Electronic Supplementary Information

Gold(I)-catalyzed tandem cyclization/peroxidation of 2-alkynyl-1-carbonylbenzenes with TBHP

Lang Chen,[a] Qibo Ni,[a] Yan Zhou[a] and Yunkui Liu*[a]

[a]State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, 310014, P. R. China.

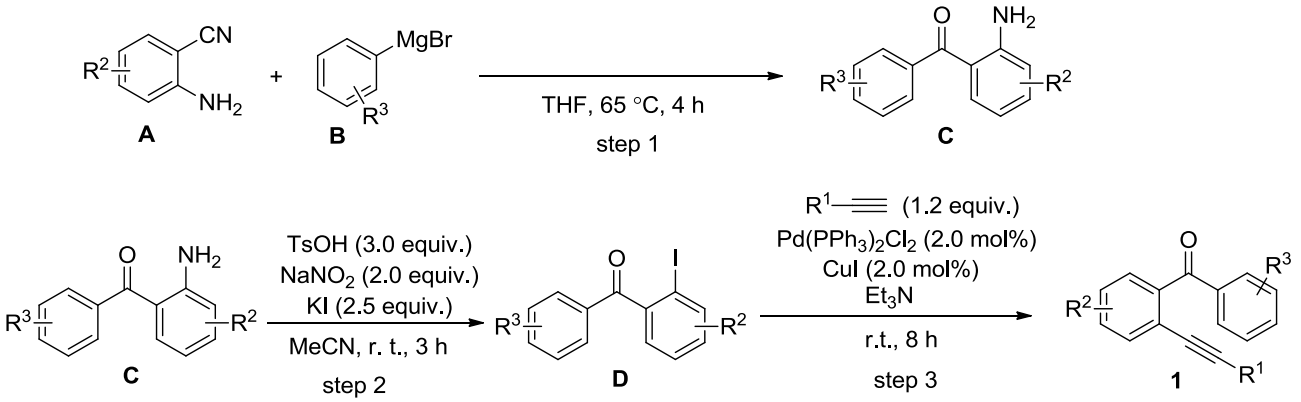
E-mail: ykuiliu@zjut.edu.cn.

Contents

1. General Information

All glassware was thoroughly oven-dried. Solvents were dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash chromatography was carried out using silica gel (100-200 mesh). Melting points are uncorrected. NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded at 400 and 101 MHz (Bruker Avance), respectively and resonances (δ) are given in parts per million relatives to tetramethylsilane. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), mul-tiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector with EI source; High resolution mass spectra (HRMS) were obtained on a TOF MS instrument with EI or ESI source.

2. General Procedure for the Preparation of the Starting Material



General procedure: All *o*-alkynylarylketones **1a-1zc** are known compounds, which were prepared according to the reported literature.[1,2] A typical procedure for their synthesis was described as follows:

Synthesis of intermediate C (step 1): To a round-bottom flask (100 mL) was added compound **A** (10 mmol, 1.0 equiv.) which was dissolved in 10 mL THF. The mixture was cooled to 0 °C. Then, to the above mixture was dropwise added Grignard reagent **B** (30.0 mL, 1.0 M solution in THF, 30 mmol, 3.0 equiv.) at 0 °C under N_2 atmosphere. The reaction mixture was stirred at 65 °C for 4 hours. After completion, the reaction mixture was cooled down to 0 °C. Saturated NH_4Cl solution (20 mL) was added dropwise to quench the reaction and the reaction mixture was stirred at room temperature

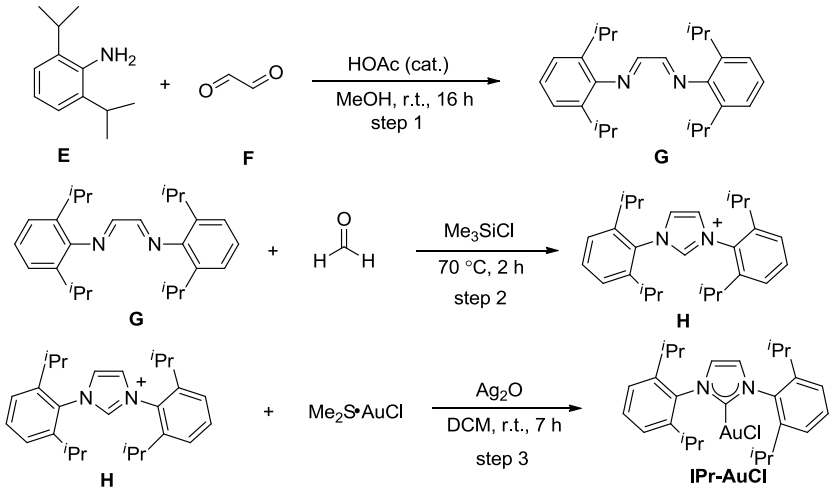
for 30 minutes. The resultant reaction mixture was extracted with EA (3 × 30 mL). The combined organic layer was washed with brine solution, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude residue. The residue was purified by a flash column chromatograph on silica gel using (petroleum ether/ethyl acetate=20:1) as the eluent to give pure **C**.

Synthesis of intermediate D (step 2): To a 150 mL flask charged with C (5.0 mmol, 1.0 equiv.) and TsOH (15 mmol, 3.0 equiv.) in MeCN (25 mL) was added $NaNO_2$ (10 mmol, 2.0 equiv) and KI (12.5 mmol, 2.5 equiv) dissolved in H_2O (15 mL) dropwise at room temperature for 1 hour and the resulting solution was stirred at room temperature for another 2 h. Upon completion, saturated aqueous sodium sulfite was added to the solution to quench the reaction until the reaction mixture turned to be yellow. After removal of the most of MeCN solvent under reduced pressure, the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether/ethyl acetate = 50 / 1) to give pure **D**.

Synthesis of 1 (step 3): To a stirred solution of **D** (5 mmol, 1.0 equiv.) and terminal aromatic alkynes (1.2 equiv.) in Et_3N (30 mL) was added $PdCl_2(PPh_3)_2$ (2 mol%) and CuI (2 mol%). The resulted mixture was stirred at room temperature for 8 h. After the separation of ammonium salt by filtration and the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 40 / 1) to afford pure **1**.

o-Alkynylbenzaldehyde **1zc** was synthesized according to the reported literature.[3]

3. Preparation of the Catalyst IPrAuCl[4]



Synthesis of intermediate G (step 1): In air, to a solution of 2,6-diisopropylaniline (1.97 g, 10 mmol, 2 equiv.) and HOAc (0.1 mL, 0.018 mol, 0.035 equiv.) in 25 mL of MeOH at 50 ºC in a flask was added a solution of glyoxal (0.73 g, 40% in water, 10 mol, 1.0 equiv.) in 250 mL of MeOH. The reaction mixture was stirred at 50 ºC for 15 min and then stirred at 25 ºC for 16 h. The reaction mixture was filtered. The filter cake was washed with MeOH (3 × 10 mL) and dried in vacuo to afford intermediate **G** as a yellow solid.

