100 |
| H | -1.08536900 | -0.98450700 | 2.44769400 |
| H | 0.47348000 | 0.94773700 | 2.37267800 |
| H | -2.87723900 | 3.63875700 | 2.37988900 |
| H | -4.42583600 | 1.70605000 | 2.44054300 |
| S | -0.01380300 | 3.76969700 | 2.25893600 |
| O | -0.55461500 | 4.86954300 | 3.05561200 |
| O | 1.33765500 | 3.29303300 | 2.55516900 |
| C | -3.80688500 | -0.93886100 | 2.51498900 |
| H | -4.72733100 | -0.73606400 | 1.96507600 |
| H | -3.35115000 | -1.84453800 | 2.11296000 |
| H | -4.08220700 | -1.13849900 | 3.55479400 |
| C | -0.74864900 | 3.56151400 | -0.37580100 |
| C | -0.10053000 | 4.27642500 | 0.50191500 |
| C | -1.54022600 | 2.41473800 | -0.80656100 |
| H | -2.60552900 | 2.65131900 | -0.73504200 |
| H | -1.32216000 | 2.17759800 | -1.85167400 |
| H | -1.34185200 | 1.51962300 | -0.20763200 |
| C | 0.55568700 | 5.58518800 | 0.22330800 |
| C | -0.10133100 | 6.51466500 | -0.58821500 |
| C | 1.81714700 | 5.89553900 | 0.73961800 |
| C | 0.49819100 | 7.73189400 | -0.88783900 |
| H | -1.08648100 | 6.27884000 | -0.97612100 |
| C | 2.40924400 | 7.11839100 | 0.44181600 |
| H | 2.34328500 | 5.17905200 | 1.35977900 |
| C | 1.75465600 | 8.03789600 | -0.37187900 |
| H | -0.02072200 | 8.44546100 | -1.51813100 |
| H | 3.38919600 | 7.34872800 | 0.84449100 |
| H | 2.22044200 | 8.98965300 | -0.60157600 |

**IV**

E = -1166.912695 a.u.

1 1

| | | | |
|---|---|---|---|
| C | 1.28656300 | -0.13477200 | 3.38733200 |
| C | 1.39696500 | 1.24956600 | 3.38430100 |
| C | 0.24244400 | 2.00036500 | 3.19360400 |
| C | -1.00966700 | 1.41625900 | 3.01480000 |
| C | -1.09251700 | 0.03347900 | 3.02319200 |
| C | 0.05062700 | -0.75875100 | 3.19474500 |
| H | 2.17478100 | -0.73897800 | 3.53519300 |
| H | 2.35785700 | 1.73346900 | 3.51840000 |
| H | -1.89140300 | 2.02918600 | 2.86612300 |
| H | -2.05701800 | -0.44446500 | 2.88694700 |
| S | 0.40983400 | 3.73063600 | 2.91410100 |
| O | -0.85438600 | 4.41167900 | 3.11208900 |
| O | 1.62366900 | 4.23600500 | 3.52424700 |
| C | -0.06721000 | -2.25535000 | 3.16476800 |
| H | 0.89708700 | -2.73647400 | 3.32850300 |
| H | -0.76223400 | -2.60206600 | 3.93323600 |
| H | -0.46020900 | -2.58738700 | 2.19991700 |
| C | 0.76667500 | -1.14888100 | -1.01321000 |
| C | -0.44472900 | -0.44414200 | -0.97203000 |
| C | -0.46384400 | 0.84009600 | -0.48492000 |
| C | 0.75780200 | 1.42750100 | -0.03179300 |
| C | 1.98318600 | 0.69324000 | -0.07908500 |
| C | 1.97369200 | -0.58891500 | -0.57125100 |
| H | 0.76967300 | -2.16232000 | -1.39912400 |
| H | -1.35558900 | -0.91323100 | -1.32097900 |
| H | -1.37854600 | 1.41840000 | -0.43198600 |
| H | 2.89193800 | 1.16302300 | 0.27797700 |
| H | 2.88766300 | -1.16677300 | -0.61646800 |
| C | 0.74444800 | 2.67426100 | 0.50439300 |
| C | 0.71731000 | 3.81139200 | 1.08852000 |
| C | 0.88619100 | 5.20407400 | 0.55437900 |
| H | 1.72950200 | 5.67853100 | 1.05896600 |
| H | 1.06753600 | 5.17799000 | -0.51759700 |
| H | -0.02130900 | 5.77374900 | 0.76157100 |

**TS2**

E = -1166.901025 a.u.

1 1

| | | | |
|---|---|---|---|
| C | 0.09866400 | -0.20448800 | 3.07057000 |
| C | 0.97498600 | 0.85091000 | 3.11865600 |
| C | 0.43680900 | 2.15950900 | 3.07672200 |

| | | | |
|---|---|---|---|
| C | -0.94102200 | 2.40043600 | 3.29443700 |
| C | -1.79510100 | 1.32678100 | 3.24433100 |
| C | -1.29453300 | 0.02056100 | 3.05881900 |
| H | 0.47255300 | -1.22036400 | 3.01613200 |
| H | 2.04922700 | 0.70578900 | 3.09371000 |
| H | -1.30264800 | 3.41713200 | 3.40092700 |
| H | -2.86547900 | 1.47876000 | 3.32230200 |
| S | 1.54706000 | 3.55472600 | 2.87955800 |
| O | 0.95421100 | 4.76416900 | 3.41547500 |
| O | 2.90535000 | 3.18539500 | 3.22709100 |
| C | -2.23310500 | -1.11224000 | 2.82959000 |
| H | -3.19684000 | -0.94095400 | 3.30961200 |
| H | -2.41315700 | -1.19247600 | 1.74780000 |
| H | -1.81249000 | -2.06092100 | 3.16325000 |
| C | -1.95246000 | -0.35195100 | -0.96194200 |
| C | -2.49992200 | 0.86908000 | -0.56039500 |
| C | -1.70893000 | 1.79392900 | 0.09392900 |
| C | -0.34532300 | 1.50205800 | 0.32608300 |
| C | 0.19485400 | 0.25668200 | -0.06893000 |
| C | -0.61064000 | -0.65723100 | -0.72093700 |
| H | -2.58094900 | -1.07656100 | -1.46736400 |
| H | -3.54245000 | 1.08815500 | -0.75518800 |
| H | -2.11277200 | 2.74388700 | 0.42490400 |
| H | 1.23676000 | 0.03945900 | 0.13684600 |
| H | -0.20339100 | -1.60895100 | -1.03891700 |
| C | 0.45699300 | 2.42158200 | 1.01596500 |
| C | 1.28400800 | 3.43283900 | 1.11684600 |
| C | 1.91632300 | 4.31370600 | 0.09699400 |
| H | 1.60320300 | 4.01972600 | -0.90376300 |
| H | 1.62630700 | 5.35071200 | 0.27948400 |
| H | 3.00286300 | 4.23621900 | 0.17629700 |

**V**

E = -1166.921937 a.u.

1 1

| | | | |
|---|---|---|---|
| C | 1.00756300 | -0.35815500 | 3.58530700 |
| C | 1.17246500 | 0.60339200 | 2.63463800 |
| C | 0.09537700 | 1.52556500 | 2.31378800 |
| C | -1.20101200 | 1.26764600 | 2.91960100 |
| C | -1.34457300 | 0.30180300 | 3.86468700 |
| C | -0.24308300 | -0.51803900 | 4.22858800 |
| H | 1.82751400 | -1.01355400 | 3.85212000 |
| H | 2.12487600 | 0.73399500 | 2.13110300 |

| | | | |
|---|---|---|---|
| H | -2.03561200 | 1.89802900 | 2.63104100 |
| H | -2.30141100 | 0.14112200 | 4.34744900 |
| S | 0.73489300 | 3.33976500 | 2.94733400 |
| O | -0.30276200 | 4.01846900 | 3.68941000 |
| O | 2.07588300 | 3.30415900 | 3.48290100 |
| C | -0.41205400 | -1.52704800 | 5.29857200 |
| H | 0.41607300 | -2.23202900 | 5.33482600 |
| H | -0.46152500 | -0.99854000 | 6.25949600 |
| H | -1.36153700 | -2.05528300 | 5.18659000 |
| C | -1.10949800 | 0.33920200 | -2.61848000 |
| C | -0.98006400 | 1.72565200 | -2.57659200 |
| C | -0.57317800 | 2.35356800 | -1.40834100 |
| C | -0.28753600 | 1.59375300 | -0.26501400 |
| C | -0.44039900 | 0.20187800 | -0.30957500 |
| C | -0.84288800 | -0.42072500 | -1.48330100 |
| H | -1.42801000 | -0.14764000 | -3.53311100 |
| H | -1.20526800 | 2.31986400 | -3.45440600 |
| H | -0.50500100 | 3.43404300 | -1.37754000 |
| H | -0.23973800 | -0.40118800 | 0.57077500 |
| H | -0.95334400 | -1.49828300 | -1.50999100 |
| C | 0.14144800 | 2.24042500 | 0.97418600 |
| C | 0.62061200 | 3.48208400 | 1.18864100 |
| C | 0.99182800 | 4.68415600 | 0.40272600 |
| H | 1.39935600 | 4.38675300 | -0.56474800 |
| H | 0.12428900 | 5.32846900 | 0.24153400 |
| H | 1.75477500 | 5.26072000 | 0.92891300 |

**TS3**

E = -1166.919897 a.u.

1 1

| | | | |
|---|---|---|---|
| C | 1.00764400 | -0.19568100 | 3.82924200 |
| C | 1.11519800 | 0.60119400 | 2.70331400 |
| C | -0.03842200 | 1.24981300 | 2.17152600 |
| C | -1.31401900 | 0.94992900 | 2.72833000 |
| C | -1.39723200 | 0.16431400 | 3.84364200 |
| C | -0.23696600 | -0.41848100 | 4.41928800 |
| H | 1.89425500 | -0.65696500 | 4.24718700 |
| H | 2.07714500 | 0.75947400 | 2.22634400 |
| H | -2.19822500 | 1.39364600 | 2.28479000 |
| H | -2.36155700 | -0.03073300 | 4.29984500 |
| S | 0.73118300 | 3.24171400 | 2.97590700 |
| O | -0.38916800 | 3.72159100 | 3.73770800 |
| O | 2.06737800 | 3.35997000 | 3.49059200 |

| | | | |
|---|---|---|---|
| C | -0.37385000 | -1.25809300 | 5.64411400 |
| H | 0.56111200 | -1.75206500 | 5.90405000 |
| H | -0.68447700 | -0.62944300 | 6.48481900 |
| H | -1.15550900 | -2.00905300 | 5.50474700 |
| C | -1.11187700 | 0.54973400 | -2.84425100 |
| C | -1.13374500 | 1.92496300 | -2.62239400 |
| C | -0.75166000 | 2.43831900 | -1.39131000 |
| C | -0.34464000 | 1.57063400 | -0.36835700 |
| C | -0.34779600 | 0.18709900 | -0.59011200 |
| C | -0.72209000 | -0.31791100 | -1.82744100 |
| H | -1.40877600 | 0.15352100 | -3.80856300 |
| H | -1.45693400 | 2.59771600 | -3.40796700 |
| H | -0.80266900 | 3.50661600 | -1.21439400 |
| H | -0.04503400 | -0.49000200 | 0.20223600 |
| H | -0.71332500 | -1.38796300 | -1.99769000 |
| C | 0.07525300 | 2.08427800 | 0.93656200 |
| C | 0.60754100 | 3.29288100 | 1.20073600 |
| C | 1.12896300 | 4.45416900 | 0.43393000 |
| H | 1.38776900 | 4.12524800 | -0.57360300 |
| H | 0.39012900 | 5.25624500 | 0.37700600 |
| H | 2.03285900 | 4.84734900 | 0.90329700 |

**VI**

E = -1166.940867 a.u.

1 1

| | | | |
|---|---|---|---|
| C | 0.76828300 | 0.55349500 | 4.40390700 |
| C | 1.06428400 | 1.06763600 | 3.06886800 |
| C | 0.05711900 | 0.89043000 | 2.01334300 |
| C | -1.01814300 | 0.05895100 | 2.23143100 |
| C | -1.20897100 | -0.44921700 | 3.51598200 |
| C | -0.34605900 | -0.19755500 | 4.62427400 |
| H | 1.49436700 | 0.72718000 | 5.19155900 |
| H | 2.03669500 | 0.67816300 | 2.72786000 |
| H | -1.75956600 | -0.11282000 | 1.46107200 |
| H | -2.10055600 | -1.04230100 | 3.70060400 |
| S | 1.34543800 | 2.91053200 | 2.93591100 |
| O | 0.32317300 | 3.57868700 | 3.71904500 |
| O | 2.74009900 | 3.24056300 | 3.14019100 |
| C | -0.68057000 | -0.78347200 | 5.96262400 |
| H | -1.67001400 | -0.44981600 | 6.28293300 |
| H | -0.70093900 | -1.87398200 | 5.90638900 |
| H | 0.04953500 | -0.48447900 | 6.71334800 |
| C | -1.51131500 | 0.97075800 | -2.92209700 |

| | | | |
|---|---|---|---|
| C | -1.62854700 | 2.24169400 | -2.36658300 |
| C | -1.06115200 | 2.51635600 | -1.12815500 |
| C | -0.37533600 | 1.51314500 | -0.43656600 |
| C | -0.27025400 | 0.23364200 | -0.99273100 |
| C | -0.83217600 | -0.03212600 | -2.23481800 |
| H | -1.95315500 | 0.76014700 | -3.88934400 |
| H | -2.16557600 | 3.02038000 | -2.89549200 |
| H | -1.16903600 | 3.50158000 | -0.68702800 |
| H | 0.26489800 | -0.54675400 | -0.46093500 |
| H | -0.73948000 | -1.02203700 | -2.66610800 |
| C | 0.23462300 | 1.79143200 | 0.87852900 |
| C | 0.93374000 | 2.90799500 | 1.19163400 |
| C | 1.39929000 | 4.05509900 | 0.37727600 |
| H | 1.32171100 | 3.83039000 | -0.68546900 |
| H | 0.80577800 | 4.94725300 | 0.60105200 |
| H | 2.44027100 | 4.28307800 | 0.62061900 |

**TS4**

E = -1166.893256 a.u.

1 1

| | | | |
|---|---|---|---|
| C | -2.04392500 | 0.58724000 | 3.59919900 |
| C | -0.96508300 | 1.34072400 | 3.06252000 |
| C | -1.07825700 | 2.76317000 | 3.07825200 |
| C | -2.19832300 | 3.42697000 | 3.62978800 |
| C | -3.22822700 | 2.64940900 | 4.07601700 |
| C | -3.16893100 | 1.21655500 | 4.06794500 |
| H | -1.95652100 | -0.49157900 | 3.63318500 |
| H | -0.00510000 | 0.86816800 | 2.89002600 |
| H | -2.23340800 | 4.50986300 | 3.64492100 |
| H | -4.12141300 | 3.12412700 | 4.46856500 |
| S | 0.31721600 | 3.57813800 | 2.27308500 |
| O | 0.08611200 | 5.00598400 | 2.19576000 |
| O | 1.58397000 | 3.05708900 | 2.73828500 |
| C | -4.34202100 | 0.44938200 | 4.58730600 |
| H | -4.61319900 | 0.79474900 | 5.58759300 |
| H | -5.20620800 | 0.62262900 | 3.93893200 |
| H | -4.13798000 | -0.61992800 | 4.61953900 |
| C | -5.03483900 | 0.85475100 | -0.32165500 |
| C | -4.71899400 | 2.20489500 | -0.21025000 |
| C | -3.50693600 | 2.58776900 | 0.35181500 |
| C | -2.61755900 | 1.60914400 | 0.81065100 |
| C | -2.94027400 | 0.25088300 | 0.70414000 |
| C | -4.14402000 | -0.12122000 | 0.12737600 |

| | | | |
|---|---|---|---|
| H | -5.97995100 | 0.55756500 | -0.76158200 |
| H | -5.41297500 | 2.95958000 | -0.56043700 |
| H | -3.24395700 | 3.63663000 | 0.44424100 |
| H | -2.24410000 | -0.50070600 | 1.05911300 |
| H | -4.39303600 | -1.17109000 | 0.02925500 |
| C | -1.35320600 | 2.06613600 | 1.37110900 |
| C | -0.35598700 | 2.78190900 | 0.82905300 |
| C | -0.03598800 | 3.13133200 | -0.57163400 |
| H | 1.01306400 | 2.90334400 | -0.77770100 |
| H | -0.67378100 | 2.57488600 | -1.25749000 |
| H | -0.18462400 | 4.20401800 | -0.72668800 |

**VII**

E = -1166.917737 a.u.

1 1

| | | | |
|---|---|---|---|
| C | -3.00938900 | 1.31073400 | 3.43487600 |
| C | -1.81950500 | 1.76820700 | 2.71607400 |
| C | -1.00780800 | 2.75008600 | 3.41949600 |
| C | -1.18821100 | 3.07756200 | 4.71815100 |
| C | -2.27296600 | 2.46275200 | 5.38965100 |
| C | -3.19410600 | 1.59985400 | 4.76996500 |
| H | -3.69445500 | 0.64353900 | 2.91990300 |
| H | -1.22027300 | 0.81502200 | 2.79418800 |
| H | -0.58264300 | 3.82265100 | 5.22082800 |
| H | -2.42868100 | 2.71152500 | 6.43574800 |
| S | 0.05010600 | 3.58755100 | 2.23869900 |
| O | -0.06658000 | 5.02187700 | 2.43144100 |
| O | 1.37095200 | 2.98129300 | 2.22006600 |
| C | -4.34890400 | 1.04460900 | 5.55133700 |
| H | -3.99018100 | 0.31914100 | 6.28489700 |
| H | -4.86294300 | 1.84074700 | 6.09184700 |
| H | -5.06175200 | 0.54848100 | 4.89423100 |
| C | -4.48533000 | 0.12821700 | -1.45001600 |
| C | -4.36036700 | 1.51352300 | -1.50339500 |
| C | -3.50399000 | 2.17129200 | -0.62839500 |
| C | -2.76765900 | 1.44188900 | 0.30969200 |
| C | -2.90528100 | 0.05067500 | 0.36766500 |
| C | -3.75627400 | -0.60227000 | -0.51494700 |
| H | -5.15210600 | -0.38220100 | -2.13552600 |
| H | -4.93132900 | 2.08411600 | -2.22663400 |
| H | -3.41387900 | 3.25181700 | -0.65926400 |
| H | -2.32870400 | -0.52319100 | 1.08678100 |
| H | -3.84843900 | -1.68135800 | -0.47413200 |

| | | | |
|---|---|---|---|
| C | -1.83887800 | 2.13031100 | 1.22315900 |
| C | -0.91981200 | 3.02830500 | 0.85209200 |
| C | -0.53046500 | 3.56294100 | -0.48397600 |
| H | 0.55758700 | 3.55334900 | -0.58984600 |
| H | -0.96000300 | 2.95612200 | -1.28002600 |
| H | -0.87139300 | 4.59434700 | -0.60059700 |

**TS5**

E = -1166.904507 a.u.

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| | | | |
|---|---|---|---|
| C | -2.87645300 | 0.88672000 | 3.21154500 |
| C | -1.98104000 | 1.76126700 | 2.53512200 |
| C | -1.15671600 | 2.62502600 | 3.32682200 |
| C | -1.20220400 | 2.63598600 | 4.71727500 |
| C | -2.08452300 | 1.76156400 | 5.32438900 |
| C | -2.91504400 | 0.87586800 | 4.59450900 |
| H | -3.50774400 | 0.22119900 | 2.63448400 |
| H | -0.88059900 | 1.28413500 | 2.85623700 |
| H | -0.57037700 | 3.30362800 | 5.29028500 |
| H | -2.13837700 | 1.74245100 | 6.40785700 |
| S | -0.26751200 | 3.73434400 | 2.20790900 |
| O | -0.70032600 | 5.08514100 | 2.50303400 |
| O | 1.14669000 | 3.41812500 | 2.17936200 |
| C | -3.82139200 | -0.05692000 | 5.33584100 |
| H | -4.51454200 | -0.55570800 | 4.66014000 |
| H | -3.22790400 | -0.81727300 | 5.85028000 |
| H | -4.38825500 | 0.48596100 | 6.09445200 |
| C | -4.26789100 | -0.04985400 | -1.78532500 |
| C | -2.88541400 | 0.02176800 | -1.92887200 |
| C | -2.12288700 | 0.71640700 | -0.99679800 |
| C | -2.74408400 | 1.33737900 | 0.08951400 |
| C | -4.13348200 | 1.26408500 | 0.23097400 |
| C | -4.89102100 | 0.57435500 | -0.70773000 |
| H | -4.86083100 | -0.58893600 | -2.51533600 |
| H | -2.39877100 | -0.46220800 | -2.76766800 |
| H | -1.04471100 | 0.77352800 | -1.10290300 |
| H | -4.62102400 | 1.76708300 | 1.06024300 |
| H | -5.96846400 | 0.52899900 | -0.59997000 |
| C | -1.93366100 | 2.09340500 | 1.06746900 |
| C | -1.09466000 | 3.08861400 | 0.75768200 |
| C | -0.73268800 | 3.71595000 | -0.54150400 |
| H | 0.27377900 | 3.41495300 | -0.84439100 |
| H | -1.43848200 | 3.41469400 | -1.31473300 |

| | | | |
|---|---|---|---|
| H | -0.74813800 | 4.80496100 | -0.45252100 |

**VIII**

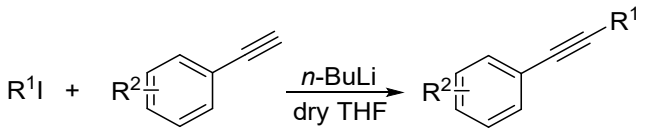
E = -1166.945009 a.u.

1 1

| | | | |
|---|---|---|---|
| C | -2.88255000 | 0.92021100 | 3.17476500 |
| C | -1.92850600 | 1.63645400 | 2.50249400 |
| C | -0.78314900 | 2.21064600 | 3.23857900 |
| C | -0.89225100 | 2.29333000 | 4.70122500 |
| C | -1.89979300 | 1.64949600 | 5.32812100 |
| C | -2.88550400 | 0.92411000 | 4.58250800 |
| H | -3.69004200 | 0.42919000 | 2.64481700 |
| H | 0.11175000 | 1.61142800 | 2.99866300 |
| H | -0.10455100 | 2.79492100 | 5.25271100 |
| H | -1.96960500 | 1.65003900 | 6.40953100 |
| S | -0.46853500 | 3.76833800 | 2.30379500 |
| O | -1.29662700 | 4.82397400 | 2.85784400 |
| O | 0.95178400 | 3.99037100 | 2.11931700 |
| C | -3.94769800 | 0.21675100 | 5.33044800 |
| H | -4.65634800 | -0.28664300 | 4.67705200 |
| H | -3.48226200 | -0.51210800 | 6.00373500 |
| H | -4.47317200 | 0.92920000 | 5.97544900 |
| C | -4.20415200 | -0.09598200 | -1.85916500 |
| C | -2.81338800 | -0.14574800 | -1.87921900 |
| C | -2.07727800 | 0.53657400 | -0.91658800 |
| C | -2.73636800 | 1.26867600 | 0.07236800 |
| C | -4.13173800 | 1.32282700 | 0.08944300 |
| C | -4.86165900 | 0.63980500 | -0.87726700 |
| H | -4.77580300 | -0.62678600 | -2.61189400 |
| H | -2.29925100 | -0.71420000 | -2.64559400 |
| H | -0.99274300 | 0.50304700 | -0.92809200 |
| H | -4.64128600 | 1.90951200 | 0.84672900 |
| H | -5.94443700 | 0.68811600 | -0.86588300 |
| C | -1.94132300 | 2.00464900 | 1.08805600 |
| C | -1.20811900 | 3.10229900 | 0.81080200 |
| C | -0.95222500 | 3.82072100 | -0.45820500 |
| H | 0.10006900 | 3.71628300 | -0.73915100 |
| H | -1.57349900 | 3.41567600 | -1.25618200 |
| H | -1.15988700 | 4.88816900 | -0.34319200 |

**Preparation of the starting materials**

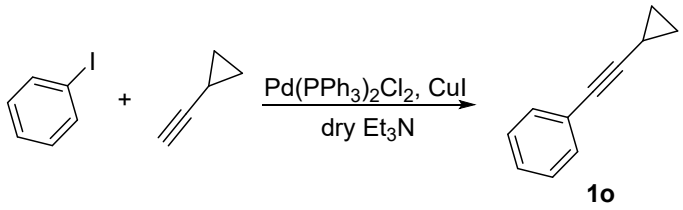
**Preparation of substrates 1**




**1b-1n, 1r, 1s, 1B-1I**

The compounds **1b** – **1n, 1r, 1s, 1B** – **1I** were prepared according to previously described methods.[4] To a flame-dried round-bottom flask under $N_2$ was added alkyne (10 mmol, 1 equiv.) followed by dry THF (50 mL, 0.2 M). Cool the flask to 0 °C. *n*-Butyllithium (8 mL, 2.5 M in hexanes, 20 mmol, 2 equiv.) was added slowly and the reaction was allowed to stir for 1 hour. Iodoalkane (21 mmol, 2.1 equiv.) was added at -20 °C and the reaction was allowed to stir at room temperature for 3 ~ 5 hour (when most of alkyne was consumed as detected by TLC). The reaction was quenched with a saturated solution of ammonium chloride and extracted with ethyl acetate. The organics were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by silica chromatography to afford the corresponding compounds **1b** – **1n, 1r, 1s, 1B** – **1I**.

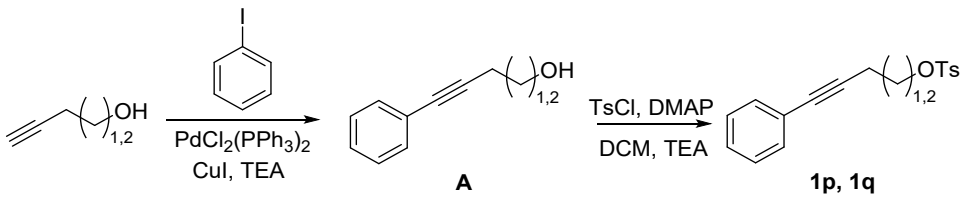
The compounds **1oa** were prepared according to previously described methods.[5]




**1o**

To a 50 mL flame-dried round-bottom flask, under $N_2$, was added $PdCl_2(PPh_3)_2$ (0.05 mmol, 0.01 equiv.), CuI (0.1 mmol, 0.02 equiv.), iodobenzene (5 mmol, 1.0 equiv.), cyclopropyl acetylene (6 mmol, 1.2 equiv.) and dry $Et_3N$ (10 mL), the reaction was allowed to stir at room temperature. The reaction was stirred overnight checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compounds **1o**.

The compounds **1p, 1q** were prepared according to previously described methods.



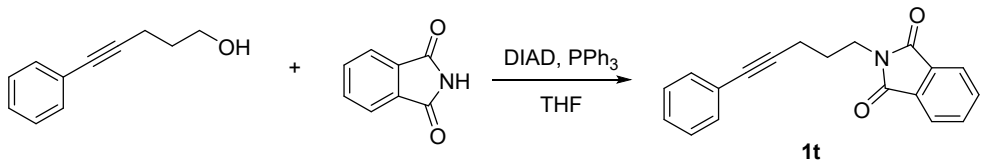

**A** **1p, 1q**

Step1: To a 50 mL flame-dried round-bottom flask, under $N_2$, was added $PdCl_2(PPh_3)_2$ (0.05 mmol, 0.01 equiv.), CuI (0.1 mmol, 0.02 equiv.), iodobenzene (6 mmol, 1.2 equiv.), alkynol (5 mmol, 1.0 equiv.) and dry $Et_3N$ (10 mL), the reaction was allowed to stir at room temperature. The reaction was stirred overnight checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The

solvent was removed and the residue purified by flash column chromatography on silica gel to give compounds **A**.[6]

Step2: To a stirred solution of Compound **A** (5 mmol, 1.0 equiv.), dimethylaminopyridine (DMAP) (0.5 mmol, 0.1 equiv.) and TEA (10 mmol, 2.0 equiv.) in dry DCM (10 mL) at 0 °C was added p-toluenesulfonyl chloride (TsCl) (6 mmol, 1.2 equiv.) portion wise. The reaction mixture was stirred for 1 h and then quenched with water, extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated and chromatography on silica gel to give compounds **1p**, **1q**.[7]

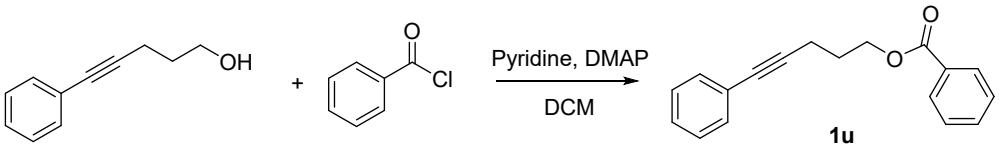
The compounds **1t** were prepared according to previously described methods.




**1t**

To a stirred solution of 5-phenylpent-4-yn-1-ol (5 mmol, 1.0 equiv.), Isoindoline-1,3-dione (6.5 mmol, 1.3 equiv.), DIAD (6.5 mmol, 1.3 equiv.) and Triphenylphosphine (6.5 mmol, 1.3 equiv.) in THF (25 mL). The reaction mixture was stirred for 6 h and then quenched with water, extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated and chromatography on silica gel to give compounds **1t**.

The compounds **1u** were prepared according to previously described methods.

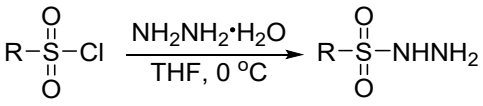



**1u**

To a stirred solution of 5-phenylpent-4-yn-1-ol (3 mmol, 1.0 equiv.), Benzoyl chloride (3.6 mmol, 1.2 equiv.), Pyridine (15 mmol, 5 equiv.) and DMAP (0.3 mmol, 0.1 equiv.) in DCM (10 mL). The reaction mixture was stirred for 3 h and then quenched with water, extracted with EtOAc, dried over anhydrous $MgSO_4$, concentrated and chromatography on silica gel to give compounds **1u**.

**Preparation of substrates 2**

The compound **2b** – **2i** according to previously described methods.[8]

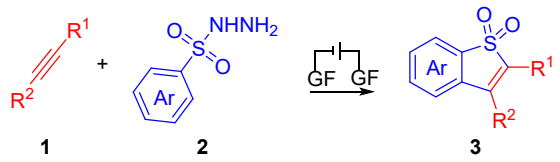



**2b-2i**

The hydrazine hydrate (80%, 30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under air at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 5

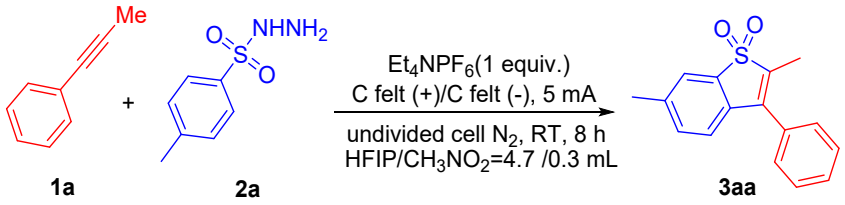
minutes. After the completion of the reaction, the esidue was extracted with dichloromethane, and the combined organic layer was ashed with water, and brine, and dried over $MgSO_4$. Concentration in vacuum followed by silicael column purification with petroleum ether/ethyl acetate eluent gave the desired products **2b-2i**.

**General procedure for the synthesis of compounds 3**




In a undivided cell (10 mL) equipped with a stir bar, **2** (0.6 mmol, 3 equiv.), and $Et_4NPF_6$ (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) (4.7 mL), $CH_3NO_2$ (0.3 mL) and **1** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h. After the reaction was completed, the residue was purified by column chromatography using petroleum ether and ethyl acetate as eluent, to afford the desired product **3**.

**Optimization of reaction conditions**

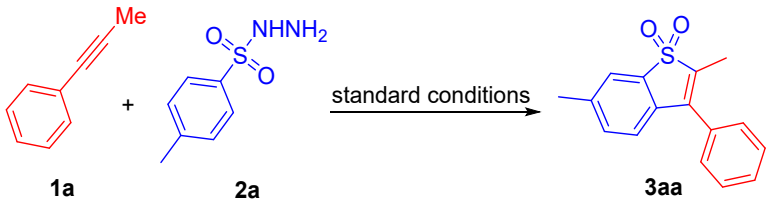



| Entry | Variation from the standard conditions | Yield (%)[b] |
|---|---|---|
| 1 | none | 75 |
| 2 | 3 mA, 13 h | 70 |
| 3 | 10 mA, 4 h | 65 |
| 4 | Nickel foam cathode[c] | 47 |
| 5 | Pt plate cathode[d] | 51 |
| 6 | $^nBu_4NPF_6$ instead of $Et_4NPF_6$ | 64 |
| 7 | $^nBu_4NBF_4$ instead of $Et_4NPF_6$ | 45 |

| | | |
|---|---|---|
| 8 | $LiClO_4$ instead of $Et_4NPF_6$ | n.r. |
| 9 | $Me_4NPF_6$ instead of $Et_4NPF_6$ | 69 |
| 10 | DCM instead of HFIP | 62 |
| 11 | DCE instead of HFIP | 60 |
| 12 | EA instead of HFIP | n.d. |
| 13 | DMF instead of HFIP | n.d. |
| 14 | THF instead of HFIP | 38 |
| 15 | DMSO instead of HFIP | n.d. |
| 16 | $CH_3CN$ instead of HFIP | trace |
| 17 | TFE instead of HFIP | n.d. |
| 18 | 1,4-dioxane instead of $CH_3NO_2$ | n.d. |
| 19 | add 10% $Cp_2Fe$ | n.r. |
| 20 | add 1 equiv. TEA | 45 |
| 21 | 50 °C | 74 |
| 22 | 60 °C | 68 |
| 23 | air instead of $N_2$ | 30 |
| 24 | 5 V instead of 5 mA | 46 |
| 25 | no electric current | n.r. |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Et_4NPF_6$ (0.2 mmol), HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL), graphite felt anode (10 mm * 10 mm * 5 mm), constant current = 5 mA, RT, 8 h, undivided cell (7.46 F, faradaic efficiency: 42%). [b] Isolated yield. [c] Nickel foam (10 mm*10 mm*0.1 mm). [d] Pt plate (10 mm*10 mm*1 mm).

**The effect of anode materials**




**1a** **2a** **3aa**

| Entry | Variation from the standard conditions | Yield (%)[b] |
|---|---|---|
| 1 | Pt plate anode[c] | 34 |
| 2 | Ni foam anode[d] | 26 |
| 3 | Glassy carbon anode[e] | 13 |
| 4 | Carbon paper anode[f] | 23 |
| 5 | Carbon cloth anode[g] | 29 |

| | | |
|---|---|---|
| 6 | Carbon felt anode[h] | 75 |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $Et_4NPF_6$ (0.2 mmol), HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL), graphite felt anode (10 mm * 10 mm * 5 mm), constant current = 5 mA, RT, 8 h, undivided cell. [b] Isolated yield. [c] Pt plate (10 mm*10 mm*0.1 mm). [d] Nickel foam (10 mm*10 mm*1 mm). [e] Glassy carbon (10 mm*10 mm*1mm). [f] Carbon paper (10 mm*10 mm*0.1 mm). [g] Carbon cloth (10 mm*10 mm*1mm). [h] Graphite felt anode (10 mm*10 mm*5 mm).

**SEM image of graphite felts:**

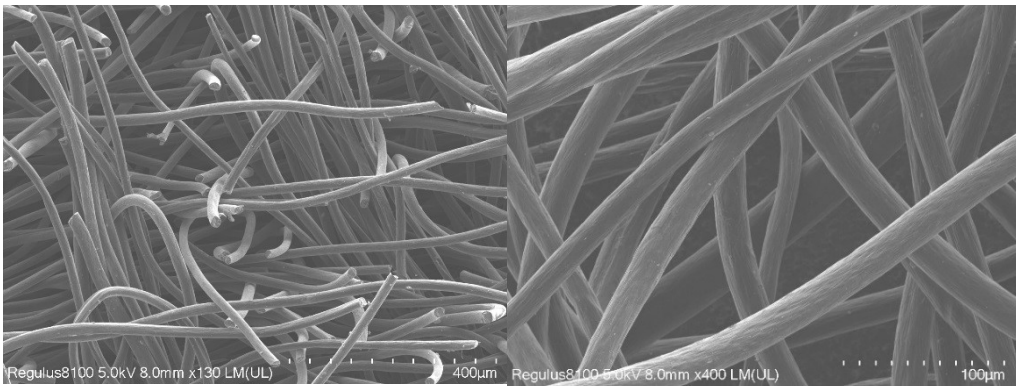
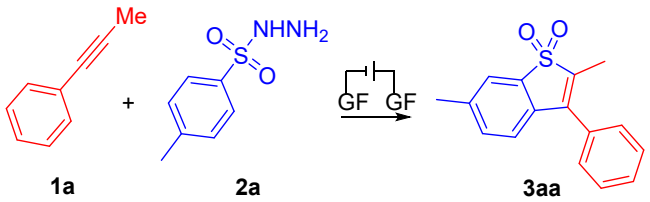



**Fig. S1** Graphite felt structure under scanning electron microscopy (SEM).

**Gram-scale reaction**




**Scheme S1** Gram-scale reaction of **3aa**.

In a undivided cell (250 mL) equipped with a stir bar, sulfonyl hydrazides **2a** (15 mmol, 3 equiv.), and $Et_4NPF_6$ (5 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 5 cm x 1.5 cm) and a graphite felt cathode (1 cm x 5 cm x 1.5 cm) and then flushed with nitrogen. Then HFIP (117.5 mL), $CH_3NO_2$ (7.5 mL) and alkyne **1a** (5 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant voltage of 15 mA at RT for 67 h. After the reaction was completed, the residue was purified by column chromatography using petroleum ether and ethyl acetate as eluent, to afford the desired product **3aa** (1.11 g, 82%).

**Cyclic voltammetry study**

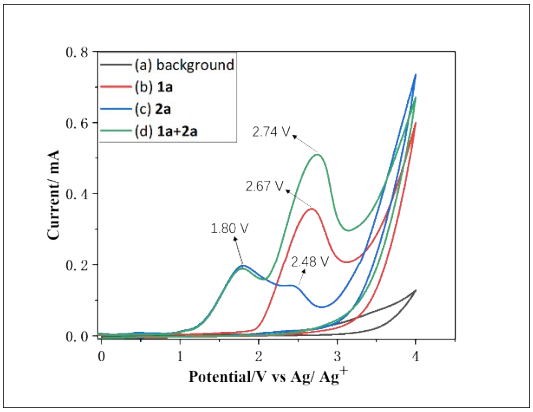



**Fig. S2** Cyclic voltammograms of **1a** (0.2 mmol), and **2a** (0.1 mmol) were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. A solvent (10 mL $CH_3CN$) containing $Et_4NPF_6$ (0.1 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0 V to 4 V.

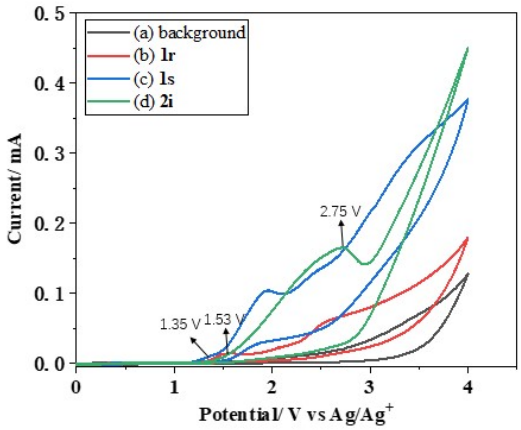
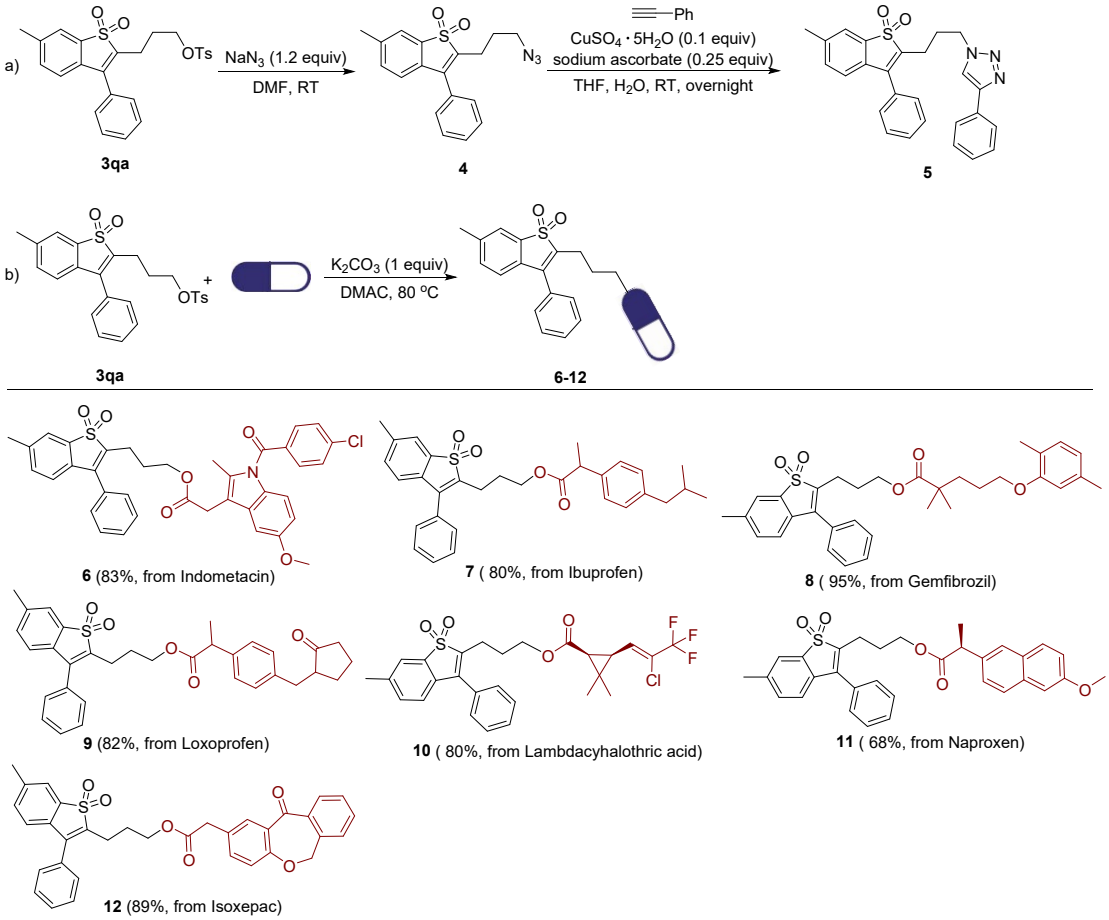



**Fig. S3** Cyclic voltammograms were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Conditions: $CH_3CN$ (5 mL), 100 $mVs^{-1}$. (a) $Et_4NPF_6$ (0.1 mmol). (b) $Et_4NPF_6$ (0.1 mmol), **1r** (0.1 mmol). (c) $Et_4NPF_6$ (0.1 mmol), **1s** (0.1 mmol). (d) $Et_4NPF_6$ (0.1 mmol), **2i** (0.1 mmol).

**Transformation of product 3qa**



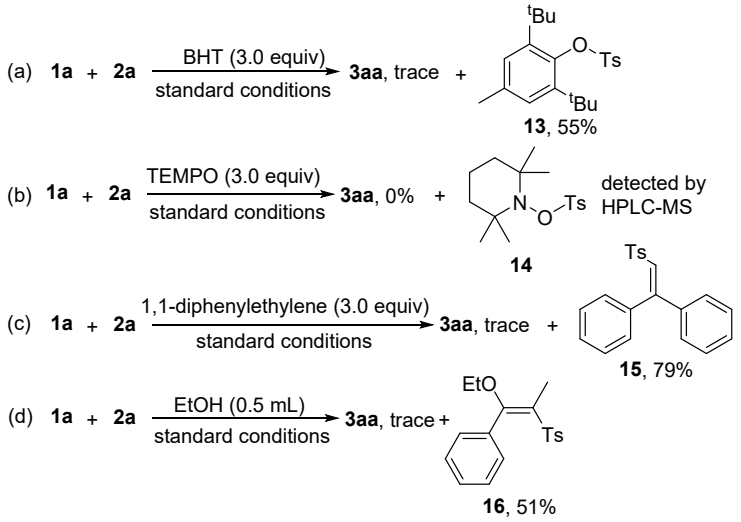

**Scheme S2** a) Step 1: Sodium azide (0.24 mmol, 1.2 equiv.) was added to a solution of **3qa** (0.2 mmol, 1 equiv.) in DMF (1.1 mL) and stirred at room temperature overnight. $H_2O$ was added to the mixture and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound **4** (yellow solid, 92%).

Step 2: To a solution of compound **4** (0.2 mmol, 1 equiv.) in a 1:1 mixture of THF:$H_2O$ (5 mL) were added copper (II) sulfate (0.02 mmol, 0.1 equiv.), sodium ascorbate (0.05 mmol, 0.25 equiv.) and the phenylacetylene (0.26 mmol, 1.3 equiv.). The mixture was brine, dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum and purified by silica gel column chromatography to avail products **5** (yellow solid, 89%).

b) To a solution of compound **3qa** (0.2 mmol, 1 equiv.) in a DMAC (2 mL) were added $K_2CO_3$ (0.2 mmol, 1 equiv.), pharmaceutical motifs such as Indometacin, Ibuprofen, Gemfibrozil, Loxoprofen, Lambdacyhalothric acid, Naproxen and Isoxepac (0.2 mmol, 1 equiv.). The mixture was stirred at 80 °C

temperature overnight. The combined organic phase was washed with brine, dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum and purified by silica gel column chromatography to avail products **6-12**.

**Control experiments**




**Scheme S3** (a) In a undivided cell (10 mL) equipped with a stir bar, **2a** (0.6 mmol, 3 equiv.), BHT (0.3 mmol, 3 equiv.) and $Et_4NPF_6$ (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL) and **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h to get product **13** (white solid, 55%).

(b) In a undivided cell (10 mL) equipped with a stir bar, **1a** (0.2 mmol, 1 equiv.), **2a** (0.6 mmol, 3 equiv.), TEMPO (0.3 mmol, 3 equiv.) and $Et_4NPF_6$ (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL) and **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h to get product **14** (detected by HPLC-MS).

(c) In a undivided cell (10 mL) equipped with a stir bar, **2a** (0.6 mmol, 3 equiv.), 1,1-diphenylethylene (0.3 mmol, 3 equiv.), and $Et_4NPF_6$ (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL) and **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h to avail products **15** (white solid, 79%).

d) In a undivided cell (10 mL) equipped with a stir bar, **2a** (0.6 mmol, 3 equiv.) and $Et_4NPF_6$ (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (4.7 mL), $CH_3NO_2$ (0.3 mL), EtOH (0.5 mL) and **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h to get product **16** (colorless oil, 51%).