Synthesis of intermediate H (step 2): In air, to N,N'-1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene (**G**) (2.26 g, 6 mol, 1.00 equiv.) and paraformaldehyde (1.81 g, 6 mmol, 1.03 equiv.) in 54 mL of EtOAc in a flask at 70 ºC was added a solution of TMSCl (0.8 mL, 6 mol, 1.03 equiv.) in 8 mL of EtOAc dropwise over 45 min with vigorous stirring. The reaction mixture was stirred at 70 ºC for 2 h. After cooling to 10 ºC with stirring, the reaction mixture was filtered. The filter cake was washed with EtOAc (3 × 50 mL) and dried in vacuo to afford intermediate **H** as a colorless solid.

Synthesis of IPrAuCl (step 3): In the dark, IPr·HCl (**H**)(100 mg, 0.294 mmol) and Ag_2O (50 mg) were stirred in DCM for 7 h, then the reaction solution was filtered through silica. To the filtrate was added AuCl•SMe_2 (87 mg, 0.294 mmol). Concentrate the reaction solution gave precipitation which was further recrystallized in *n*-hexane to afford pure IPrAuCl.

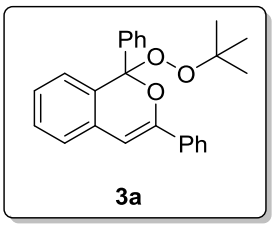
Other NHC-coordinated gold(I) chloride, such as IMeAuCl, SIMeAuCl, and SIPrAuCl were prepared in a similar procedure as that of IPrAuCl.

4. General Procedure for the Synthesis of Products 3 and Characterization Data

To a 25 mL flame-dried Schlenk tube containing a stirring bar were added IPrAuCl (5 mol%), $AgOCOCF_3$(5 mol%), MeCN (1 mL), 2-alkynyl-1-carbonylbenzenes **1** (0.2 mmol), and TBHP (1.1 equiv.) in sequence under a nitrogen atmosphere. The tube was sealed and stirred at room temperature for 4 h. The reaction was monitored by TLC. Upon completion, the solvent was removed to give a crude product which was further purified by silica gel column chromatography (petroleum ether/EtOAc = 100:1 to 50:1) to give pure **3**.

Characterization of the products 3:

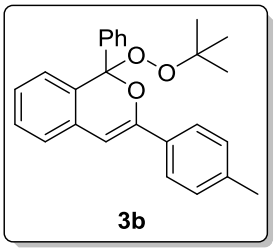
1-(*tert*-butylperoxy)-1,3-diphenyl-1*H*-isochromene (3a)



3a

White solid (64 mg, 86% yield). m.p. 88-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.88 (m, 2H), 7.74-7.67 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.44-7.33 (m, 8H), 7.23-7.19 (m, 1H), 6.10 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 139.2, 138.3, 136.0, 135.1, 129.4, 129.0, 128.79, 128.78, 128.6, 128.51, 128.47, 126.1, 125.9, 119.6, 114.4, 98.1, 81.1, 26.6. HRMS (ESI+) for $C_{25}H_{24}NaO_3^+$ ([M+Na]$^+$): Calcd. 395.1618; Found. 395.1625.

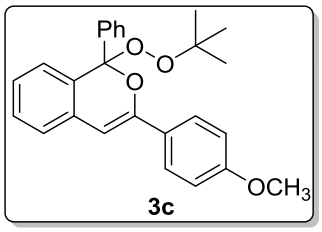
1-(*tert*-butylperoxy)-1-phenyl-3-(*p*-tolyl)-1*H*-isochromene (3b)



3b

White solid (61 mg, 75% yield). m.p. 96-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.76-7.71 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.46-7.37 (m, 5H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 2.39 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 139.1, 138.5, 135.6, 135.2, 133.2, 129.4, 129.2, 129.0, 128.61, 128.56, 128.5, 126.1, 123.4, 119.5, 114.3, 98.2, 81.1, 26.7, 21.4. HRMS (ESI+) for $C_{26}H_{26}NaO_3^+$ ([M+Na]$^+$): Calcd. 409.1780; Found. 409.1776.

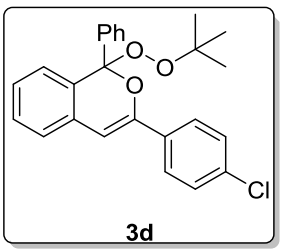
1-(*tert*-butylperoxy)-3-(4-methoxyphenyl)-1-phenyl-1*H*-isochromene (3c)



3c

White solid (60 mg, 70% yield). m.p. 95-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.82 (m, 2H), 7.71-7.67 (m, 2H), 7.58-7.54 (m, 1H), 7.42-7.36 (m, 5H), 7.31 (dd, *J* = 7.1, 1.4 Hz, 1H), 6.95-6.90 (m, 2H), 6.04 (s, 1H), 3.84 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.8, 151.3, 138.9, 138.5, 135.2, 129.8, 129.3, 128.9, 128.8, 128.5, 128.4, 126.1, 123.4, 119.3, 114.2, 113.9, 97.8, 81.0, 55.3, 26.6. HRMS (ESI+) for $C_{26}H_{26}NaO_4^+$ ([M+Na]$^+$): Calcd. 425.1729; Found. 425.1736.

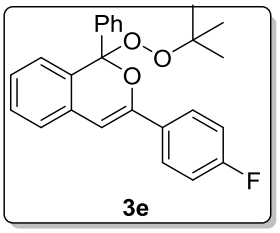
1-(*tert*-butylperoxy)-3-(4-chlorophenyl)-1-phenyl-1*H*-isochromene (3d).



3d

White solid (53 mg, 65% yield). m.p. 96-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 2H), 7.72-7.69 (m, 2H), 7.60 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.45-7.39 (m, 5H), 7.38-7.33 (m, 3H), 6.06 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3, 139.3, 138.1, 134.8, 134.5, 131.2, 129.7, 129.5, 129.1, 129.0, 128.9. 128.6, 126.1, 123.5, 119.6, 114.5, 97.0, 81.2, 26.6. HRMS (ESI+) for $C_{25}H_{23}ClNaO_3^+$ ([M+Na]$^+$): Calcd. 429.1233; Found. 429.1224.

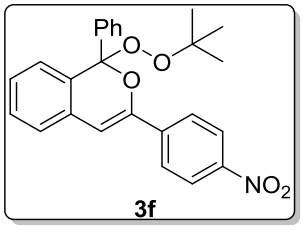
3-(4-fluorophenyl)-1-(*tert*-butyperoxy)-1-phenyl-1*H*-isochromene (3e).



3e

White solid (53 mg, 68% yield). m.p. 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.1, 5.0 Hz, 2H), 7.77-7.69 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.46-7.40 (m, 5H), 7.38-7.36 (m, 1H), 7.13-7.05 (m, 2H), 6.09 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.1 (d, *J* = 246.4 Hz) 152.4 (d, *J* = 2.0 Hz), 139.1, 138.3, 134.9, 132.1 (d, *J* = 3.0 Hz), 130.0, 129.1 (d, *J* = 63.6 Hz), 129.1, 128.8, 128.5, 126.1, 123.5, 119.5, 115.3 (d, *J* = 21.2 Hz), 114.4, 97.0, 81.1, 26.6. HRMS (ESI+) for $C_{25}H_{23}FNaO_3^+$ ([M+Na]$^+$): Calcd. 413.1529; Found. 413.1530.

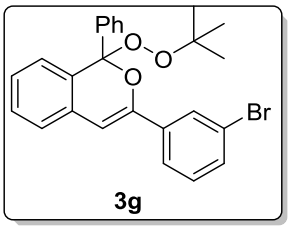
1-(*tert*-butylperoxy)-3-(4-nitrophenyl)-1-phenyl-1*H*-isochromene (3f).



3f

White solid (52 mg, 62% yield). m.p. 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.71 (m, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.03-7.93 (m, 1H), 7.70-7.66 (m, 2H), 7.64-7.62 (m, 1H), 7.49-7.40 (m, 7H), 6.12 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.0, 148.6, 139.4, 137.8, 137.7, 133.9, 129.7, 129.6, 129.3, 129.2, 128.6, 126.1, 123.7, 122.9, 120.2, 120.0, 95.9, 81.3, 26.6. HRMS (ESI+) for $C_{25}H_{23}NNaO_5^+$ ([M+Na]$^+$): Calcd. 440.1474; Found. 440.1472.

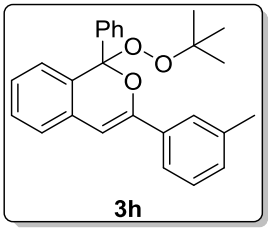
3-(3-bromophenyl)-1-(*tert*-butylperoxy)-1-phenyl-1*H*-isochromene (3g).



3g

White solid (61 mg, 68% yield). m.p. 94-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.53-7.41 (m, 6H), 7.40-7.35 (m, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.07 (s, 1H), 1.27 (s, 9H).. ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 139.4, 138.2, 138.1, 134.7, 131.2, 130.0, 129.6, 129.23, 129.16, 128.63, 128.60, 127.0, 126.1, 123.5, 122.6, 119.8, 114.7, 96.7, 81.3, 26.6. HRMS (ESI+) for $C_{25}H_{23}BrNaO_3^+$ ([M+Na]$^+$): Calcd. 473.0728; Found. 473.0729.

1-(*tert*-butylperoxy)-1-phenyl-3-(m-tolyl)-1*H*-isochromene (3h)

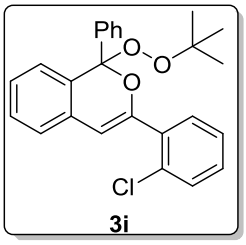


3h

White solid (46 mg, 60% yield). m.p. 88-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.71-7.66 (m, 3H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.42-7.35 (m, 5H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.05 (s, 1H), 2.37 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz,

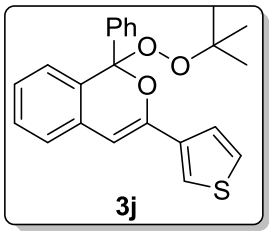
$CDCl_3$): δ 152.7, 139.2, 138.4, 137.9, 135.9, 135.1, 129.4, 129.3, 129.0, 128.7, 128.5, 128.4, 126.7, 126.1, 125.7, 123.4, 119.6, 114.4, 98.2, 81.1, 26.6, 21.6. HRMS (ESI+) for $C_{26}H_{26}NaO_3^+$ ([M+Na]$^+$): Calcd. 409.1780; Found. 409.1769.

1-(*tert*-butylperoxy)-3-(2-chlorophenyl)-1-phenyl-1*H*-isochromene (3i).



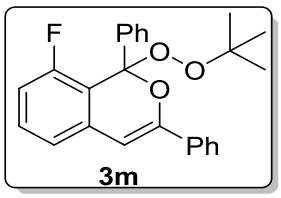
White solid (46 mg, 56% yield). m.p. 90-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 7.8 Hz, 1H), 7.71-7.68 (m, 3H), 7.49-7.35 (m, 7H), 7.33-7.25 (m, 1H), 7.14-7.10 (m, 1H), 6.61 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 139.3, 138.1, 135.0, 133.6, 132.2, 130.1, 129.6, 129.4, 129.2, 129.1, 128.6, 126.9, 126.7, 126.1, 123.4, 120.1, 114.7, 93.3, 81.2, 26.6. HRMS (ESI+) for $C_{25}H_{23}ClNaO_3^+$ ([M+Na]$^+$): Calcd. 429.1233; Found. 429.1236.

1-(*tert*-butylperoxy)-1-phenyl-3-(thiophen-3-yl)-1*H*-isochromene (3j).



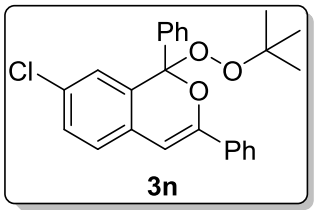
White solid (53 mg, 70% yield). m.p. 137-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.68 (m, 3H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.47-7.37 (m, 5H), 7.37-7.30 (m, 2H), 6.23 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 139.3, 138.4, 136.7, 134.7, 129.4, 129.0, 128.8, 128.7, 128.5, 126.1, 124.8, 123.5, 121.9, 119.4, 114.1, 92.9, 81.1, 26.7. HRMS (ESI+) for $C_{23}H_{22}NaO_3S^+$ ([M+Na]$^+$): Calcd. 401.1187; Found. 401.1184.

1-(*tert*-butylperoxy)-8-fluoro-1,3-diphenyl-1*H*-isochromene (3m).



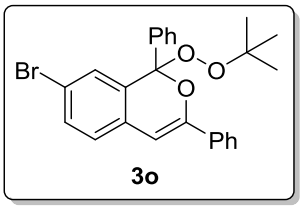
White solid (55 mg, 71% yield). m.p. 80-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.69-7.66 (m, 2H), 7.49 (d, *J* = 8.5 Hz), 7.45-7.35 (m, 6H), 7.24-7.20 (m, 1H), 6.08 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.53 (d, *J* = 253.5 Hz), 152.1, 138.5 (d, *J* = 5.1 Hz), 137.0, 135.6, 131.8 (d, *J* = 7.1 Hz), 129.3, 128.6 (d, *J* = 19.2 Hz), 128.3, 126.58, 126.56, 126.2, 125.5 (d, *J* = 16.2 Hz), 115.7 (d, *J* = 21.2 Hz), 115.4 (d, *J* = 4.0 Hz), 114.0, 98.9, 81.24, 26.5. HRMS (ESI+) for $C_{25}H_{23}FNaO_3^+$ ([M+Na]$^+$): Calcd. 413.1529; Found. 413.1533.

1-(*tert*-butylperoxy)-7-chloro-1,3-diphenyl-1*H*-isochromene (3n).



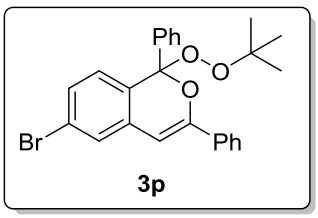
White solid (51 mg, 63% yield). m.p. 80-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.73 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.47-7.39 (m, 7H), 7.28-7.24 (m, 1H), 6.11 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 140.8, 137.8, 135.7, 134.5, 133.6, 130.0, 129.4, 128.72, 128.67, 128.6, 126.2, 126.0, 123.7, 120.7, 113.8, 98.8, 81.4, 26.6. HRMS (ESI+) for $C_{25}H_{23}ClNaO_3^+$ ([M+Na]$^+$): Calcd. 429.1233; Found. 429.1234.