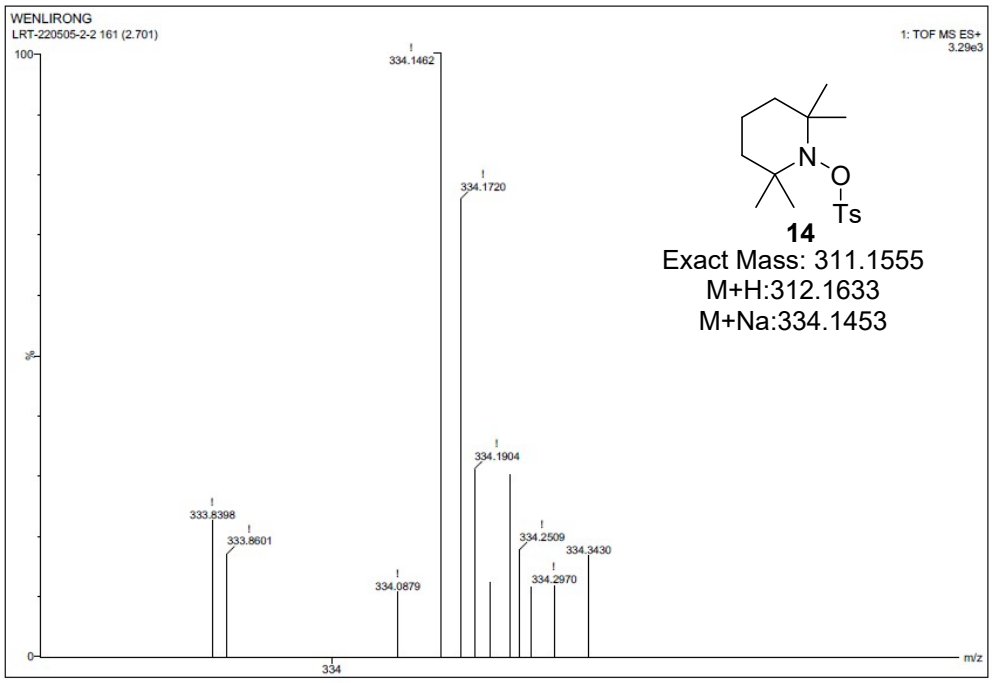



**Fig. S4** Mass spectra (MS) of compounds **14**.

**Fluorescence Microscopic Studies**

**Cell culture.** All cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) and supplemented with 10% fetal bovine serum (FBS) and 1% antibiotics (100 U $mL^{-1}$ panicillin and 100 μg $mL^{-1}$ streptomycin) at 37 °C in a humidified atmosphere of 5% $CO_2$ for 24 h**.**

**Fluorescence microscopic imaging.** All the experiments were conducted in live cells. The living cell imaging was measured by Nikon C2 plus with an excitation filter of 405 nm and the collection wavelength range is at 420-460nm.

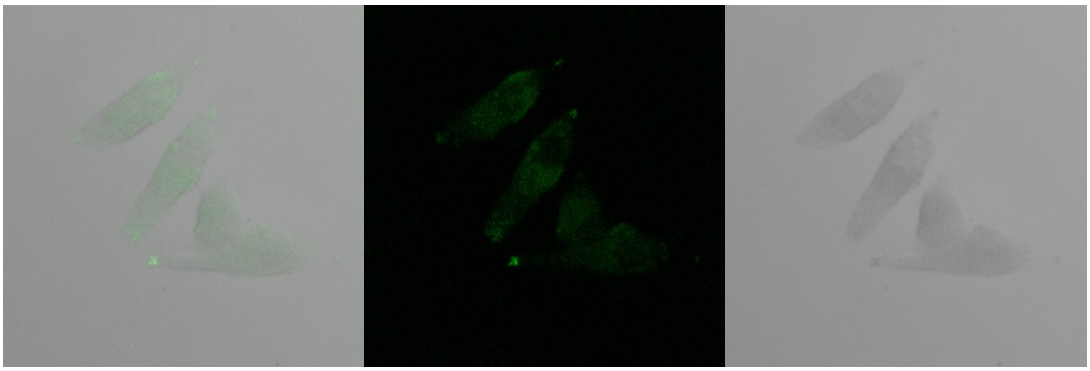


**Fig. S5** Fluorescence intensity of **3Ha** in HeLa cells.

**References**

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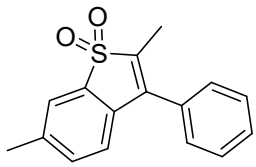
**Characterization of products**

**2,6-dimethyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3aa)**



**3aa**

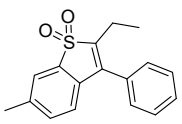
**3aa** was obtained in 75% (40.6 mg) as a white crystal after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.61 (s, 1H), 7.56 – 7.45 (m, 3H), 7.39 – 7.32 (m, 2H), 7.31 – 7.23 (m, 1H), 7.08 (d, $J$ = 7.8 Hz, 1H), 2.44 (s, 3H), 2.13 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.1, 137.9, 136.4, 134.4, 133.8, 130.9, 130.6, 129.4, 129.0, 128.6, 123.2, 122.1, 21.3, 7.5.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{16}H_{14}O_2S$, 293.0612, Found: 293.0618.

**2-ethyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ba)**



**3ba**

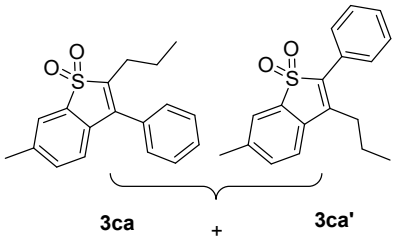
**3ba+3ba'** was obtained in 64% (36.4 mg) as a colorless crystal after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.55 – 7.45 (m, 3H), 7.34 (dd, $J$ = 7.9, 1.7 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.01 (d, $J$ = 7.8 Hz, 1H), 2.59 (q, $J$ = 7.6 Hz, 2H), 2.43 (s, 3H), 1.30 (t, $J$ = 7.6 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 139.6, 138.2, 136.5, 133.8, 130.9, 129.3, 129.0, 128.4, 123.3, 121.8, 21.3, 17.2, 13.2.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{17}H_{16}O_2S$, 285.0949, Found: 285.0955.

**6-methyl-3-phenyl-2-propylbenzo[*b*]thiophene 1,1-dioxide (3ca)**



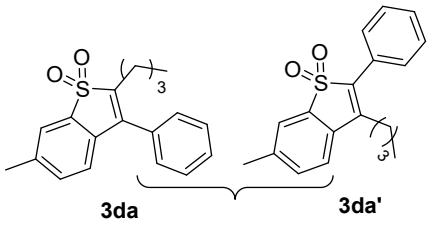

**3ca+3ca'** was obtained in 58% (34.6 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.55 – 7.45 (m, 3H), 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 6.99 (d, $J$ = 7.7 Hz, 1H), 2.62 – 2.48 (m, 2H), 2.43 (s, 3H), 1.76 (h, $J$ = 7.4 Hz, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.6, 138.5, 136.4, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.8, 25.7, 21.5, 21.3, 14.1.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{18}H_{18}O_2S$, 299.1106, Found: 299.1111.

**2-butyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3da)**



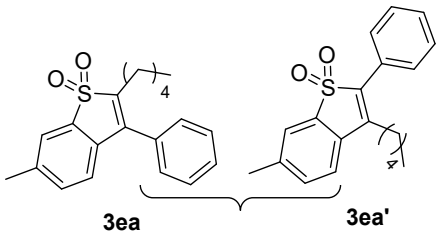

**3da+3da'** was obtained in 54% (33.7 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.56 – 7.45 (m, 3H), 7.33 (dd, $J$ = 8.1, 1.6 Hz, 2H), 7.28 – 7.23 (m, 1H), 6.99 (d, $J$ = 7.8 Hz, 1H), 2.54 (dd, $J$ = 9.0, 7.0 Hz, 2H), 2.43 (s, 3H), 1.85 – 1.65 (m, 2H), 1.43 – 1.29 (m, 2H), 0.85 (t, $J$ = 7.4 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.8, 30.1, 23.4, 22.6, 21.3, 13.5.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{19}H_{20}O_2S$, 313.1262, Found: 313.1265.

**6-methyl-2-pentyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ea)**



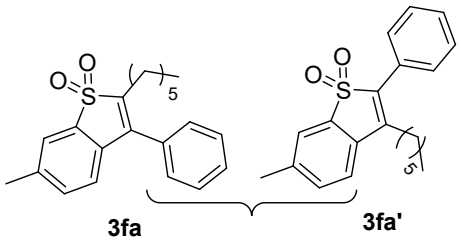

**3ea+3ea'** was obtained in 52% (33.9 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.51 (dddd, $J$ = 11.7, 6.9, 4.6, 2.4 Hz, 3H), 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 1H), 6.99 (d, $J$ = 7.8 Hz, 1H), 2.71 – 2.49 (m, 2H), 2.43 (s, 3H), 1.72 (p, $J$ = 7.5 Hz, 2H), 1.27 (tt, $J$ = 8.7, 4.8 Hz, 5H), 0.84 (t, $J$ = 6.9 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.8, 31.6, 27.7, 23.6, 22.1, 21.3, 13.9.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{20}H_{22}O_2S$, 327.1419, Found: 327.1419.

**2-hexyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3fa)**



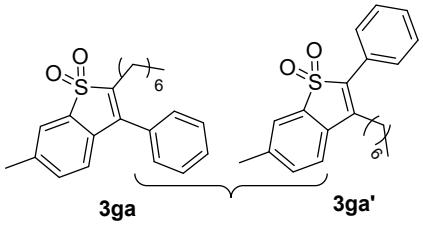

**3fa+3fa'** was obtained in 49% (33.3 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.55 – 7.46 (m, 3H), 7.38 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 6.99 (d, $J$ = 7.8 Hz, 1H), 2.61 – 2.50 (m, 2H), 2.43 (s, 3H), 1.72 (p, $J$ = 7.8 Hz, 2H), 1.44 – 1.16 (m, 7H), 0.84 (t, $J$ = 6.9 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.9, 31.2, 29.2, 28.0, 23.7, 22.4, 21.3, 14.0.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{21}H_{24}O_2S$, 341.1575, Found: 341.1570.

**2-heptyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ga)**



**3ga** **3ga'**

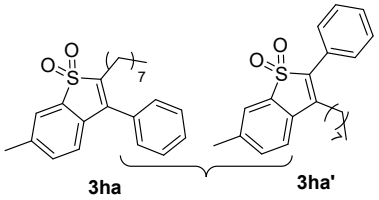
**3ga+3ga'** was obtained in 47% (32.0 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.55 – 7.44 (m, 3H), 7.33 (dd, $J$ = 8.0, 1.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.99 (d, $J$ = 7.8 Hz, 1H), 2.58 – 2.49 (m, 2H), 2.43 (s, 3H), 1.72 (p, $J$ = 7.8 Hz, 2H), 1.35 – 1.13 (m, 8H), 0.85 (t, $J$ = 6.9 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.4, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.9, 31.6, 29.4, 28.7, 28.0, 23.7, 22.6, 21.3, 14.1.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{22}H_{26}O_2S$, 355.1732, Found: 355.1725.

**6-methyl-2-octyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ha)**



**3ha** **3ha'**

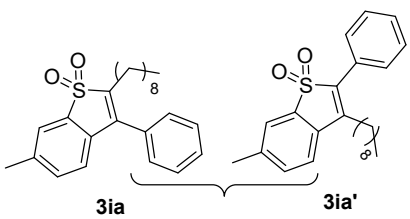
**3ha+3ha'** was obtained in 46% (33.9 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.58 (s, 1H), 7.55 – 7.44 (m, 3H), 7.35 – 7.30 (m, 2H), 7.23 (d, $J$ = 13.4 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 2.65 – 2.47 (m, 2H), 2.43 (s, 3H), 1.71 (p, $J$ = 7.8 Hz, 2H), 1.38 – 1.08 (m, 12H), 0.86 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.2, 121.8, 31.8, 29.5, 29.1, 29.0, 28.0, 23.7, 22.6, 21.3, 14.1.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{23}H_{28}O_2S$, 391.1708, Found: 391.1702.

**6-methyl-2-nonyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ia)**



**3ia** **3ia'**

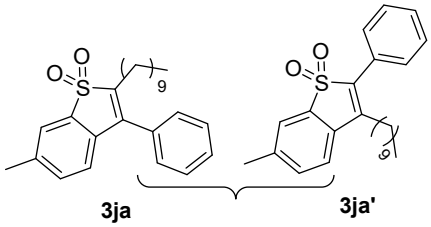
**3ia+3ia'** was obtained in 47% (35.9 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.56 – 7.46 (m, 1H), 7.34 – 7.32 (m, 3H), 7.26 – 7.20 (m, 2H), 6.99 (d, $J$ = 7.7 Hz, 1H), 2.56 – 2.50 (m, 1H), 2.43 (d, $J$ = 2.4 Hz, 2H), 1.79 – 1.67 (m, 3H), 1.31 – 1.16 (m, 12H), 0.87 (t, $J$ = 7.0 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 130.2, 129.3, 129.0, 128.5, 123.3, 121.9, 31.8, 29.5, 29.4, 29.2, 29.0, 28.0, 23.7, 22.6, 21.3, 14.1.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{24}H_{30}O_2S$, 383.2045, Found: 383.2038.

**2-decyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ja)**




**3ja** **3ja'**

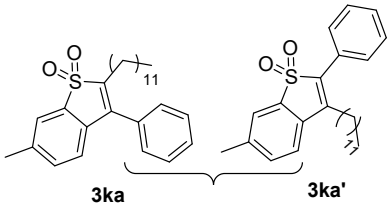
**3ja+3ja'** was obtained in 39% (30.9 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.50 (s, 1H), 7.42 (dq, $J$ = 13.9, 7.1 Hz, 3H), 7.24 (d, $J$ = 7.2 Hz, 2H), 7.17 (d, $J$ = 6.9 Hz, 1H), 6.91 (d, $J$ = 7.7 Hz, 1H), 2.45 (t, $J$ = 8.0 Hz, 2H), 2.35 (s, 3H), 1.63 (p, $J$ = 7.6 Hz, 2H), 1.24 – 1.07 (m, 14H), 0.79 (t, $J$ = 7.0 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.4, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.3, 121.9, 31.9, 29.5, 29.5, 29.4, 29.3, 29.0, 28.0, 23.7, 22.7, 21.3, 14.1.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{25}H_{32}O_2S$, 419.2021, Found: 419.2022.

**2-dodecyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ka)**




**3ka** **3ka'**

**3ka+3ka'** was obtained in 40% (33.9 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

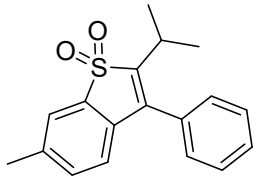
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.54 – 7.47 (m, 3H), 7.35 – 7.31 (m, 2H), 7.26 – 7.20 (m, 1H), 6.99 (d, $J$ = 7.7 Hz, 1H), 2.56 – 2.51 (m, 2H), 2.43 (s, 3H), 1.72 (p, $J$ = 7.8 Hz, 2H), 1.32 – 1.17

(m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.2, 138.7, 138.4, 136.5, 133.8, 131.0, 131.0, 129.2, 129.0, 128.5, 123.2, 121.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 28.0, 23.7, 22.7, 21.3, 14.1.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{27}H_{36}O_2S$, 447.2334, Found: 447.2328.

**2-isopropyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3la)**



**3la**

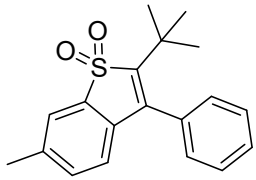
**3la** was obtained in 57% (34.0 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.55 (s, 1H), 7.54 – 7.45 (m, 3H), 7.34 – 7.29 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 3.05 (p, *J* = 7.1 Hz, 1H), 2.42 (s, 3H), 1.37 (d, *J* = 7.0 Hz, 6H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 143.1, 140.2, 137.7, 136.7, 133.7, 131.5, 131.0, 129.1, 129.0, 128.4, 123.3, 121.4, 27.2, 21.4, 21.3.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{18}H_{18}O_2S$, 299.1106, Found: 299.1108.

**2-(*tert*-butyl)-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ma)**



**3ma**

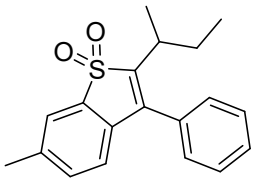
**3ma** was obtained in 69% (43.1 mg) as a colorless crystal after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.52 (s, 1H), 7.51 – 7.41 (m, 3H), 7.25 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.21 – 7.11 (m, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 1.31 (s, 9H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 145.8, 140.3, 138.2, 135.6, 133.8, 133.3, 132.2, 128.7, 128.6, 128.5, 123.3, 120.9, 35.2, 30.6, 21.3.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{19}H_{20}O_2S$, 313.1262, Found: 313.1266.

**2-(sec-butyl)-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3na)**



**3na**

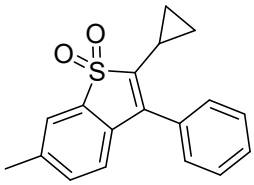
**3na** was obtained in 42% (26.2 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.55 (s, 1H), 7.54 – 7.42 (m, 3H), 7.30 – 7.28 (m, 2H), 7.23 (d, $J$ = 7.7 Hz, 1H), 6.85 (d, $J$ = 7.7 Hz, 1H), 2.86 – 2.64 (m, 1H), 2.42 (s, 3H), 1.98 – 1.79 (m, 1H), 1.67 – 1.51 (m, 1H), 1.38 (d, $J$ = 7.1 Hz, 3H), 0.89 (t, $J$ = 7.3 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 142.2, 140.2, 138.7, 136.7, 133.7, 129.0, 128.9, 128.5, 123.3, 121.4, 34.6, 28.0, 21.3, 19.5, 12.6.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{19}H_{20}O_2S$, 313.1262, Found: 313.1265.

**2-cyclopropyl-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3oa)**



**3oa**

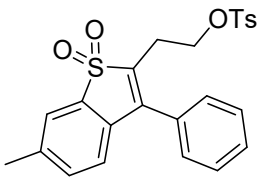
**3oa** was obtained in 56% (33.2 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.54 (s, 1H), 7.53 – 7.50 (m, 2H), 7.50 – 7.47 (m, 1H), 7.46 – 7.42 (m, 2H), 7.25 (d, $J$ = 7.1 Hz, 1H), 7.03 (d, $J$ = 7.8 Hz, 1H), 2.42 (s, 3H), 1.75 (tt, $J$ = 8.6, 5.4 Hz, 1H), 1.22 (dt, $J$ = 6.8, 4.9 Hz, 2H), 0.93 – 0.86 (m, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.0, 138.6, 138.3, 136.3, 133.8, 131.1, 130.5, 129.2, 128.9, 128.8, 21.3, 6.8, 6.6.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{18}H_{16}O_2S$, 297.0949, Found: 297.0950.

**2-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)ethyl 4-methylbenzenesulfonate (3pa)**



**3pa**

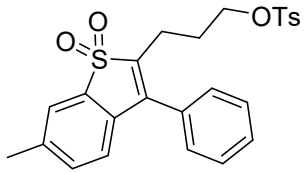
**3pa** was obtained in 36% (32.7 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.71 (dd, $J$ = 8.3, 1.9 Hz, 2H), 7.56 (s, 1H), 7.52 (dt, $J$ = 4.1, 2.1 Hz, 3H), 7.33 (dd, $J$ = 5.1, 2.2 Hz, 2H), 7.28 (t, $J$ = 7.9 Hz, 3H), 7.03 – 7.00 (m, 1H), 4.29 (td, $J$ = 7.0, 1.8 Hz, 2H), 2.90 (td, $J$ = 7.1, 1.8 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 144.9, 141.7, 141.0, 136.2, 134.0, 132.7, 132.5, 130.5, 129.8, 129.7, 129.2, 128.4, 128.0, 127.3, 123.9, 122.0, 66.6, 23.8, 21.6, 21.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{24}H_{22}O_5S_2$, 477.0806, Found: 477.0806.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 4-methylbenzenesulfonate (3qa)**




**3qa**

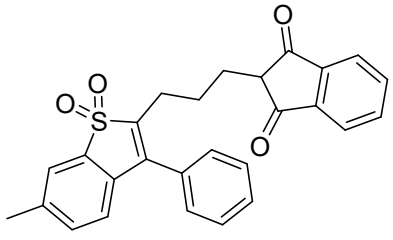
**3qa** was obtained in 55% (51.5 mg) as a colorless oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.72 – 7.69 (m, 2H), 7.57 (s, 1H), 7.56 – 7.50 (m, 3H), 7.34 – 7.28 (m, 5H), 7.01 (d, $J$ = 7.8 Hz, 1H), 4.05 (td, $J$ = 6.0, 1.6 Hz, 2H), 2.60 (dd, $J$ = 8.8, 6.8 Hz, 2H), 2.43 (s, 6H), 2.12 – 2.03 (m, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 144.8, 140.6, 139.8, 136.3 (d, $J$ = 2.0 Hz), 133.9, 132.9, 130.6, 130.3, 129.8, 129.6, 129.2, 128.4, 127.9, 123.6, 121.9, 69.3, 27.1, 21.6, 21.4, 20.0.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{25}H_{24}O_5S_2$, 491.0963, Found: 491.0952.

**2-(3-(6-Methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl)-1H-indene-1,3(2H)-dione (3ta)**




**3ta**

**3ta** was obtained in 44% (38.94 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

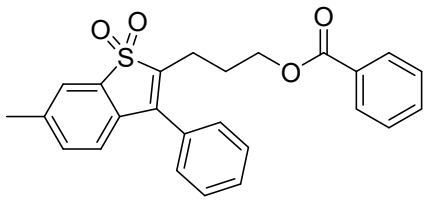
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.96 (dd, J = 8.2, 1.5 Hz, 2H), 7.78 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd,

J = 5.5, 3.0 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 3.59 (t, J = 6.9 Hz, 2H), 2.38 (s, 3H), 2.14 – 2.05 (m, 2H), 1.63 (ddd, J = 9.9, 6.5, 3.6 Hz, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 192.3, 168.2, 145.4, 134.1, 134.0, 133.2, 131.9, 129.8, 129.5, 129.1, 128.8, 123.3, 77.3, 68.9, 36.9, 25.6, 25.4, 21.7.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{27}H_{22}O_4S$, 466.1089, Found: 466.1086.

**3-(6-Methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl benzoate (3ua)**



**3ua**

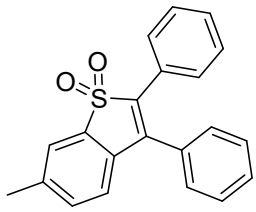
**3ua** was obtained in 30% (25.11 mg) as a colorless solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.89 – 7.85 (m, 2H), 7.61 (s, 1H), 7.57 – 7.53 (m, 1H), 7.40 (ddd, J = 15.5, 8.3, 5.0 Hz, 5H), 7.33 – 7.27 (m, 3H), 7.01 (d, J = 7.7 Hz, 1H), 4.30 (t, J = 6.0 Hz, 2H), 2.80 (dd, J = 8.6, 6.8 Hz, 2H), 2.45 (s, 3H), 2.28 – 2.19 (m, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 166.3, 140.5, 139.5, 137.1, 136.4, 133.9, 132.9, 130.7, 130.6, 130.0, 129.6, 129.3, 129.1, 128.3, 128.2, 100.00, 63.7, 27.00, 21.4, 20.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{25}H_{22}O_4S$, 441.1136, Found: 441.1131.

**6-methyl-2,3-diphenylbenzo[*b*]thiophene 1,1-dioxide (3Aa)**



**3Aa**

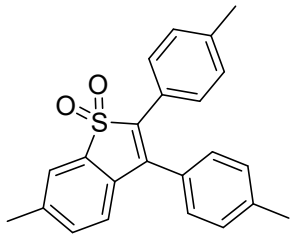
**3Aa** was obtained in 69% (45.8 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.66 (s, 1H), 7.53 – 7.45 (m, 2H), 7.44 – 7.41 (m, 3H), 7.36 – 7.23 (m, 6H), 7.17 (d, *J* = 7.9 Hz, 1H), 2.46 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 141.0, 138.2, 136.6, 136.5, 134.0, 131.1, 130.6, 129.5, 129.4, 129.3, 129.1, 129.1, 128.7, 127.2, 124.0, 122.1, 21.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{21}H_{16}O_2S$, 355.0769, Found: 355.0768.

**6-methyl-2,3-di-p-tolylbenzo[*b*]thiophene 1,1-dioxide (3Ba)**



**3Ba**

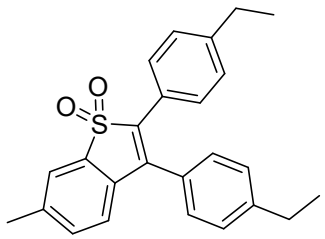
**3Ba** was obtained in 64% (46.1 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (s, 1H), 7.37 (d, $J$ = 8.3 Hz, 2H), 7.31 (d, $J$ = 7.9 Hz, 1H), 7.26 – 7.20 (m, 4H), 7.18 (d, $J$ = 7.9 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 2H), 2.47 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.6, 139.6, 139.4, 137.5, 136.5, 136.3, 133.8, 130.9, 129.8, 129.4, 129.1, 129.0, 128.2, 124.4, 123.9, 122.0, 21.4, 21.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{23}H_{20}O_2S$, 383.1082, Found: 383.1085.

**2,3-bis(4-ethylphenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Ca)**



**3Ca**

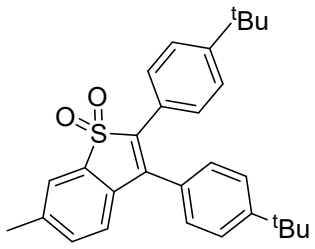
**3Ca** was obtained in 52% (40.4 mg) as a green oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (s, 1H), 7.39 (d, $J$ = 8.3 Hz, 2H), 7.31 (d, $J$ = 7.8 Hz, 1H), 7.27 – 7.23 (m, 4H), 7.18 (d, $J$ = 7.9 Hz, 1H), 7.12 (d, $J$ = 8.1 Hz, 2H), 2.70 (q, $J$ = 7.6 Hz, 2H), 2.61 (q, $J$ = 7.6 Hz, 2H), 2.46 (s, 3H), 1.28 (t, $J$ = 7.6 Hz, 3H), 1.20 (t, $J$ = 7.6 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 145.7, 145.6, 140.6, 137.4, 136.5, 136.3, 130.9, 129.1, 129.0, 128.6, 128.4, 128.2, 124.6, 123.9, 122.0, 28.7, 21.4, 15.2, 15.1.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{25}H_{24}O_2S$, 411.1395, Found: 411.1395.

**2,3-bis(4-(*tert*-butyl)phenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Da)**




**3Da**

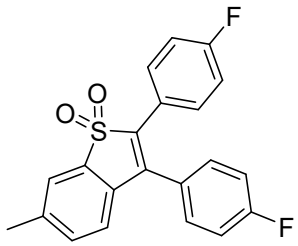
**3Da** was obtained in 43% (38.2 mg) as a brown oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.58 (s, 1H), 7.37 (ddd, $J$ = 18.4, 8.7, 2.2 Hz, 4H), 7.26 – 7.21 (m, 4H), 7.20 (s, 1H), 7.11 (dd, $J$ = 7.7, 2.2 Hz, 1H), 2.39 (s, 3H), 1.30 (s, 9H), 1.22 (s, 9H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 152.5, 140.6, 137.3, 136.4, 136.2, 133.8, 131.1, 128.8, 128.3, 126.0, 125.7, 124.3, 124.0, 122.0, 34.9, 34.8, 31.3, 31.1, 21.4.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{29}H_{32}O_2S$, 467.2021, Found: 467.2011.

**2,3-bis(4-fluorophenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Ea)**




**3Ea**

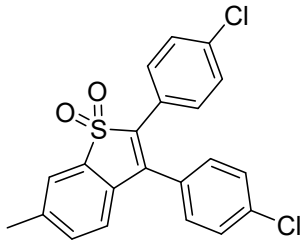
**3Ea** was obtained in 58% (42.7 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.67 (s, 1H), 7.44 (dd, $J$ = 8.7, 5.4 Hz, 2H), 7.35 (d, $J$ = 7.9 Hz, 1H), 7.31 (dd, $J$ = 8.5, 5.3 Hz, 2H), 7.20 – 7.12 (m, 3H), 7.01 (t, $J$ = 8.7 Hz, 2H), 2.48 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 141.3, 137.2, 136.3, 135.9, 134.1, 131.4, 131.3, 131.1, 131.0, 130.2, 126.7, 126.7, 123.8, 123.1, 123.0, 122.3, 116.6, 116.5, 116.2, 116.1, 21.5.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{21}H_{14}F_2O_2S$, 369.0761, Found: 369.0758.

**2,3-bis(4-chlorophenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Fa)**




**3Fa**

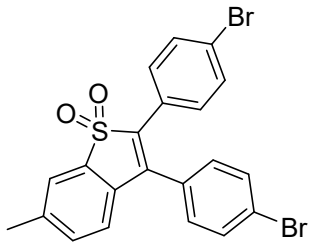
**3Fa** was obtained in 49% (39.2 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.67 (s, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.38 (m, 2H), 7.37 – 7.34 (m, 1H), 7.30 (d, $J$ = 8.6 Hz, 2H), 7.27 (d, $J$ = 3.8 Hz, 2H), 7.15 (d, $J$ = 7.9 Hz, 1H), 2.49 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 141.5, 137.5, 136.4, 136.0, 135.9, 134.1, 130.5, 130.4, 129.9, 129.7, 129.3, 125.4, 123.8, 122.4, 21.5.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{21}H_{14}Cl_2O_2S$, 401.0170, Found: 401.0176.

**2,3-bis(4-bromophenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Ga)**




**3Ga**

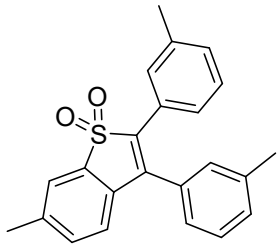
**3Ga** was obtained in 44% (42.9 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.67 (s, 1H), 7.60 (d, $J$ = 8.1 Hz, 2H), 7.45 (d, $J$ = 8.4 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.19 (d, $J$ = 8.3 Hz, 2H), 7.14 (d, $J$ = 7.8 Hz, 1H), 2.48 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 141.5, 137.5, 136.4, 136.0, 134.2, 132.7, 132.2, 130.7, 130.6, 129.8, 129.6, 125.9, 124.4, 124.1, 123.8, 122.4, 21.5.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{21}H_{14}Br_2O_2S$, 488.9160, Found: 488.9164.

**6-methyl-2,3-di-m-tolylbenzo[*b*]thiophene 1,1-dioxide (3Ha)**



**3Ha**

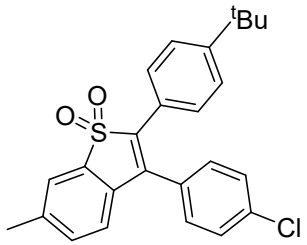
**3Ha** was obtained in 41% (29.5 mg) as a yellow oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (s, 1H), 7.37 (s, 1H), 7.34 – 7.27 (m, 2H), 7.23 (d, $J$ = 7.7 Hz, 1H), 7.16 (dd, $J$ = 5.1, 2.6 Hz, 2H), 7.13 (dd, $J$ = 7.3, 2.1 Hz, 3H), 7.10 (d, $J$ = 8.1 Hz, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 140.8, 138.8, 138.3, 138.1, 136.5, 133.9, 131.1, 130.8, 130.3, 130.1, 129.5, 129.4, 129.0, 128.5, 127.1, 126.6, 126.2, 124.0, 122.0, 21.5, 21.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{23}H_{20}O_2S$, 383.1082, Found: 383.1075.

**2-(4-(*tert*-butyl)phenyl)-3-(4-chlorophenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Ia)**



**3Ia**

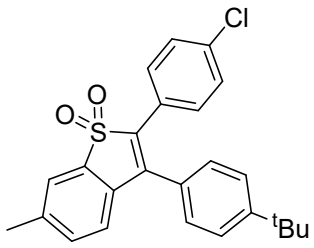
**3Ia** was obtained in 26% (21.9 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (s, 1H), 7.44 (d, $J$ = 8.0 Hz, 2H), 7.40 (d, $J$ = 8.4 Hz, 2H), 7.33 (d, $J$ = 7.7 Hz, 1H), 7.26 (d, $J$ = 7.7 Hz, 2H), 7.22 (d, $J$ = 8.0 Hz, 3H), 2.47 (s, 3H), 1.35 (s, 9H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 153.0, 141.1, 138.8, 136.4, 135.5, 135.0, 134.0, 130.5 (d, $J$ = 6.0 Hz), 129.6, 129.0, 128.7, 127.6, 126.2, 125.9, 124.3, 122.1, 34.9, 31.2, 21.5.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{25}H_{23}ClO_2S$, 445.1005, Found: 445.1000.

**3-(4-(*tert*-butyl)phenyl)-2-(4-chlorophenyl)-6-methylbenzo[*b*]thiophene 1,1-dioxide (3Ia')**




**3Ia'**

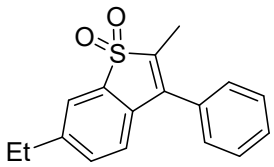
**3Ia'** was obtained in 24% (20.2 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.66 (s, 1H), 7.44 (d, $J$ = 8.2 Hz, 2H), 7.39 (d, $J$ = 8.2 Hz, 2H), 7.31 (dt, $J$ = 11.2, 6.6 Hz, 5H), 7.11 (d, $J$ = 7.8 Hz, 1H), 2.47 (s, 3H), 1.28 (s, 9H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 153.0, 141.0, 137.1, 136.4, 136.0, 135.4, 134.0, 130.5, 130.4, 129.6, 129.0, 128.8, 125.9, 123.8, 123.6, 122.2, 34.8, 31.1, 21.4.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{25}H_{23}ClO_2S$, 445.1005, Found: 445.1001.

**6-ethyl-2-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ab)**




**3ab**

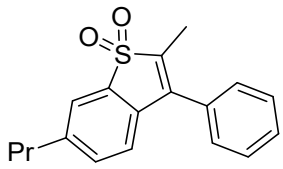
**3ab** was obtained in 69% (39.2 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (s, 1H), 7.58 – 7.45 (m, 3H), 7.39 – 7.33 (m, 2H), 7.30 (dd, $J$ = 7.8, 1.7 Hz, 1H), 7.11 (d, $J$ = 7.8 Hz, 1H), 2.73 (q, $J$ = 7.6 Hz, 2H), 2.14 (s, 3H), 1.27 (t, $J$ = 7.6 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 146.4, 137.9, 136.4, 134.5, 132.8, 131.2, 130.7, 129.4, 129.0, 128.6, 123.3, 121.0, 28.6, 15.2, 7.5.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{17}H_{16}O_2S$, 285.0949, Found: 285.0951.

**2-methyl-3-phenyl-6-propylbenzo[*b*]thiophene 1,1-dioxide (3ac)**




**3ac**

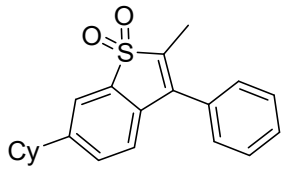
**3ac** was obtained in 51% (30.4 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.62 (s, 1H), 7.51 (ddd, $J$ = 13.6, 7.9, 6.1 Hz, 3H), 7.38 – 7.32 (m, 2H), 7.28 (dd, $J$ = 7.8, 1.6 Hz, 1H), 7.10 (d, $J$ = 7.8 Hz, 1H), 2.67 (t, $J$ = 7.6 Hz, 2H), 2.14 (s, 3H), 1.68 (dt, $J$ = 15.0, 7.5 Hz, 2H), 0.95 (t, $J$ = 7.3 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 144.9, 138.0, 136.3, 134.5, 133.4, 131.2, 130.6, 129.4, 129.0, 128.7, 123.2, 121.5, 37.7, 24.2, 13.6, 7.5.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{18}H_{18}O_2S$, 321.0925, Found: 321.0927.

**6-cyclohexyl-2-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ad)**




**3ad**

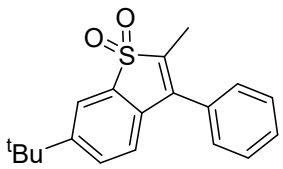
**3ad** was obtained in 64% (43.3 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.67 (s, 1H), 7.57 – 7.45 (m, 3H), 7.39 – 7.33 (m, 2H), 7.31 (dd, $J$ = 7.9, 1.7 Hz, 1H), 7.10 (d, $J$ = 7.9 Hz, 1H), 2.59 (td, $J$ = 11.4, 9.7, 5.5 Hz, 1H), 2.13 (s, 3H), 1.96 – 1.81 (m, 5H), 1.48 – 1.35 (m, 5H), 1.26 (d, $J$ = 5.8 Hz, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 149.6, 137.2, 135.6, 133.9, 131.2, 130.5, 130.0, 128.6, 128.3, 127.9, 122.6, 119.3, 43.7, 33.5, 25.9, 25.2, 6.8.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{21}H_{22}O_2S$, 339.1419, Found: 339.1418.

**6-(*tert*-butyl)-2-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ae)**




**3ae**

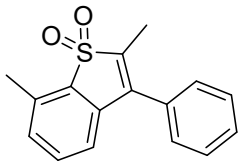
**3ae** was obtained in 55% (34.3 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.85 (s, 1H), 7.57 – 7.46 (m, 4H), 7.40 – 7.33 (m, 2H), 7.14 (d, $J$ = 7.9 Hz, 1H), 2.15 (s, 3H), 1.35 (s, 9H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 153.5, 137.8, 136.2, 134.8, 130.9, 130.6, 130.4, 129.4, 129.0, 128.6, 123.1, 118.7, 35.3, 31.1, 7.5.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{19}H_{20}O_2S$, 313.1262, Found: 313.1263.

**2,7-dimethyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3af)**



**3af**

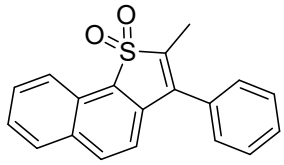
**3af** was obtained in 56% (30.3 mg) as a yellow oil after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.40 – 7.34 (m, 3H), 7.30 (dd, $J$ = 16.3, 8.0 Hz, 2H), 7.22 (t, $J$ = 7.5 Hz, 1H), 7.15 (d, $J$ = 8.1 Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 142.8, 139.4, 139.0, 137.2, 134.3, 133.6, 132.2, 129.1, 128.5, 128.0, 127.6, 124.8, 21.1, 21.1.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{16}H_{14}O_2S$, 293.0612, Found: 293.0610.

**2-methyl-3-phenylnaphtho[1,2-*b*]thiophene 1,1-dioxide (3ag)**



**3ag**

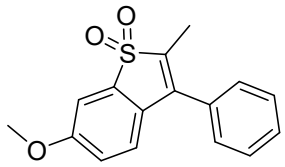
**3ag** was obtained in 43% (26.3 mg) as a yellow solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.00 (d, $J$ = 8.4 Hz, 1H), 7.87 (t, $J$ = 8.0 Hz, 2H), 7.62 – 7.55 (m, 3H), 7.47 (ddd, $J$ = 8.2, 6.3, 1.7 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.22 – 7.13 (m, 2H), 2.05 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 139.1, 137.0, 136.8, 134.1, 133.9, 131.2, 129.4, 129.3, 129.3, 128.5, 128.1, 127.8, 127.5, 125.2, 116.7, 7.6.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{19}H_{14}O_2S$, 307.0793, Found: 307.0793.

**6-methoxy-2-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (3ah)**



**3ah**

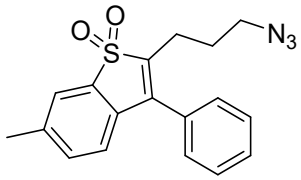
**3ah** was obtained in 67% (38.3 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.57 – 7.46 (m, 3H), 7.37 – 7.34 (m, 3H), 7.11 (d, $J$ = 8.4 Hz, 1H), 6.97 (dd, $J$ = 8.4, 2.5 Hz, 1H), 3.88 (s, 3H), 2.12 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 161.0, 138.0, 137.8, 133.5, 130.7, 129.4, 129.0, 128.6, 125.8, 124.5, 118.8, 107.3, 56.0, 7.5.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{16}H_{14}O_3S$, 309.0561, Found: 309.0563.

**2-(3-azidopropyl)-6-methyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (4)**



**4**

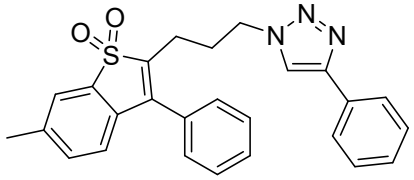
**4** was obtained in 92% (62.4 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.60 (s, 1H), 7.58 – 7.48 (m, 3H), 7.34 (d, $J$ = 6.9 Hz, 2H), 7.29 (d, $J$ = 7.9 Hz, 1H), 7.02 (d, $J$ = 7.8 Hz, 1H), 3.32 (t, $J$ = 6.5 Hz, 2H), 2.76 – 2.62 (m, 2H), 2.44 (s, 3H), 2.00 (p, $J$ = 6.8 Hz, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 140.6, 139.6, 136.9, 136.3, 134.0, 130.7, 130.5, 129.6, 129.2, 128.3, 123.5, 121.9, 50.6, 27.0, 21.4, 20.8.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{18}H_{17}N_3O_2S$, 362.0939, Found: 362.0939.

**6-methyl-3-phenyl-2-(3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propyl)benzo[*b*]thiophene 1,1-dioxide (5)**



**5**

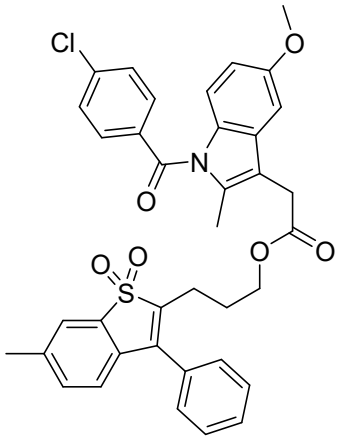
**5** was obtained in 89% (78.6 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.77 (d, $J$ = 7.3 Hz, 2H), 7.62 (s, 1H), 7.60 (s, 1H), 7.46 (dd, $J$ = 8.1, 6.3 Hz, 2H), 7.41 (dd, $J$ = 8.4, 6.7 Hz, 3H), 7.31 (dd, $J$ = 24.3, 7.6 Hz, 3H), 7.25 (s, 1H), 7.02 (d, $J$ = 7.8 Hz, 1H), 4.41 (t, $J$ = 6.9 Hz, 2H), 2.65 (t, $J$ = 7.5 Hz, 2H), 2.44 (s, 3H), 2.41 – 2.34 (m, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 147.8, 140.8, 140.0, 136.2, 136.2, 134.1, 130.6, 130.5, 130.2, 129.7, 129.3, 128.8, 128.2, 128.1, 125.8, 123.6, 122.0, 119.7, 49.3, 28.2, 21.4, 20.6.