7-bromo-1-(*tert*-butylperoxy)-1,3-diphenyl-1*H*-isochromene (3o).



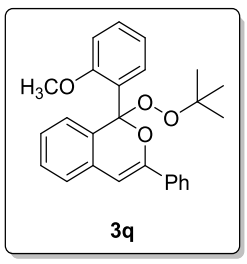
White solid (57 mg, 63% yield). m.p. 85-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.69-7.66 (m, 2H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.49 (d, *J* = 17.5 Hz, 1H), 7.45-7.35 (m, 6H), 7.24-7.20 (m, 1H), 6.07 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 147.1, 137.7, 135.6, 134.1, 129.3, 128.68, 128.66, 128.63, 128.5, 126.0, 123.7, 122.4, 121.0, 120.7, 113.7, 98.9, 81.4, 26.6. HRMS (ESI+) for $C_{25}H_{23}BrNaO_3^+$ ([M+Na]$^+$): Calcd. 473.0728; Found. 473.0721.

6-bromo-1-(*tert*-butylperoxy)-1,3-diphenyl-1*H*-isochromene (3p).



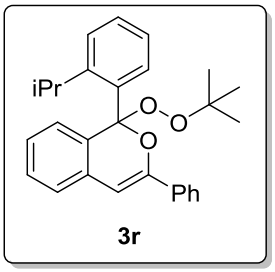
White solid (56 mg, 62% yield). m.p. 86-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.86 (m, 2H), 7.74-7.64 (m, 2H), 7.47-7.37 (m, 7H), 7.22 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.58 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.8, 139.1, 134.2, 129.5, 129.2, 129.1, 128.6, 128.4, 128.0, 126.9, 126.8, 125.8, 123.7, 105.2, 99.1, 80.6, 26.5. HRMS (ESI+) for $C_{25}H_{23}BrNaO_3^+$ ([M+Na]$^+$): Calcd. 473.0728; Found. 473.0720.

1-(*tert*-butylperoxy)-1-(2-methoxyphenyl)-3-phenyl-1*H*-isochromene (3q).



White solid (51 mg, 63% yield). m.p. 103-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.60-7.56 (m, 2H), 7.41-7.30 (m, 5H), 7.18-7.15 (m, 1H), 7.00-6.93 (m, 2H), 6.04 (s, 1H), 3.73 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.9, 153.3, 139.5, 136.3, 135.9, 130.5, 129.2, 128.5, 128.4, 128.3, 128.0, 126.5, 125.5, 123.6, 120.5, 119.1, 113.9, 113.4, 97.3, 80.9, 56.4, 26.6. HRMS (ESI+) for $C_{26}H_{26}NaO_4$ ([M+Na]$^+$): Calcd. 425.1729; Found. 425.1737.

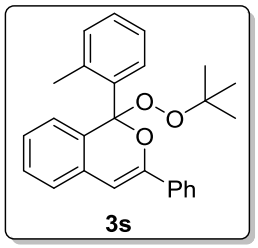
1-*(tert*-butylperoxy)-1-(2-isopropylphenyl)-3-phenyl-1*H*-isochromene (3r).



3r

White solid (48 mg, 58% yield). m.p. 89-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.54-7.45 (m, 3H), 7.44-7.41 (m, 2H), 7.36-7.29 (m, 3H), 7.18-7.10 (m, 2H), 6.03 (s, 1H), 4.12-4.06 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7, 149.3, 136.1, 135.9, 133.8, 129.5, 129.3, 128.4, 128.3, 128.2, 127.7, 127.6, 125.7, 125.3, 124.9, 119.6, 116.9, 97.8, 80.59, 27.0, 26.7, 25.2, 24.5. HRMS (ESI+) for $C_{28}H_{30}NaO_3^+$ ($[M+Na]^+$): Calcd. 437.2093; Found. 437.2085.

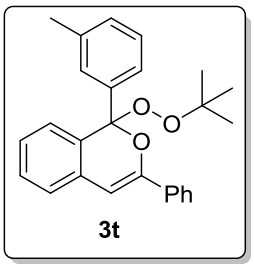
1-(*tert*-butylperoxy)-3-phenyl-1-(o-tolyl)-1*H*-isochromene (3s).



3s

White solid (51 mg, 66% yield). m.p. 99-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 1H), 7.44-7.31 (m, 6H), 7.30-7.28 (m, 1H), 7.23-7.16 (m, 2H), 6.09 (s, 1H), 2.37 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 139.4, 138.3, 136.1, 135.1, 129.9, 129.4, 128.8, 128.6, 128.50, 128.47, 126.6, 125.9, 123.5, 123.2, 119.6, 114.5, 98.1, 81.1, 26.7, 21.7. HRMS (ESI+) for $C_{29}H_{26}NaO_3^+$ ($[M+Na]^+$): Calcd. 409.1780; Found. 409.1776.

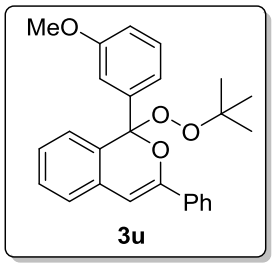
1-(*tert*-butylperoxy)-3-phenyl-1-(m-tolyl)-1*H*-isochromene (3t).



3t

White solid (51 mg, 66% yield). m.p. 99-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 7.7 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.37 (d, J = 7.0 Hz, 4H), 7.31 – 7.19 (m, 4H), 6.13 (s, 1H), 2.43 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 138.4, 137.4, 136.1, 135.9, 135.6, 132.4, 129.5, 129.0, 128.6, 128.5, 128.4, 127.4, 125.8, 125.6, 124.0, 119.4, 115.4, 98.5, 80.9, 26.6, 21.3. HRMS (ESI+) for $C_{26}H_{26}NaO_3^+$ ($[M+Na]^+$):Calcd. 409.1780; Found. 409.1782.

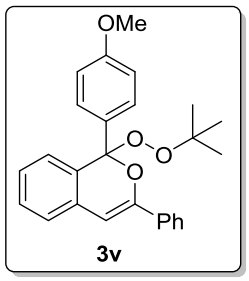
1-(*tert*-butylperoxy)-1-(3-methoxyphenyl)-3-phenyl-1*H*-isochromene (3u).



3u

White solid (51 mg, 64% yield). m.p. 103-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.46-7.41 (m, 3H), 7.40-7.33 (m, 4H), 7.29-7.23 (m, 1H), 6.98-6.94 (m, 1H), 6.16 (s, 1H), 3.84 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 152.9, 139.9, 139.2, 136.0, 135.1, 129.7, 129.5, 128.9, 128.7, 128.5, 126.0, 123.5, 119.7, 118.6, 114.2, 112.2, 98.3, 81.2, 55.3, 26.7. HRMS (ESI+) for $C_{26}H_{26}NaO_4^+$ ([M+Na]$^+$): Calcd. 425.1729; Found. 425.1735.

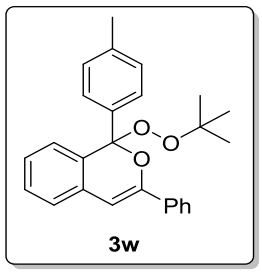
1-(*tert*-butylperoxy)-1-(4-methoxyphenyl)-3-phenyl-1*H*-isochromene (3v).



3v

White solid (55 mg, 68% yield). m.p. 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.92 (m, 2H), 7.74-7.68 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.50-7.37 (m, 5H), 7.29-7.23 (m, 1H), 7.02-6.94 (m, 2H), 6.14 (s, 1H), 3.85 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.2, 152.8, 139.4, 136.0, 135.1, 130.5, 129.3, 128.8, 128.6, 128.5, 127.5, 125.8, 123.3, 119.6, 114.4, 113.8, 98.0, 81.0, 55.3, 26.6. HRMS (ESI+) for $C_{26}H_{26}NaO_4^+$ ([M+Na]$^+$): Calcd. 425.1729; Found. 425.1718.

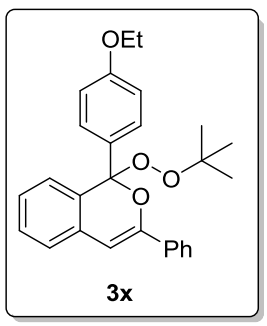
1-(*tert*-butylperoxy)-3-phenyl-1-(p-tolyl)-1*H*-isochromene (3w).



3w

White solid (52 mg, 67% yield). m.p. 99-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 2H), 7.66-7.58 (m, 3H), 7.48-7.32 (m, 5H), 7.27-7.20 (m, 3H), 6.15-6.05 (m, 1H), 2.39 (s, 3H), 1.23 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$): δ 153.0, 139.4, 139.0, 136.1, 135.5, 135.1, 129.4, 129.3, 128.9, 128.7, 128.5, 126.1, 125.9, 123.4, 119.6, 114.5, 98.1, 81.1, 26.7, 21.3. HRMS (ESI+) for $C_{26}H_{26}NaO_3^+$ ([M+Na]$^+$): Calcd. 409.1780; Found. 409.1774.

1-(*tert*-butylperoxy)-1-(4-ethoxyphenyl)-3-phenyl-1*H*-isochromene (3x).

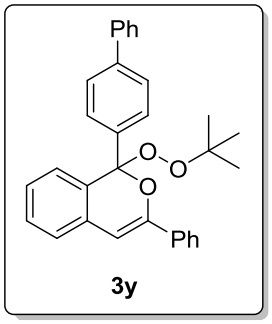


3x

White solid (56 mg, 67% yield). m.p. 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.69-7.64 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.48-7.36 (m, 5H), 7.26-7.21 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.11 (d, *J* = 2.8 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H), 1.24 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 152.9, 139.4, 136.1, 135.1, 130.3, 129.3, 128.8, 128.6, 128.5, 127.5, 125.8, 123.4, 119.6, 114.5, 114.4, 98.0, 81.0, 63.5, 26.7,

14.9. HRMS (ESI+) for $C_{27}H_{28}NaO_4^+$ ([M+Na]$^+$): Calcd. 439.1885; Found. 439.1890.

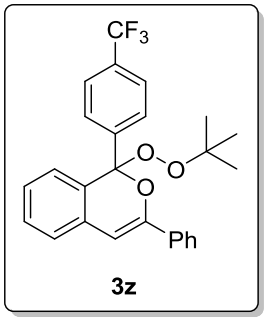
1-([1,1'-biphenyl]-4-yl)-1-(*tert*-butylperoxy)-3-phenyl-1*H*-isochromene (3y).



3y

White solid (65 mg, 72% yield). m.p. 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 15.6, 8 Hz, 5H), 7.54-7.39 (m, 8H), 7.28 (d, *J* = 7.0 Hz, 1H), 6.18 (s, 1H), 1.28 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 142.0, 140.7, 139.2, 137.3, 136.0, 135.2, 129.6, 128.9, 128.7, 128.6, 127.6, 127.4, 127.3, 126.6, 126.0, 123.5, 119.7, 114.5, 98.3, 81.2, 26.7. HRMS (ESI+) for $C_{31}H_{28}NaO_3^+$ ([M+Na]$^+$): Calcd. 471.1935; Found. 471.1923.

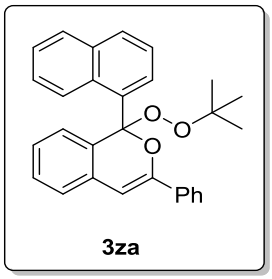
1-(*tert*-butylperoxy)-3-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-isochromene (3z).



3z

White solid (51 mg, 58% yield). m.p. 84-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.84 (m, 2H), 7.77-7.69 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.48-7.40 (m, 5H), 7.37 (d, *J* = 7.4 Hz, 1H),7.14-7.03 (m, 2H), 6.09 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 142.3, 138.5, 135.7, 135.0, 131.04 (q, *J* = 32.0 Hz), 129.9, 129.0, 128.7, 128.6, 126.7, 126.2, 125.6 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 270.6 Hz), 123.4, 119.8, 113.7, 99.0, 81.4, 26.6. HRMS (ESI+) for $C_{26}H_{23}F_3NaO_3^+$ ([M+Na]$^+$): Calcd. 463.1492; Found. 463.1496.

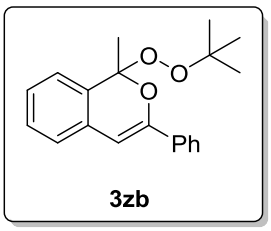
1-(*tert*-butylperoxy)-1-(naphthalen-1-yl)-3-phenyl-1*H*-isochromene (3za).



3za

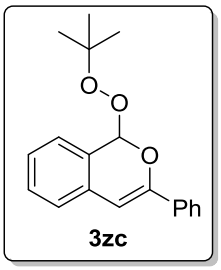
White solid (49 mg, 58% yield). m.p. 150-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71-7.65 (m, 3H), 7.46-7.36 (m, 9H), 7.30-7.24 (m, 2H), 7.15-7.07 (m, 1H), 6.58 (s, 1H), 1.19 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 138.7, 135.9, 135.7, 134.7, 133.6, 130.9, 130.4, 129.6, 128.7, 128.6, 128.5, 128.4, 127.3, 126.1, 125.9, 125.8, 125.7, 124.8, 124.3, 119.7, 116.3, 98.3, 81.0, 26.7. HR-MS (ESI+) for $C_{29}H_{26}NaO_3^+$ ([M+Na]$^+$): Calcd. 445.1780; Found. 445.1770.

1-(*tert*-butylperoxy)-1-methyl-3-phenyl-1*H*-isochromene (3zb).



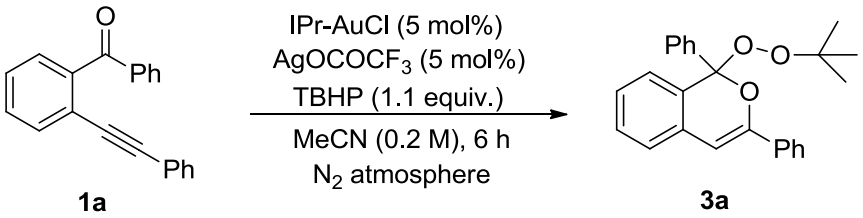
White solid (48 mg, 77% yield). m.p. 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.96 (m, 2H), 7.82 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.50-7.44 (m, 1H), 7.41-7.32 (m, 3H), 7.29-7.22 (m, 1H), 7.18 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.75 (s, 1H), 1.67 (s, 9H), 1.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.1, 166.8, 137.2, 135.8, 133.0, 132.3, 132.1, 131.6, 130.8, 128.6, 128.2, 127.1, 125.3, 81.2, 44.9, 28.1. HRMS (ESI+) for $C_{20}H_{22}NaO_3^+$ ([M+Na]$^+$): Calcd.333.1467; Found. 333.1471.