**HRMS (ESI-TOF, $[M + H]^+$):** For $C_{26}H_{23}N_3O_2S$, 442.1589, Found: 442.1588.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (6)**



**6**

**6** was obtained in 83% (108.3 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

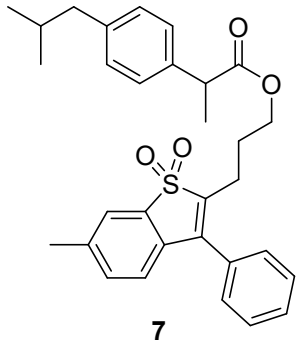
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.72 (d, $J$ = 7.9 Hz, 1H), 7.64 (d, $J$ = 8.2 Hz, 2H), 7.58 (s, 1H), 7.54 – 7.47 (m, 3H), 7.45 (d, $J$ = 8.3 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.00 (d, $J$ = 7.8 Hz, 1H), 6.91 (d, $J$ = 2.5 Hz, 1H), 6.88 (d, $J$ = 9.0 Hz, 1H), 6.65 (dd, $J$ = 9.1, 2.6 Hz, 1H), 4.08 (t, $J$ = 6.2 Hz, 2H), 3.81 (s, 3H), 3.55 (s, 2H), 2.64 (t, $J$ = 7.7 Hz, 2H), 2.60 (d, $J$ = 5.3 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 2.07 (dd, $J$ = 6.8, 2.2 Hz, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 170.7, 168.3, 156.1, 140.6, 139.4, 139.2, 137.0, 136.3, 135.9, 134.0,

131.2, 130.6, 129.7, 129.5, 129.2, 129.1, 128.4, 127.3, 123.5, 121.9, 115.0, 112.5, 111.7, 101.2, 63.9, 55.7, 30.1, 26.9, 21.4, 20.2, 13.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{37}H_{32}ClNO_6S$, 676.1537, Found: 676.1544.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 2-(4-isobutylphenyl)propanoate (7)**



**7**

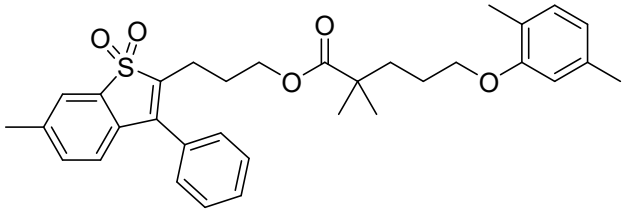
**7** was obtained in 80% (80.1 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.57 (s, 1H), 7.53 – 7.45 (m, 3H), 7.33 – 7.24 (m, 3H), 7.09 (d, $J$ = 7.8 Hz, 2H), 7.03 (d, $J$ = 7.9 Hz, 2H), 6.98 (d, $J$ = 7.8 Hz, 1H), 4.03 (ddt, $J$ = 39.6, 11.5, 6.1 Hz, 2H), 3.54 (q, $J$ = 7.1 Hz, 1H), 2.56 (t, $J$ = 8.3 Hz, 2H), 2.46 – 2.39 (m, 5H), 2.03 (dh, $J$ = 13.5, 7.0 Hz, 2H), 1.87 – 1.76 (m, $J$ = 6.8 Hz, 1H), 1.39 (d, $J$ = 7.2 Hz, 3H), 0.87 (s, 3H), 0.86 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 174.5, 140.5, 139.2, 137.6, 137.2, 136.4, 133.9, 130.7, 130.7, 129.4, 129.3, 129.1, 128.4, 127.1, 123.4, 121.9, 100.0, 63.6, 45.0, 30.2, 27.0, 22.4, 21.4, 20.3, 18.4.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{31}H_{34}O_4S$, 525.2075, Found: 525.2079.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (8)**



**8**

**8** was obtained in 95% (103.5 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

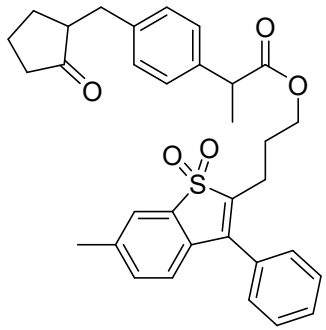
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.58 (s, 1H), 7.48 (dtd, $J$ = 12.7, 6.9, 1.6 Hz, 3H), 7.34 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 6.98 (dt, $J$ = 8.0, 1.8 Hz, 2H), 6.64 (d, $J$ = 7.5 Hz, 1H), 6.59 (s, 1H), 4.05 (td, $J$ =

6.1, 1.5 Hz, 2H), 3.86 (dt, *J* = 6.7, 3.4 Hz, 2H), 2.64 (dd, *J* = 9.1, 6.8 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H), 2.07 (dt, *J* = 10.5, 3.8 Hz, 2H), 1.73 – 1.58 (m, 4H), 1.11 (s, 6H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 177.6, 157.0, 140.5, 139.3, 137.2, 136.4, 136.4, 133.9, 130.7, 130.7, 130.3, 129.5, 129.2, 128.4, 123.6, 123.5, 121.9, 120.7, 112.0, 67.9, 63.4, 42.1, 37.0, 27.3, 25.1, 25.1, 21.4, 21.4, 20.5, 15.8.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{33}H_{38}O_5S$, 569.2338, Found: 569.2327.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (9)**



**9**

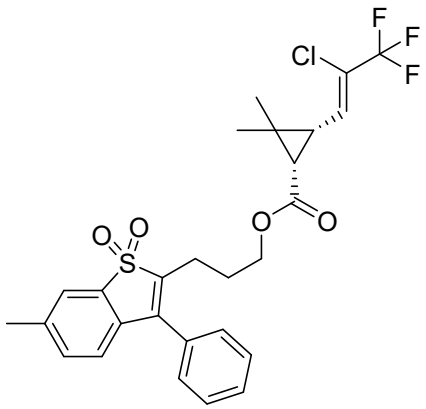
**9** was obtained in 82% (89.2 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.55 – 7.48 (m, 3H), 7.34 – 7.28 (m, 3H), 7.14 – 7.04 (m, 4H), 7.00 (d, *J* = 7.8 Hz, 1H), 4.04 (ddt, *J* = 34.5, 11.5, 6.2 Hz, 2H), 3.56 (q, *J* = 7.1 Hz, 1H), 3.11 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.63 (dd, *J* = 5.5, 1.2 Hz, 1H), 2.57 (t, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.36 – 2.28 (m, 2H), 2.06 – 2.00 (m, 4H), 1.97 – 1.89 (m, 1H), 1.77 – 1.65 (m, 1H), 1.60 – 1.47 (m, 1H), 1.40 (dd, *J* = 7.3, 1.3 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 174.4, 140.5, 139.3, 138.8, 138.2, 137.1, 136.3, 133.9, 130.7, 130.6, 129.7, 129.5, 129.1, 129.1, 128.4, 127.5, 127.3, 123.5, 121.9, 63.7, 51.0, 45.0, 38.2, 35.2, 29.2, 27.0, 21.4, 20.5, 20.2, 18.3.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{33}H_{34}O_5S$, 565.2015, Found: 565.2019.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl (1*S*,3*S*)-3-((*Z*)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl)-2,2-dimethylcyclopropane-1-carboxylate (10)**



**10**

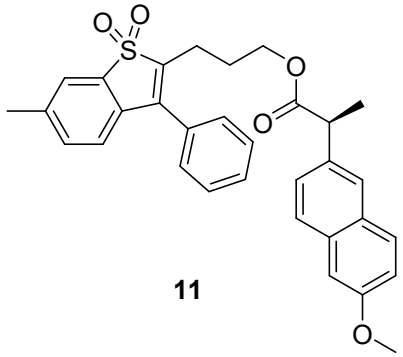
**10** was obtained in 80% (85.8 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59 (s, 1H), 7.51 (q, $J$ = 7.5, 7.1 Hz, 3H), 7.35 – 7.31 (m, 2H), 7.29 (s, 1H), 7.01 (d, $J$ = 7.8 Hz, 1H), 6.90 (d, $J$ = 9.4 Hz, 1H), 4.04 (qt, $J$ = 11.4, 6.0 Hz, 2H), 2.68 (t, $J$ = 7.7 Hz, 2H), 2.44 (s, 3H), 2.14 – 2.01 (m, 3H), 1.81 (d, $J$ = 8.3 Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 170.1, 140.5, 139.4, 137.0, 136.4, 133.9, 130.7, 130.6, 130.2 (q, $J$ = 4.5 Hz), 129.4, 129.1, 128.4, 123.5, 121.9, 63.4, 32.7, 30.8, 28.6, 28.3, 26.9, 21.3, 20.2, 14.8.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{27}H_{26}ClF_3O_4S$, 561.1090, Found: 561.1082.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (11)**



**11**

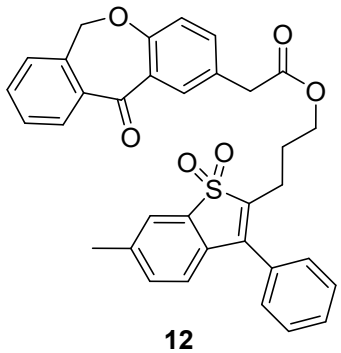
**11** was obtained in 68% (71.4 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.66 (t, $J$ = 8.5 Hz, 2H), 7.58 (t, $J$ = 2.2 Hz, 2H), 7.52 – 7.44 (m, 3H), 7.29 (ddd, $J$ = 16.8, 6.9, 2.8 Hz, 4H), 7.18 – 7.08 (m, 2H), 6.98 (d, $J$ = 7.9 Hz, 1H), 4.05 (ddt, $J$ = 45.4, 11.6, 6.2 Hz, 2H), 3.90 (s, 3H), 3.71 (q, $J$ = 7.2 Hz, 1H), 2.58 (ddd, $J$ = 8.7, 6.9, 2.1 Hz, 2H), 2.43 (s, 3H), 2.08 – 2.00 (m, 2H), 1.49 (d, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 174.4, 157.6, 140.5, 139.3, 137.1, 136.3, 135.6, 133.9, 133.6, 130.7, 130.6, 129.4, 129.3, 129.1, 128.9, 128.4, 127.1, 126.2, 125.9, 123.4, 121.9, 118.9, 105.6, 63.7, 55.3, 45.3, 26.9, 21.3, 20.2, 18.4.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{32}H_{30}O_5S$, 549.1712, Found: 549.1710.

**3-(6-methyl-1,1-dioxido-3-phenylbenzo[*b*]thiophen-2-yl)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (12)**



**12**

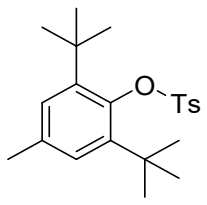
**12** was obtained in 89% (100.9 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.04 (d, $J$ = 2.4 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.59 – 7.58 (m, 1H), 7.57 – 7.50 (m, 4H), 7.48 – 7.44 (m, 1H), 7.38 – 7.32 (m, 4H), 7.28 (d, $J$ = 7.8 Hz, 1H), 7.00 (t, $J$ = 8.1 Hz, 2H), 5.17 (s, 2H), 4.08 (t, $J$ = 6.0 Hz, 2H), 3.48 (s, 2H), 2.66 (dd, $J$ = 8.6, 6.7 Hz, 2H), 2.43 (s, 3H), 2.07 (p, $J$ = 6.8 Hz, 2H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 190.7, 171.1, 170.6, 160.4, 140.5, 140.4, 139.4, 136.9, 136.3, 135.6, 133.9, 132.7, 132.3, 130.6, 130.5, 129.5, 129.4, 129.2, 129.1, 128.4, 127.8, 127.6, 125.0, 123.4, 121.8, 121.0, 73.6, 63.7, 39.9, 26.8, 21.3, 20.1.

**HRMS (ESI-TOF, $[M + Na]^+$):** For $C_{34}H_{28}O_6S$, 587.1504, Found: 587.1506.

**2,6-di-*tert*-butyl-4-methylphenyl 4-methylbenzenesulfonate (13)**



**13**

**13** was obtained in 55% (123.60 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

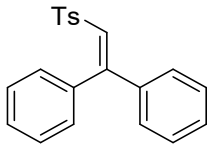
**$^1$H NMR (500 MHz, $CDCl_3$):** δ. 7.51 (d, $J$ = 8.2 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 2H), 6.63 (s, 2H), 2.36 (s,

3H), 1.81 (s, 3H), 1.10 (s, 18H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ = 183.7, 151.2, 145.3, 135.7, 130.6, 130.3, 128.8, 77.4, 77.0, 76.7, 65.8, 35.2, 29.0, 21.6, 18.5.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{22}H_{30}NaO_3S$, 397.1813, Found: 397.1814.

**(2-tosylethene-1,1-diyl)dibenzene (15)**




**15**

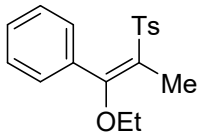
**15** was obtained in 79% (158.4 mg) as a white solid after column chromate-graphy (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** *δ* 7.47 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.30 (dd, *J* = 8.3, 6.8 Hz, 4H), 7.20 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** *δ* 154.5, 143.5, 139.0, 138.4, 135.4, 130.0, 129.6, 129.1, 128.8, 128.6, 128.4, 128.0, 127.6, 127.5, 21.4.

**HRMS (ESI-TOF, [M + H]$^+$):** For $C_{21}H_{18}O_2S$, 335.1106, Found: 335.1106.

**(*E*)-1-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (14)**




**16**

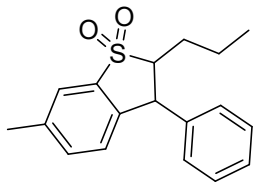
**16** was obtained in 51% (49.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.40 (d, J = 7.9 Hz, 3H), 7.38 – 7.28 (m, 2H), 7.23 – 7.17 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.48 (q, J = 7.0, 7.0, 7.1 Hz, 2H), 2.37 (s, 3H), 2.10 (s, 3H), 1.14 (t, J = 7.0, 7.0 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)**: δ = 162.8, 143.0, 139.3, 132.3, 129.8, 129.5, 129.2, 127.8, 127.3, 118.8, 77.3, 77.1, 76.8, 65.1, 21.5, 15.2, 12.8.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{18}H_{20}NaO_3S$, 339.1031, Found: 339.1038.

**6-Methyl-3-phenyl-2-propyl-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (17)**



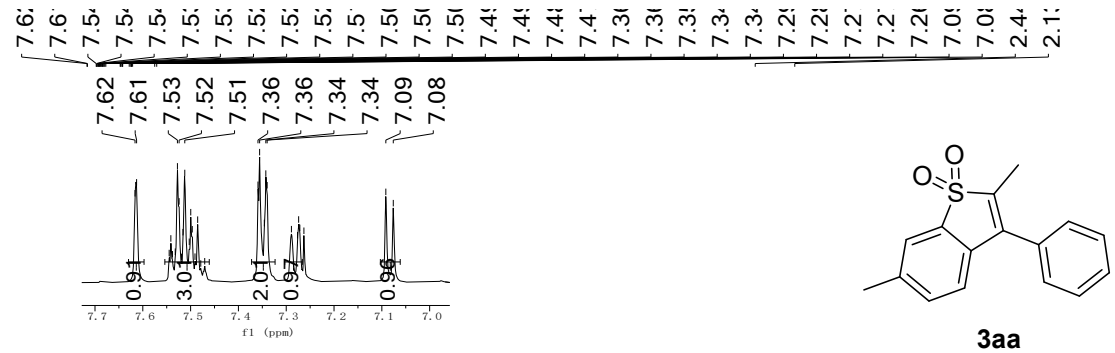
**17**

**17** was obtained in <5% yield under the reaction conditions as a colorless solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1, v/v).

**$^1$H NMR (500 MHz, $CDCl_3$)** $\delta$ 7.65 (s, 1H), 7.35 (d, $J$ = 7.9 Hz, 1H), 7.29 (d, $J$ = 7.4 Hz, 3H), 7.13 – 7.08 (m, 3H), 4.67 (d, $J$ = 8.6 Hz, 1H), 3.76 (td, $J$ = 8.4, 6.0 Hz, 1H), 2.45 (s, 3H), 1.65 (dtt, $J$ = 16.7, 8.4, 4.0 Hz, 2H), 1.55 – 1.23 (m, 2H), 0.88 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 139.7, 138.9, 138.1, 137.6, 134.8, 129.6, 128.5, 127.7, 127.7, 121.3, 64.0, 48.5, 27.4, 21.2, 20.3, 13.9.

**HRMS (ESI-TOF, [M + Na]$^+$):** For $C_{18}H_{20}O_2S$, 323.1082, Found: 323.1087.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7.53
7.52
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7.36
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7.34
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7.09
7.08
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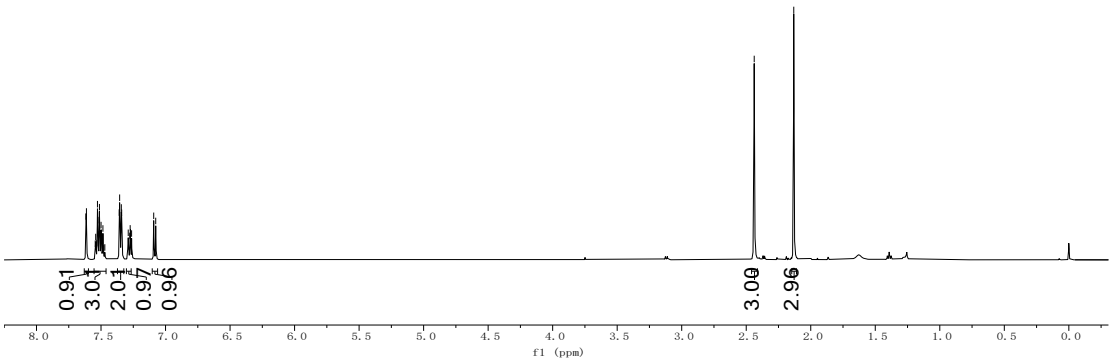
3.01
2.01
0.97
0.96
f1 (ppm)



3aa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2.01
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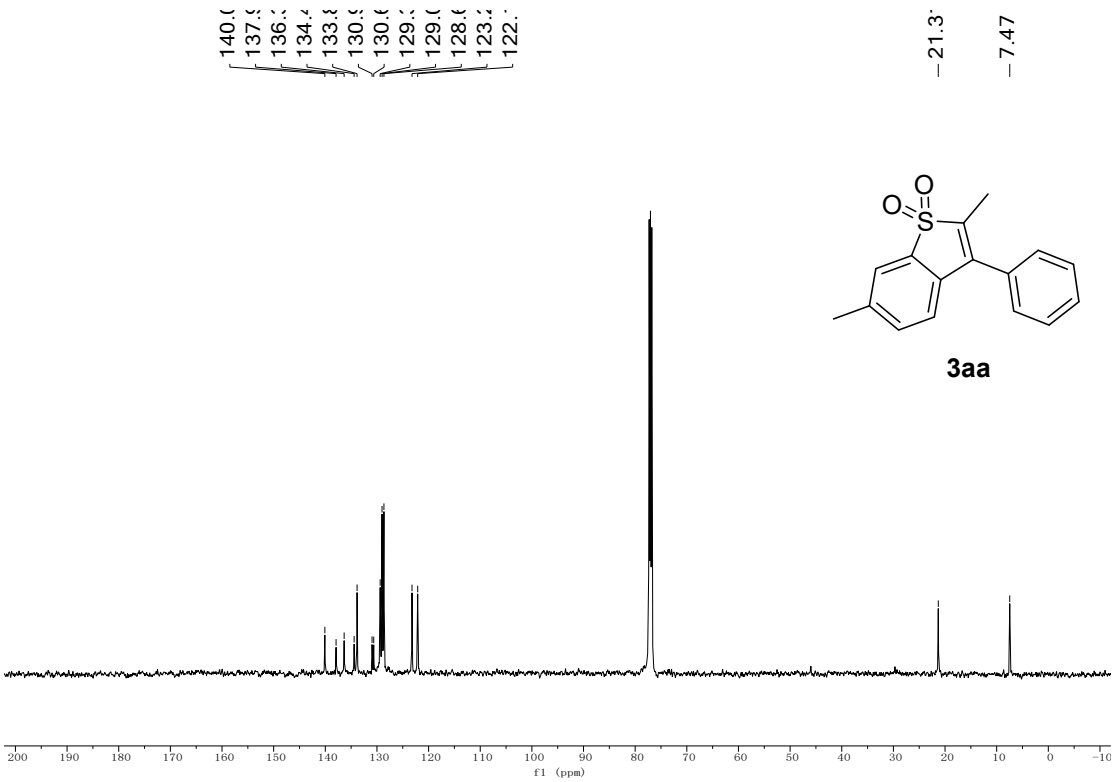
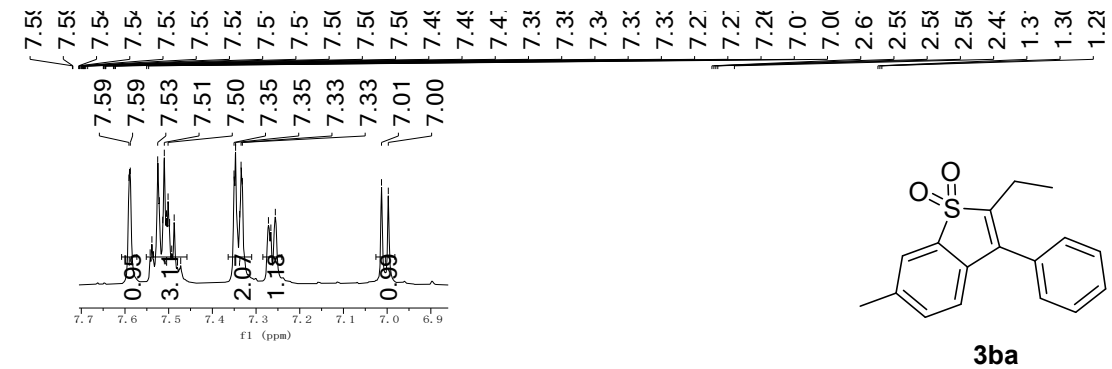
3.00
2.96
f1 (ppm)


21.3
7.47
f1 (ppm)

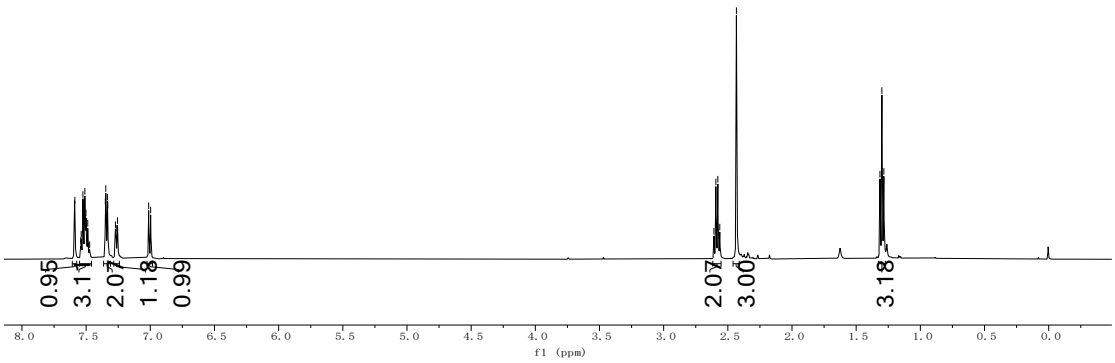


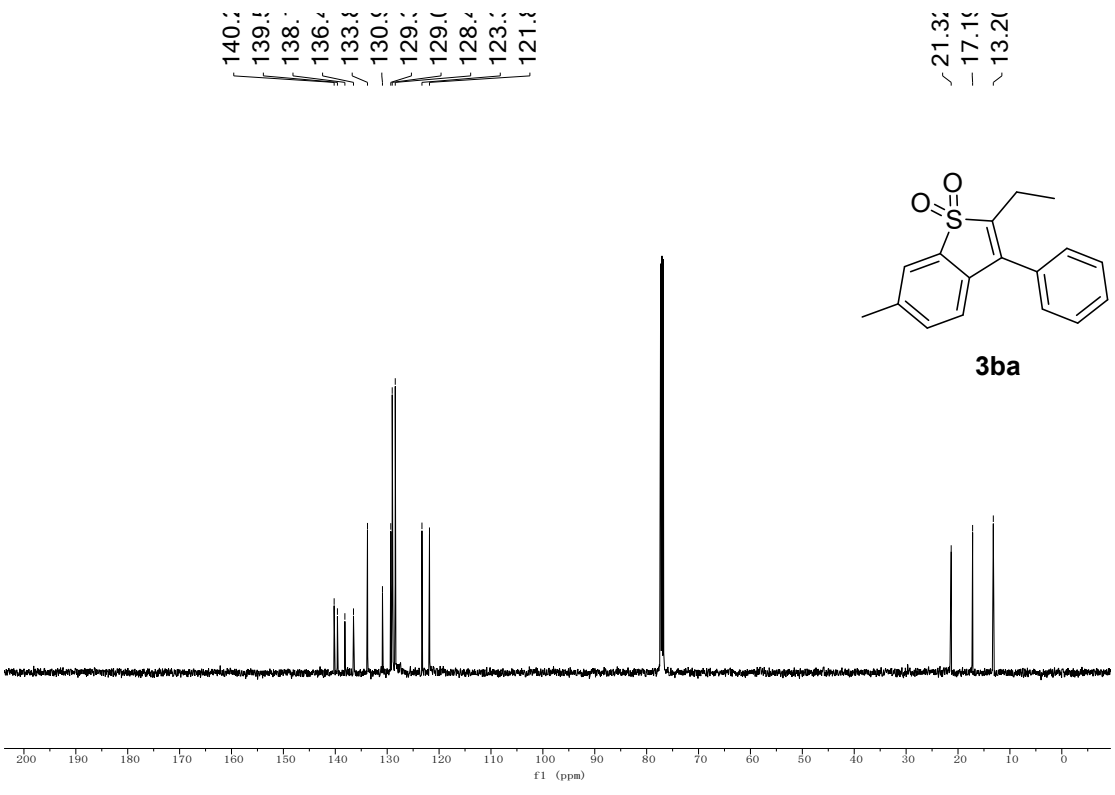
3aa





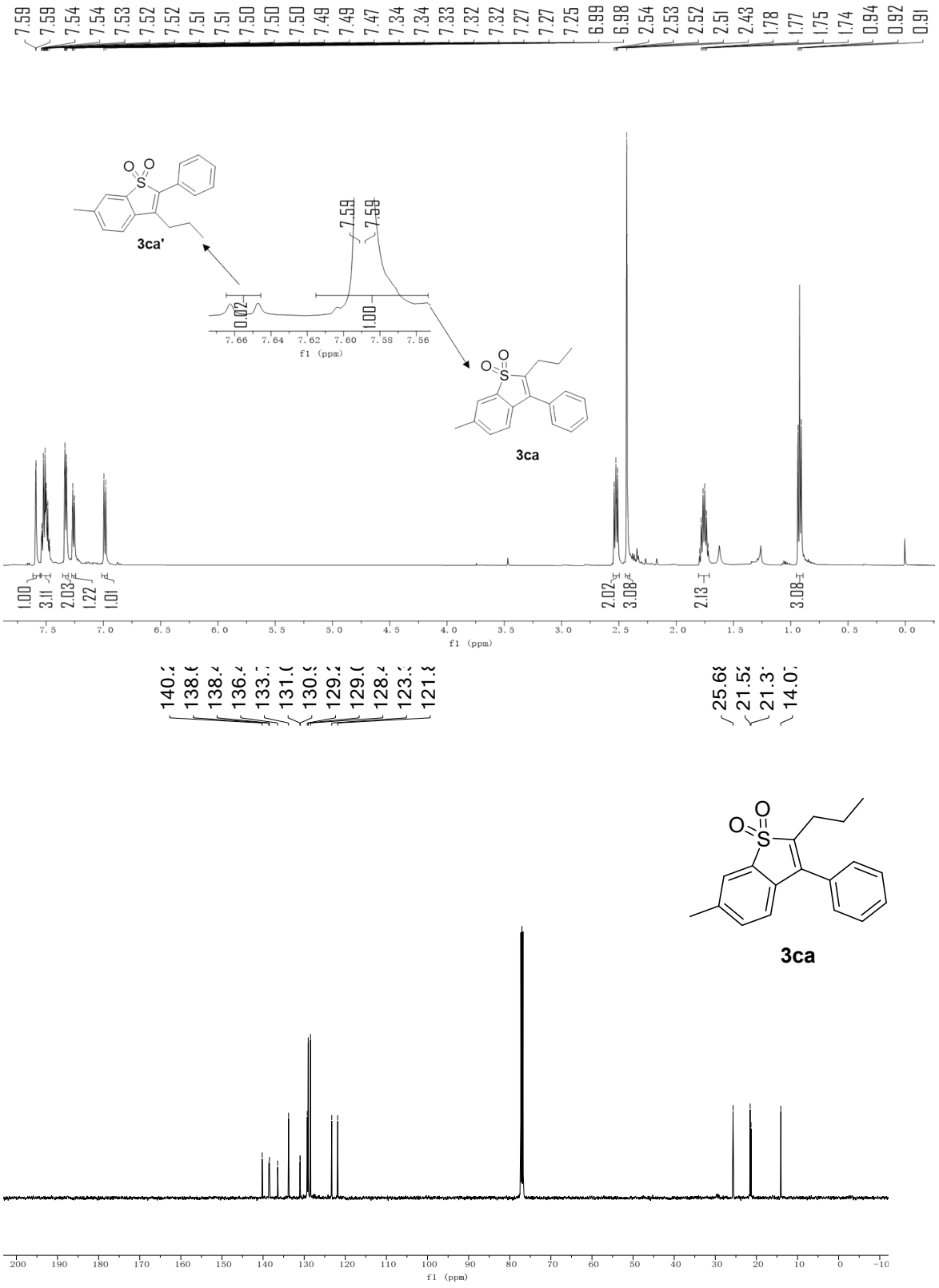
**3ba**







**3ba**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6.98
2.54
2.53
2.52
2.51
2.43
1.78
1.77
1.75
1.74
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0.92
0.91
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3ca
f1 (ppm)
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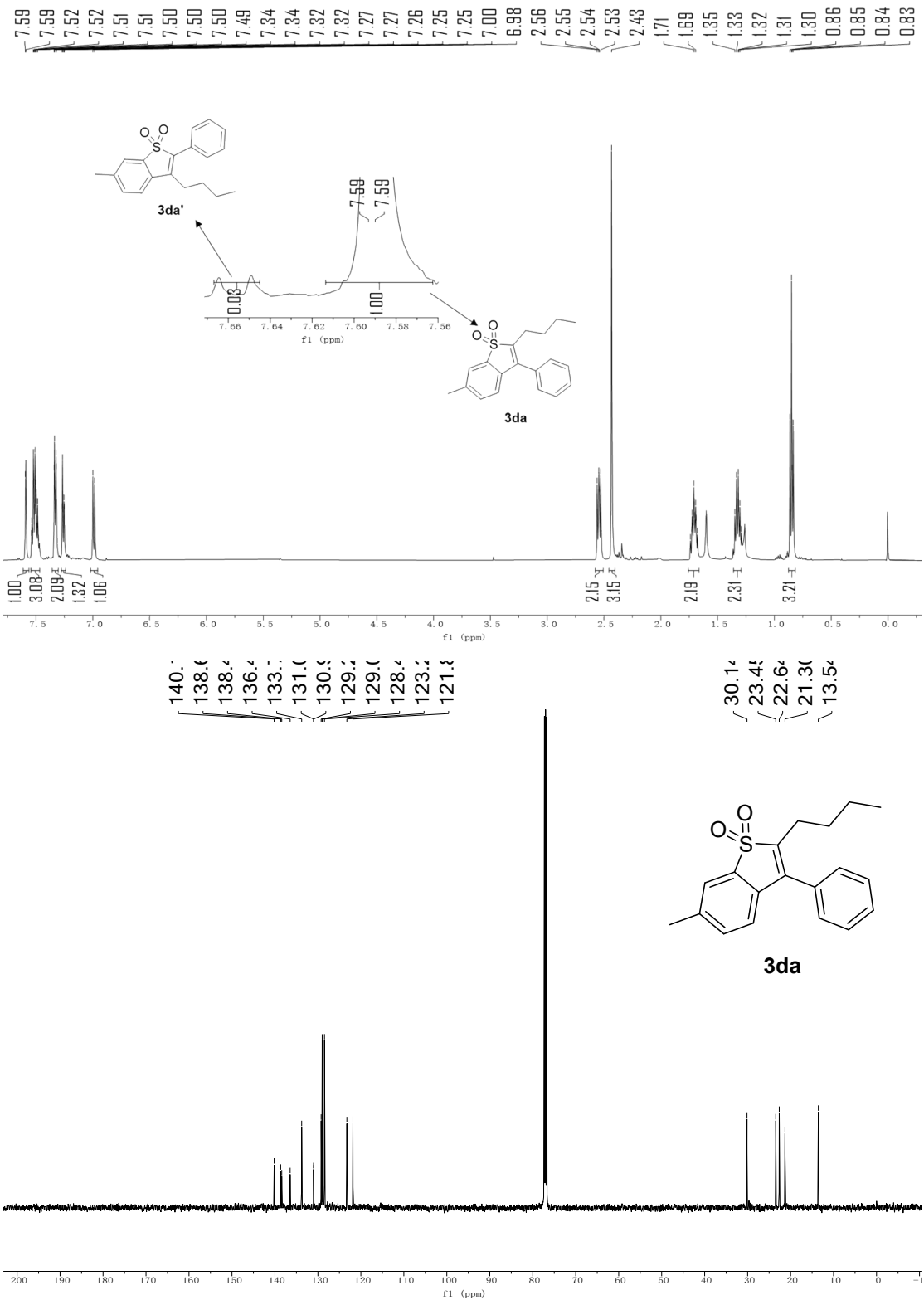
3.11
2.03
1.22
1.01
2.02
3.08
2.13
3.08
25.6
21.5
21.3
14.0
3ca
f1 (ppm)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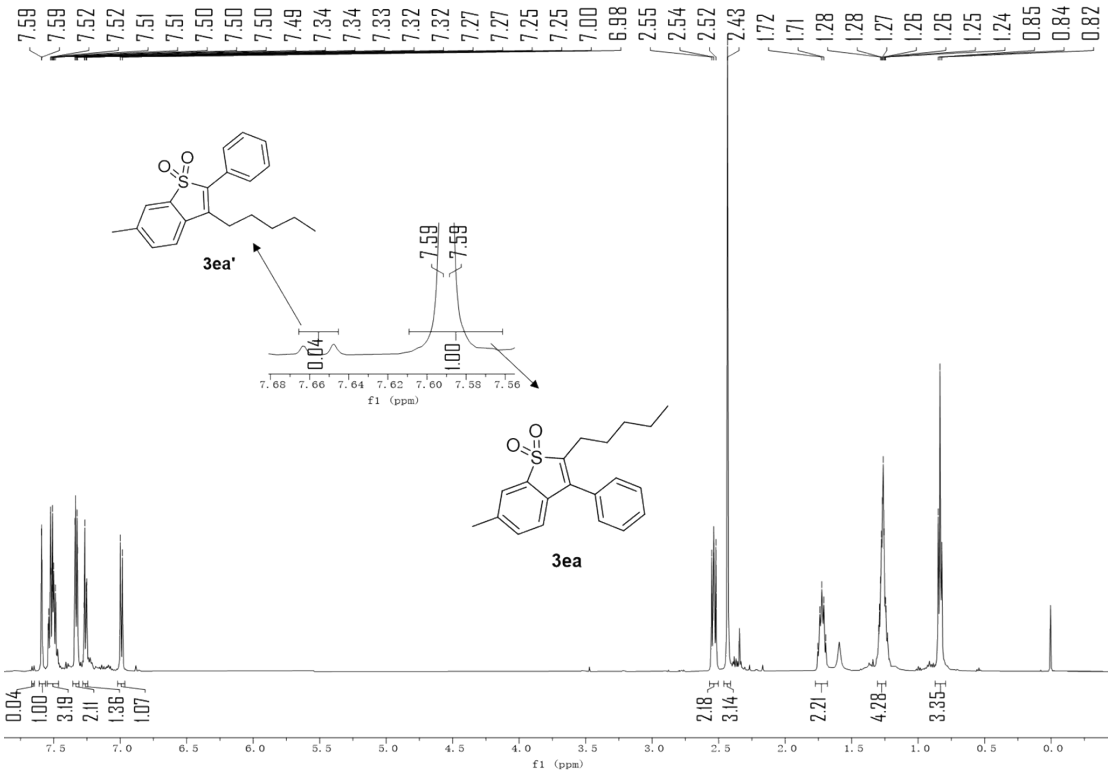
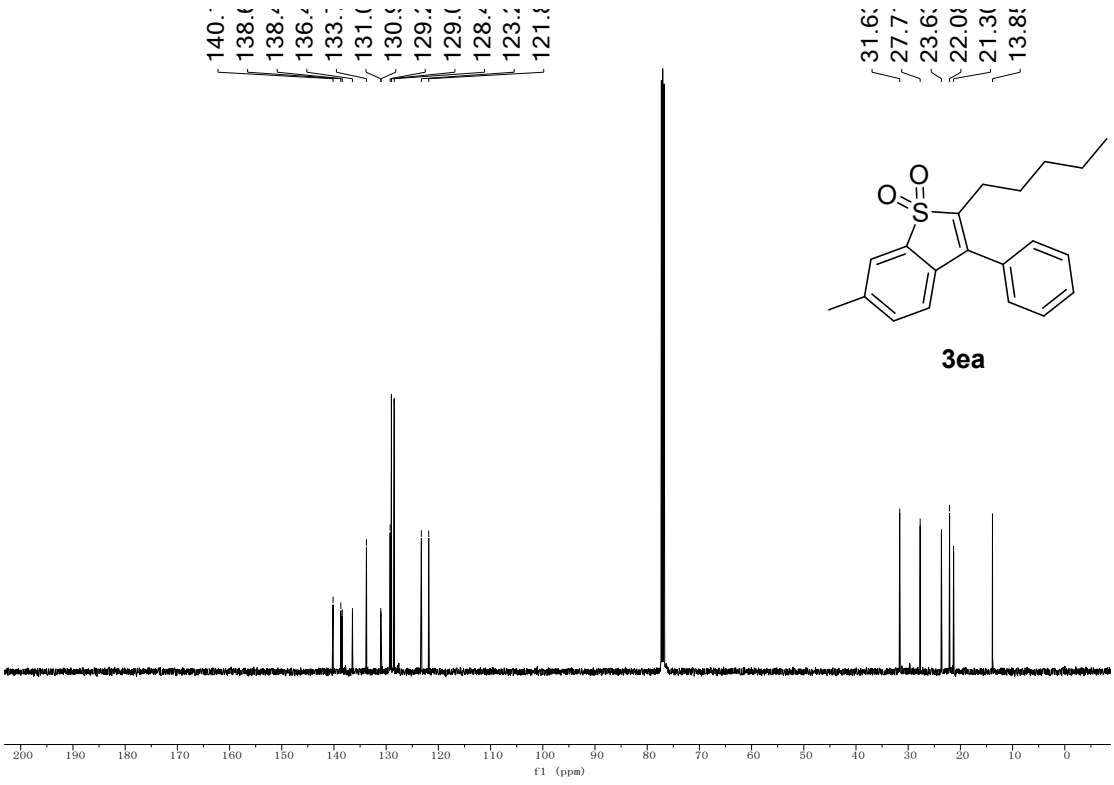
f1 (ppm)
3da


3ea'
3ea
f1 (ppm)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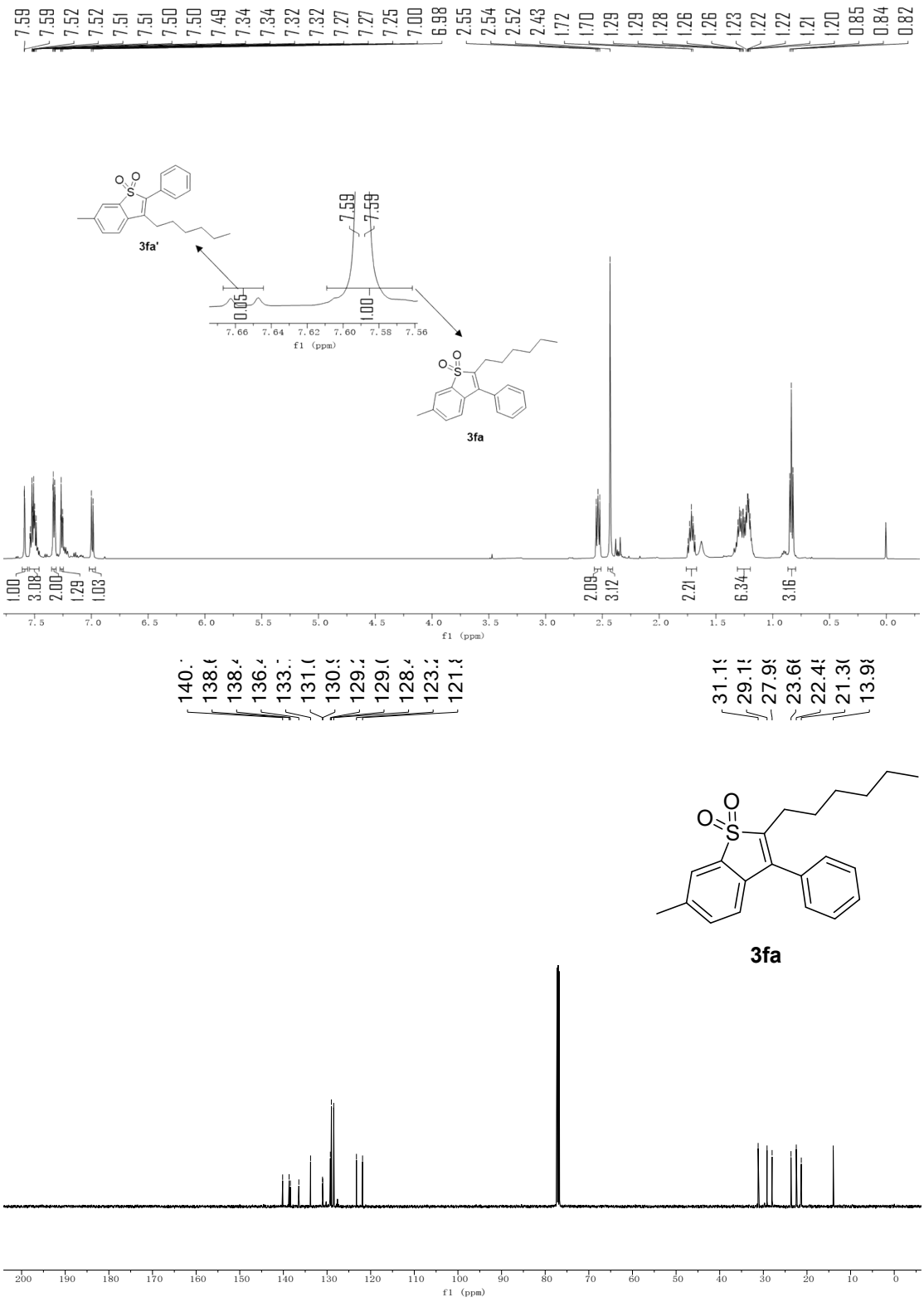
f1 (ppm)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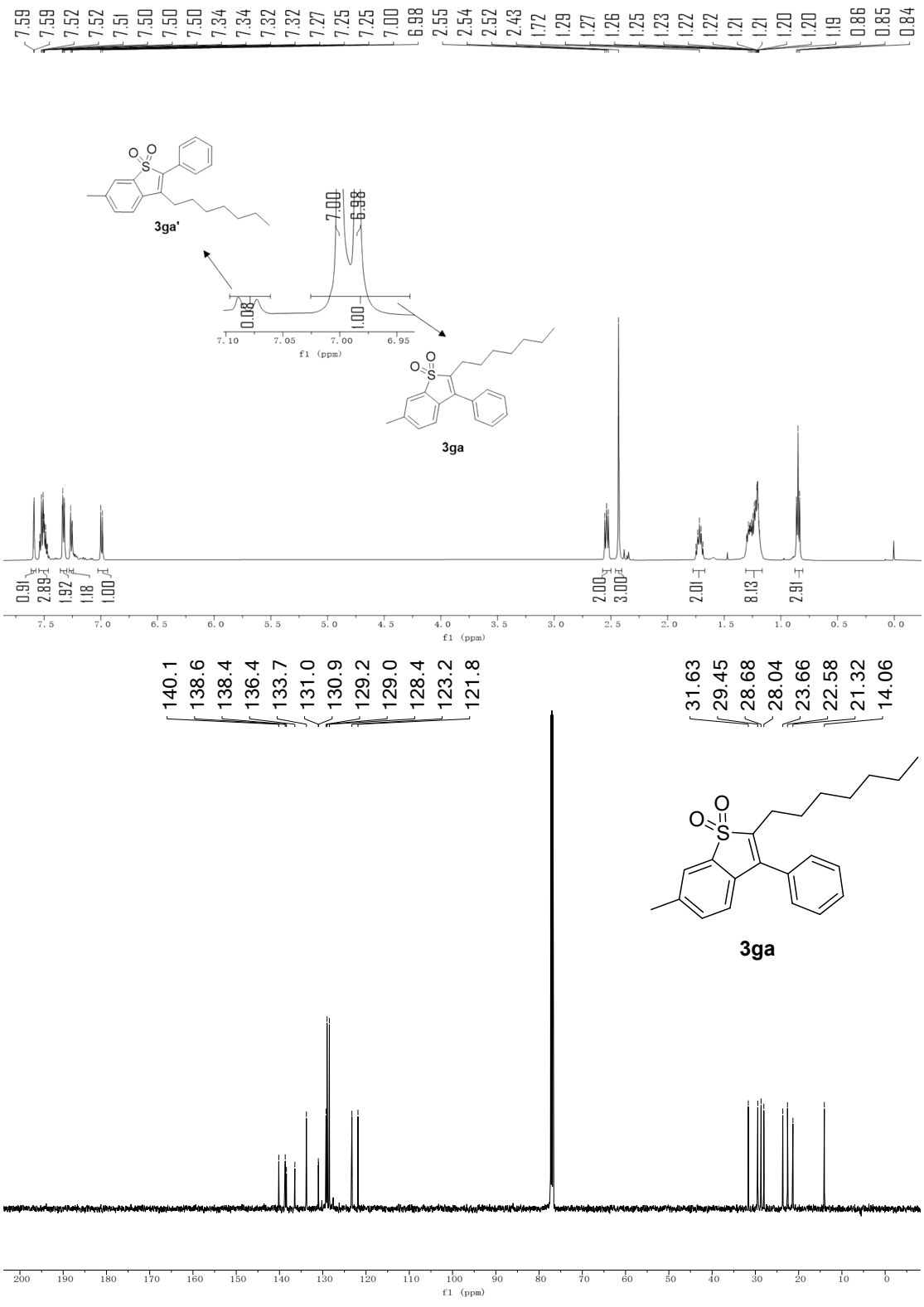
f1 (ppm)