1-(*tert*-butylperoxy)-3-phenyl-1*H*-isochromene (3zc).



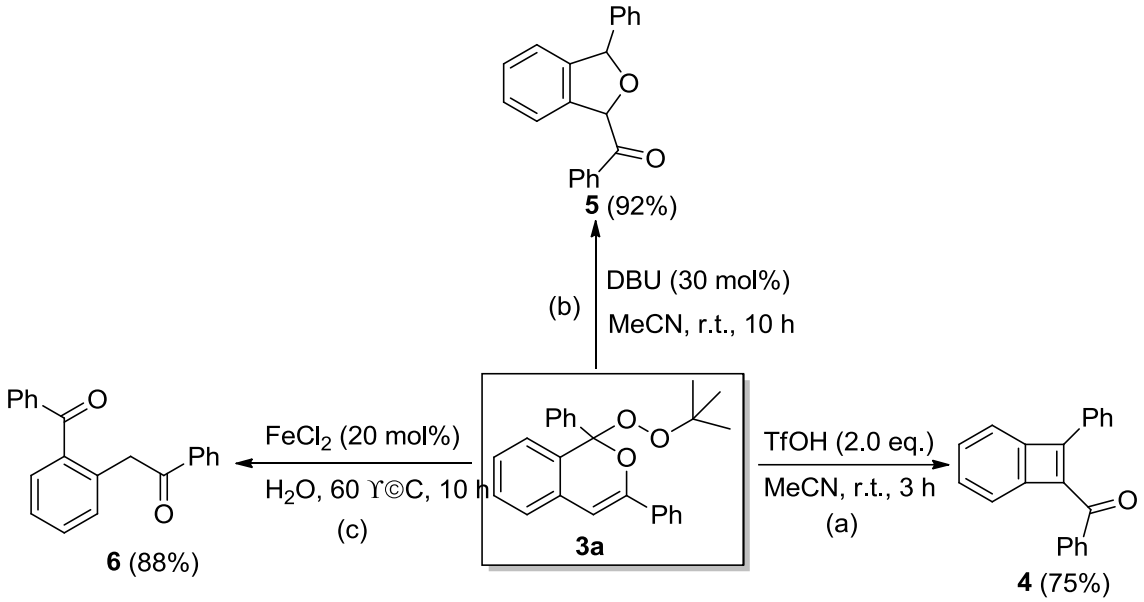
Colorless liquid (45 mg, 75% yield). ^{1} H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (m, 2H), 7.48-7.37 (m, 5H), 7.32 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.74 (s, 1H), 6.61 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 134.7, 131.7, 130.1, 128.8, 128.4, 127.0, 126.6, 125.5, 124.6, 123.5, 100.5, 100.1, 81.1, 26.5. HRMS (ESI+) for $C_{19}H_{20}NaO_3^+$ ([M+Na]$^+$): Calcd.319.1305; Found. 319.1306.

5. Scale-up Experiment



To a 50 mL flame-dried Schlenk tube containing a stirring bar were added IPrAuCl (0.16 g, 5 mol%), $AgOCOCF_3$(0.055g, 5 mol%), MeCN (23 mL), 2-alkynyl-1-carbonylbenzenes **1a** (1.41 g, 5 mmol), and TBHP (0.55 mL (1 M in hexane), 1.1 equiv.) in sequence under a nitrogen atmosphere. The tube was sealed and stirred at room temperature for 6 h. The reaction was monitored by TLC. Upon completion, the solvent was removed to give a crude product which was further purified by silica gel column chromatography (petroleum ether/EtOAc = 100:1 to 50:1) to give pure **3a** in 83% yield (1.54 g).

6. Application of 3a for the Synthesis of 4-6.

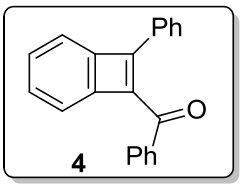


Synthesis of 4 (equation a): To a 25 mL Schlenk tube containing a stirring bar were added (74.5 mg, 0.2 mmol), MeCN (2 mL), TfOH (0.037 mL, 2 equiv.) in sequence under a nitrogen atmosphere. The tube was sealed and stirred at room temperature for 3 h which was monitored by TLC. Upon completion, the solvent was removed and concentrated to give crude product which was further purified by silica gel column chromatography (petroleum ether/EtOAc = 20:1) to give pure **4** in 75% yield (42 mg).

Synthesis of 5 (equation b): To a 25 mL Schlenk tube containing a stirring bar were added **3a** (74.5 mg, 0.2 mmol), MeCN (2 mL), DBU (0.009 mL, 30 mol%) in sequence under a nitrogen atmosphere. The tube was sealed and stirred at room temperature for 10 h. The reaction was monitored by TLC. Upon completion, the solvent was removed and concentrated to give crude product which was further purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1) to give pure **5** in 92% yield (55 mg).

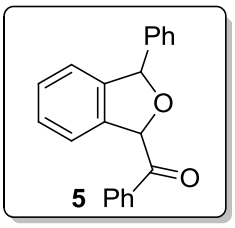
Synthesis of 6 (equation c): To a 25 mL Schlenk tube containing a stirring bar were added **3a** (74.5 mg, 0.2 mmol), H_2O (2 mL), $FeCl_2$ (7.1 mg, 20 mol%) in sequence under a nitrogen atmosphere. The tube was sealed and stirred at 60 °C for 10 h. , monitored by TLC, The reaction was monitored by TLC. Upon completion, the solvent was removed and concentrated to give crude product which was further purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give pure **6** in 88% yield (53 mg).

phenyl(8-phenylbicyclo[4.2.0]octa-1(6),2,4,7-tetraen-7-yl)methanone (4).



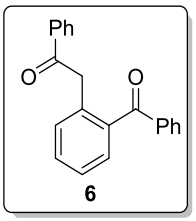
Red liquid (43 mg, 75% yield) . ^{1}H NMR (400 MHz, DMSO-d6): δ 7.55 (d, *J* = 7.0 Hz, 1H), 7.51-7.44 (m, 4H), 7.41-7.36 (m, 3H), 7.32-7.26 (m, 3H), 7.22-7.18 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d6): δ 196.2, 155.7, 145.0, 134.6, 132.5, 132.4, 131.0, 130.4, 130.2, 130.0, 129.9, 129.4, 128.8, 128.5, 128.3, 123.2, 121.9. HR-MS (ESI+) for $C_{21}H_{15}NaO^{+}$ ([M+Na]$^{+}$): Calcd.283.1123; Found. 283.1118.

phenyl(3-phenyl-1,3-dihydroisobenzofuran-1-yl)methanone (5).