3fa
f1 (ppm)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2.55 2.54 2.52 2.43 1.72 1.29 1.27 1.26 1.25 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.19 0.86 0.85 0.84
3ga'
7.00
6.98
0.08
1.00
7.10 7.05 7.00 6.95
f1 (ppm)
3ga
0.91 2.89 1.92 1.18 1.00
2.00 3.00 2.01 8.13 2.91
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)
140.1 138.6 138.4 136.4 133.7 131.0 130.9 129.2 129.0 128.4 123.2 121.8
31.63 29.45 28.68 28.04 23.66 22.58 21.32 14.06
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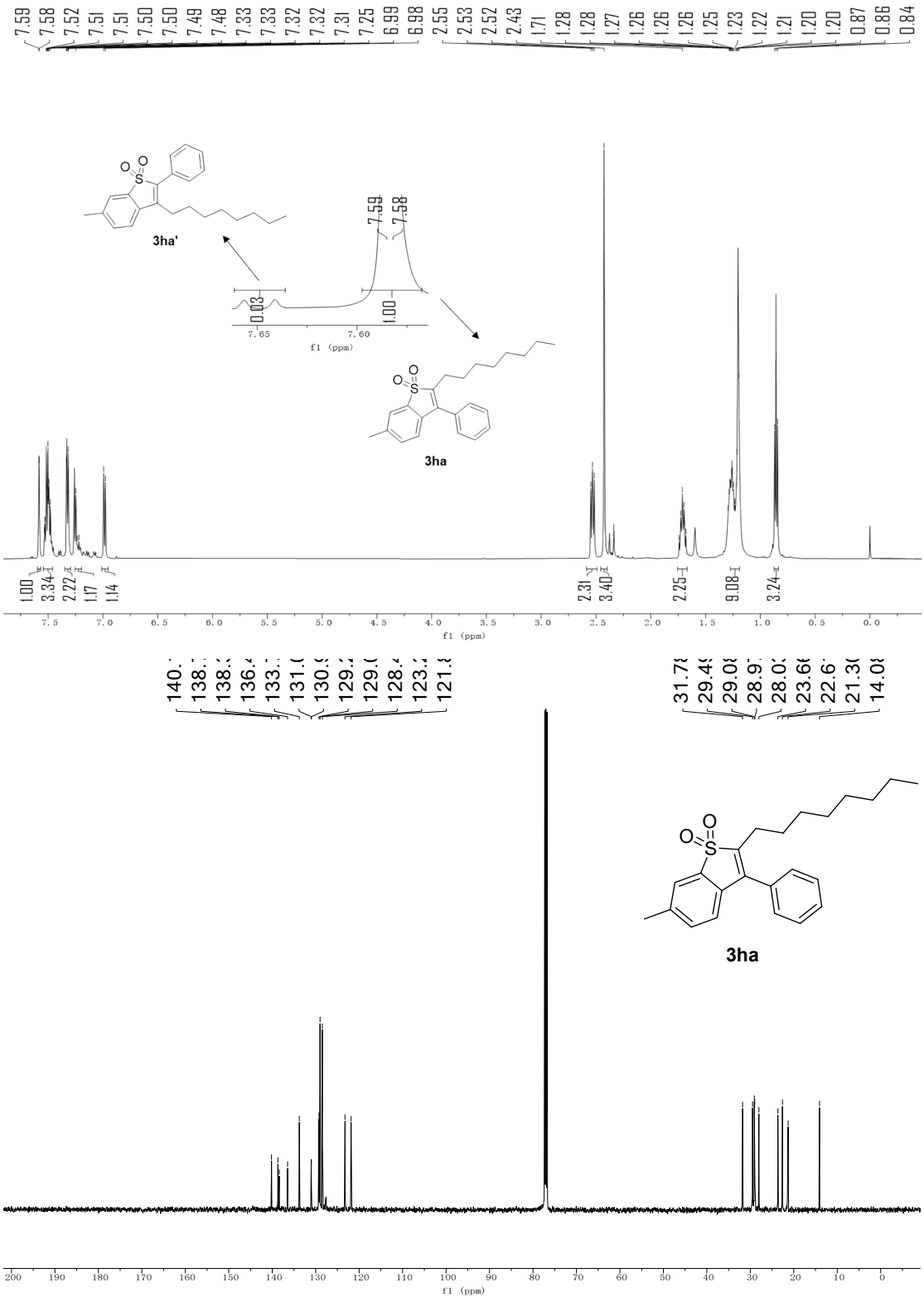
f1 (ppm)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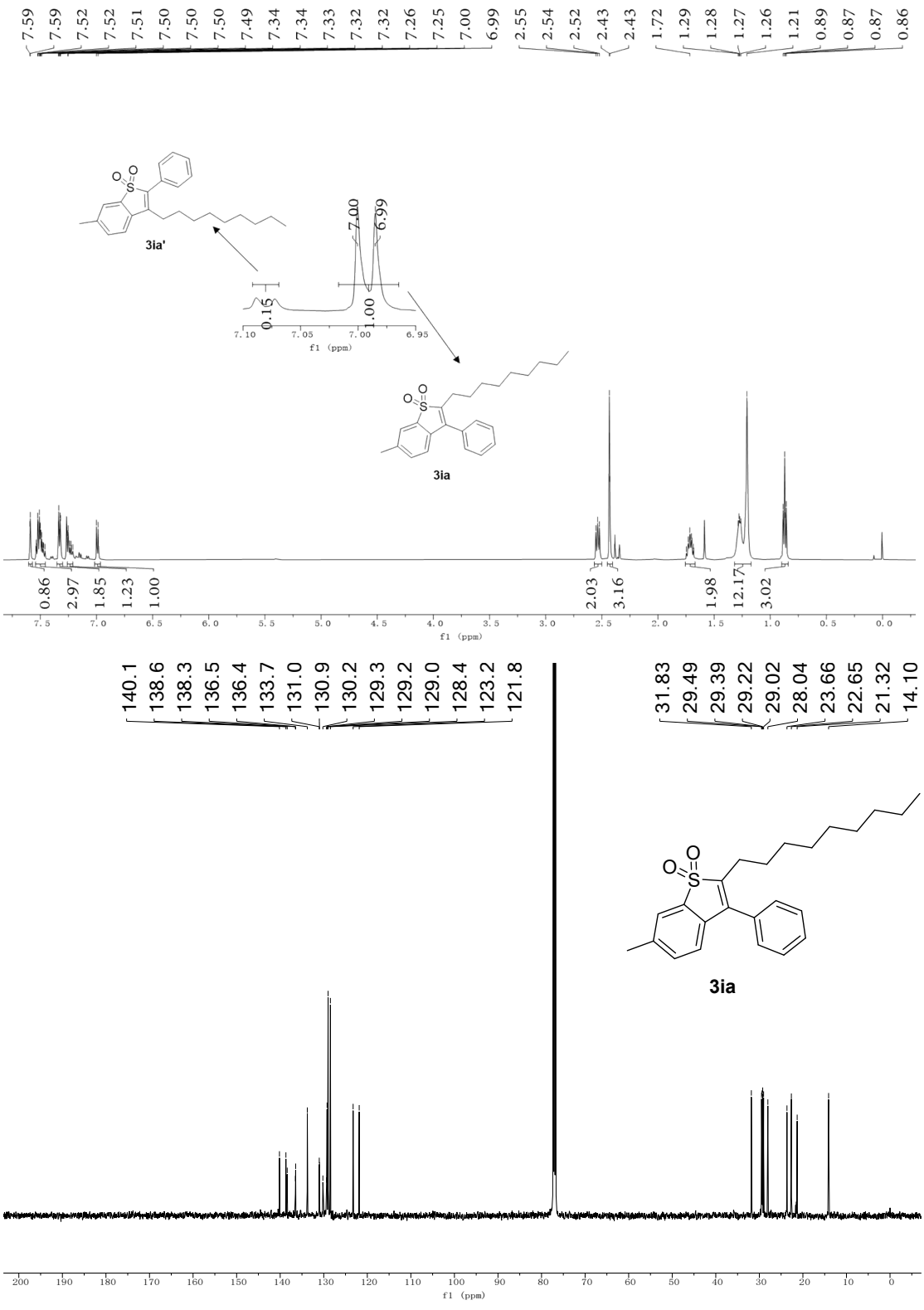
3ha
f1 (ppm)
3ha
f1 (ppm)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1.72 1.29 1.28 1.27 1.26 1.21 0.89 0.87 0.87 0.86
3ia'
7.00
6.99
0.15
1.00
7.10 7.05 7.00 6.95
f1 (ppm)
3ia
0.86 2.97 1.85 1.23 1.00
2.03 3.16 1.98 12.17 3.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
140.1 138.6 138.3 136.5 136.4 133.7 131.0 130.9 130.2 129.3 129.2 129.0 128.4 123.2 121.8
31.83 29.49 29.39 29.22 29.02 28.04 23.66 22.65 21.32 14.10
3ia
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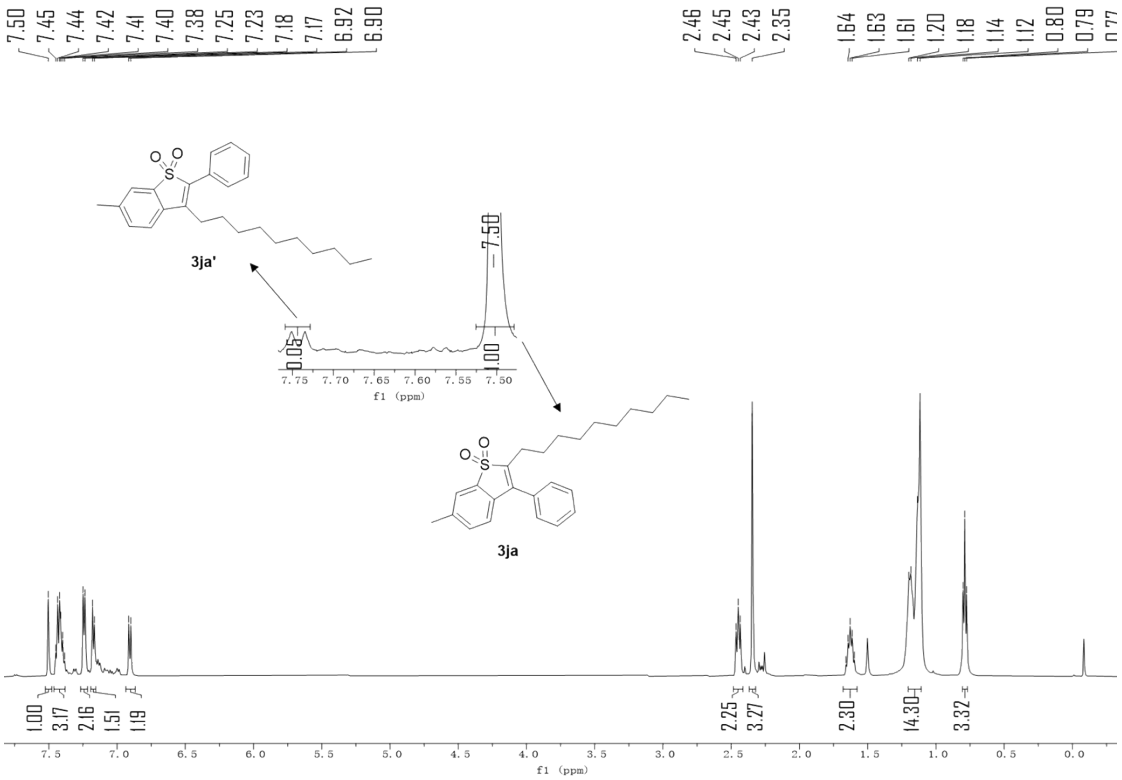
f1 (ppm)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7.23
7.18
7.17
6.92
6.90
2.46
2.45
2.43
2.35
1.64
1.63
1.61
1.20
1.18
1.14
1.12
0.80
0.79
3ja'
3ja
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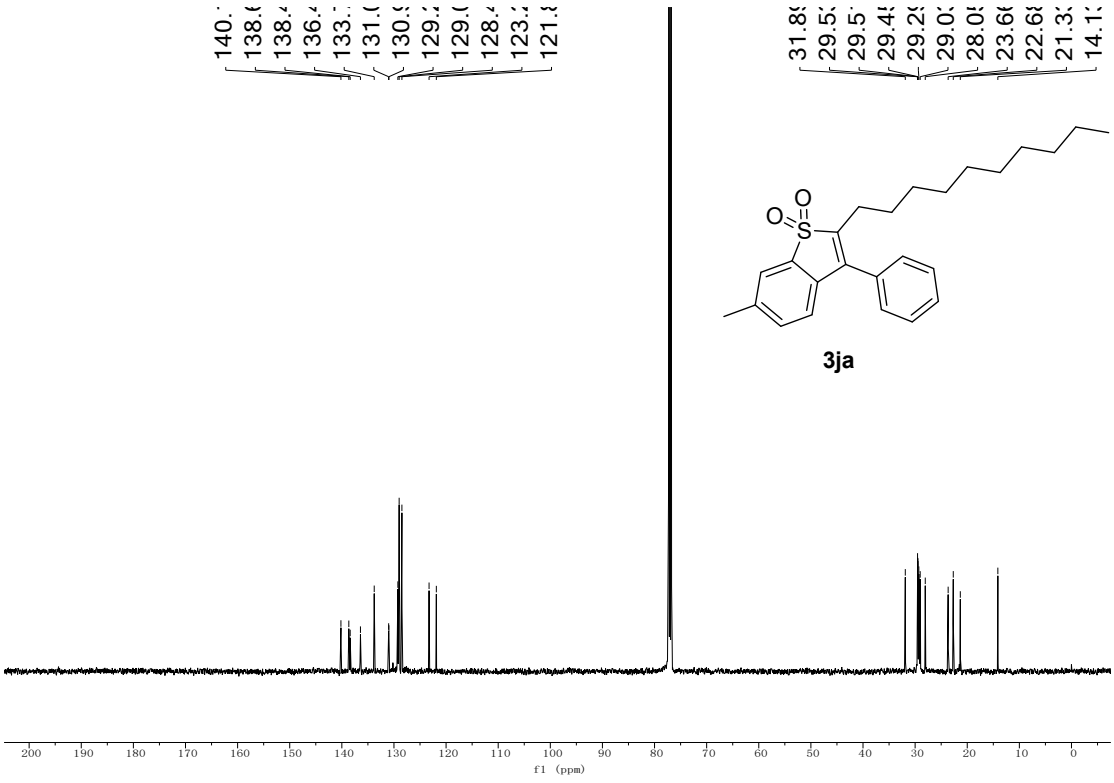
1.19
2.25
3.27
2.30
14.30
3.32
f1 (ppm)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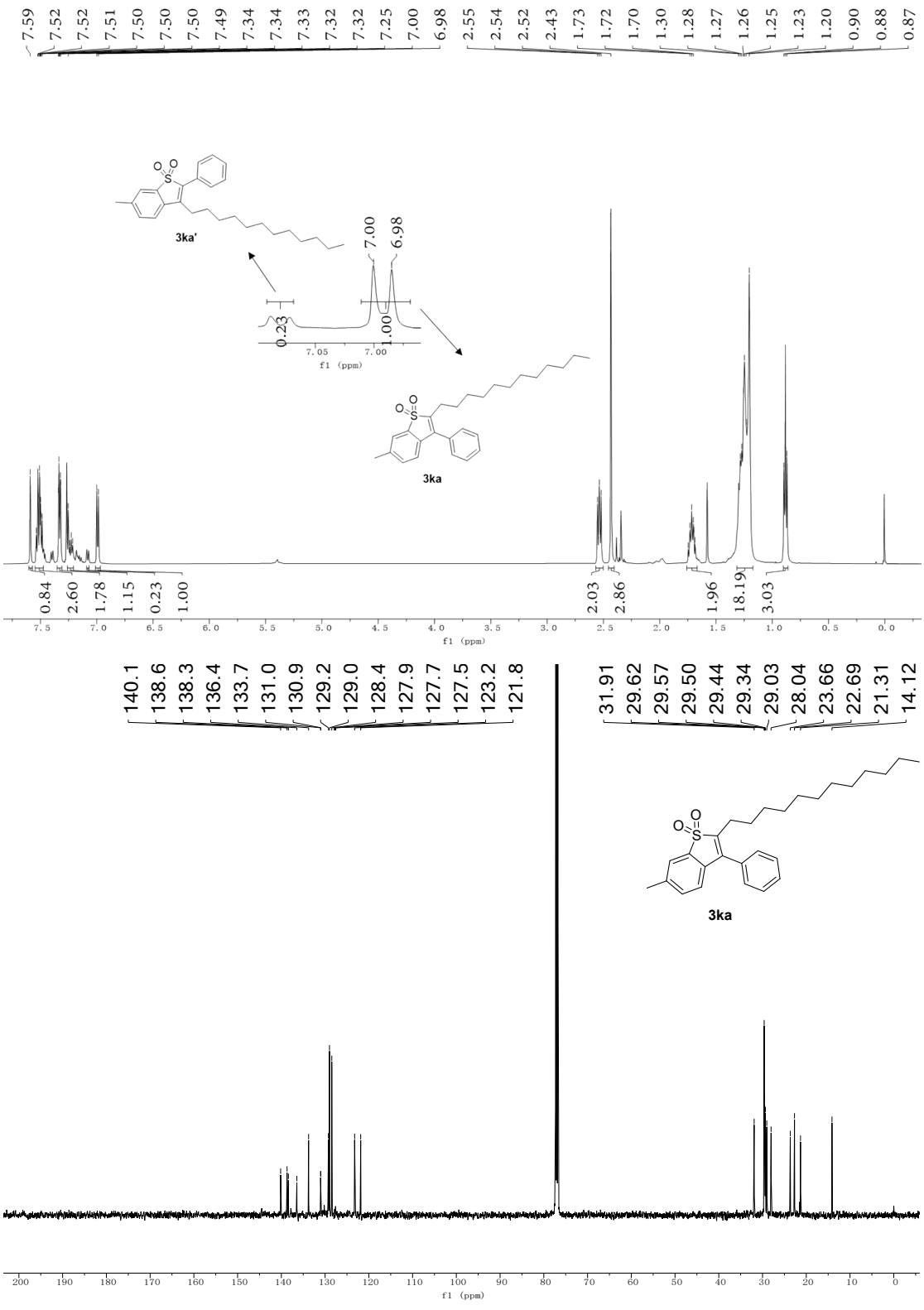
f1 (ppm)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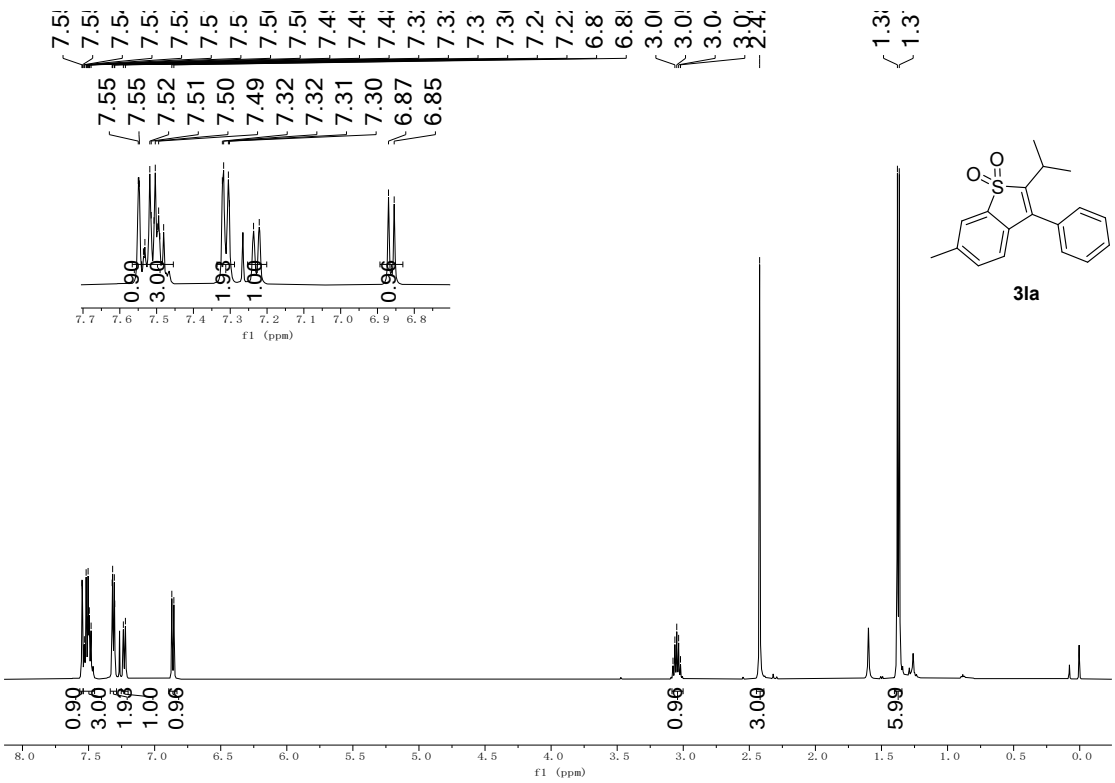
2.55 2.54 2.52 2.43 1.73 1.72 1.70 1.30 1.28 1.27 1.26 1.25 1.23 1.20 0.90 0.88 0.87
3ka'
7.00 6.98
0.23 1.00
7.05 7.00
f1 (ppm)
3ka
0.84 2.60 1.78 1.15 0.23 1.00
2.03 2.86 1.96 18.19 3.03
f1 (ppm)
140.1 138.6 138.3 136.4 133.7 131.0 130.9 129.2 129.0 128.4 127.9 127.7 127.5 123.2 121.8
31.91 29.62 29.57 29.50 29.44 29.34 29.03 28.04 23.66 22.69 21.31 14.12
3ka
f1 (ppm)


7.55
7.55
7.52
7.51
7.50
7.49
7.32
7.32
7.31
7.30
6.87
6.85
0.90
3.00
1.93
1.00
0.96
f1 (ppm)
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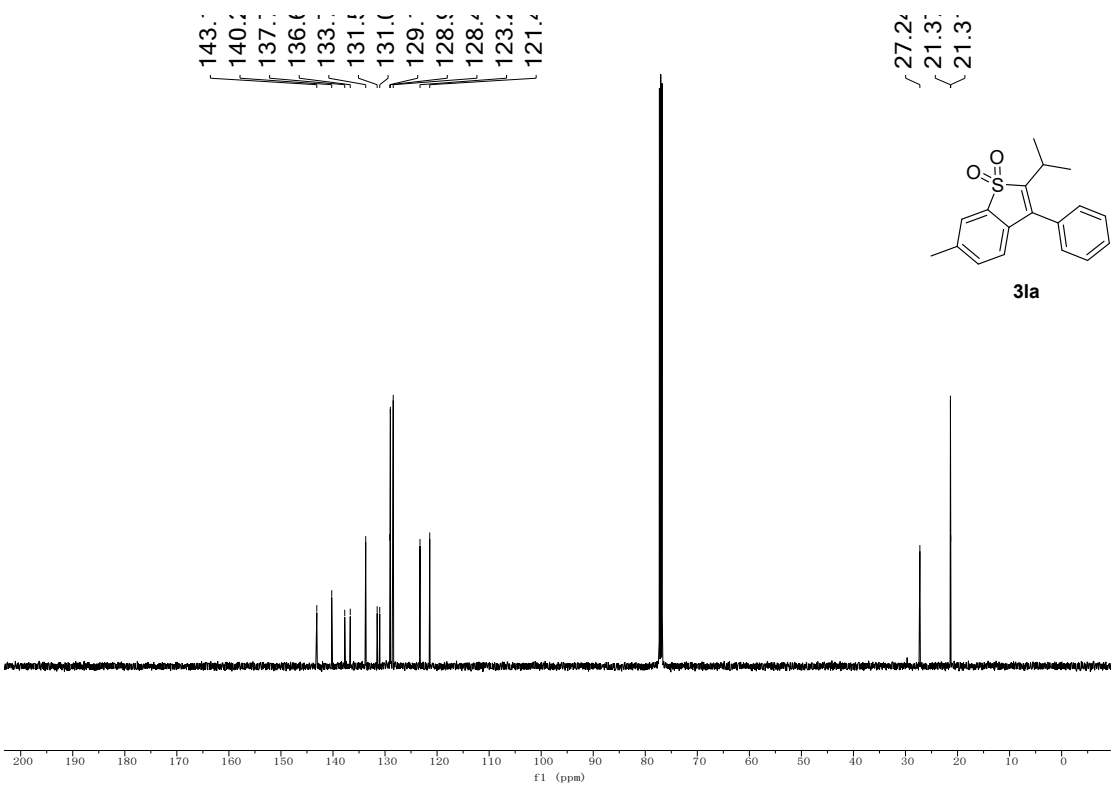
3.00
1.93
1.00
0.96
0.96
3.00
5.99
f1 (ppm)
3la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21.37
21.36
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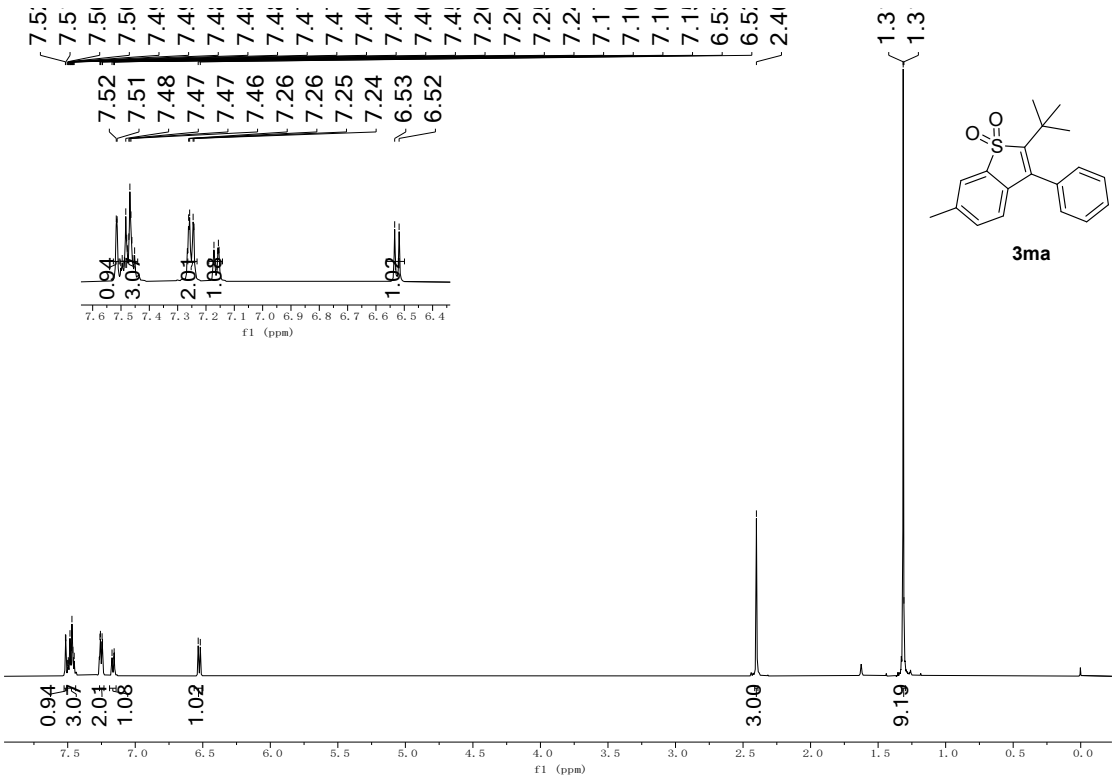
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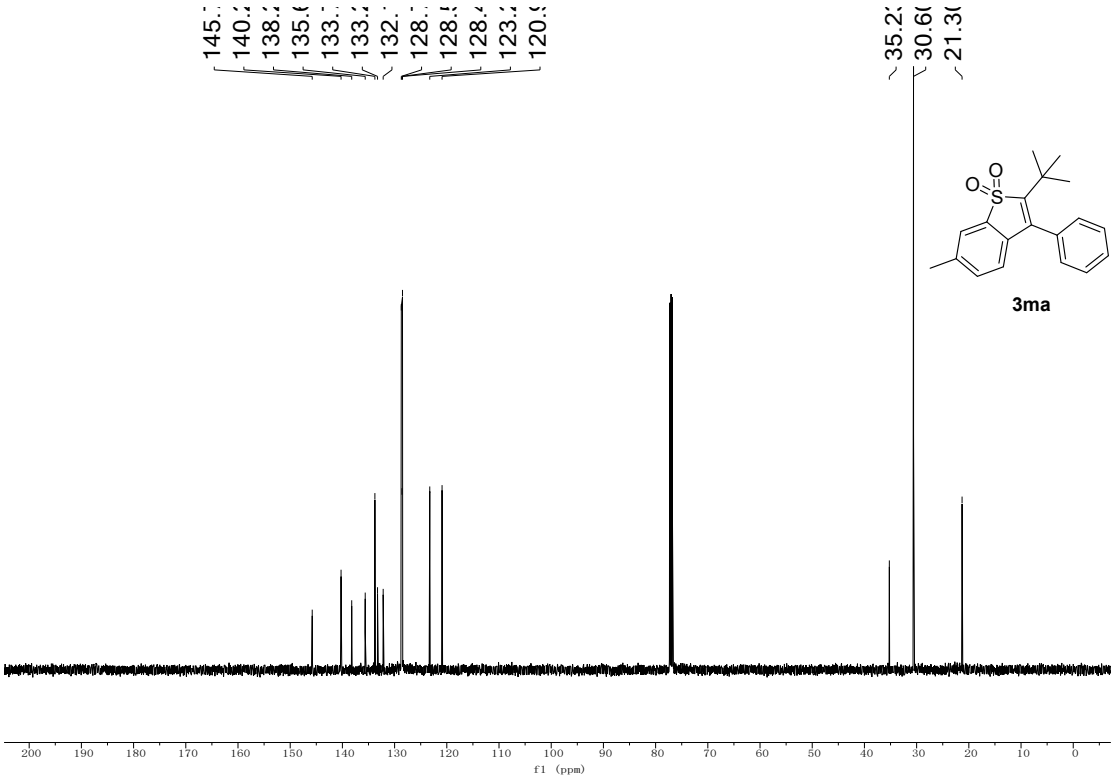
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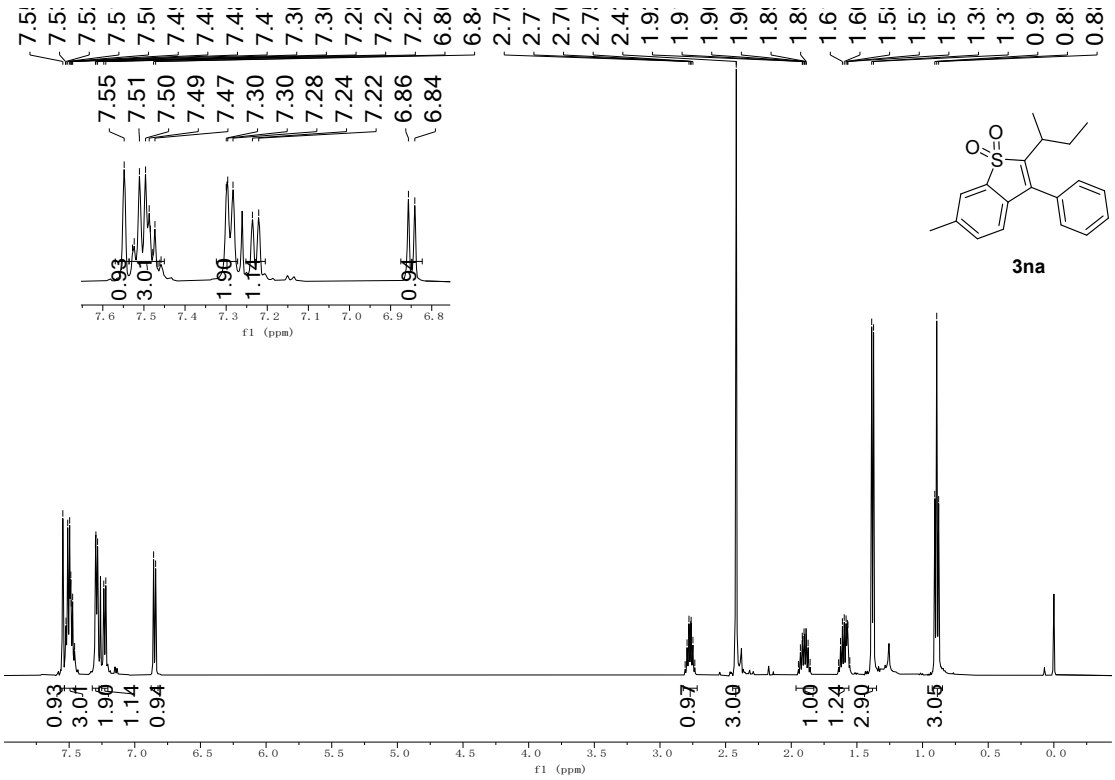
f1 (ppm)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3.01
1.90
1.14
0.94
f1 (ppm)
O
O
S
3na
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1.14
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0.97
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1.00
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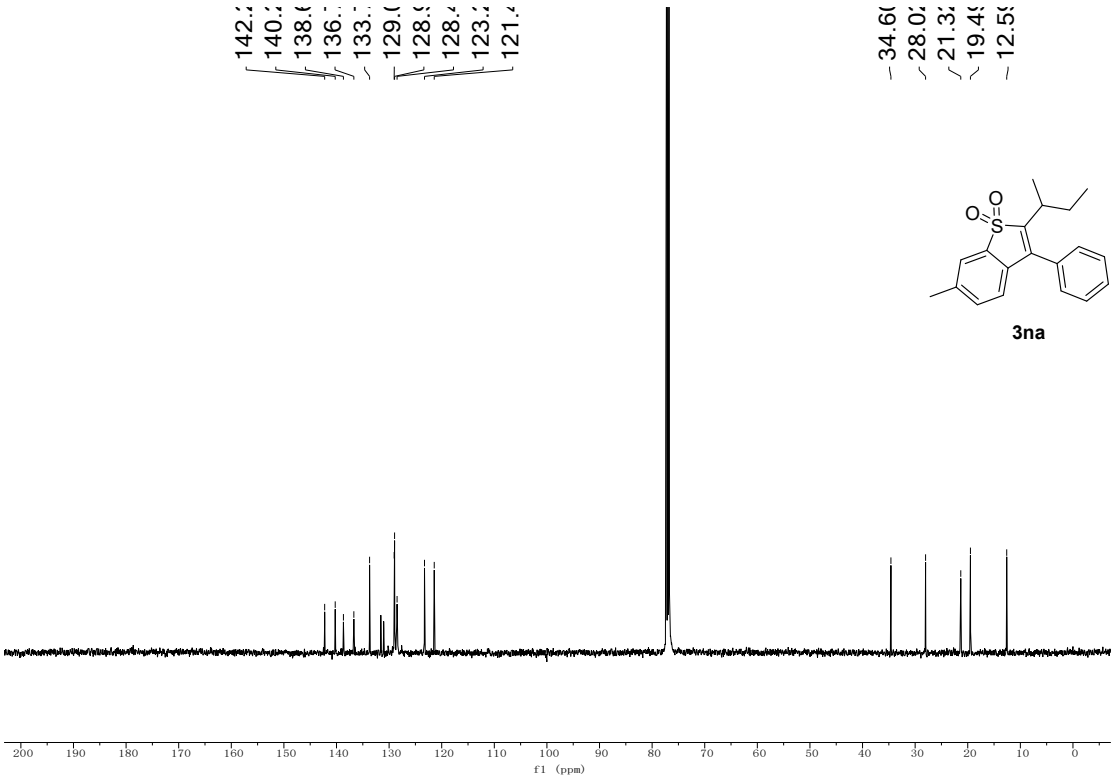
f1 (ppm)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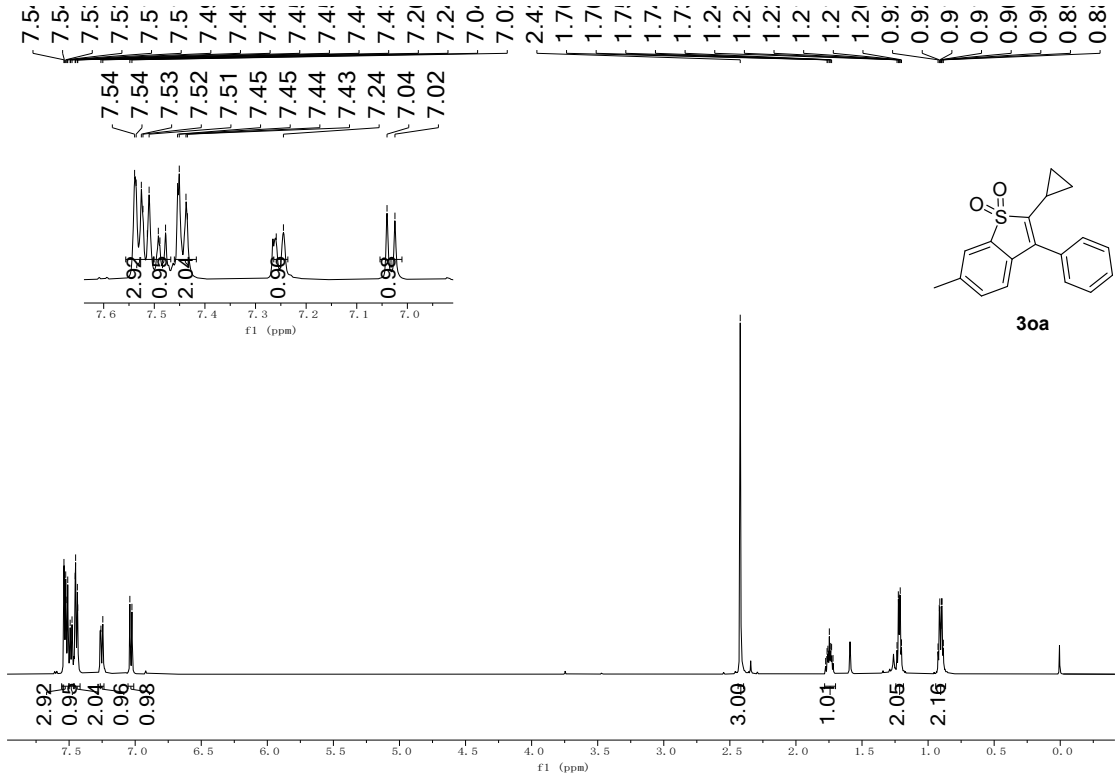
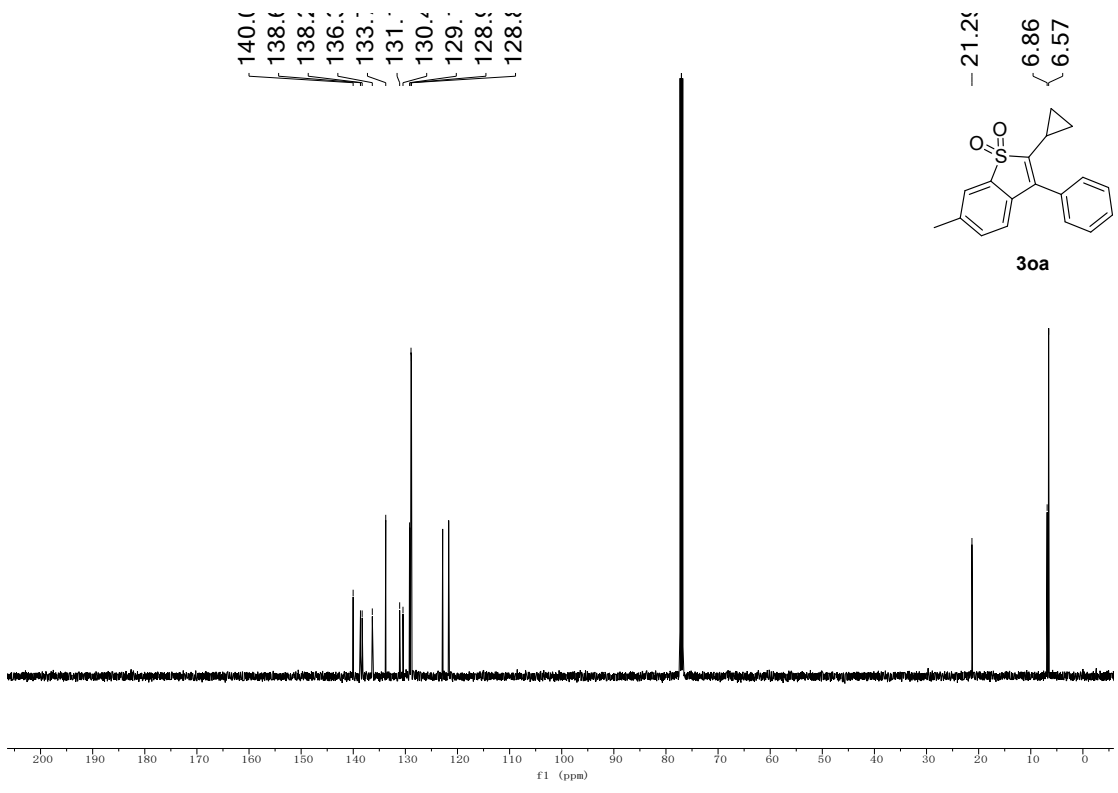
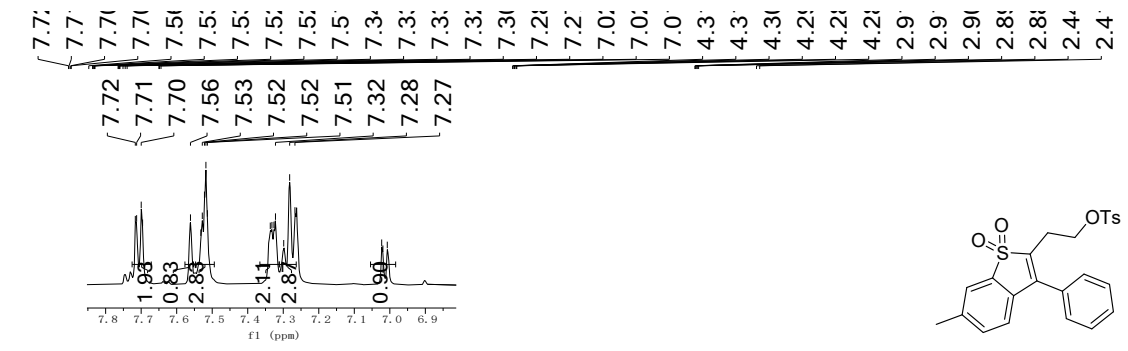
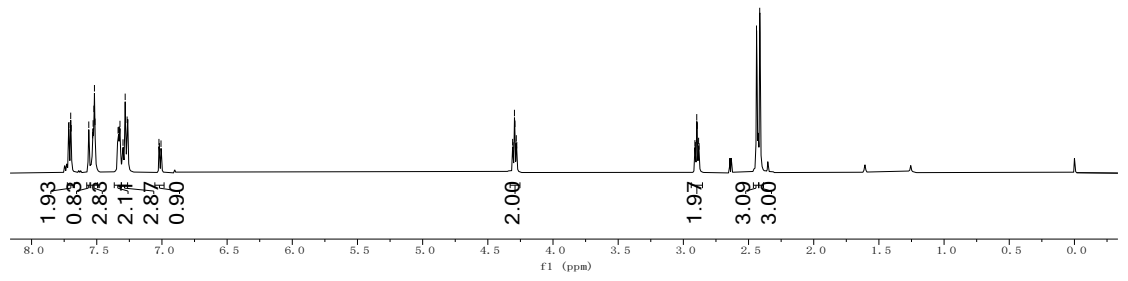
138.
136.
133.
129.
128.
128.
123.
121.
34.6
28.0
21.3
19.4
12.5
O
O
S
3na
f1 (ppm)

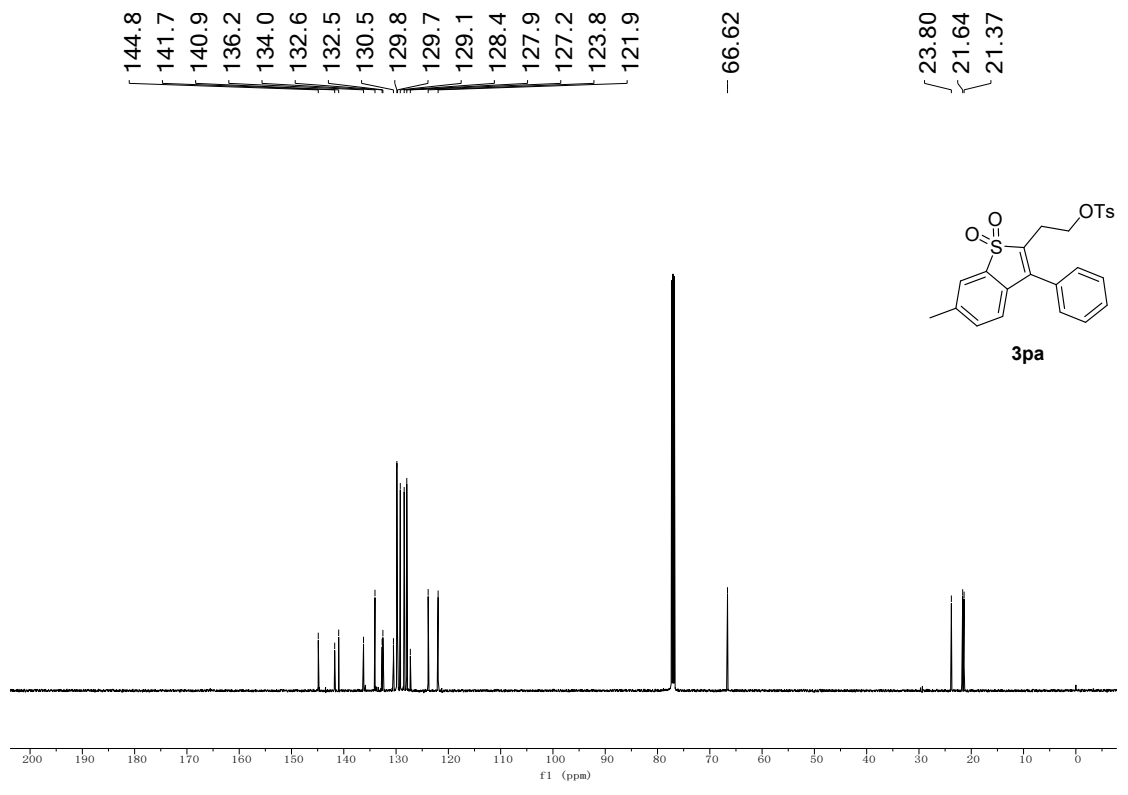

3oa
f1 (ppm)


3oa
f1 (ppm)

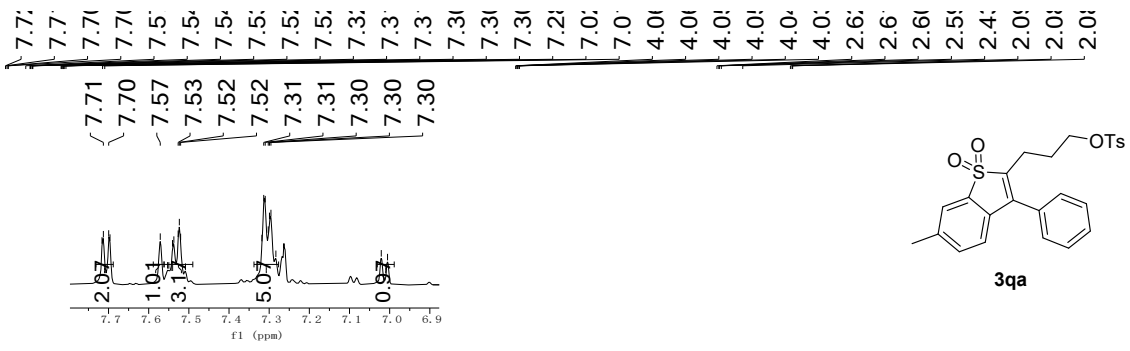

7.72
7.71
7.70
7.56
7.53
7.52
7.52
7.51
7.32
7.28
7.27
1.93
0.83
2.85
2.11
2.87
0.90
f1 (ppm)
OTs
O
O
S

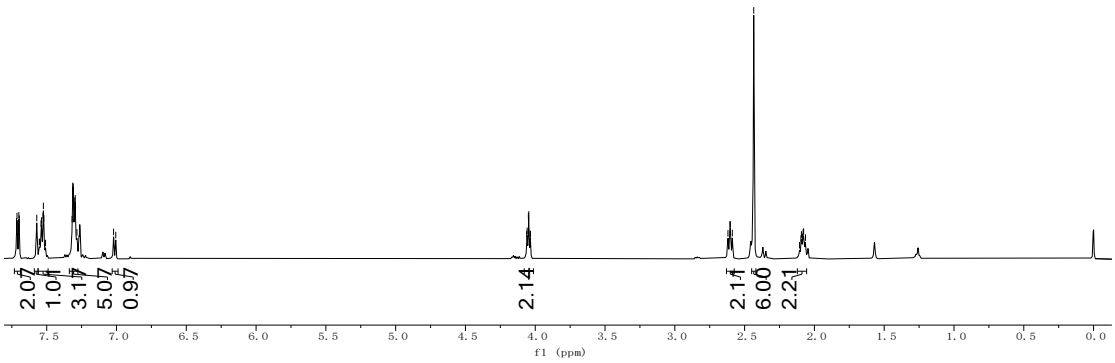
**3pa**

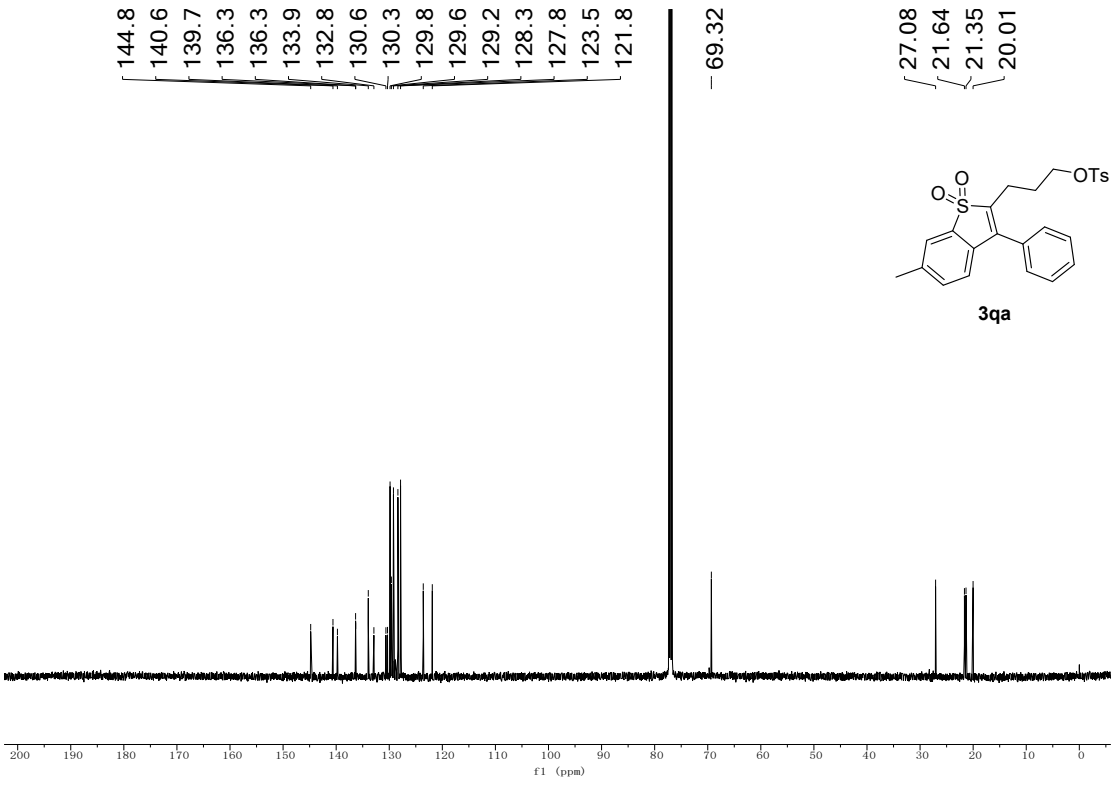

1.93
0.83
2.83
2.14
2.87
0.90
2.00
1.97
3.09
3.00
f1 (ppm)

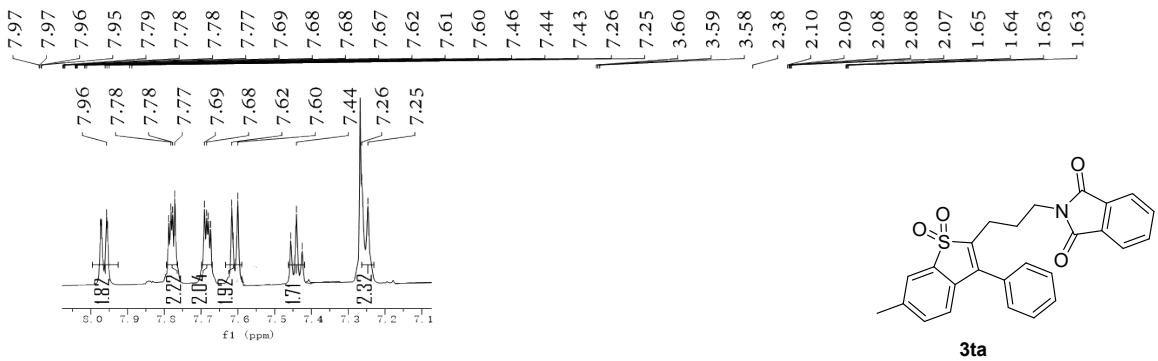

144.8
141.7
140.9
136.2
134.0
132.6
132.5
130.5
129.8
129.7
129.1
128.4
127.9
127.2
123.8
121.9
66.62
23.80
21.64
21.37
OTs
O
O
S
f1 (ppm)

**3pa**


7.71
7.70
7.57
7.53
7.52
7.52
7.31
7.31
7.30
7.30
7.30
2.07
1.01
3.14
5.07
0.97
f1 (ppm)
OTs
3qa

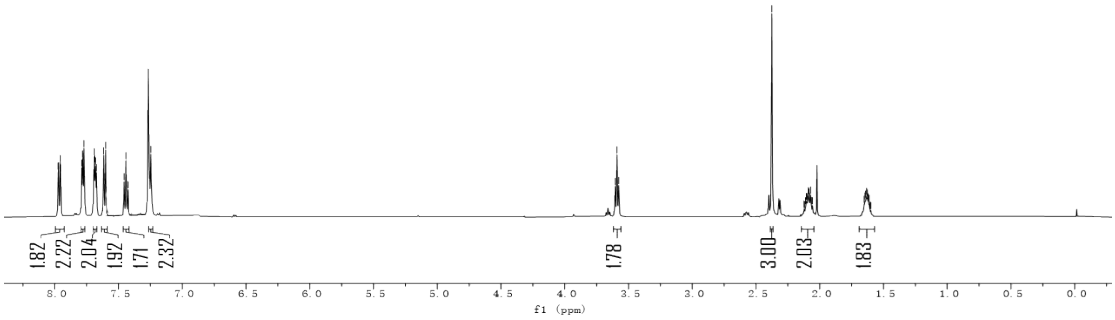

2.07
1.04
3.17
5.07
0.97
2.14
2.14
6.00
2.21
f1 (ppm)

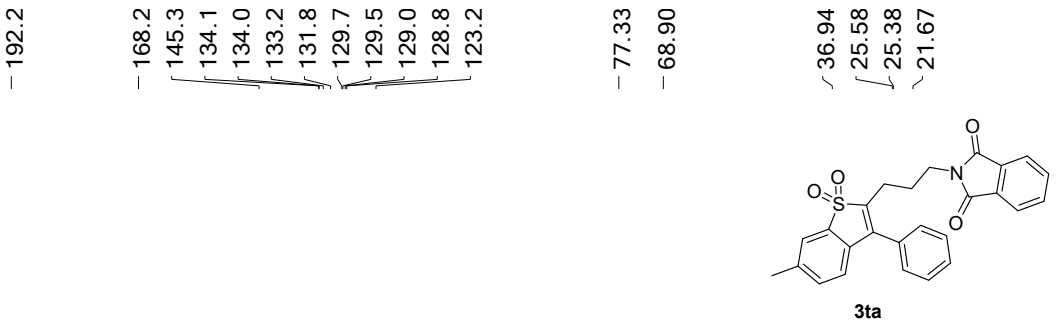

144.8
140.6
139.7
136.3
136.3
133.9
132.8
130.6
130.3
129.8
129.6
129.2
128.3
127.8
123.5
121.8
69.32
27.08
21.64
21.35
20.01
f1 (ppm)
OTs
3qa


7.97 7.97 7.96 7.95 7.79 7.78 7.78 7.77 7.69 7.68 7.68 7.67 7.62 7.61 7.60 7.46 7.44 7.43 7.26 7.25 3.60 3.59 3.58 2.38 2.10 2.09 2.08 2.08 2.07 1.65 1.64 1.63 1.63
7.96 7.78 7.78 7.77 7.69 7.68 7.62 7.60 7.44 7.26 7.25
1.82 2.22 2.04 1.92 1.71 2.32
f1 (ppm)



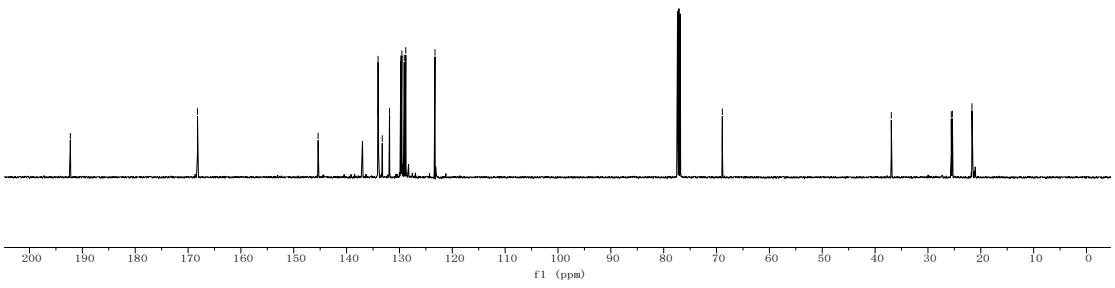
3ta

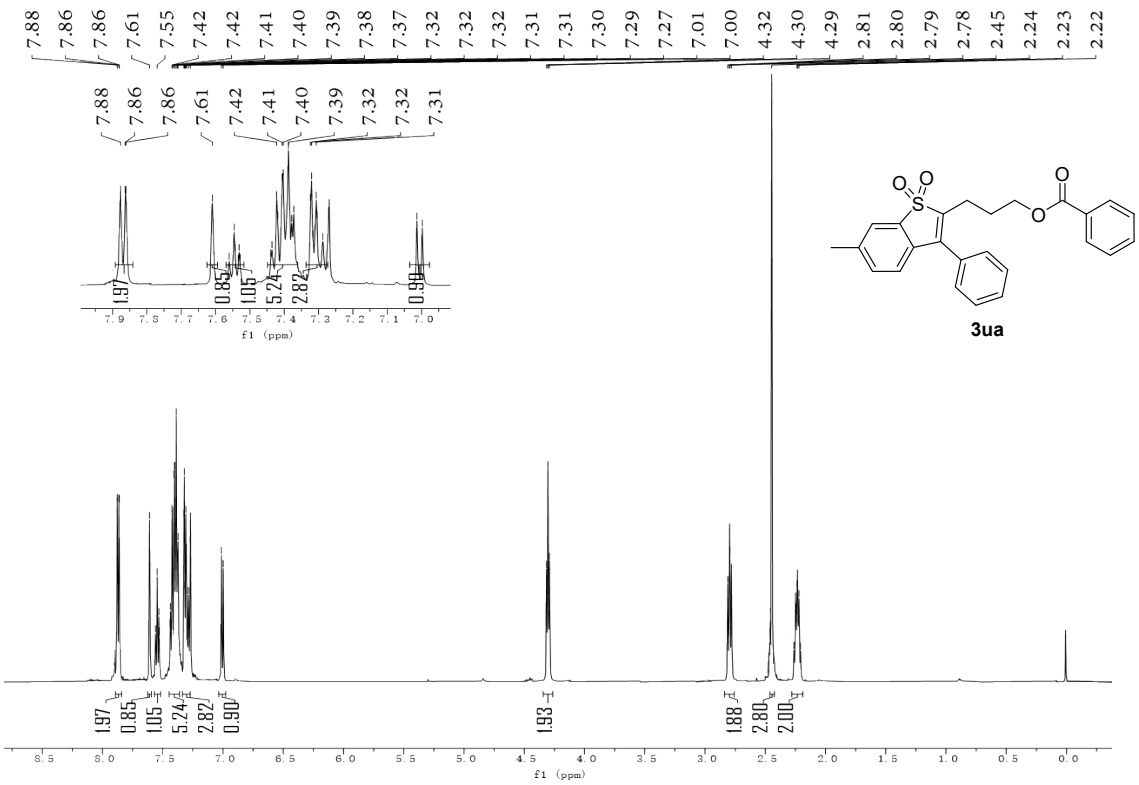

1.82 2.22 2.04 1.92 1.71 2.32 1.78 3.00 2.03 1.83
f1 (ppm)

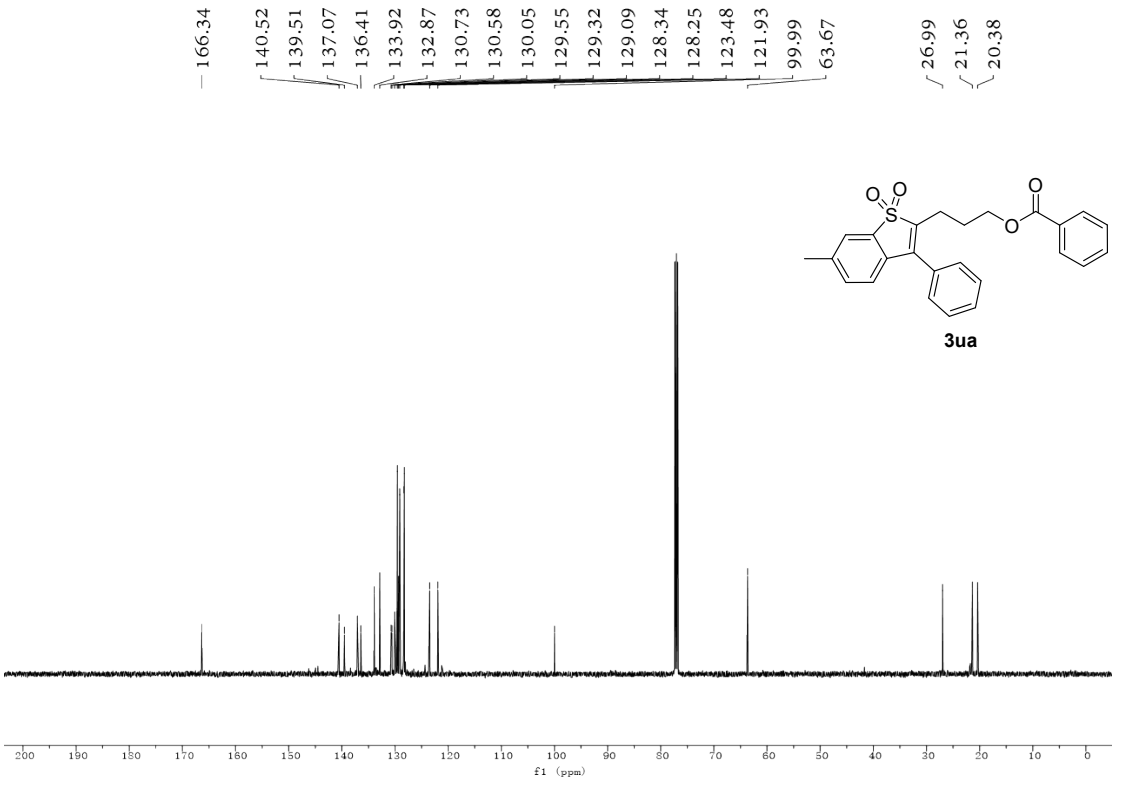

192.2
168.2 145.3 134.1 134.0 133.2 131.8 129.7 129.5 129.0 128.8 123.2
77.33 68.90
36.94 25.58 25.38 21.67

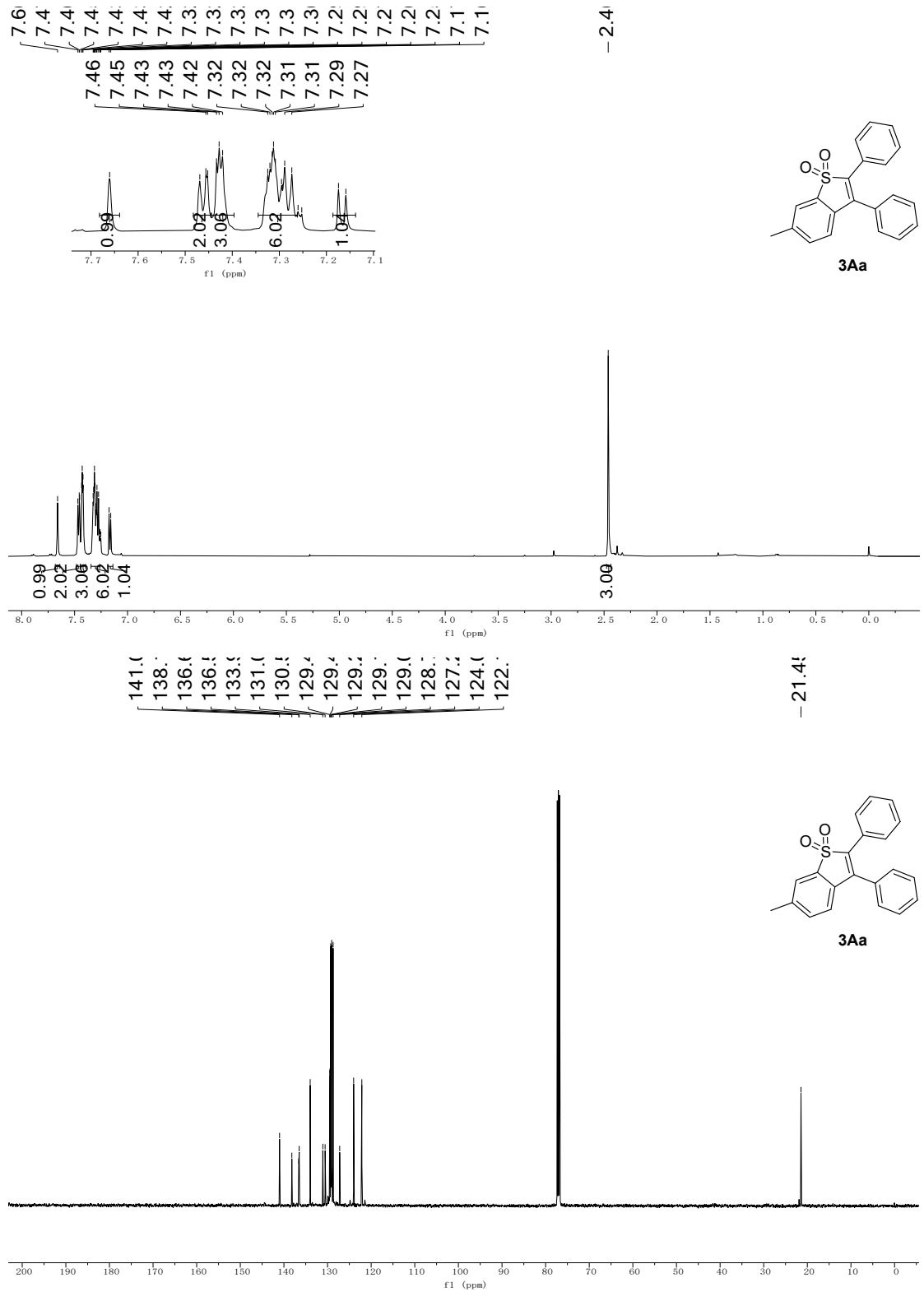


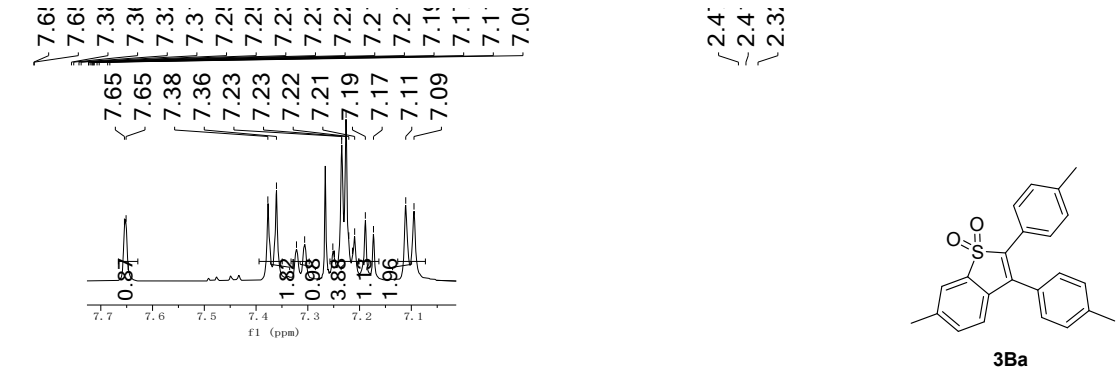
3ta


f1 (ppm)


7.88 7.86 7.86 7.61 7.55 7.42 7.42 7.41 7.40 7.39 7.38 7.37 7.32 7.32 7.32 7.31 7.31 7.30 7.29 7.27 7.01 7.00 4.32 4.30 4.29 2.81 2.80 2.79 2.78 2.45 2.24 2.23 2.22
1.97 0.85 1.05 5.24 2.82 0.90 1.93 1.88 2.80 2.00
f1 (ppm)
3ua

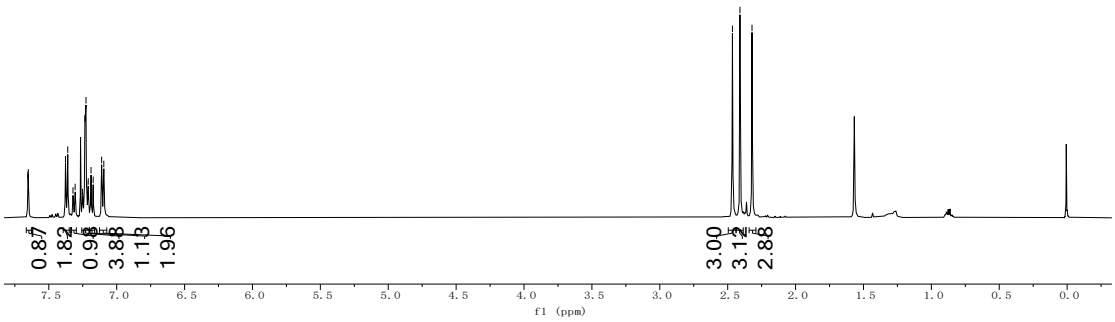

166.34 140.52 139.51 137.07 136.41 133.92 132.87 130.73 130.58 130.05 129.55 129.32 129.09 128.34 128.25 123.48 121.93 99.99 63.67 26.99 21.36 20.38
f1 (ppm)
3ua

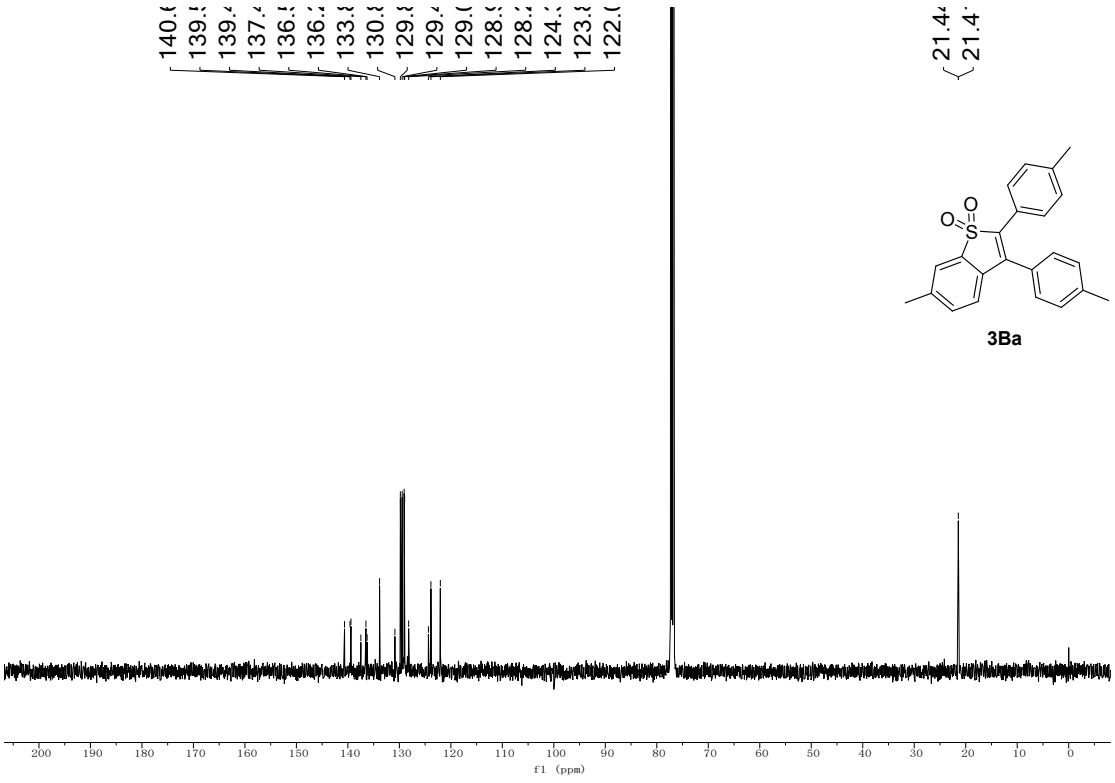

3Aa
3Aa


7.65
7.65
7.38
7.36
7.23
7.23
7.22
7.21
7.19
7.17
7.11
7.09
0.87
1.82
0.98
3.88
1.13
1.96
f1 (ppm)
2.4
2.4
2.3


O
O
S

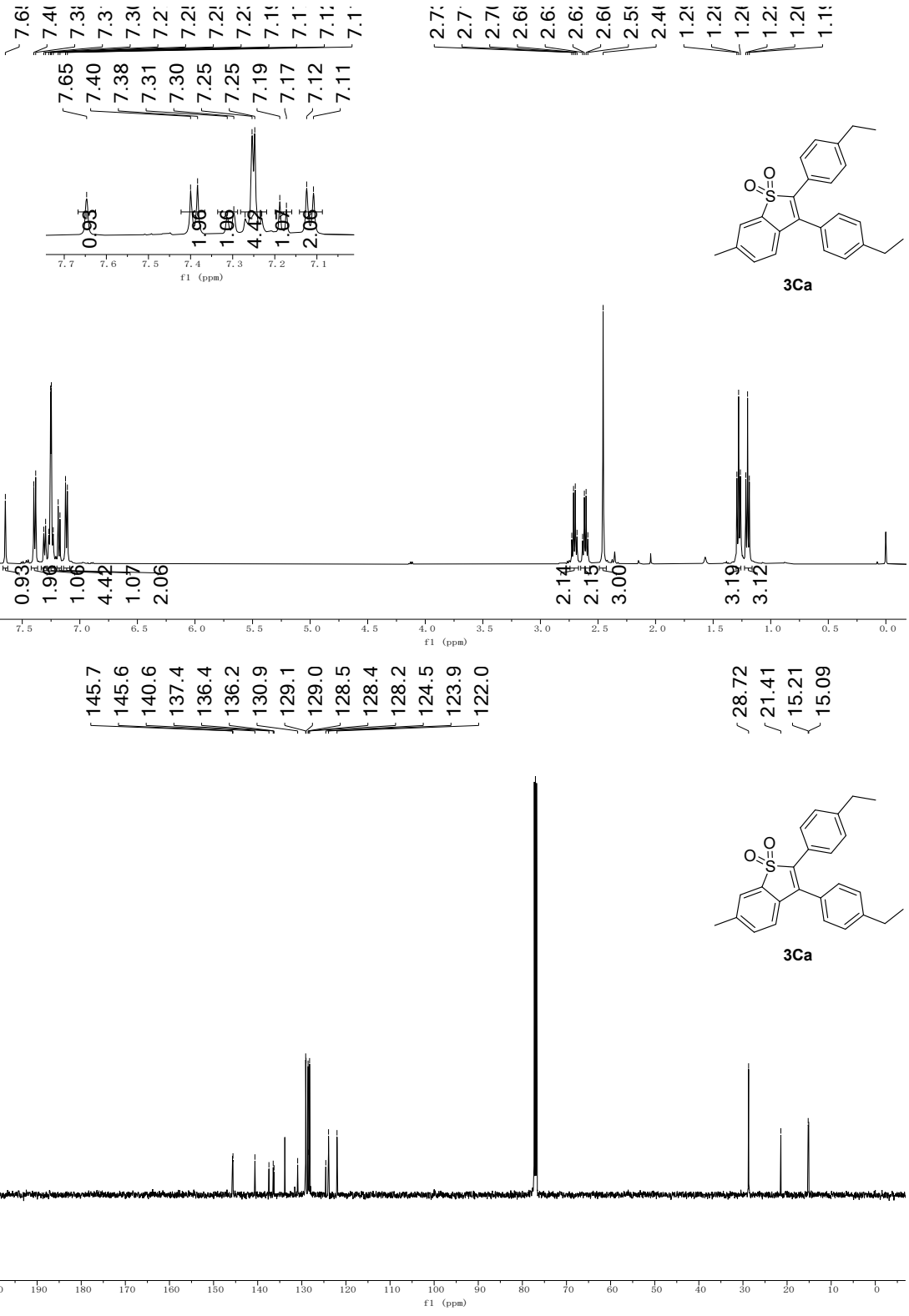
**3Ba**

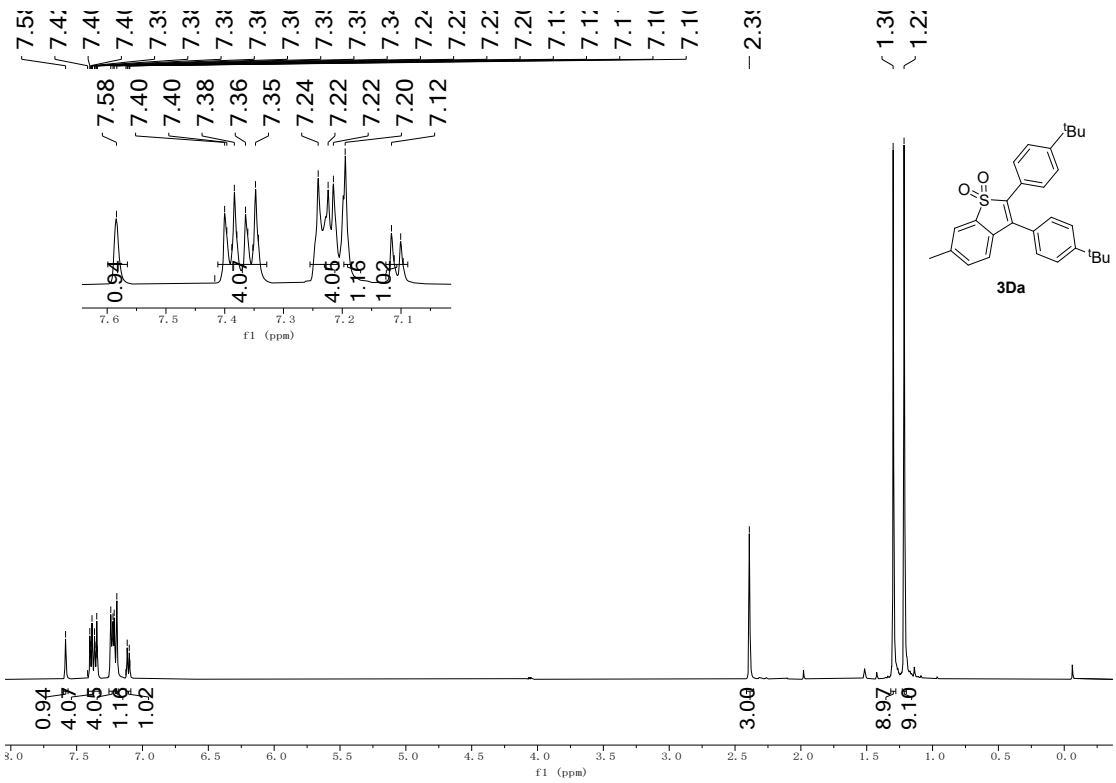

0.87
1.82
0.98
3.88
1.13
1.96
3.00
3.12
2.88
f1 (ppm)

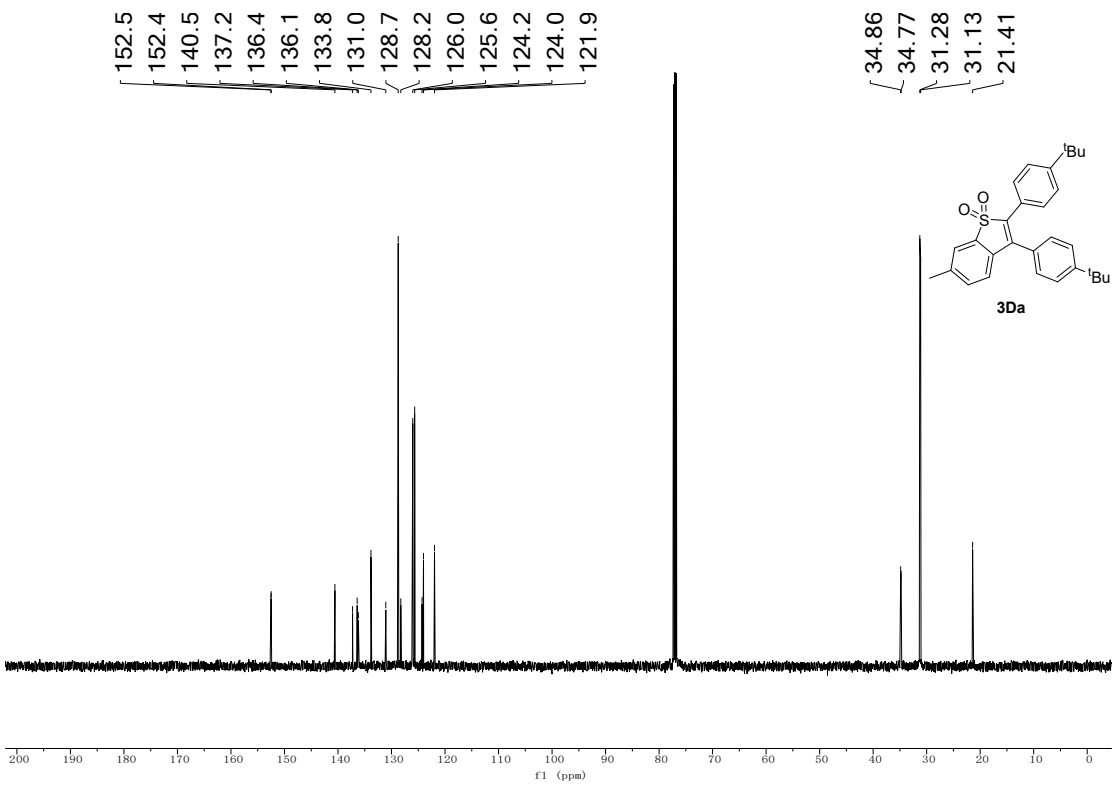

140.
139.
139.
137.
136.
136.
133.
130.
129.
129.
129.
128.
128.
124.
123.
122.
21.4
21.4
f1 (ppm)

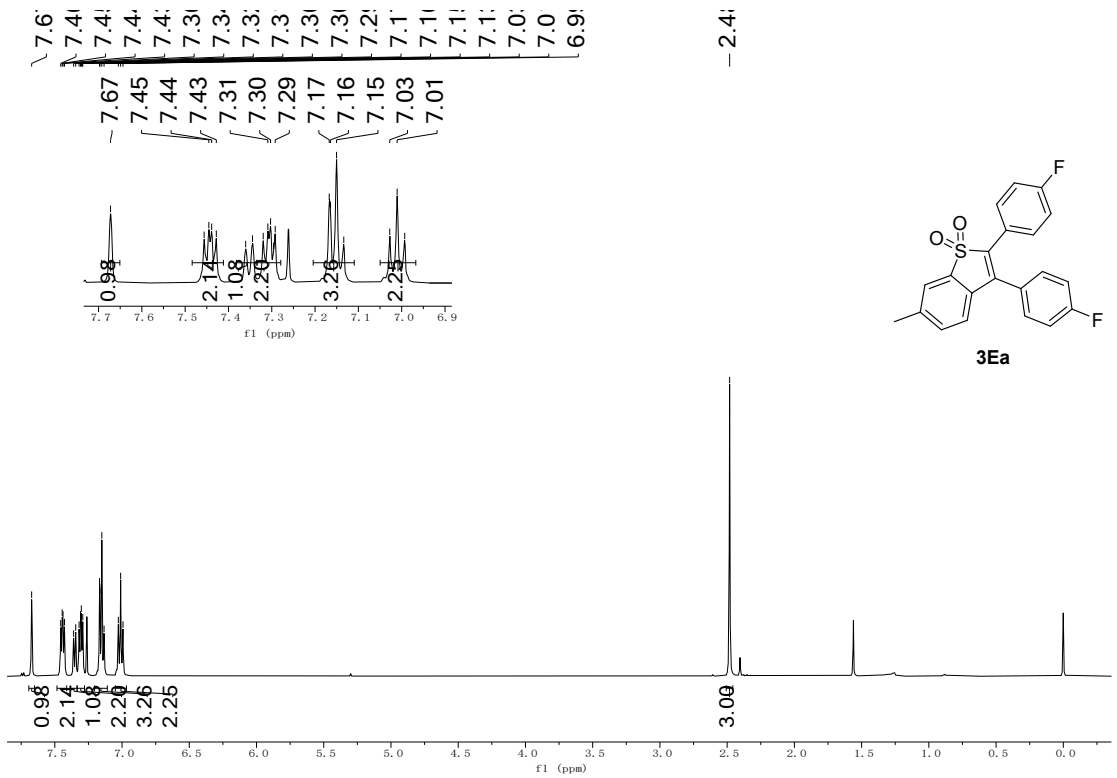

O
O
S

**3Ba**


7.65
7.40
7.38
7.31
7.30
7.25
7.25
7.19
7.17
7.12
7.11
2.73
2.70
2.68
2.63
2.61
2.58
2.41
1.25
1.23
1.21
1.20
1.19
0.93
1.90
1.06
4.42
1.07
2.06
2.14
2.15
3.00
3.19
3.12
f1 (ppm)
3Ca
145.7
145.6
140.6
137.4
136.4
136.2
130.9
129.1
129.0
128.5
128.4
128.2
124.5
123.9
122.0
28.72
21.41
15.21
15.09
f1 (ppm)
3Ca

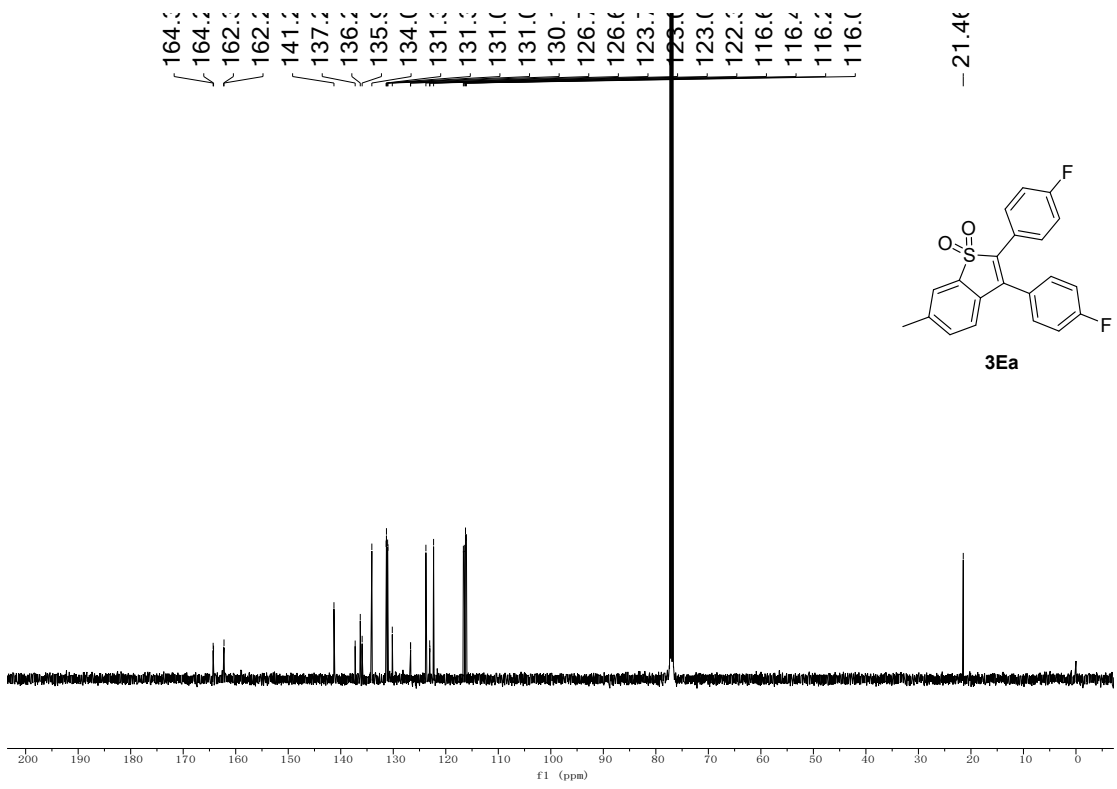

7.58
7.40
7.40
7.38
7.36
7.35
7.24
7.22
7.22
7.20
7.12
0.94
4.07
4.05
1.16
1.02
f1 (ppm)
3Da


152.5
152.4
140.5
137.2
136.4
136.1
133.8
131.0
128.7
128.2
126.0
125.6
124.2
124.0
121.9
34.86
34.77
31.28
31.13
21.41
f1 (ppm)
3Da


7.67
7.45
7.44
7.43
7.31
7.30
7.29
7.17
7.16
7.15
7.03
7.01
2.41
0.98
2.14
1.08
2.20
3.26
2.25
3.00
f1 (ppm)

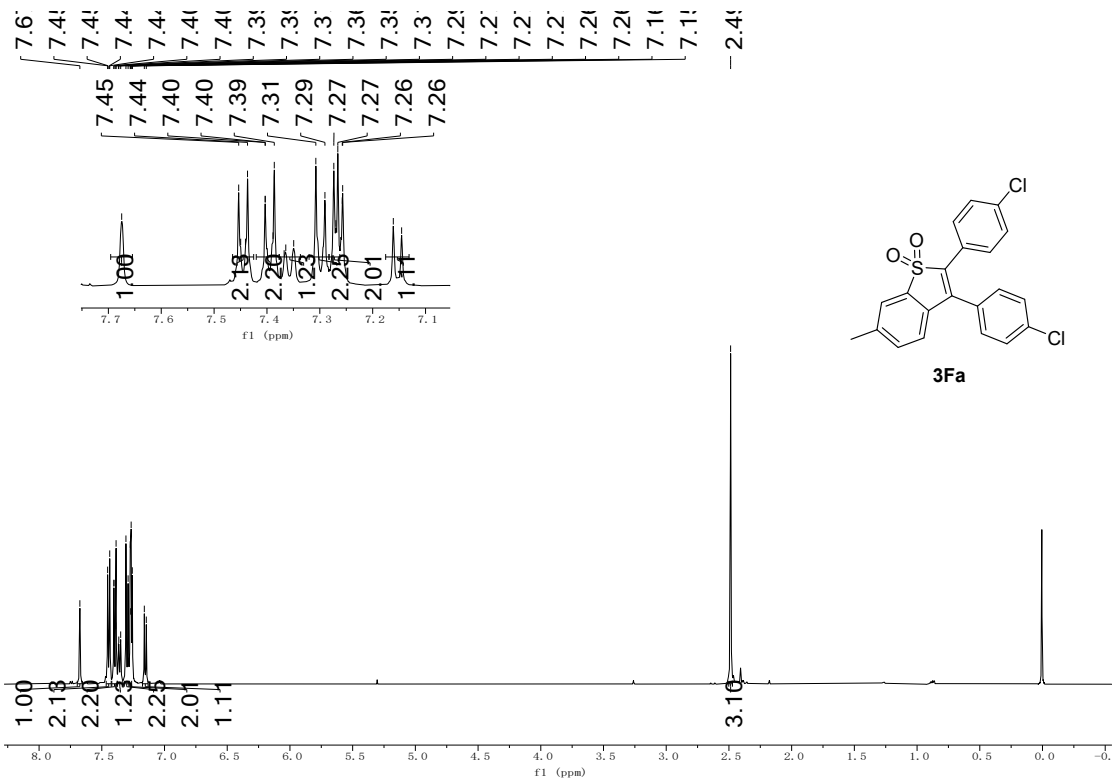


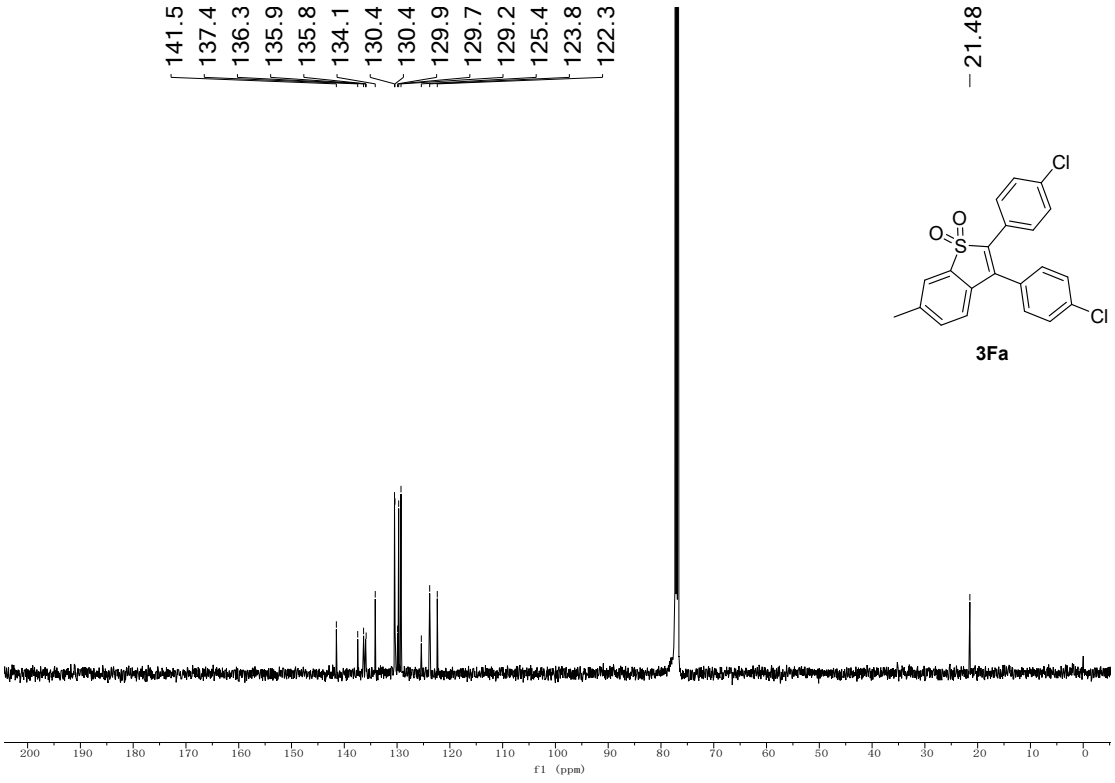
3Ea

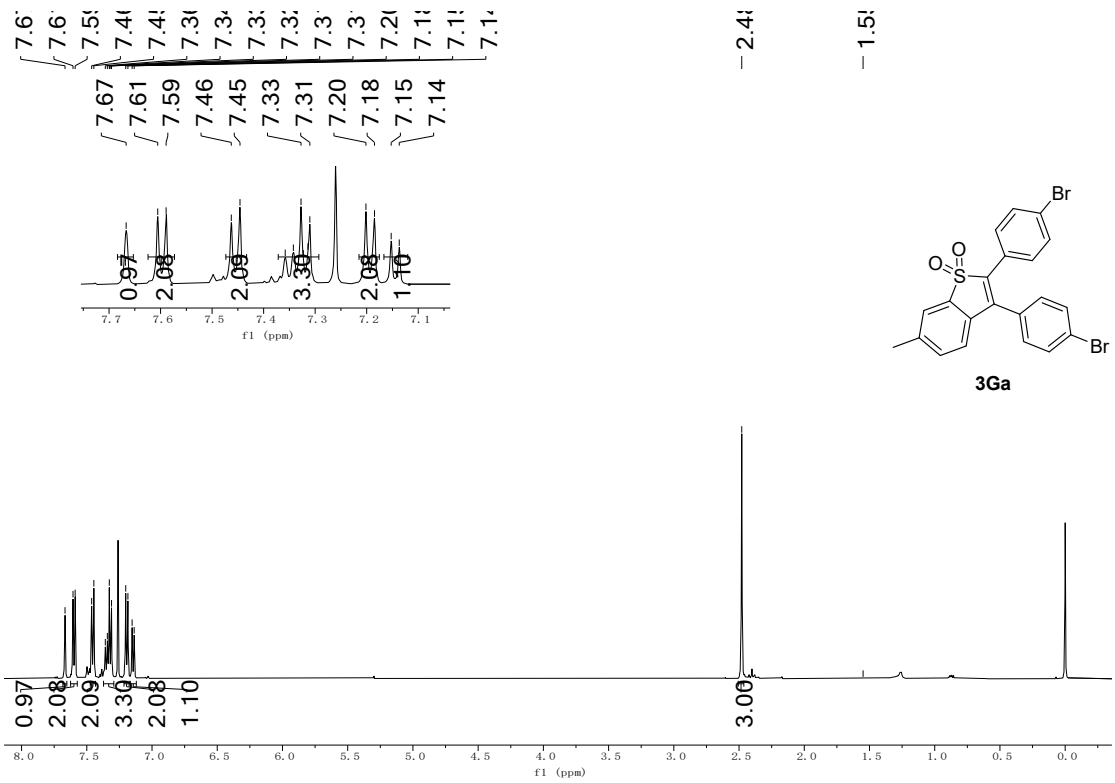

21.46
f1 (ppm)