Colorless liquid (55.3 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.89 (m, 2H), 7.71-7.59 (m, 4H), 7.53-7.46 (m, 4H), 7.32-7.19 (m, 4H), 7.06-7.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.4, 143.1, 136.8, 133.8, 133.6, 133.4, 131.5, 131.4, 130.3, 128.7, 128.6, 128.2, 122.4, 122.3, 120.8, 96.3, 86.5. HR-MS (ESI+) for $C_{21}H_{16}NaO_2^{+}$ ([M+Na]$^{+}$): Calcd.323.1048; Found. 323.1040.

2-(2-benzoylphenyl)-1-phenylethan-1-one (6).[5]



Colorless liquid (53.9 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.92 (m, 2H), 7.85-7.79 (m, 2H), 7.58-7.49 (m, 3H), 7.48-7.40 (m, 5H), 7.37-7.33 (m, 2H), 4.62 (s, 2H).

7. References

[1] L.-Z. Yu, Y. Wei and M. Shi, *ACS Catalysis*, 2017, **7**, 4242-4247.

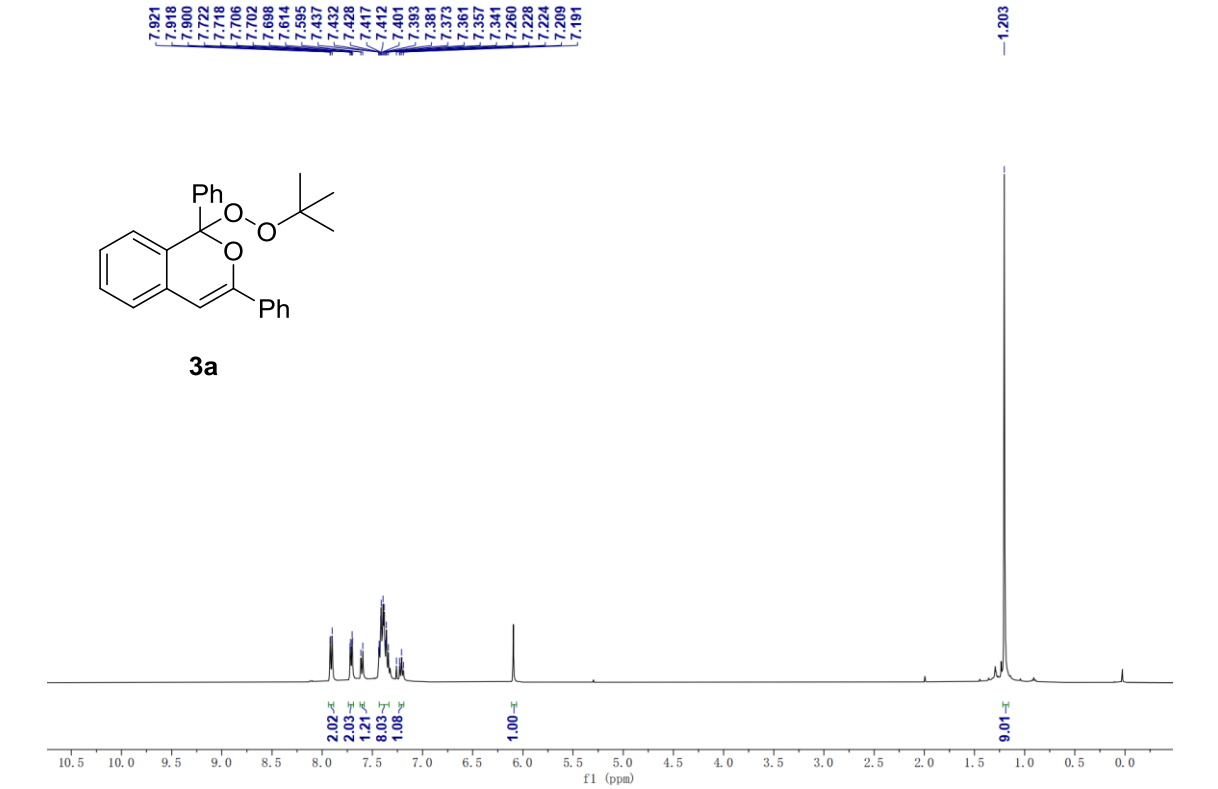
[2] E. Olivieri, N. Shao, R. Rosas, J.-V. Naubron and A. Quintard, *Angew. Chem. Int. Ed.*, 2022, **61**, e202214763.

[3] Y. Yuan, C. Faure, D. Menigaux, M. Berthelot, P. Belmont and E. Brachet, *J. Org. Chem.*, 2023, **88**, 15750-15760.

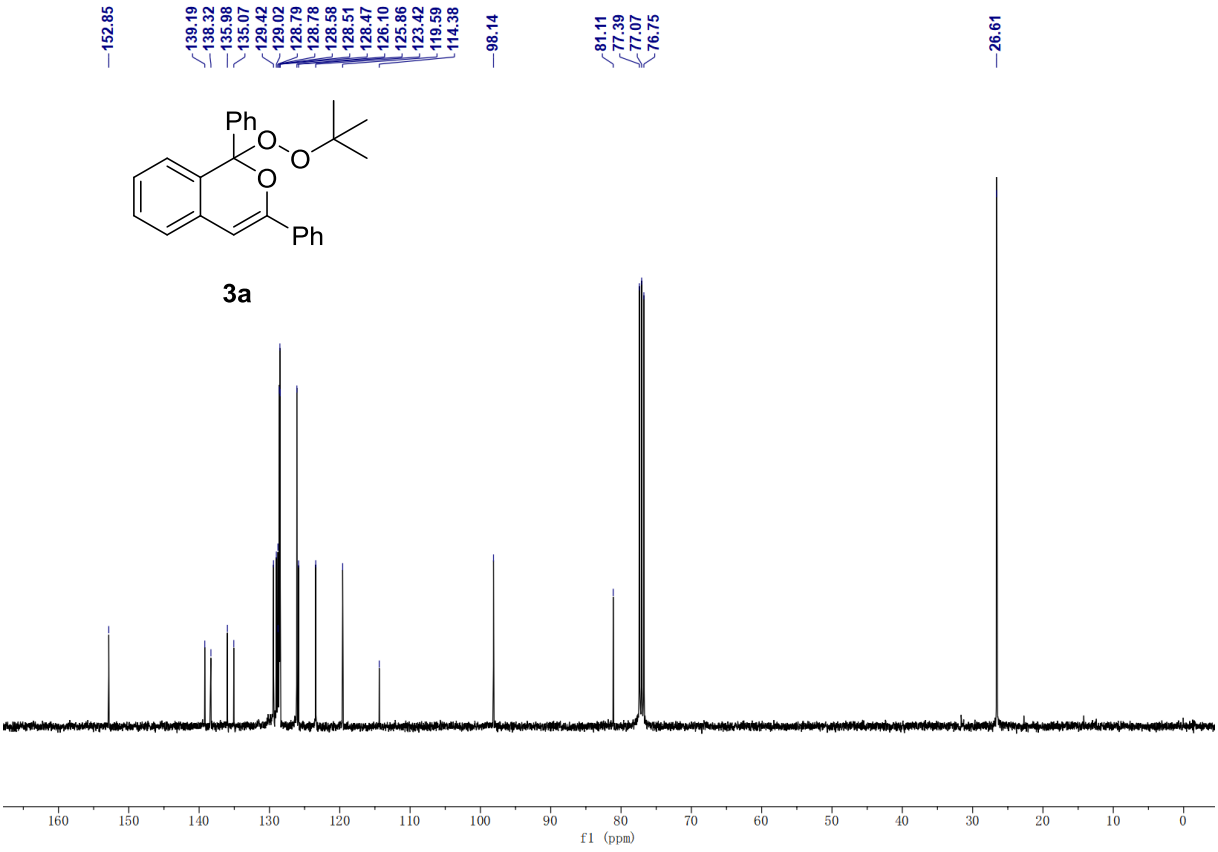
[4] J. Jelen and G. Tavčar, *Org. Lett.*, 2023**, 25**, 3649-3653.