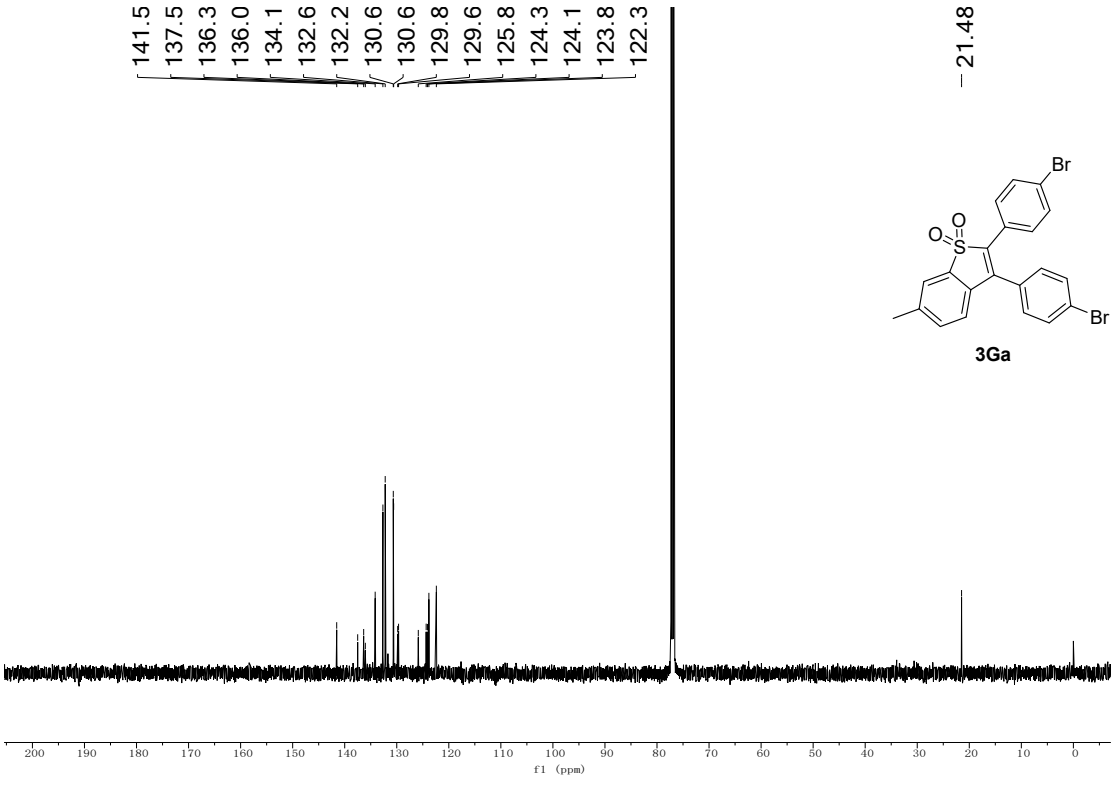
3Ea


7.45
7.44
7.40
7.40
7.39
7.31
7.29
7.27
7.27
7.26
7.26
1.00
2.13
2.20
1.23
2.25
2.01
1.11
f1 (ppm)
Cl
O
O
S
Cl
3Fa
3.10
f1 (ppm)

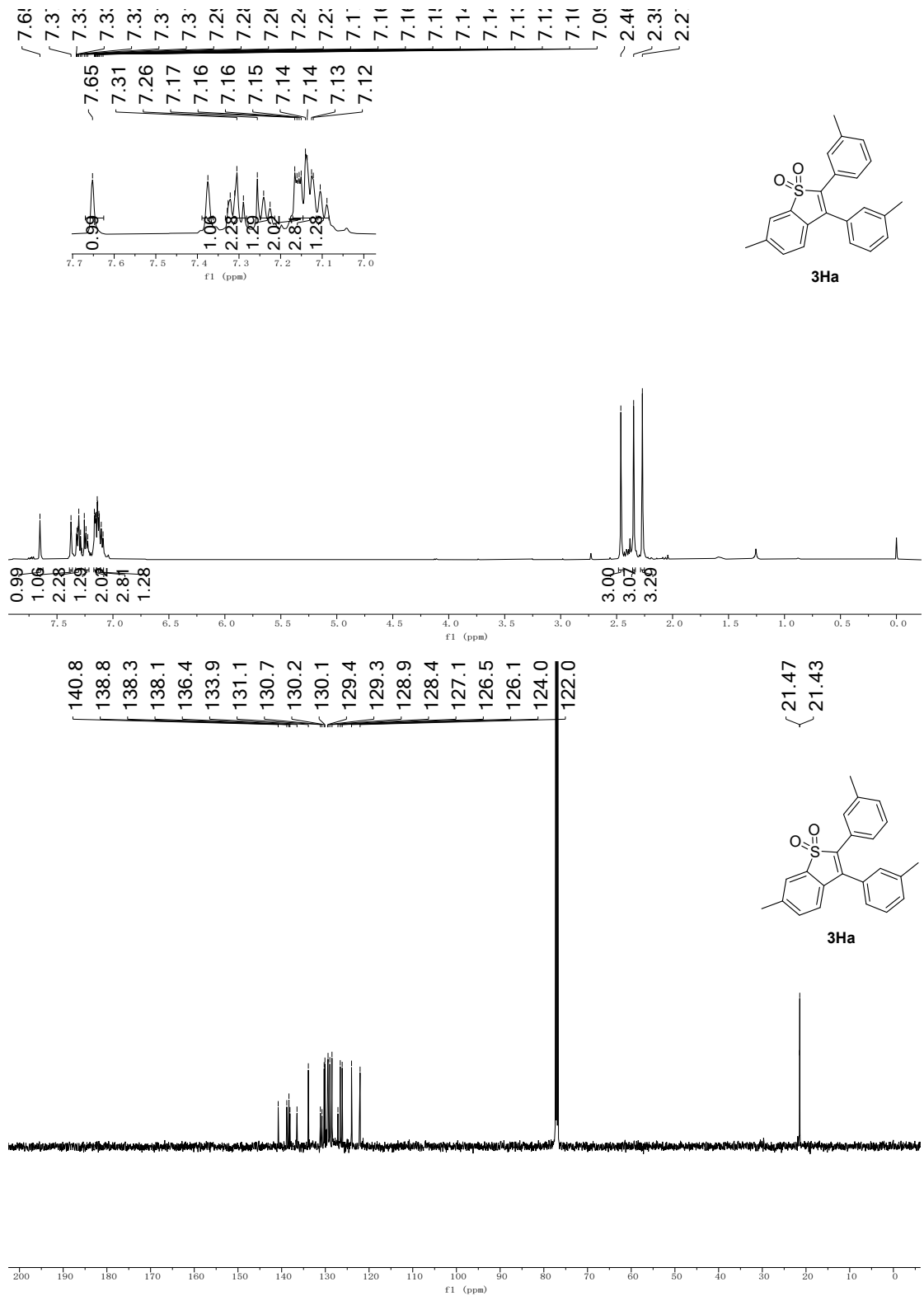

141.5
137.4
136.3
135.9
135.8
134.1
130.4
130.4
129.9
129.7
129.2
125.4
123.8
122.3
21.48
Cl
O
O
S
Cl
3Fa
f1 (ppm)

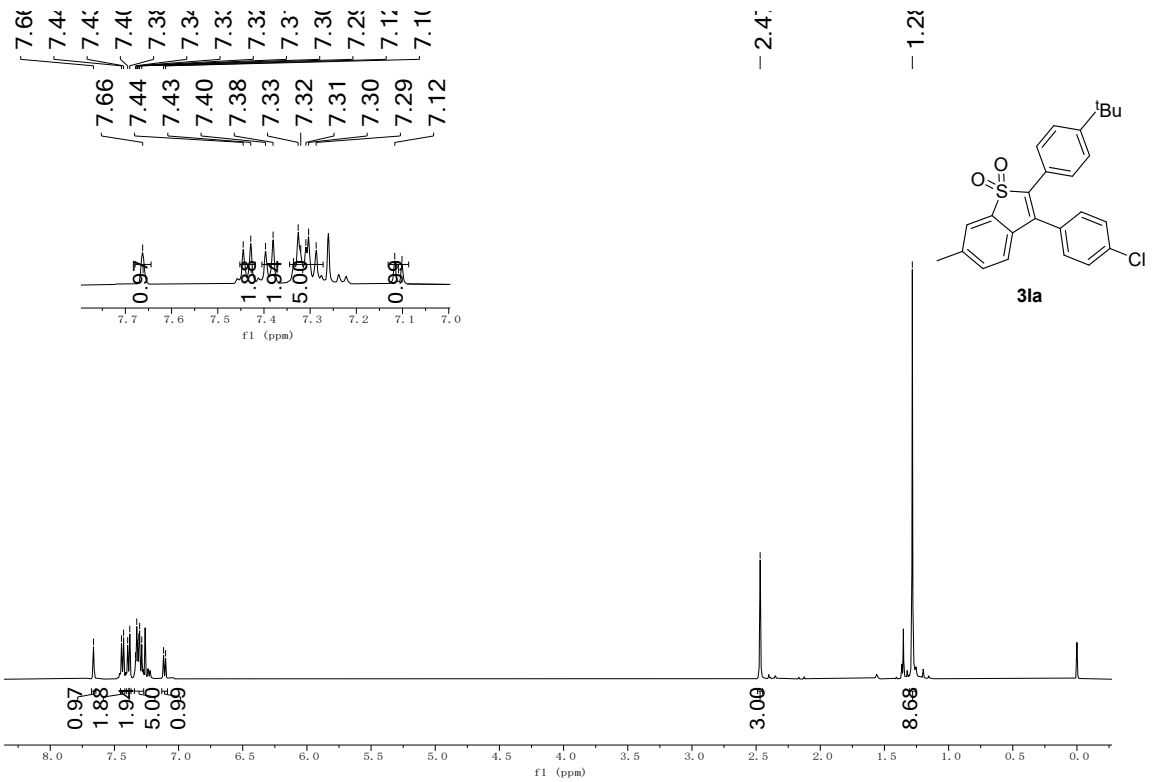

7.67
7.61
7.59
7.46
7.45
7.33
7.31
7.20
7.18
7.15
7.14
2.41
1.51
0.97
2.08
2.09
3.30
2.08
1.10
3.00
f1 (ppm)
Br
Br
O
O
S

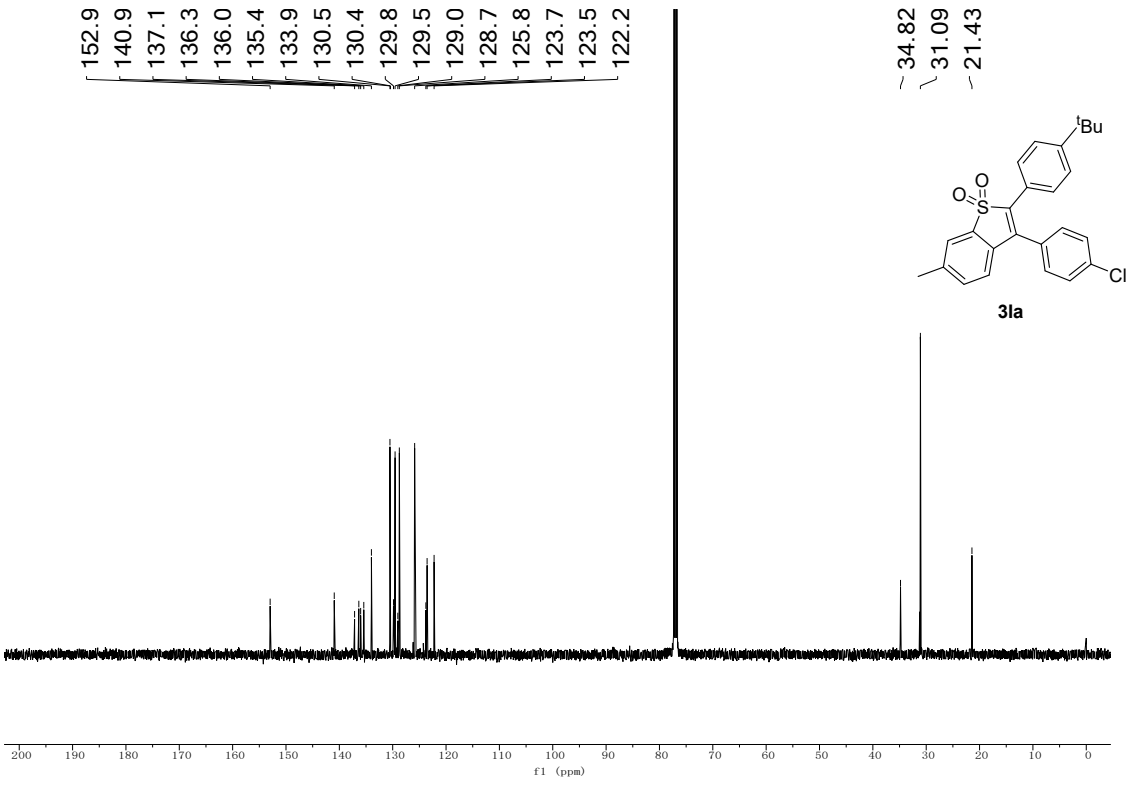
**3Ga**

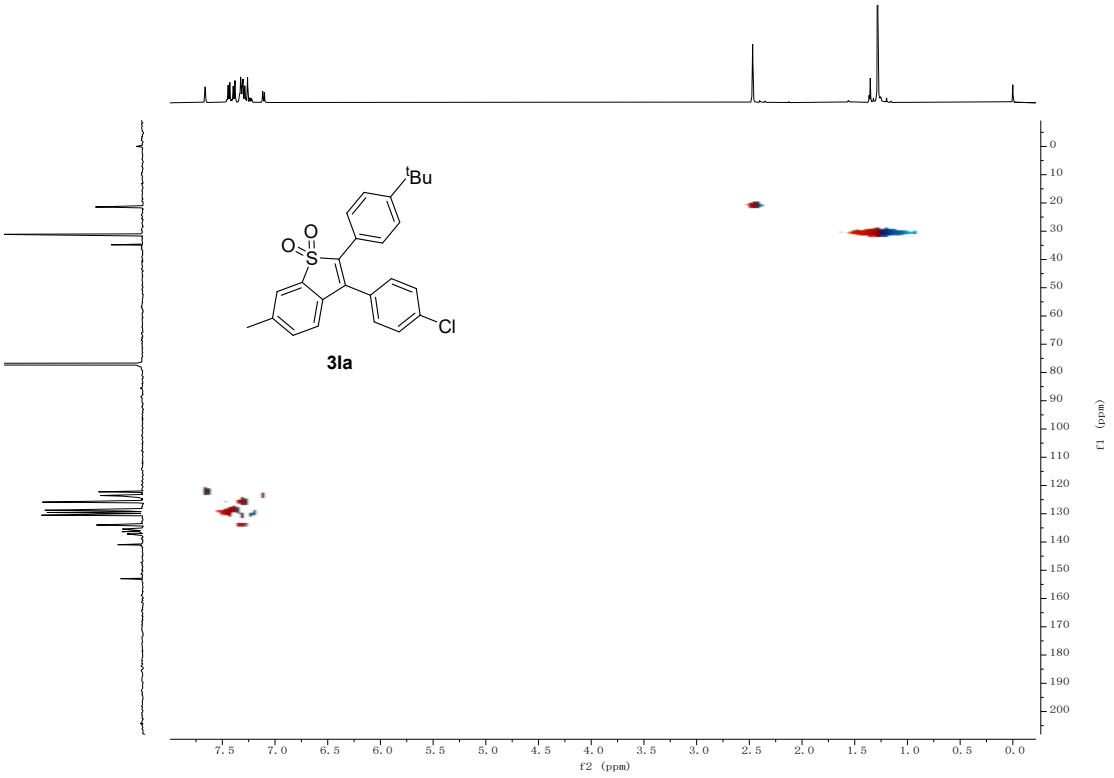

141.5
137.5
136.3
136.0
134.1
132.6
132.2
130.6
130.6
129.8
129.6
125.8
124.3
124.1
123.8
122.3
21.48
f1 (ppm)
Br
Br
O
O
S

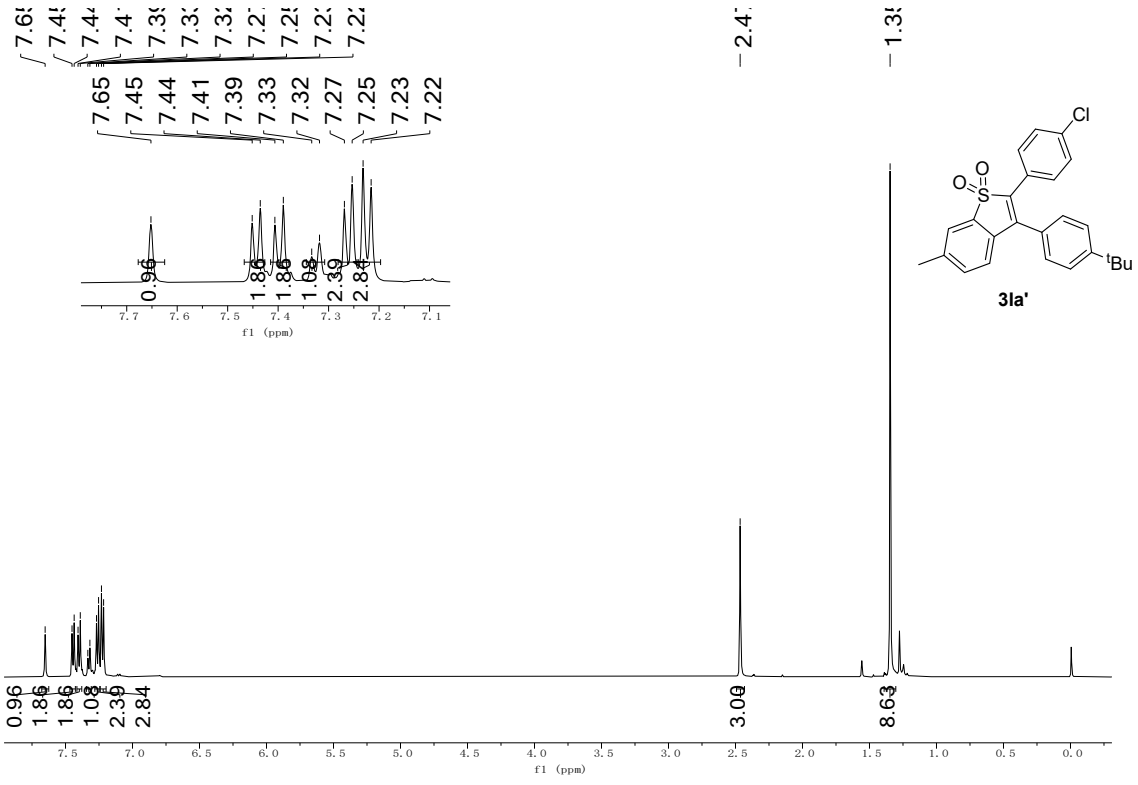
**3Ga**

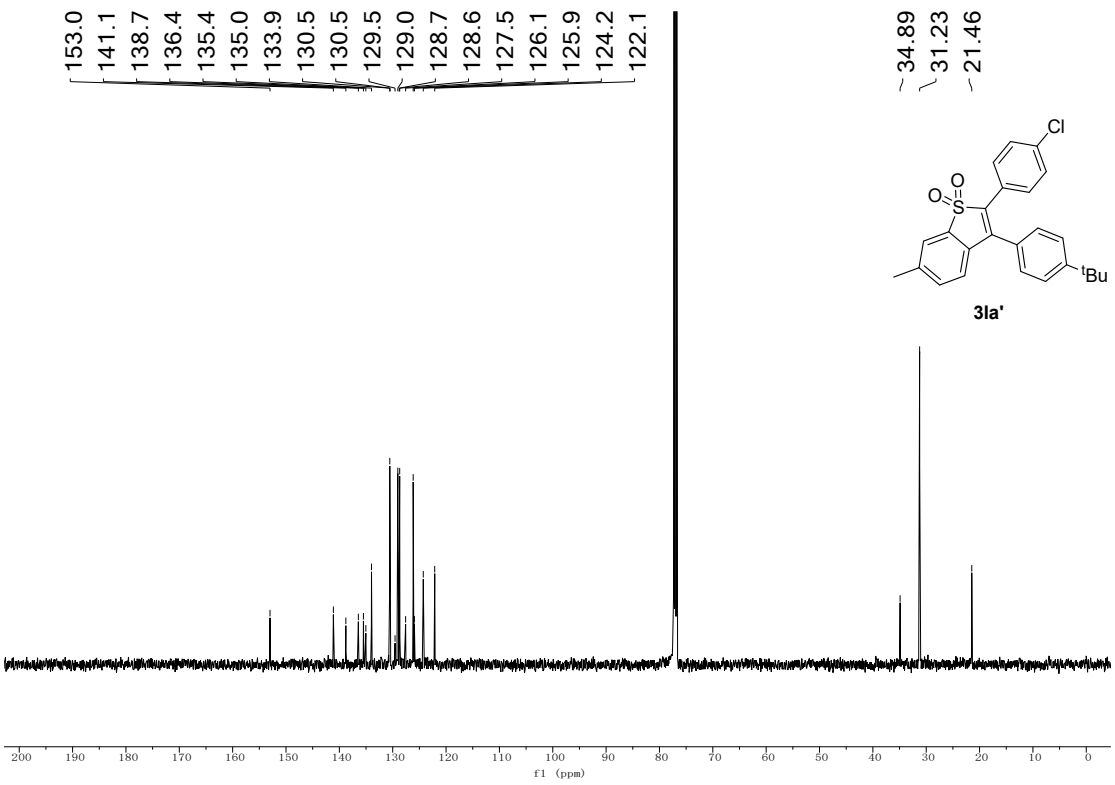

3Ha
3Ha
f1 (ppm)

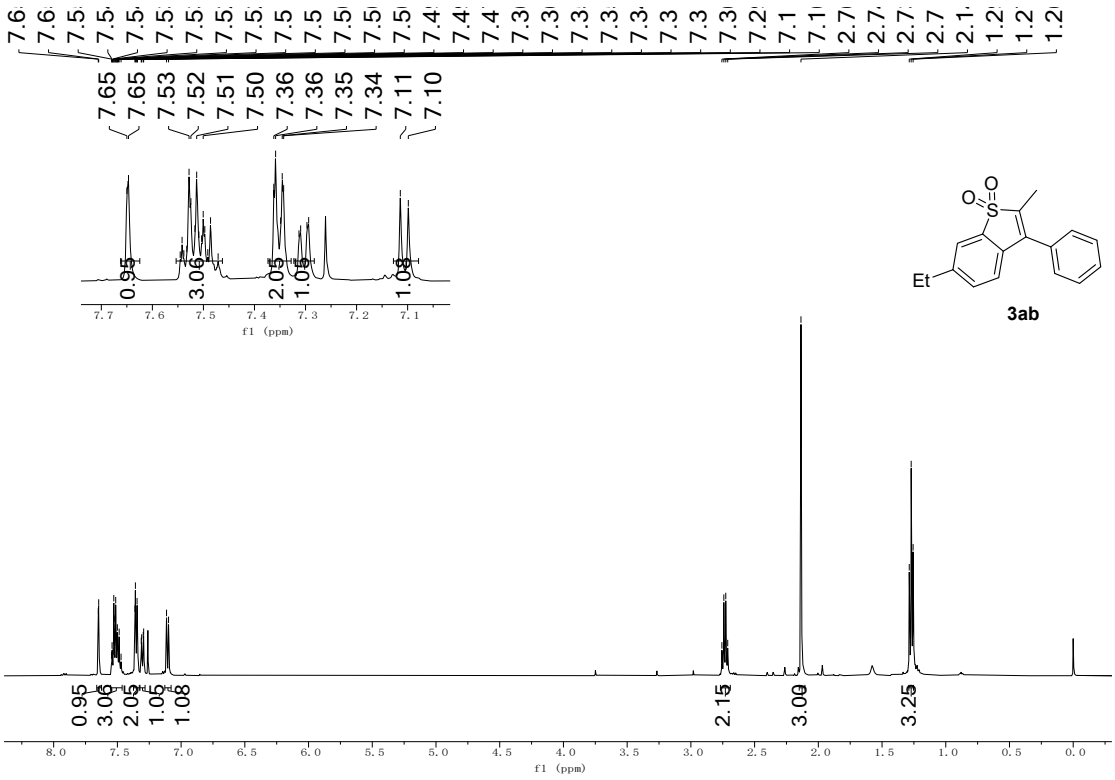

7.66
7.44
7.43
7.40
7.38
7.33
7.32
7.31
7.30
7.29
7.12
2.47
1.28
0.97
1.88
1.94
5.00
0.99
3.09
8.68
f1 (ppm)
tBu
O
O
S
Cl
3la

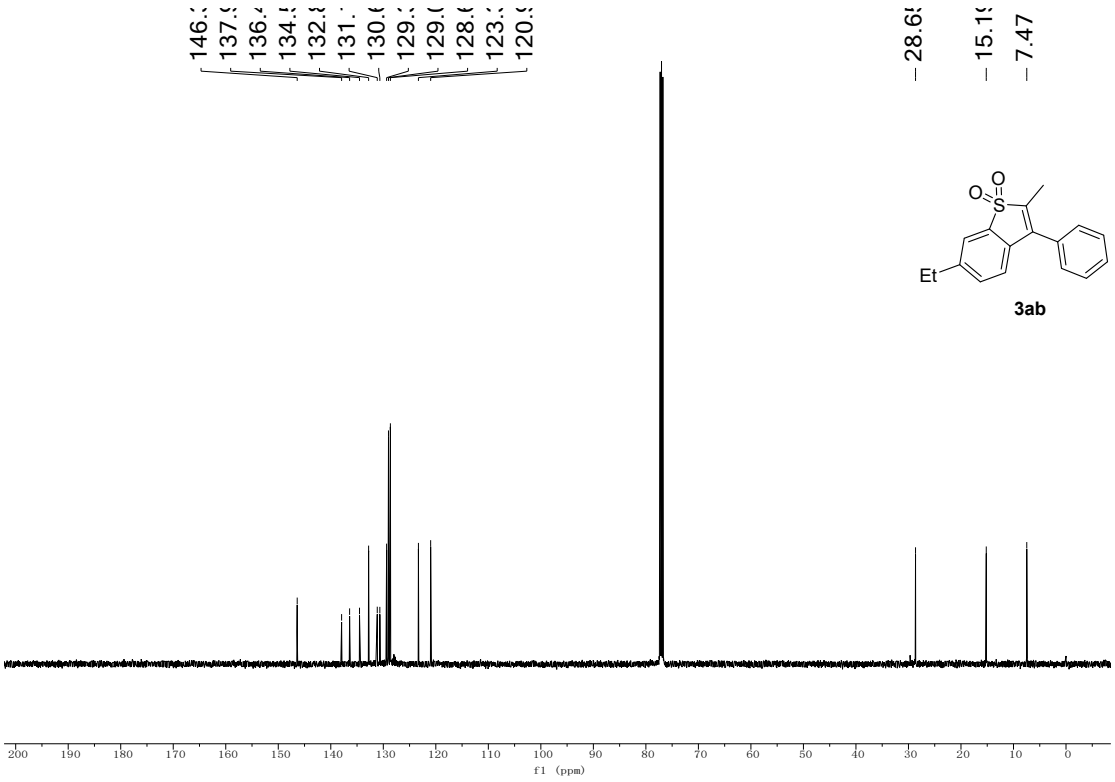

152.9
140.9
137.1
136.3
136.0
135.4
133.9
130.5
130.4
129.8
129.5
129.0
128.7
125.8
123.7
123.5
122.2
34.82
31.09
21.43
f1 (ppm)
tBu
O
O
S
Cl
3la

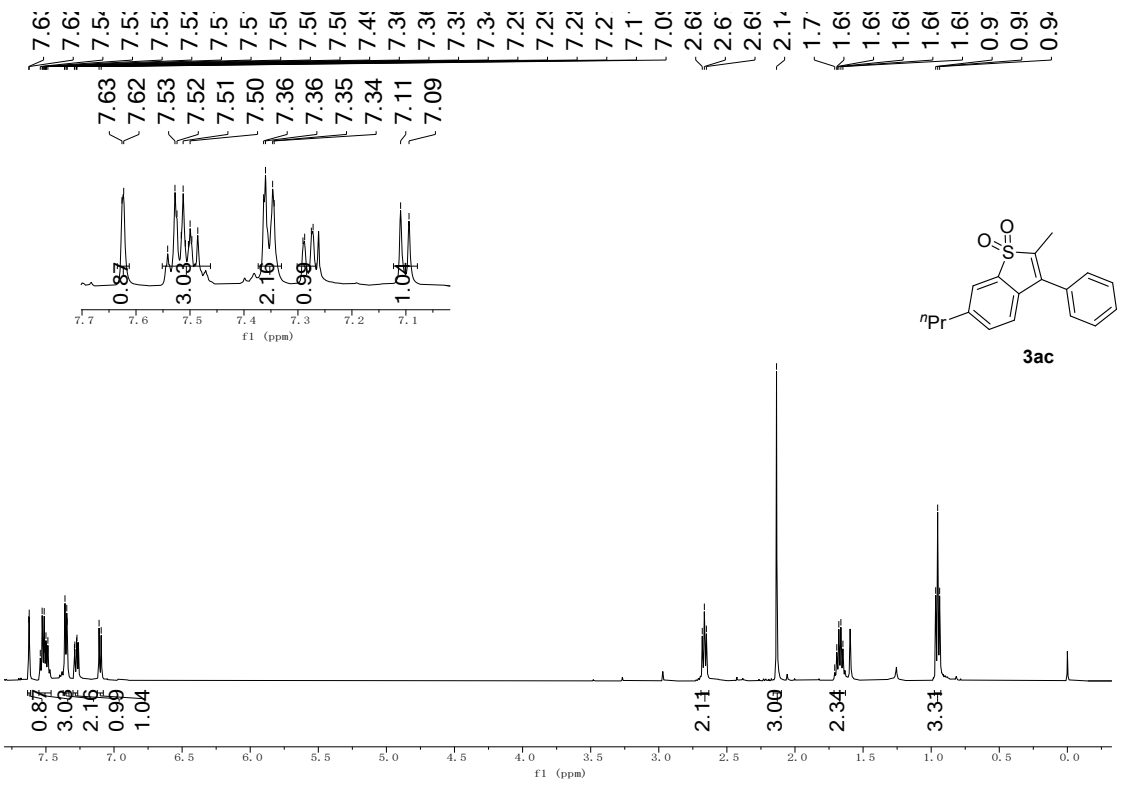

tBu
O
O
S
Cl
3la
f2 (ppm)
f1 (ppm)

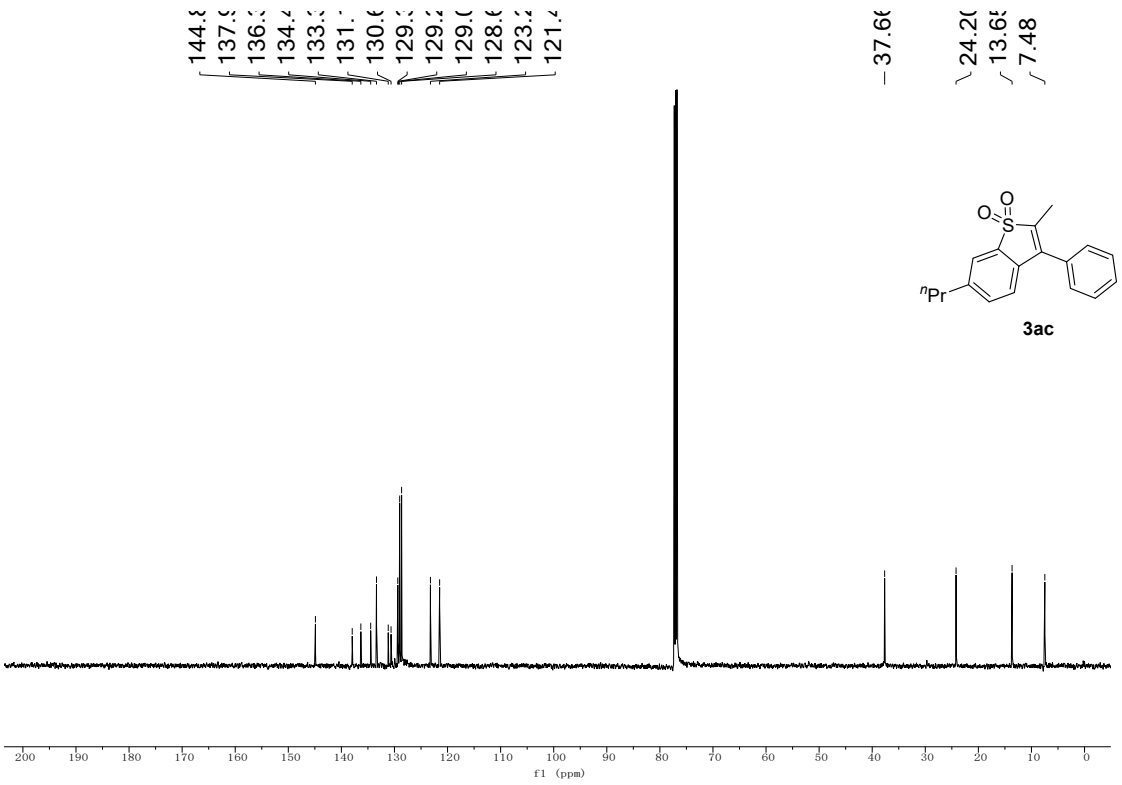

7.65
7.45
7.44
7.41
7.39
7.33
7.32
7.27
7.25
7.23
7.22
2.47
1.31
0.96
1.86
1.86
1.08
2.39
2.84
3.00
8.63
Cl
O
O
S
tBu
3la'
f1 (ppm)

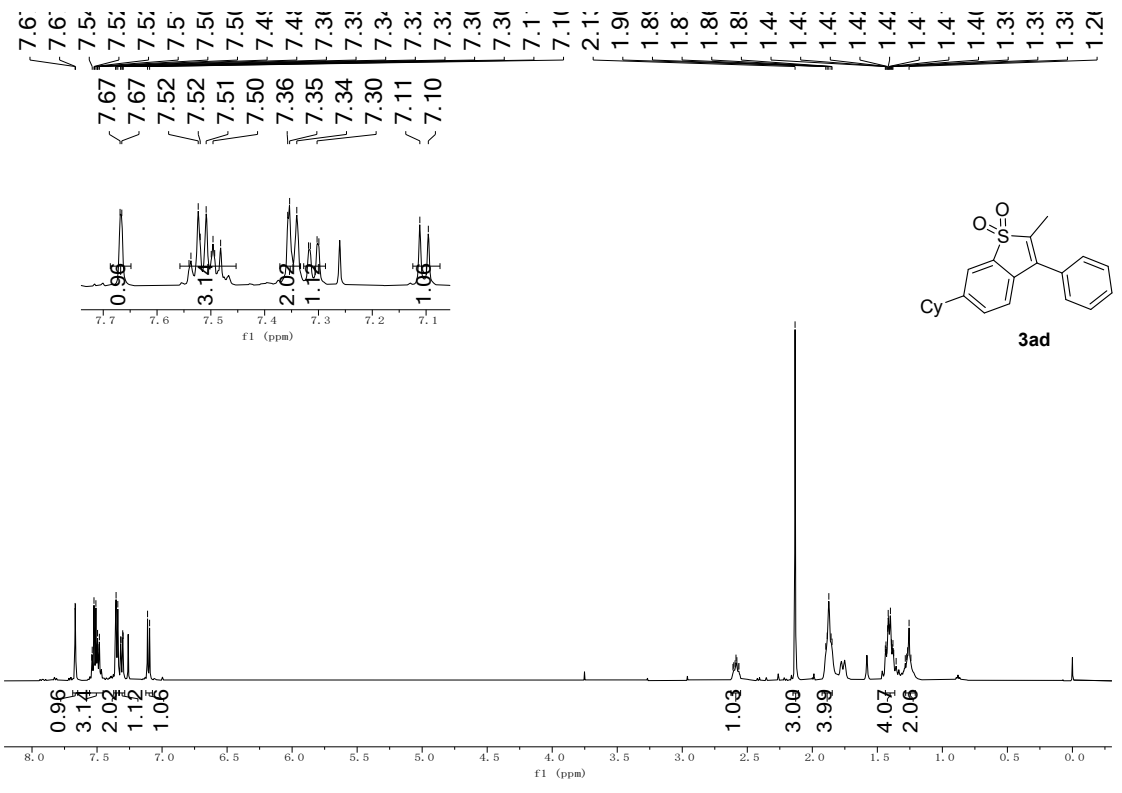

153.0
141.1
138.7
136.4
135.4
135.0
133.9
130.5
130.5
129.5
129.0
128.7
128.6
127.5
126.1
125.9
124.2
122.1
34.89
31.23
21.46
Cl
O
O
S
tBu
3la'
f1 (ppm)

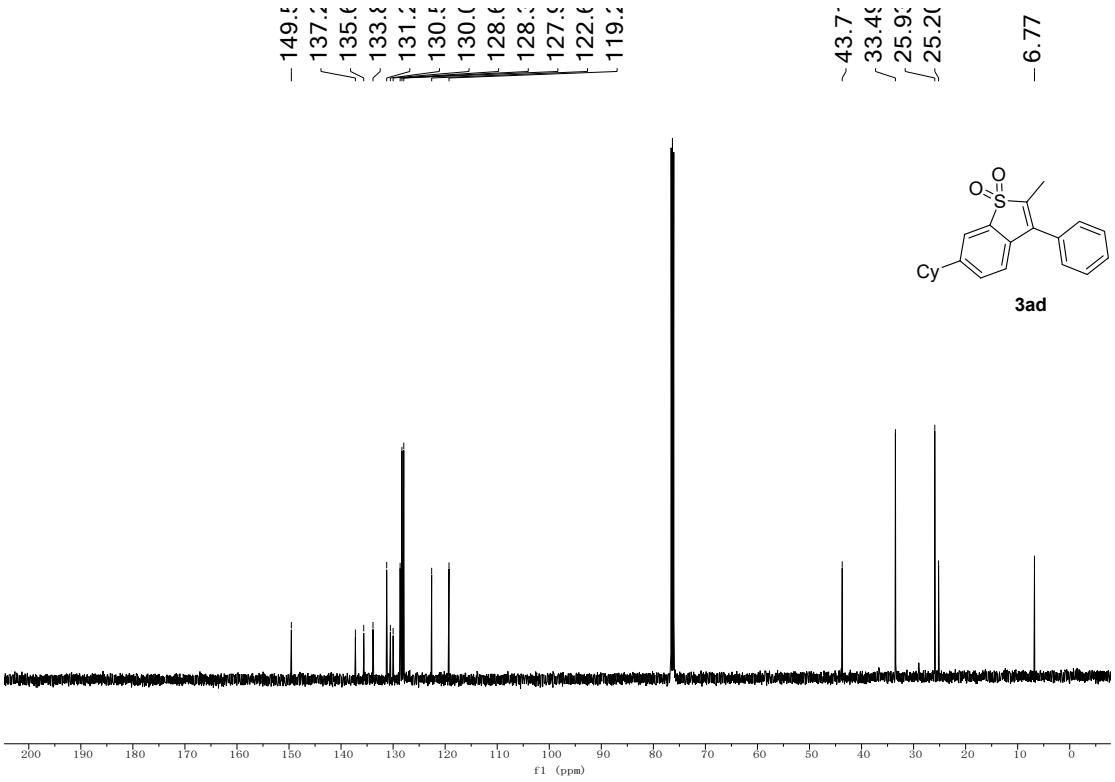

7.65
7.65
7.53
7.52
7.51
7.50
7.36
7.36
7.35
7.34
7.11
7.10
0.95
3.06
2.05
1.05
1.08
O
O
S
Et
3ab
f1 (ppm)

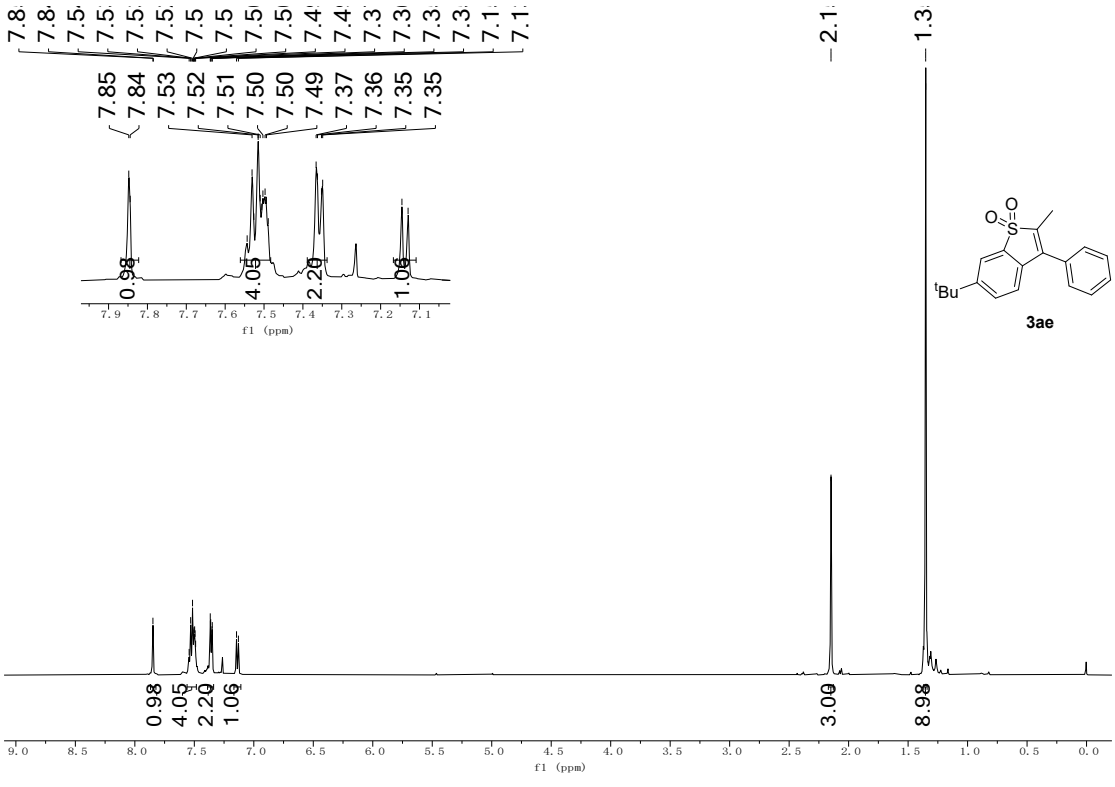

28.68
15.19
7.47
Et
3ab
f1 (ppm)

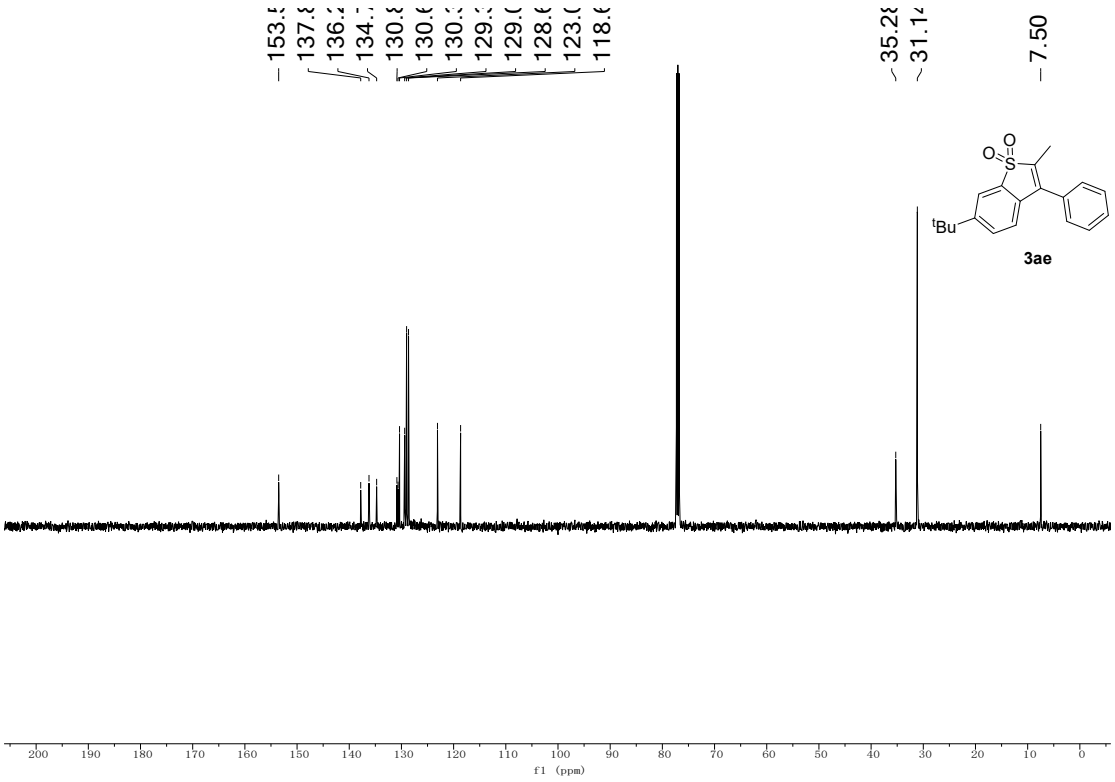

7.63
7.62
7.53
7.52
7.51
7.50
7.36
7.35
7.34
7.11
7.09
0.87
3.03
2.16
0.99
1.04
2.11
3.00
2.34
3.31
nPr
3ac
f1 (ppm)

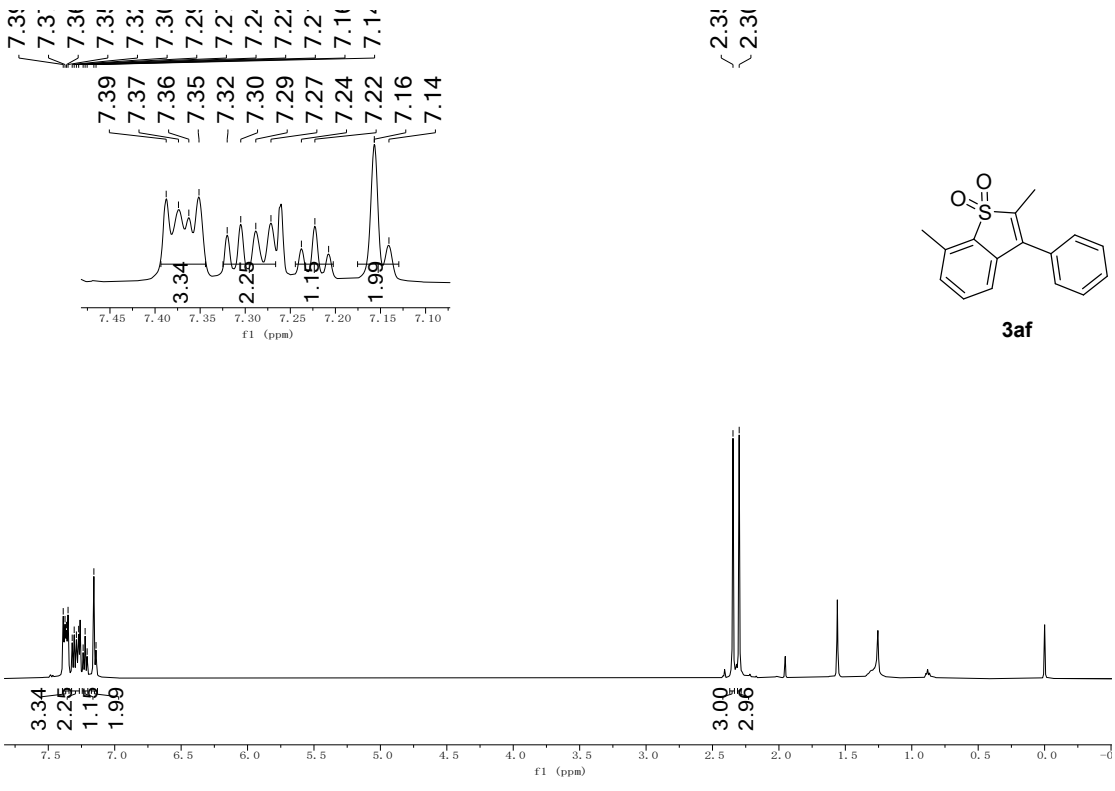

144.8
137.9
136.3
134.4
133.3
131.1
130.6
129.3
129.2
129.0
128.6
123.2
121.4
37.6
24.2
13.6
7.48
O
O
S
nPr
3ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

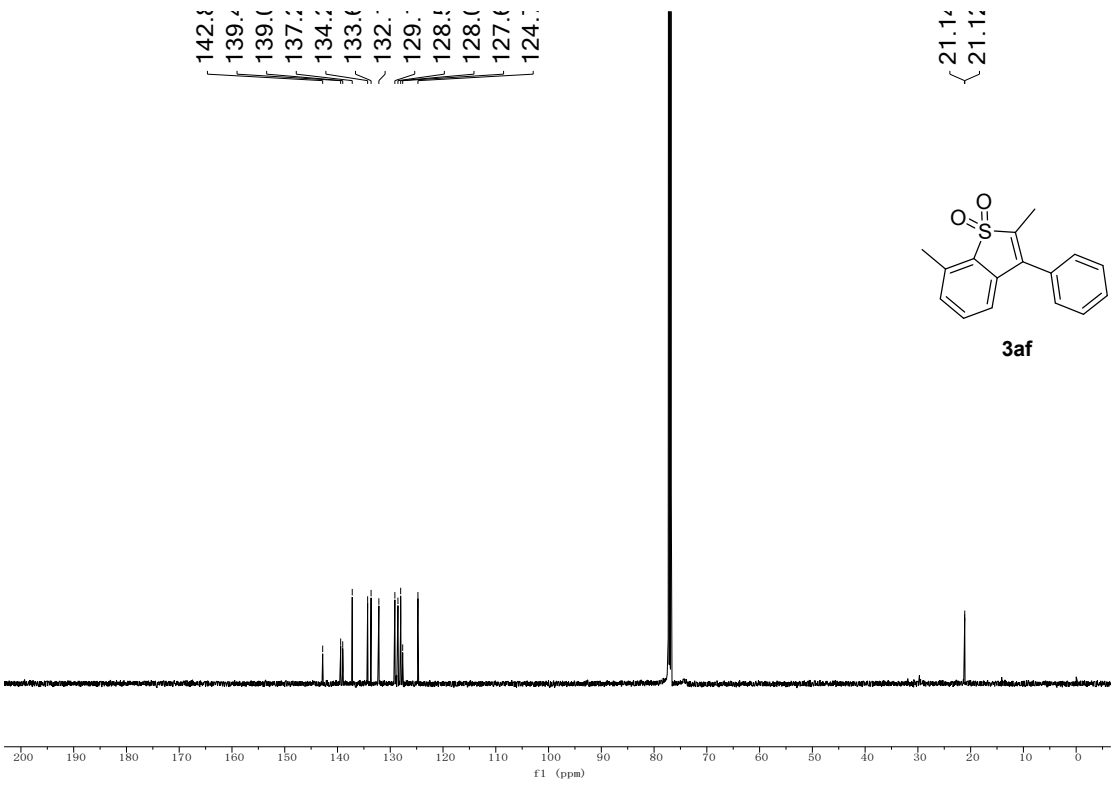

7.67
7.67
7.52
7.52
7.51
7.50
7.36
7.35
7.34
7.30
7.11
7.10
2.13
1.90
1.85
1.80
1.80
1.80
1.44
1.43
1.42
1.42
1.42
1.41
1.40
1.39
1.39
1.38
1.21
0.96
3.14
2.02
1.12
1.06
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
O
O
S
Cy
3ad
0.96
3.14
2.02
1.12
1.06
1.03
3.00
3.99
4.07
2.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.5
137.2
135.6
133.8
131.2
130.5
130.0
128.6
128.3
127.9
122.6
119.2
43.7
33.4
25.9
25.2
6.77
Cy
3ad
f1 (ppm)

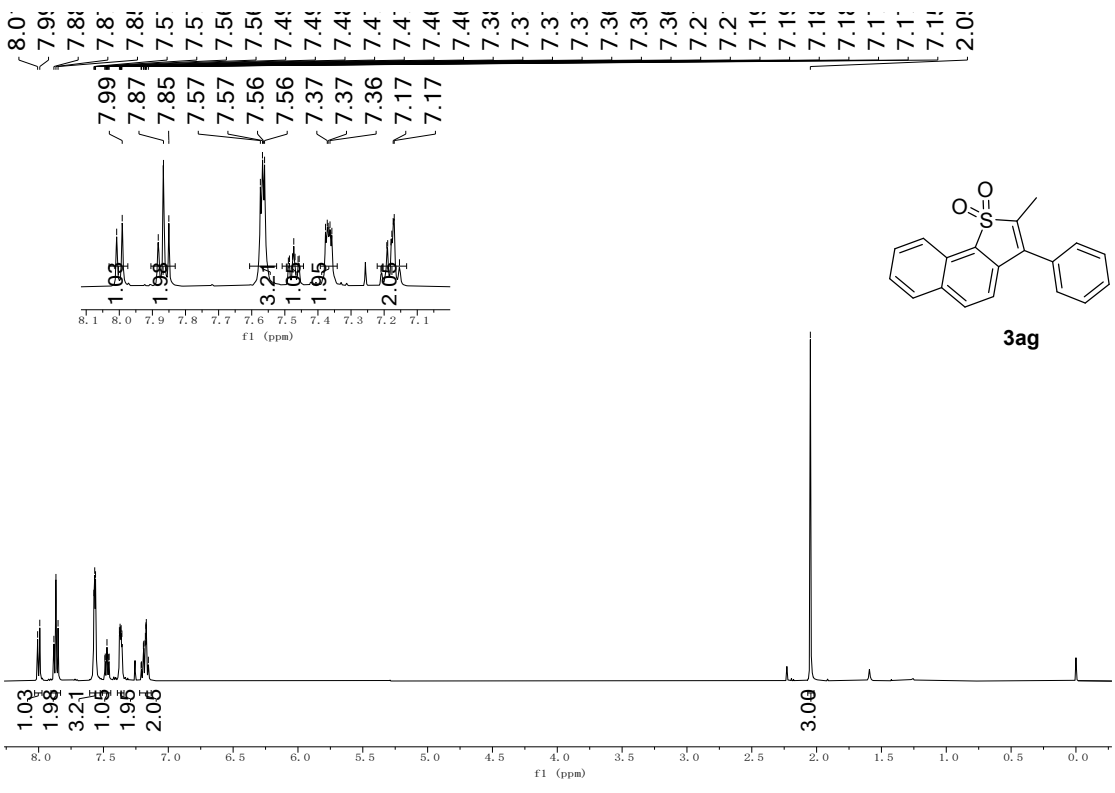

7.85
7.84
7.53
7.52
7.51
7.50
7.50
7.49
7.37
7.36
7.35
7.35
2.11
1.30
0.98
4.05
2.20
1.06
3.00
8.98
tBu
3ae
f1 (ppm)


35.28
31.14
7.50
tBu
3ae
f1 (ppm)

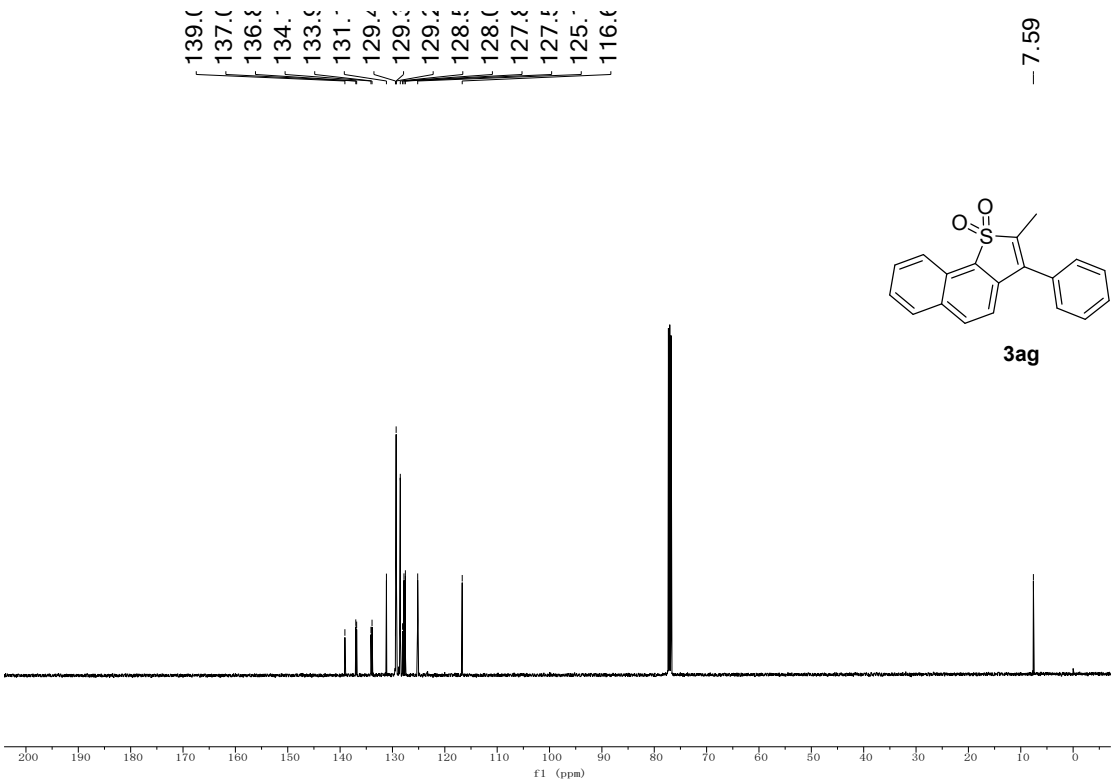

7.39
7.37
7.36
7.35
7.32
7.30
7.29
7.27
7.24
7.22
7.16
7.14
2.31
2.30
3.34
2.25
1.15
1.99
3af
3.00
2.96
f1 (ppm)

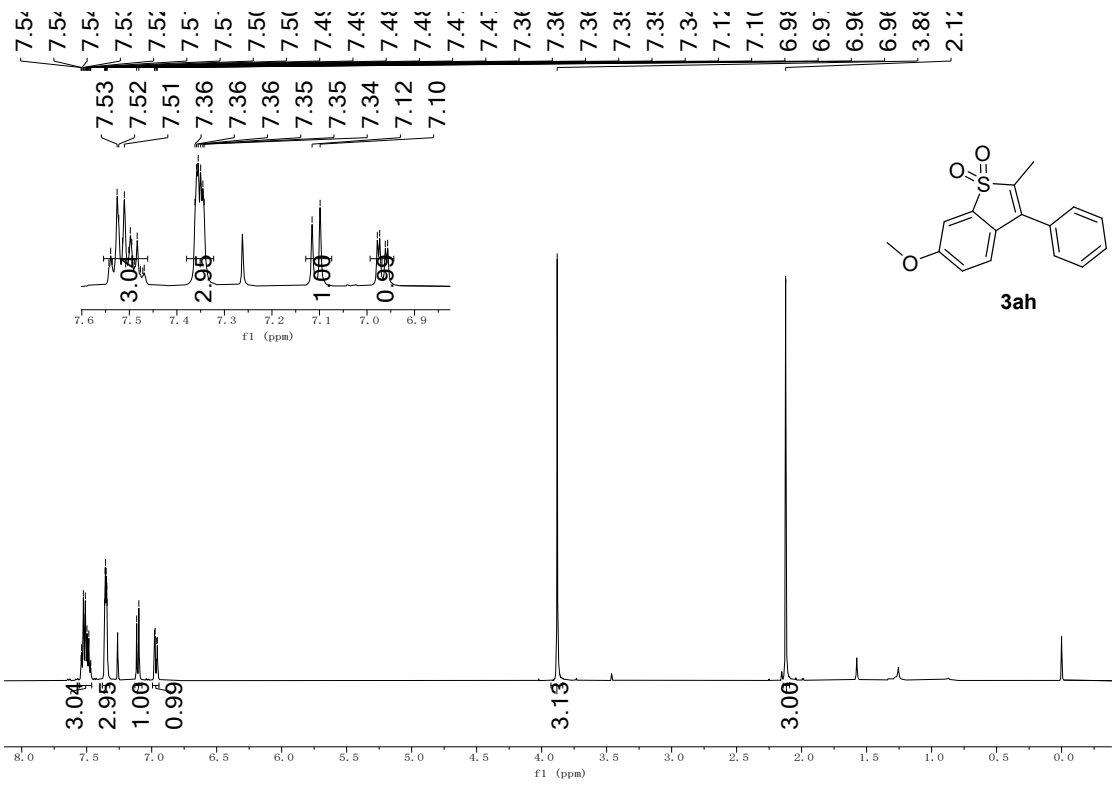


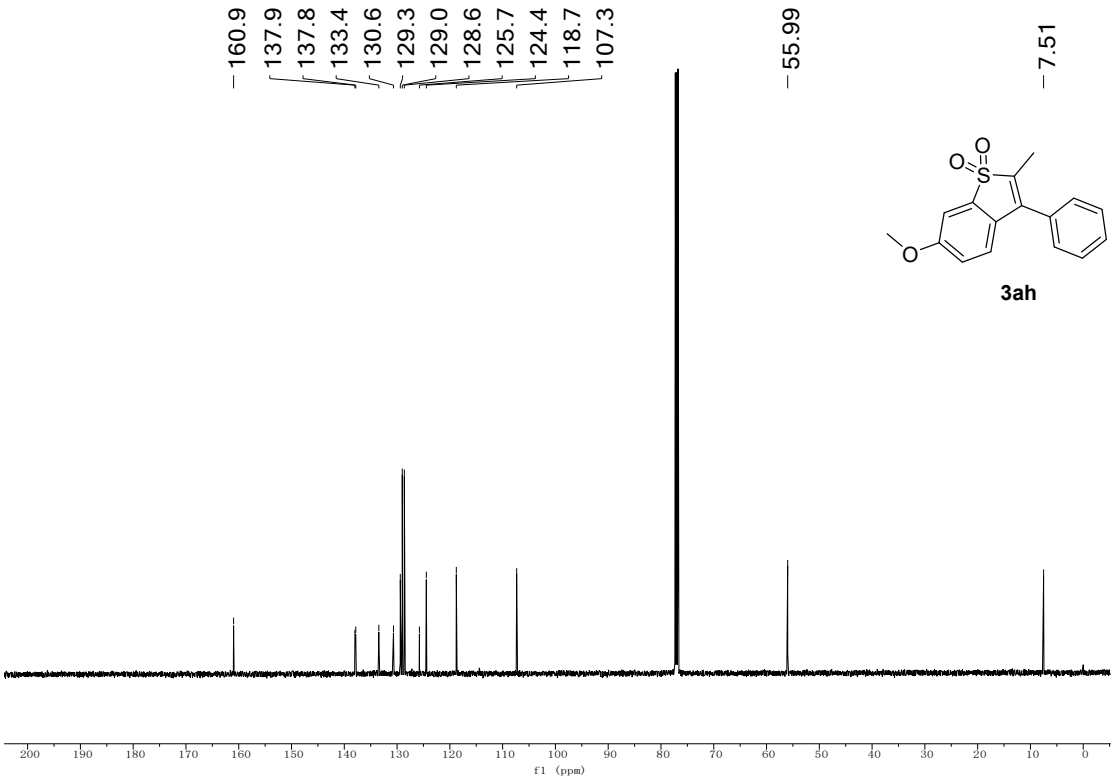
3af



3ag

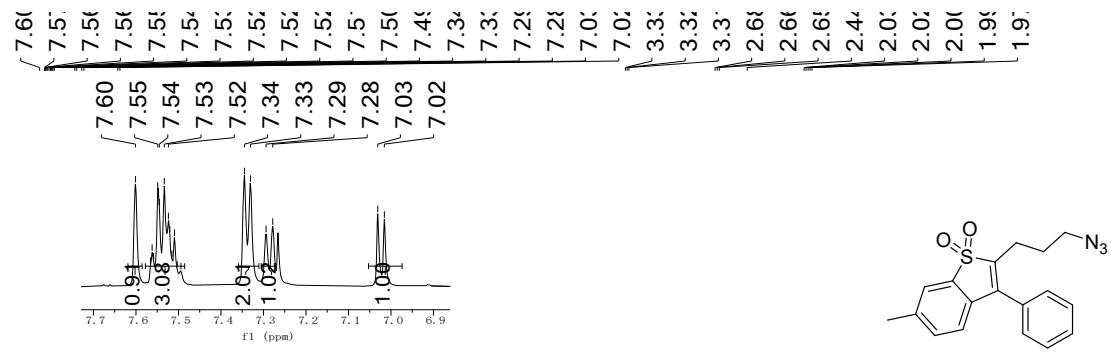

139.0
137.0
136.8
134.
133.9
131.
129.4
129.
129.2
128.8
128.0
127.8
127.5
125.
116.6
7.59
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.53
7.52
7.51
7.36
7.36
7.36
7.35
7.35
7.34
7.12
7.10
3.04
2.95
1.00
0.99
f1 (ppm)
3ah
3.04
2.95
1.00
0.99
3.13
3.00
f1 (ppm)


160.9
137.9
137.8
133.4
130.6
129.3
129.0
128.6
125.7
124.4
118.7
107.3
55.99
7.51
f1 (ppm)

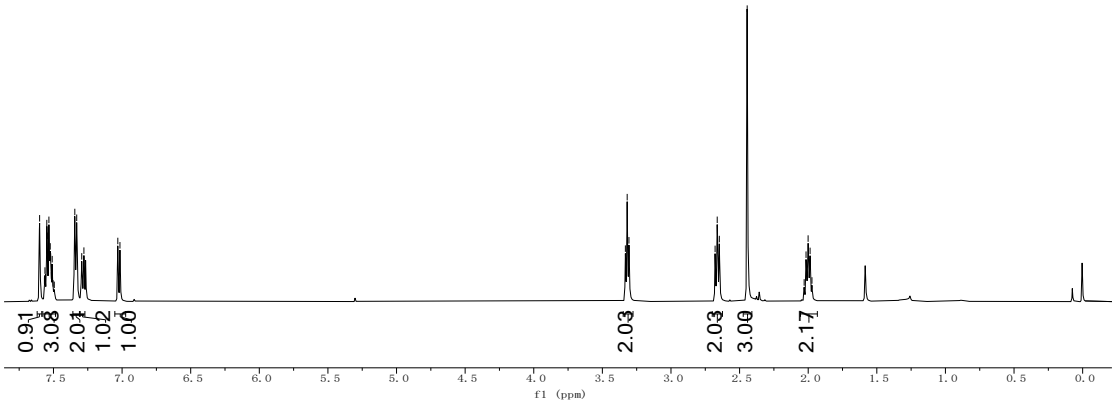


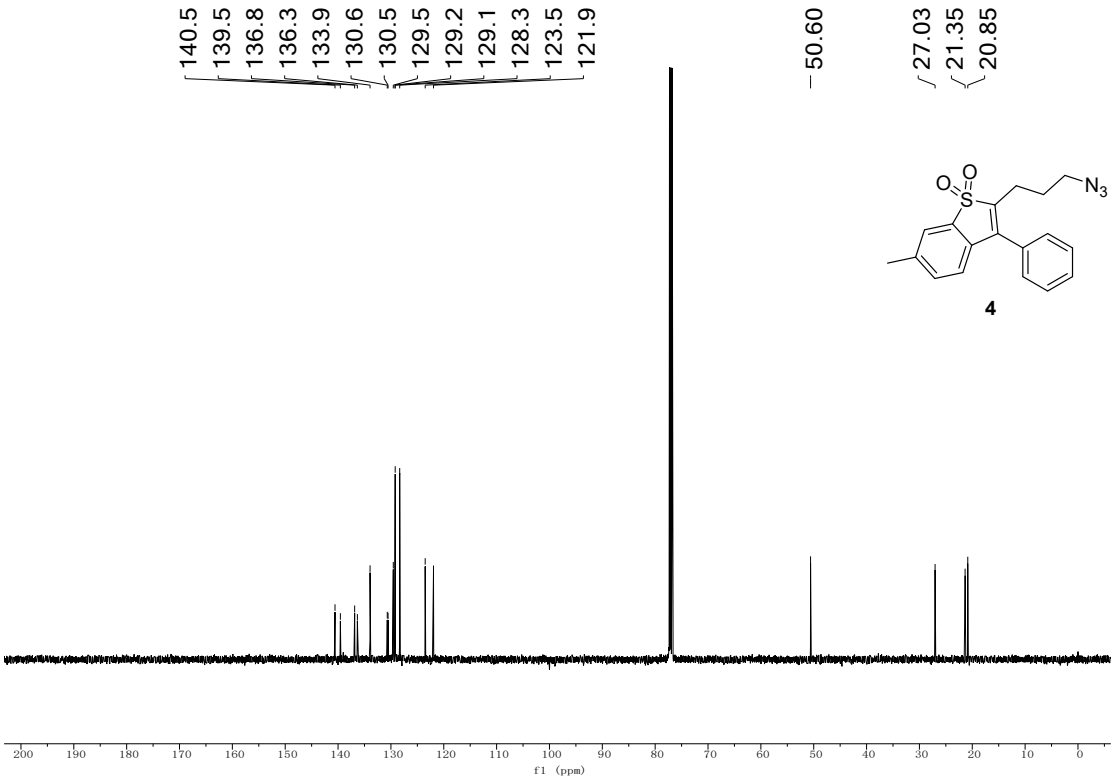
3ah


7.60
7.55
7.54
7.53
7.52
7.34
7.33
7.29
7.28
7.03
7.02
0.91
3.08
2.01
1.02
1.00
f1 (ppm)



4


0.91
3.08
2.01
1.02
1.00
2.03
2.03
3.09
2.17
f1 (ppm)


140.5
139.5
136.8
136.3
133.9
130.6
130.5
129.5
129.2
129.1
128.3
123.5
121.9
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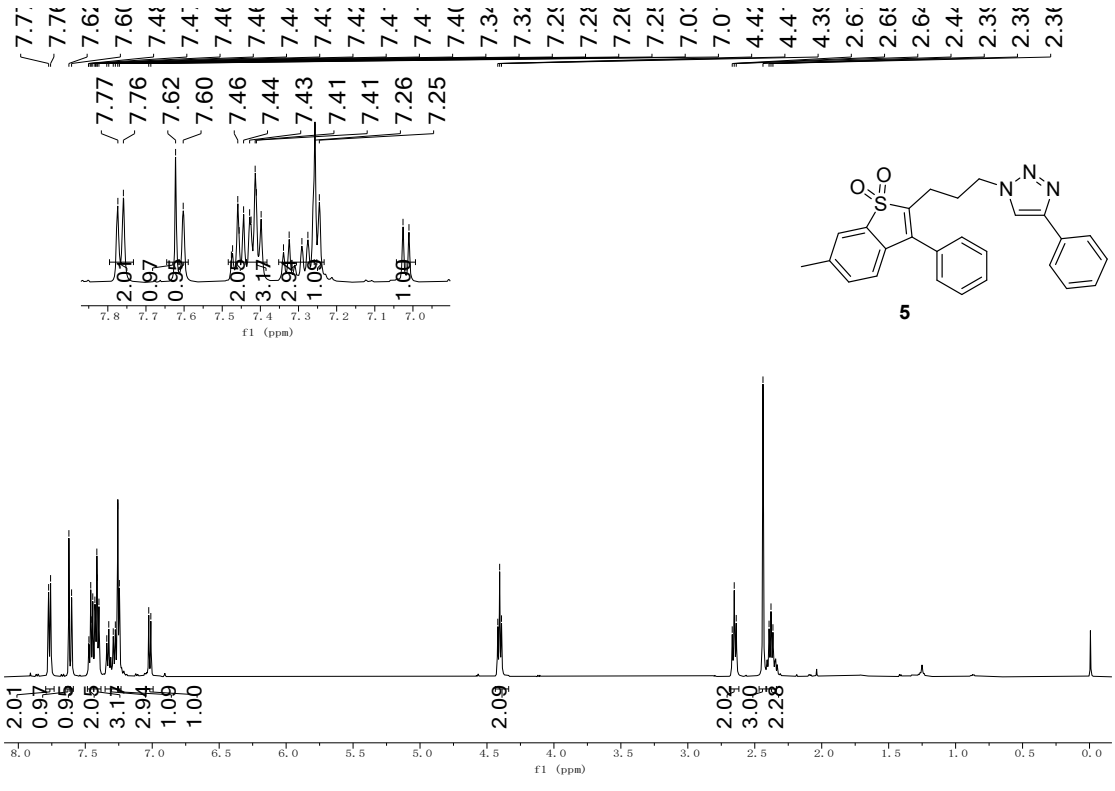
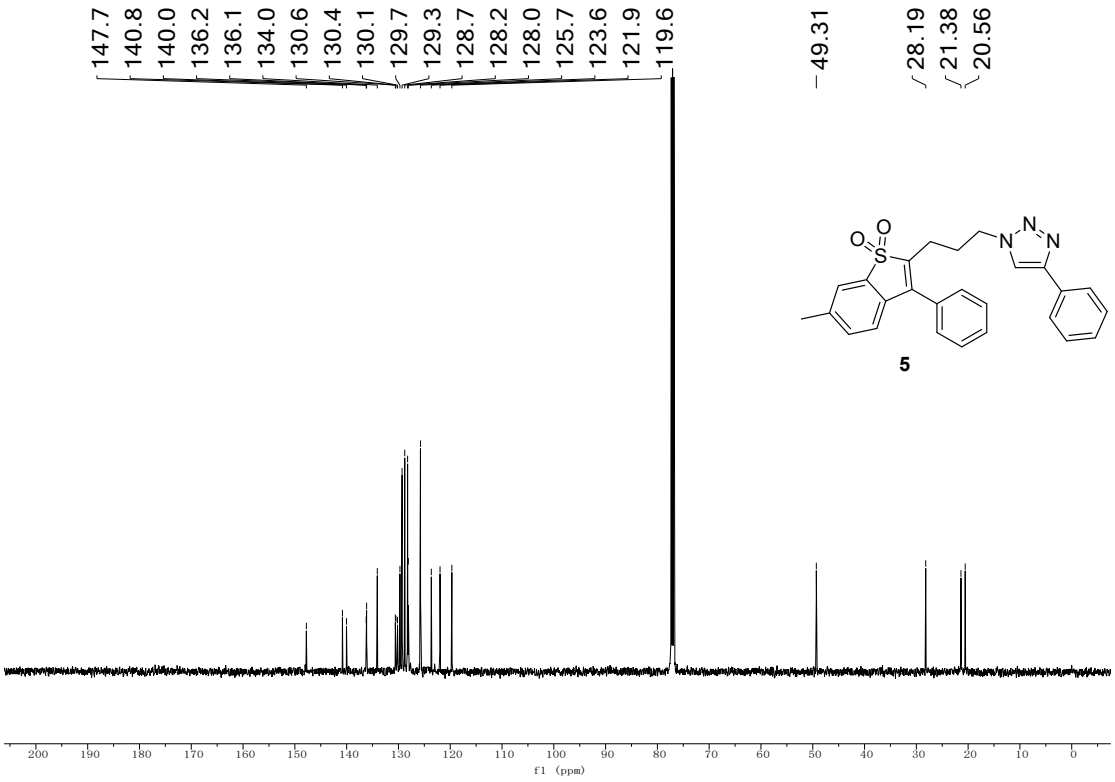
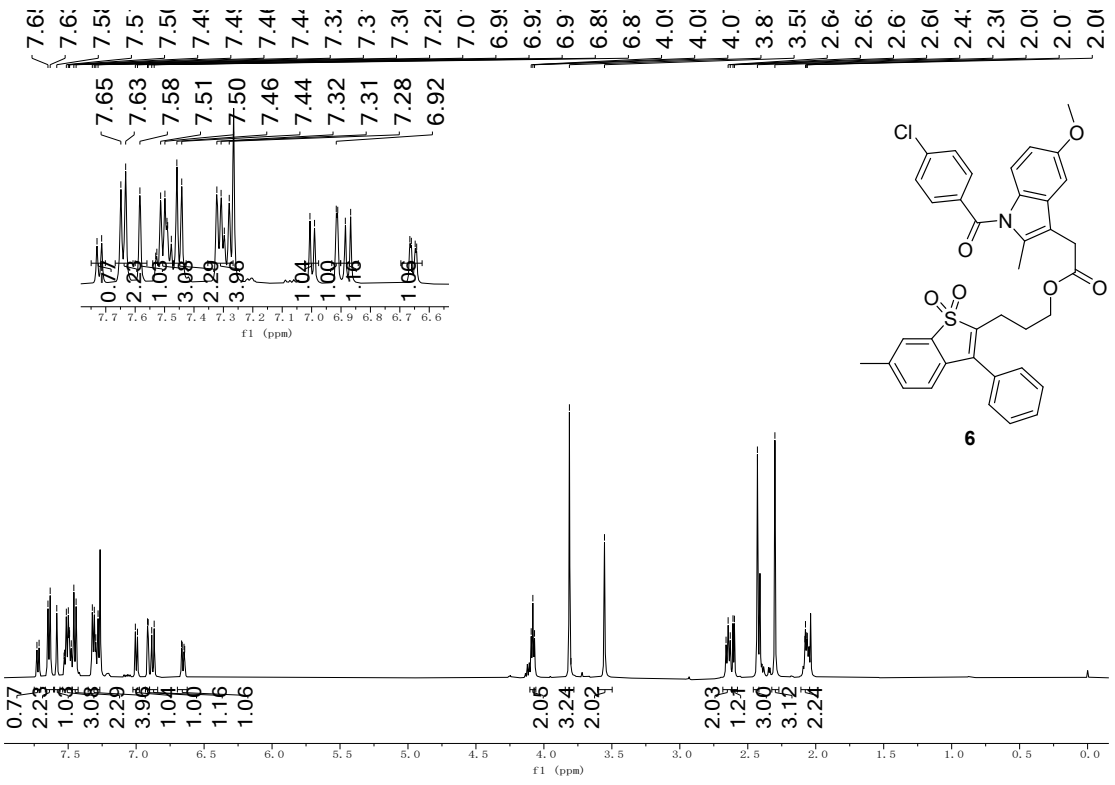
21.35
20.85
O
O
S
N3
4
f1 (ppm)

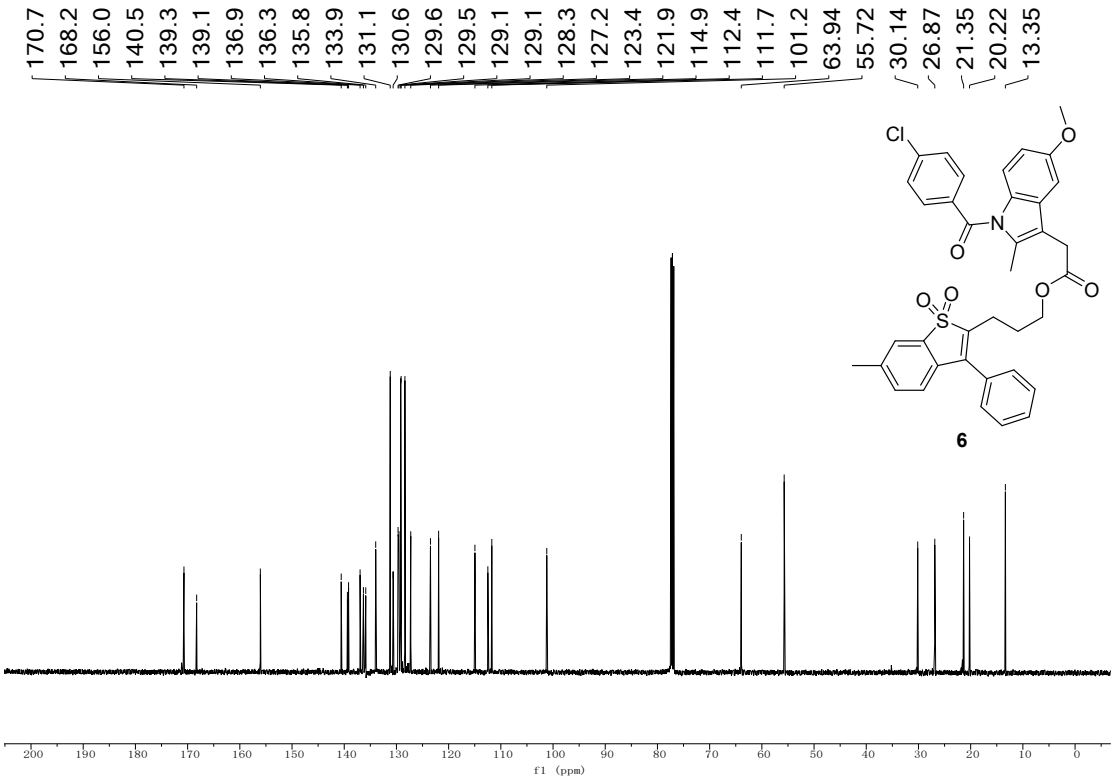

7.77
7.76
7.62
7.60
7.46
7.44
7.43
7.41
7.41
7.26
7.25
2.01
0.97
0.95
2.05
3.17
2.94
1.09
1.00
O
O
S
N
N
N
5
f1 (ppm)

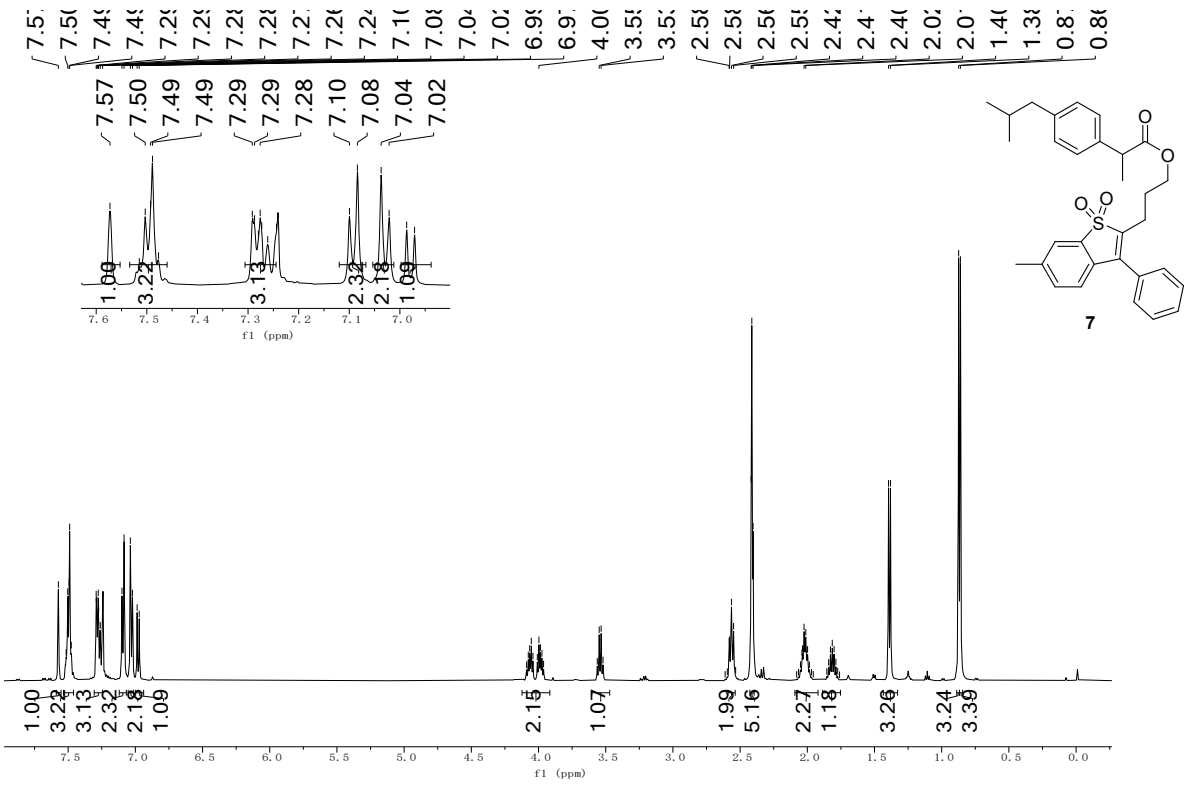

147.7
140.8
140.0
136.2
136.1
134.0
130.6
130.4
130.1
129.7
129.3
128.7
128.2
128.0
125.7
123.6
121.9
119.6
49.31
28.19
21.38
20.56
f1 (ppm)

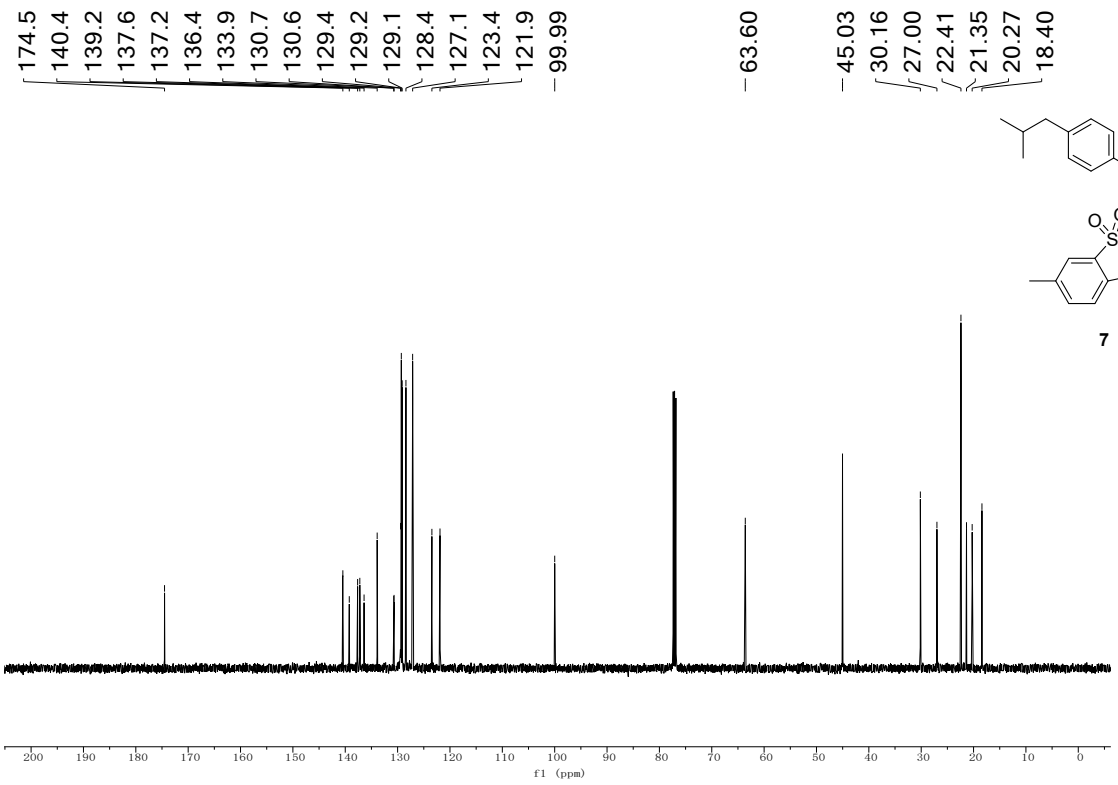
5


7.65
7.63
7.58
7.51
7.50
7.46
7.44
7.32
7.31
7.28
6.92
0.77
2.23
1.09
3.08
2.29
3.96
1.04
1.00
1.16
1.06
2.05
3.24
2.02
2.03
1.24
3.00
3.12
2.24
f1 (ppm)

6


170.7
168.2
156.0
140.5
139.3
139.1
136.9
136.3
135.8
133.9
131.1
130.6
129.6
129.5
129.1
129.1
128.3
127.2
123.4
121.9
114.9
112.4
111.7
101.2
63.94
55.72
30.14
26.87
21.35
20.22
13.35
Cl
O
N
O
O
O
O
O
S
O
6
f1 (ppm)


7.57
7.50
7.49
7.49
7.29
7.29
7.28
7.10
7.08
7.04
7.02
1.00
3.22
3.13
2.32
2.18
1.09
O
O
O
O
S
7
f1 (ppm)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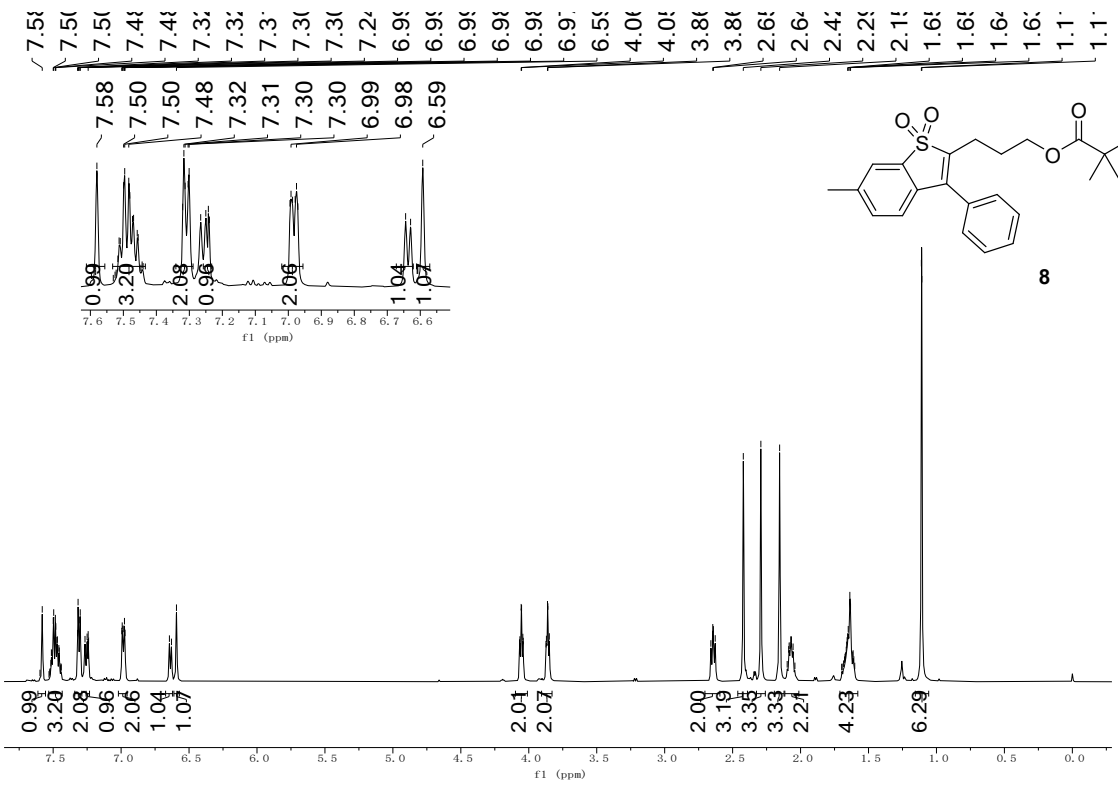
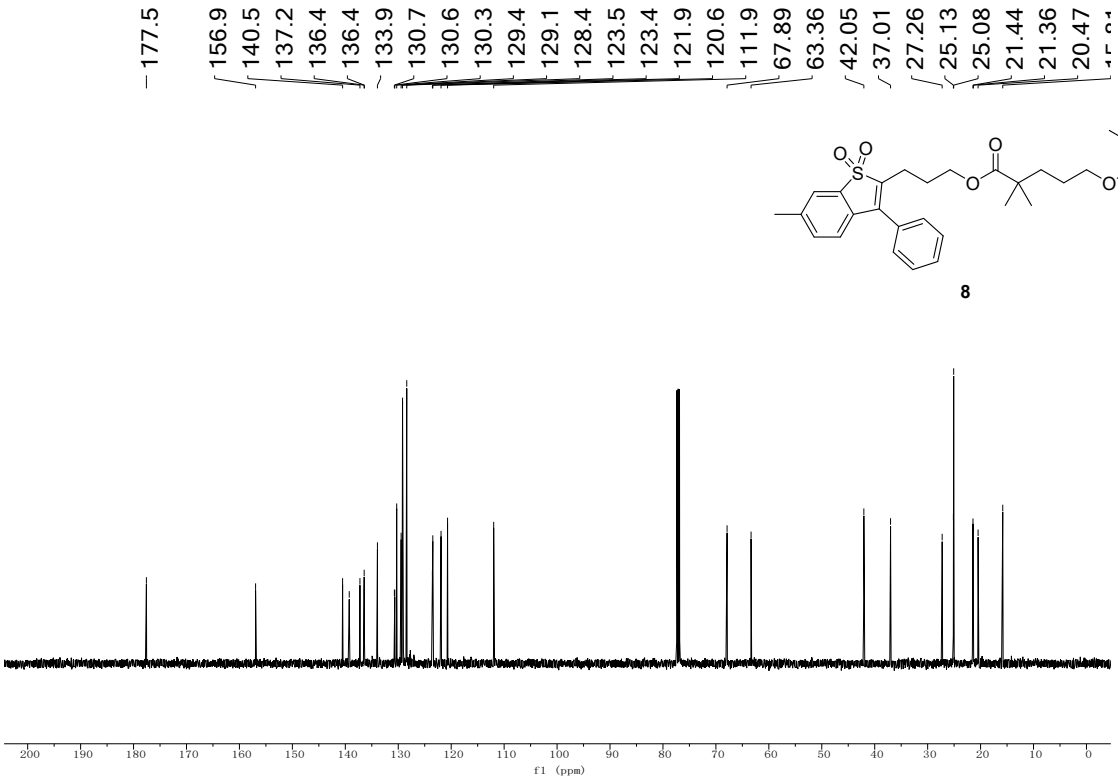
140.4
139.2
137.6
137.2
136.4
133.9
130.7
130.6
129.4
129.2
129.1
128.4
127.1
123.4
121.9
99.99
63.60
45.03
30.16
27.00
22.41
21.35
20.27
18.40
f1 (ppm)

7


7.58
7.50
7.50
7.48
7.32
7.31
7.30
7.30
6.99
6.98
6.59
0.99
3.20
2.08
0.96
2.06
1.04
1.07
2.01
2.07
2.00
3.19
3.35
3.33
2.24
4.23
6.29
f1 (ppm)

8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156.9
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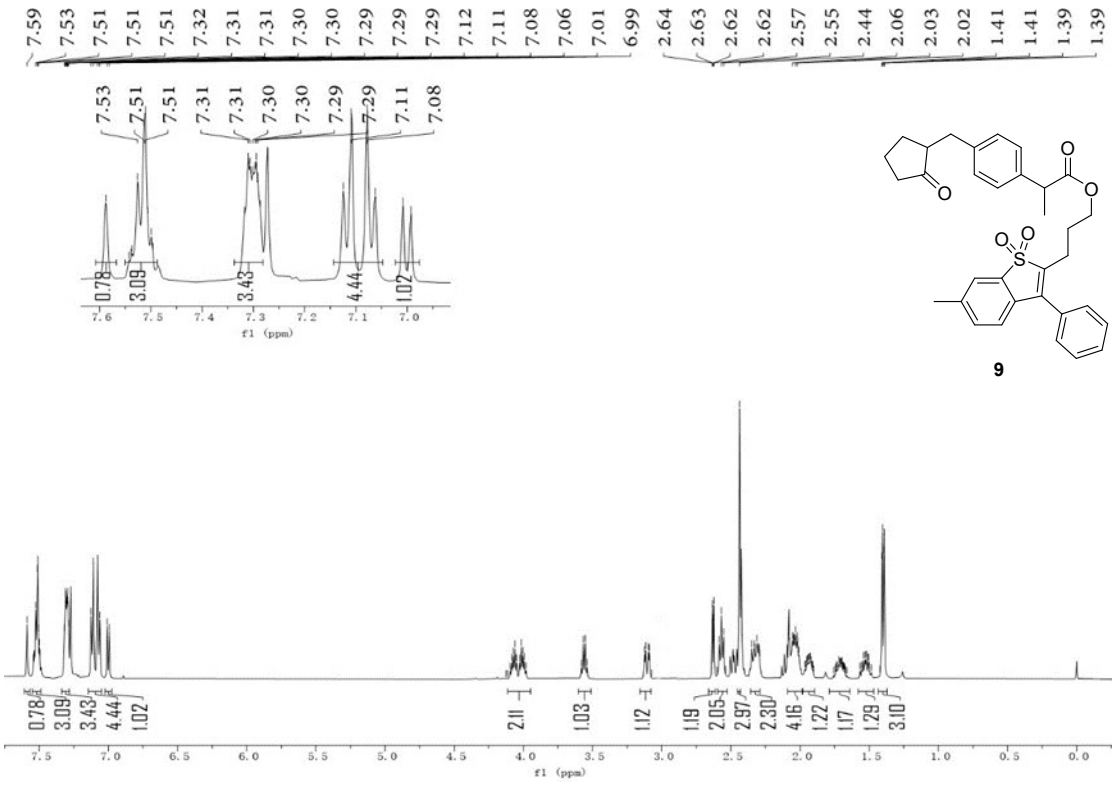
137.2
136.4
136.4
133.9
130.7
130.6
130.3
129.4
129.1
128.4
123.5
123.4
121.9
120.6
111.9
67.89
63.36
42.05
37.01
27.26
25.13
25.08
21.44
21.36
20.47
f1 (ppm)

**8**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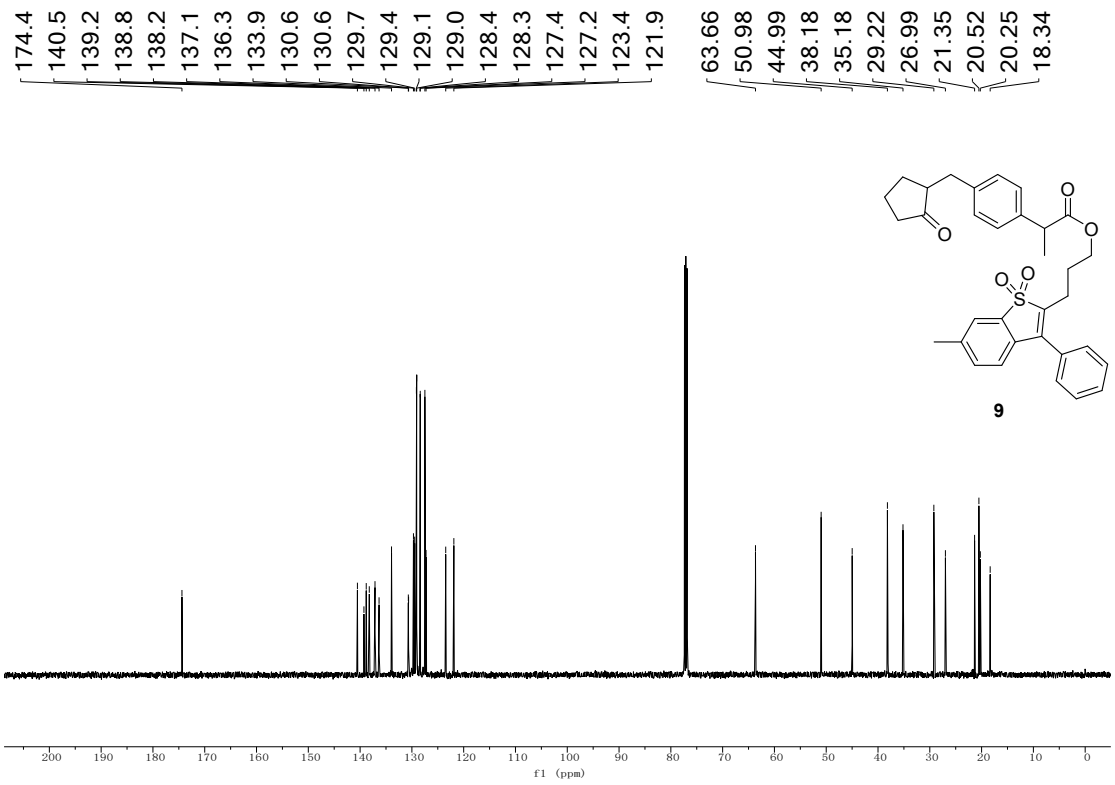
7.53
7.51
7.51
7.51
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.12
7.11
7.08
7.06
7.01
6.99
2.64
2.63
2.62
2.62
2.57
2.55
2.44
2.06
2.03
2.02
1.41
1.41
1.39
1.39
0.78
3.09
3.43
4.44
1.02
2.11
1.03
1.12
1.19
2.05
2.97
2.30
4.16
1.22
1.17
1.29
3.10
f1 (ppm)

**9**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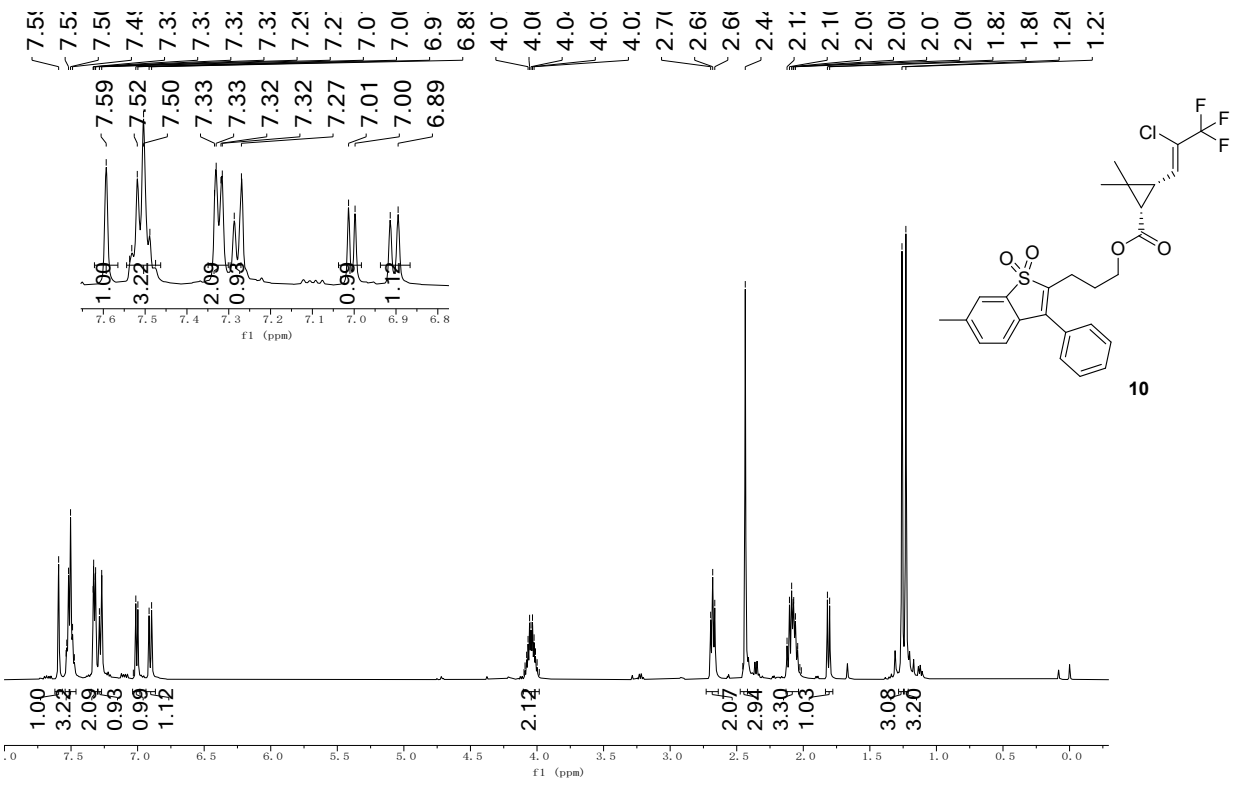
140.5
139.2
138.8
138.2
137.1
136.3
133.9
130.6
130.6
129.7
129.4
129.1
129.0
128.4
128.3
127.4
127.2
123.4
121.9
63.66
50.98
44.99
38.18
35.18
29.22
26.99
21.35
20.52
20.25
18.34
9
f1 (ppm)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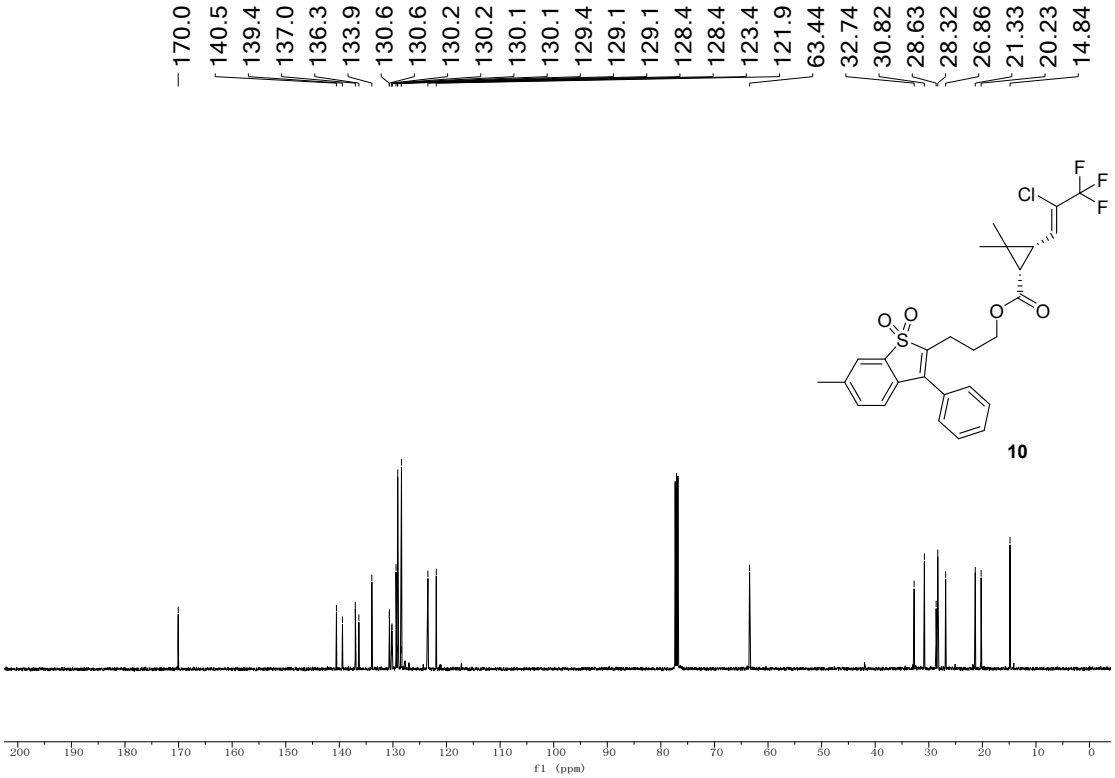
7.33
7.33
7.32
7.32
7.27
7.01
7.00
6.89
1.00
3.22
2.09
0.93
0.99
1.12
2.12
2.07
2.94
3.30
1.03
3.08
3.20
F
F
F
Cl
O
O
O
O
S
10
f1 (ppm)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136.3
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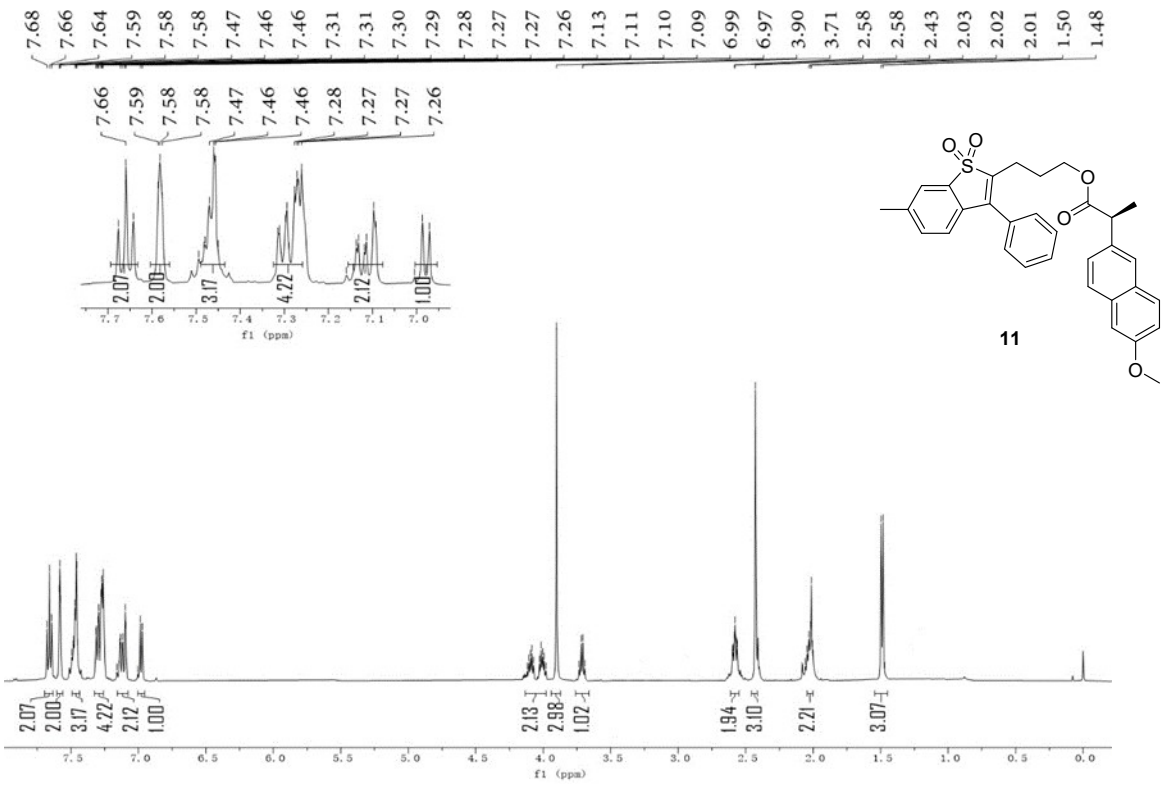
130.6
130.6
130.2
130.2
130.1
130.1
129.4
129.1
129.1
128.4
128.4
123.4
121.9
63.44
32.74
30.82
28.63
28.32
26.86
21.33
20.23
14.84
F
F
F
Cl
O
O
S
O
O
10
f1 (ppm)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7.58
7.47
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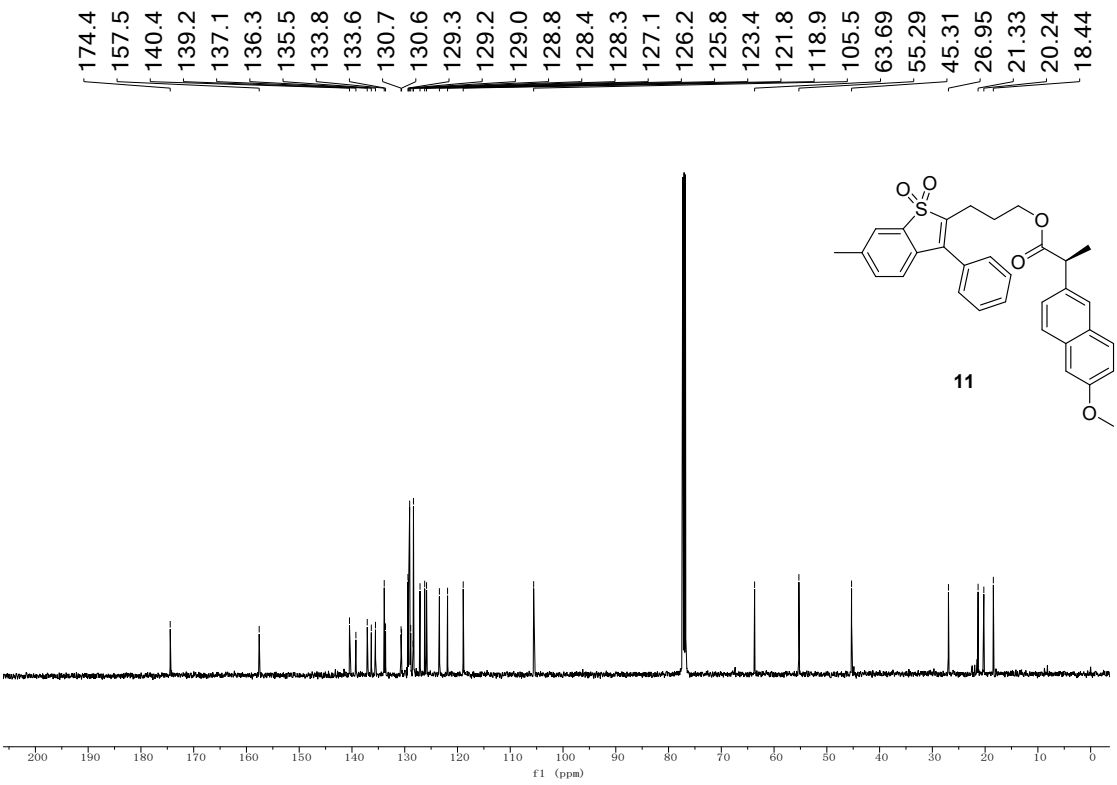
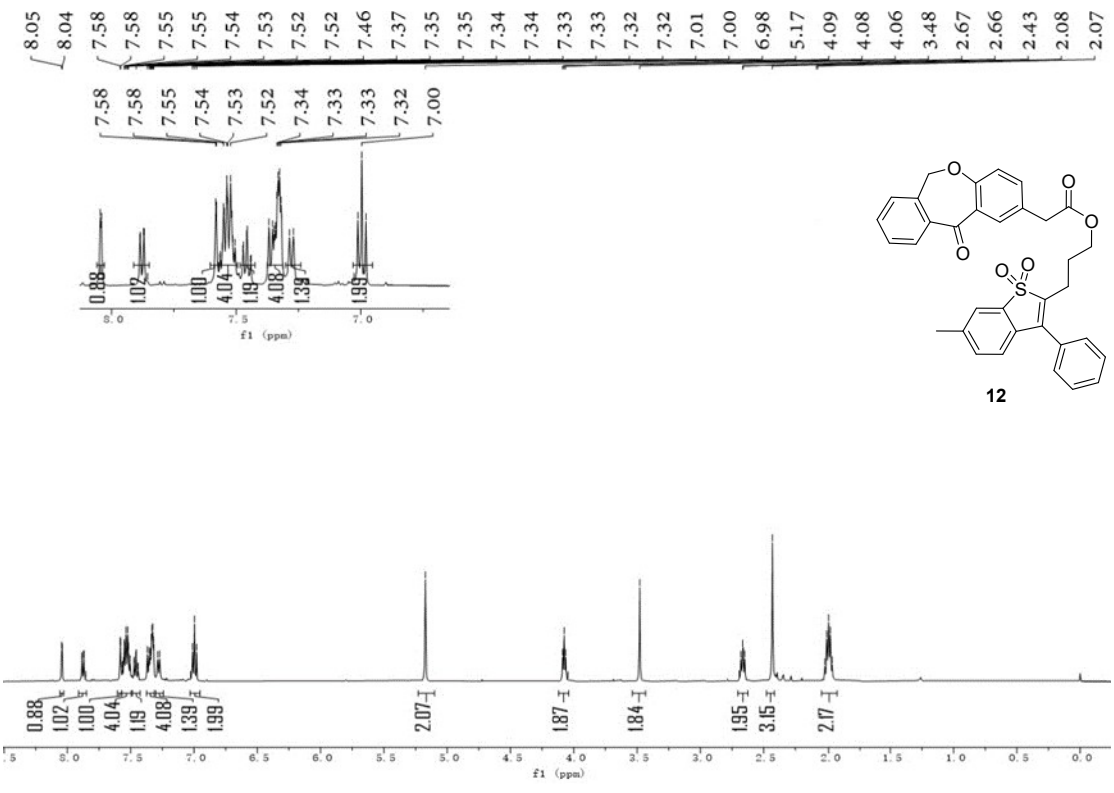
7.46
7.31
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.13
7.11
7.10
7.09
6.99
6.97
3.90
3.71
2.58
2.58
2.43
2.03
2.02
2.01
1.50
1.48
2.07
2.00
3.17
4.22
2.12
1.00
2.13
2.98
1.02
1.94
3.10
2.21
3.07
O
O
S
O
O
O
11
f1 (ppm)


174.4
157.5
140.4
139.2
137.1
136.3
135.5
133.8
133.6
130.7
130.6
129.3
129.2
129.0
128.8
128.4
128.3
127.1
126.2
125.8
123.4
121.8
118.9
105.5
63.69
55.29
45.31
26.95
21.33
20.24
18.44
11
f1 (ppm)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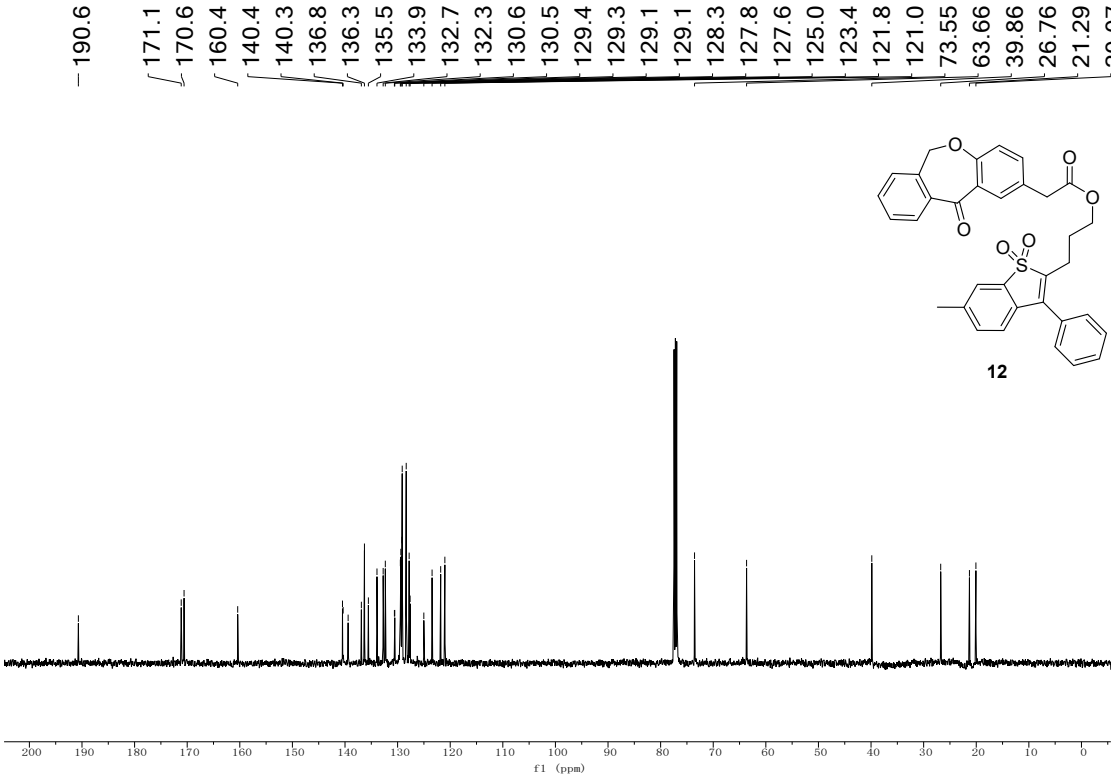
8.04
7.58
7.58
7.55
7.55
7.54
7.53
7.52
7.52
7.46
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.01
7.00
6.98
5.17
4.09
4.08
4.06
3.48
2.67
2.66
2.43
2.08
2.07
12
f1 (ppm)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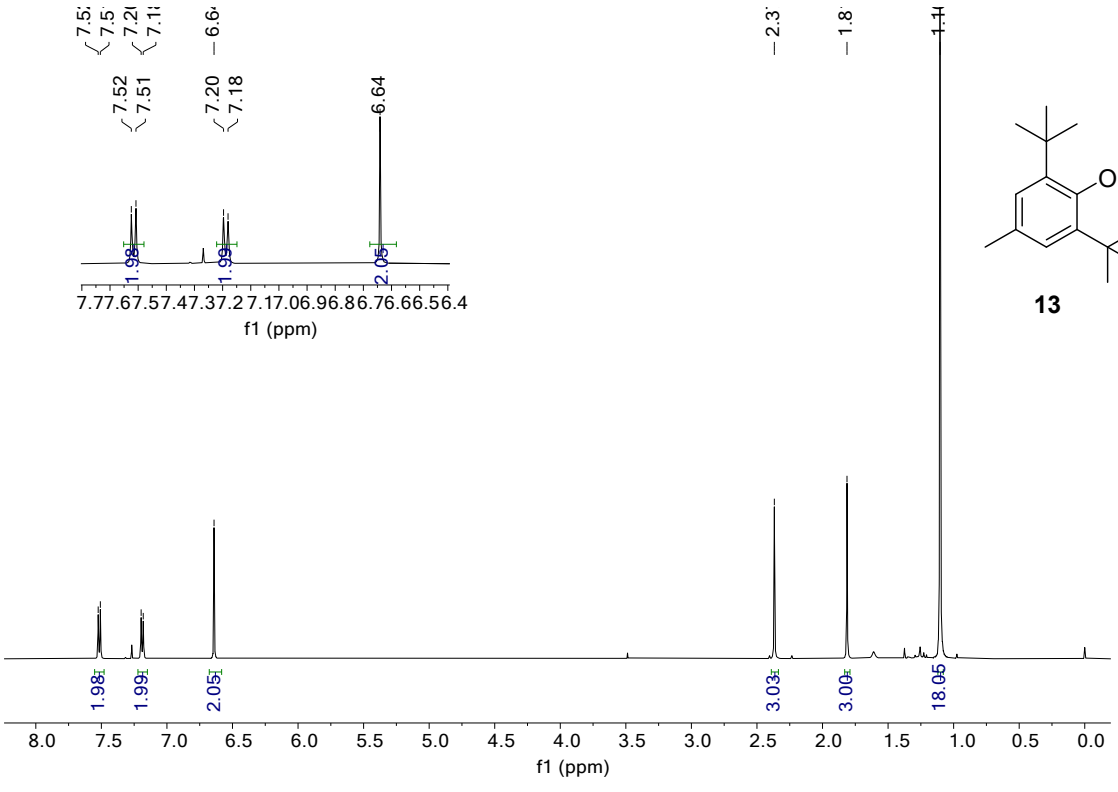
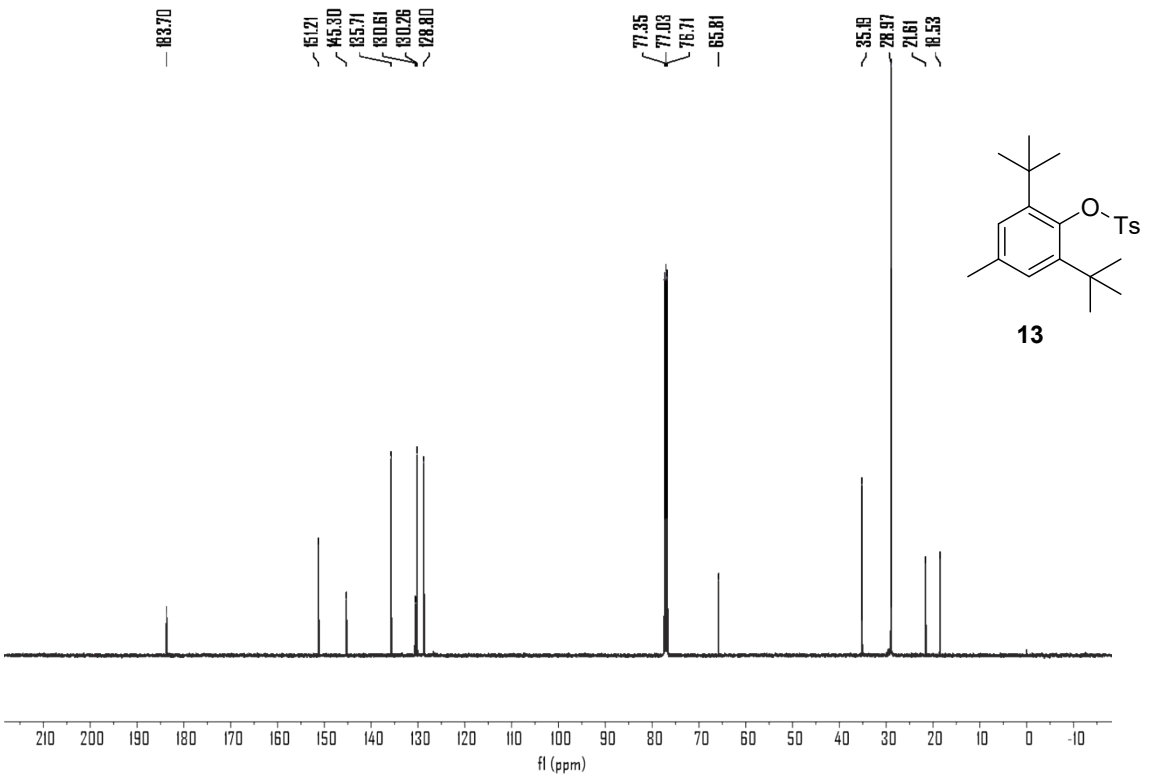
171.1
170.6
160.4
140.4
140.3
136.8
136.3
135.5
133.9
132.7
132.3
130.6
130.5
129.4
129.3
129.1
129.1
128.3
127.8
127.6
125.0
123.4
121.8
121.0
73.55
63.66
39.86
26.76
21.29
f1 (ppm)

12


7.52
7.51
7.20
7.18
6.64
2.3
1.8
1.1
1.98
1.99
2.05
3.03
3.00
18.05
f1 (ppm)

13


153.70
145.30
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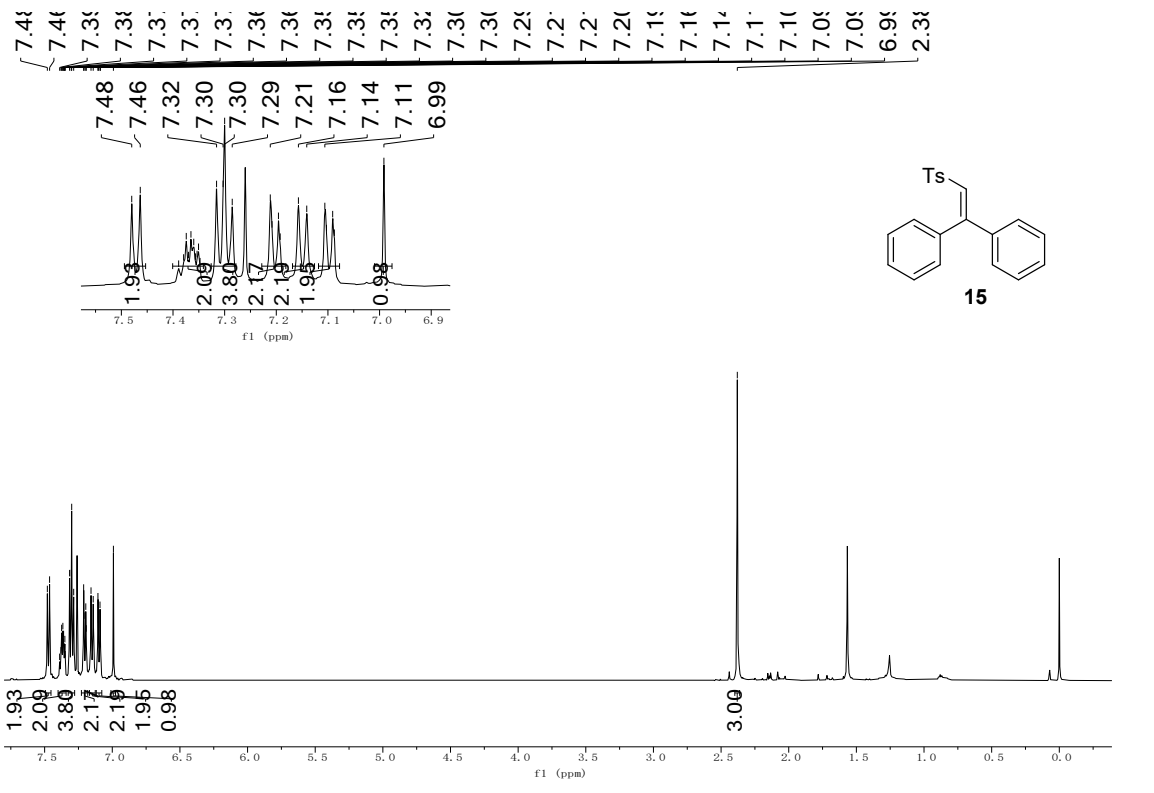
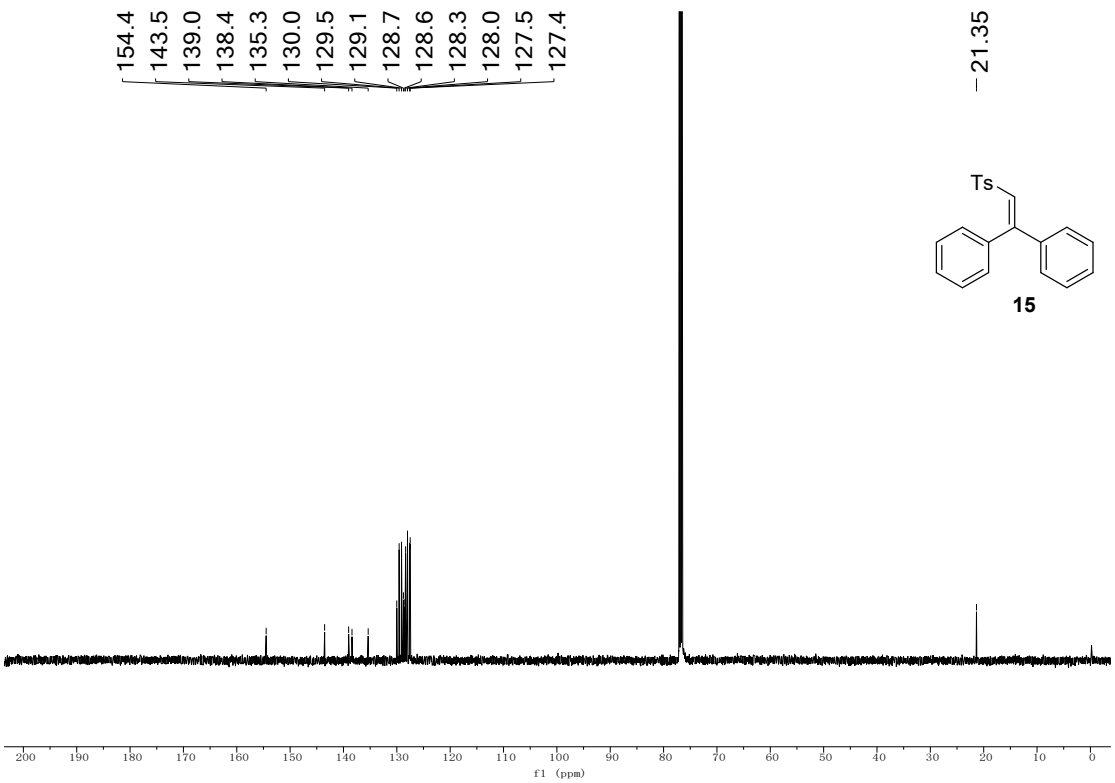
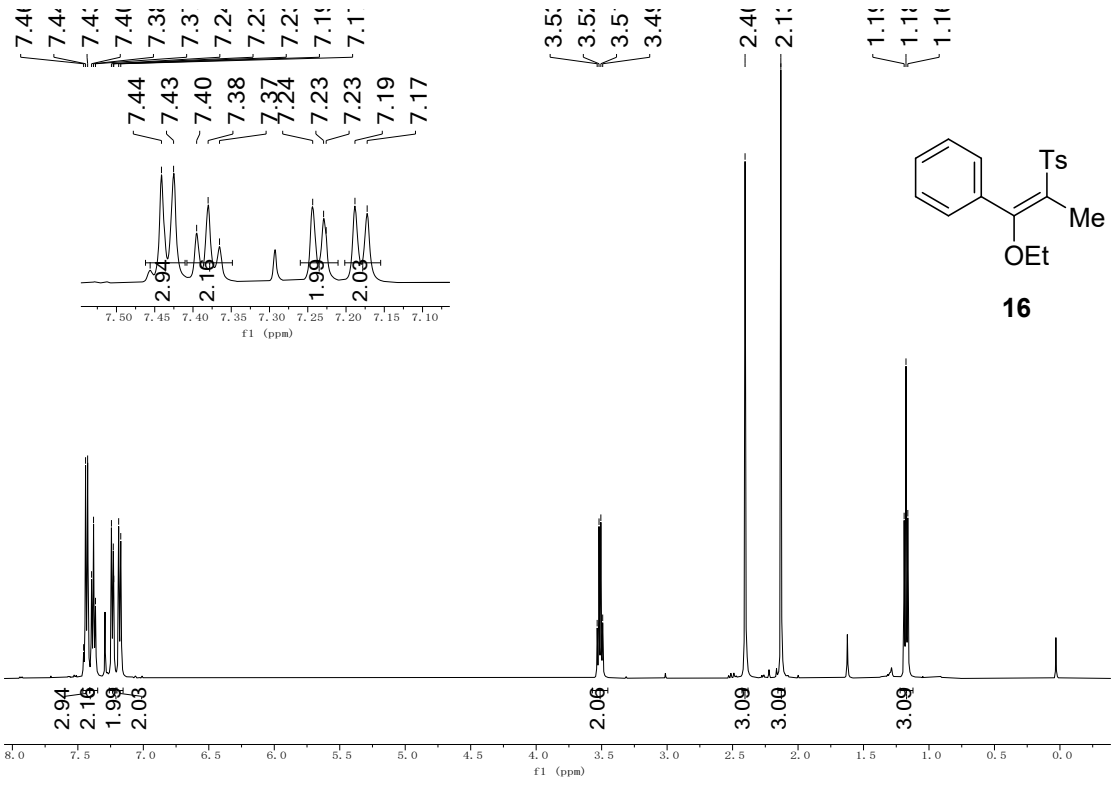
130.26
128.80
77.35
77.03
76.71
65.81
35.48
28.97
21.61
18.53
O
Ts
13
fl (ppm)

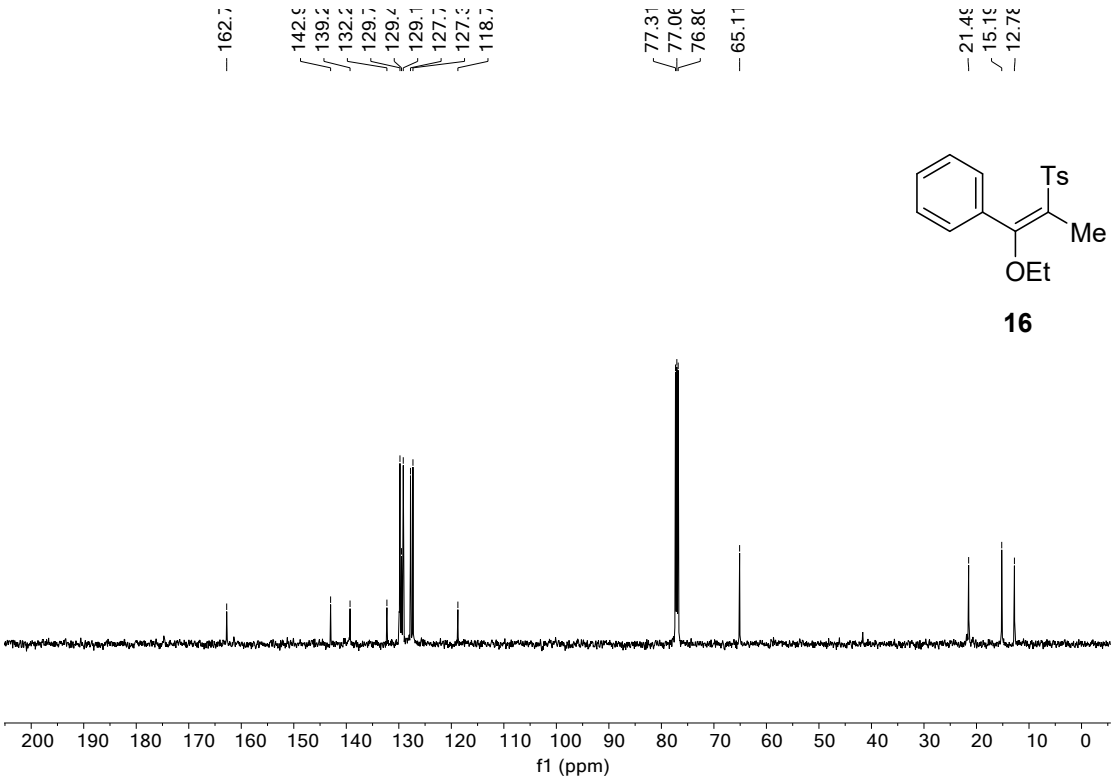

7.48
7.46
7.32
7.30
7.30
7.29
7.21
7.16
7.14
7.11
6.99
1.93
2.09
3.80
2.17
2.10
1.95
0.98
3.00
f1 (ppm)


Ts

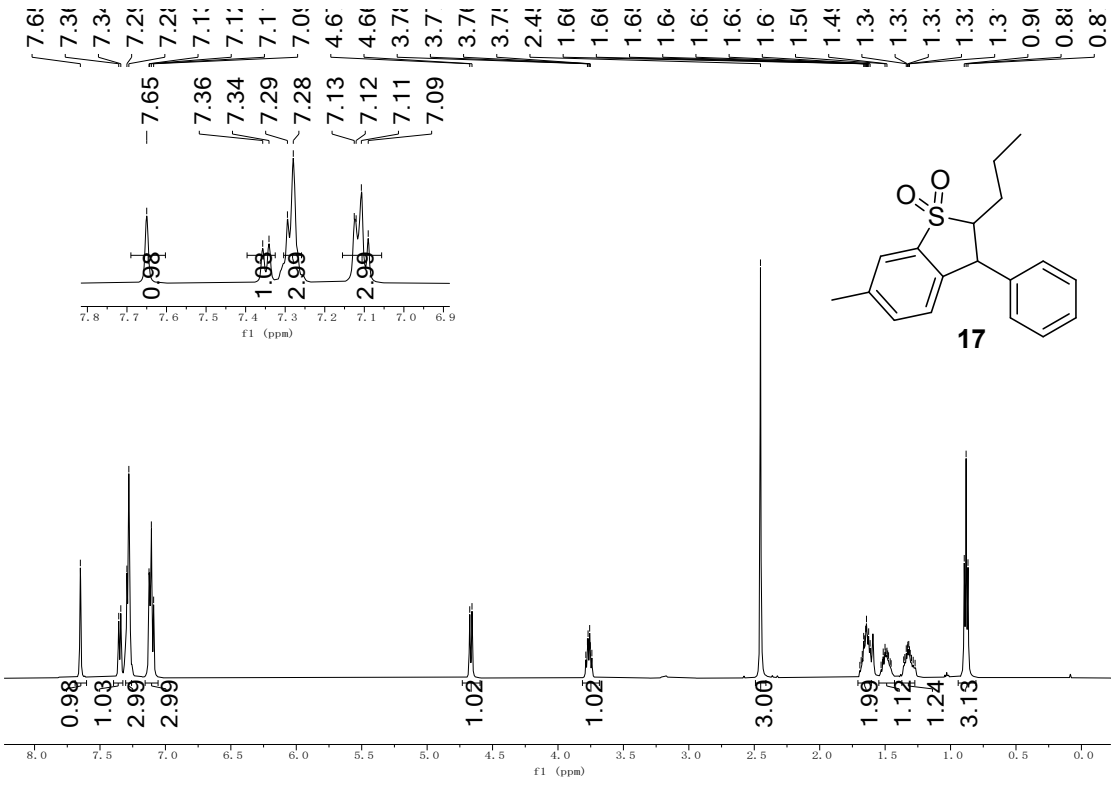
15


154.4
143.5
139.0
138.4
135.3
130.0
129.5
129.1
128.7
128.6
128.3
128.0
127.5
127.4
21.35
Ts
15
f1 (ppm)


7.44
7.43
7.40
7.38
7.37
7.24
7.23
7.23
7.19
7.17
3.52
3.52
3.48
2.41
2.13
1.15
1.14
1.14
Ts
Me
OEt
16
2.94
2.16
1.99
2.03
2.06
3.09
3.00
3.09
f1 (ppm)

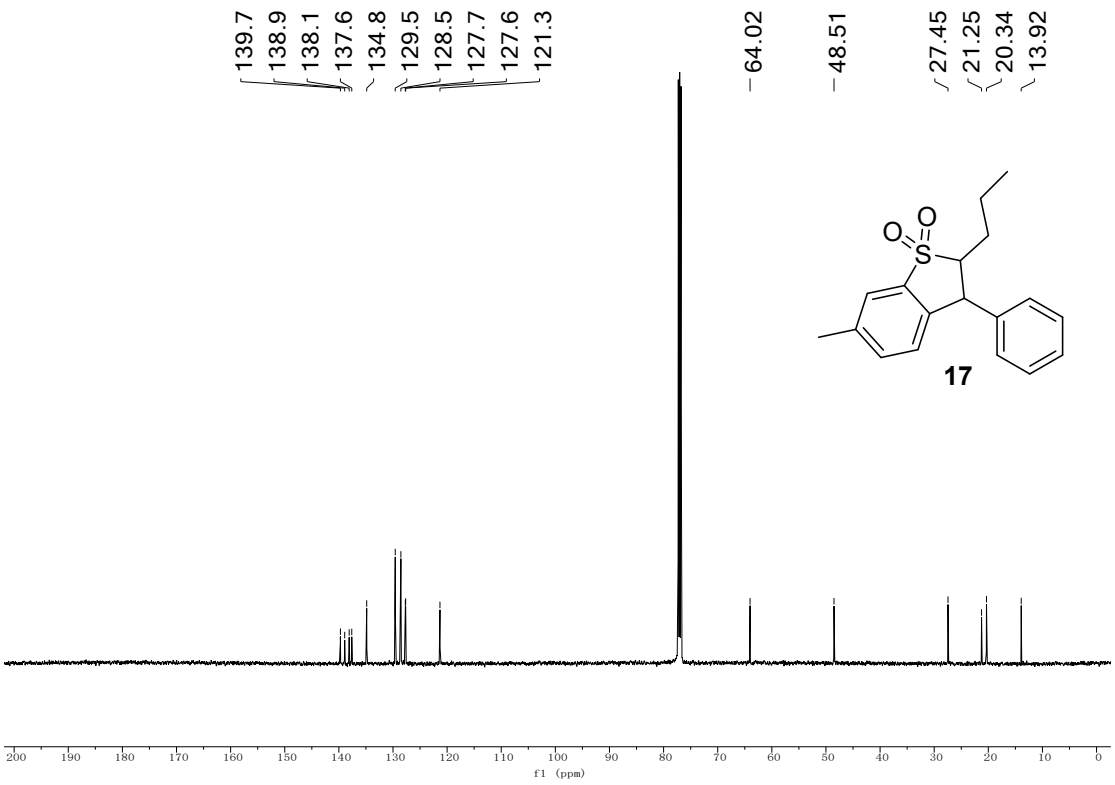



**16**






**17**


139.7
138.9
138.1
137.6
134.8
129.5
128.5
127.7
127.6
121.3
64.02
48.51
27.45
21.25
20.34
13.92
O
O
S
17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)