[5] M. Minoshima, K. Uchida, Y. Nakamura, T. Hosoya and S. Yoshida, *Org. Lett.*, 2021, **23**, 1868-1873

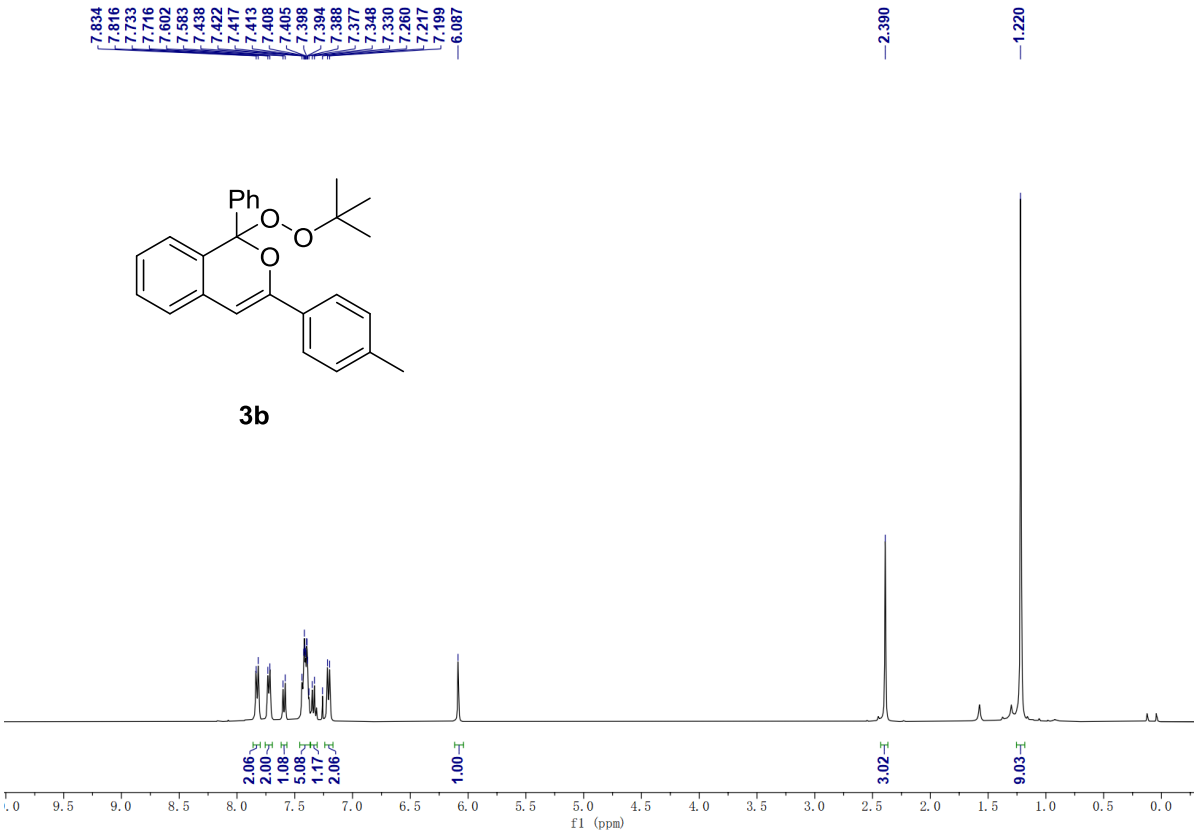
8. Copies of NMR Spectra of Products



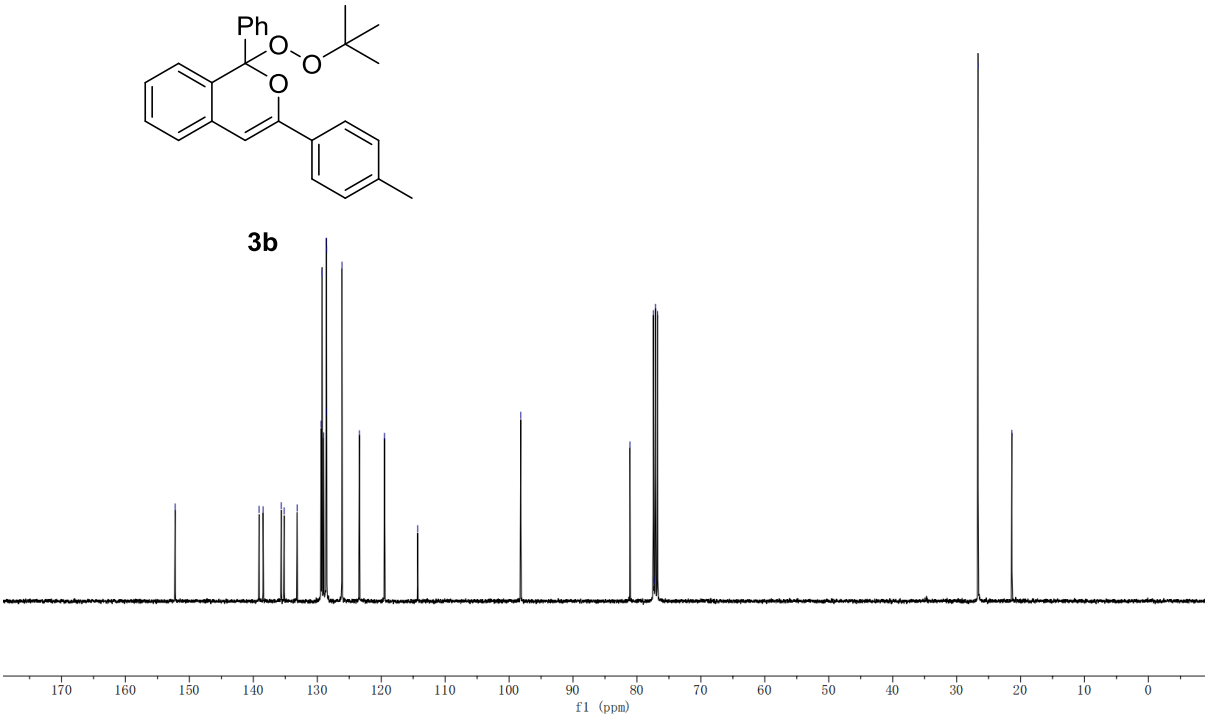
3a



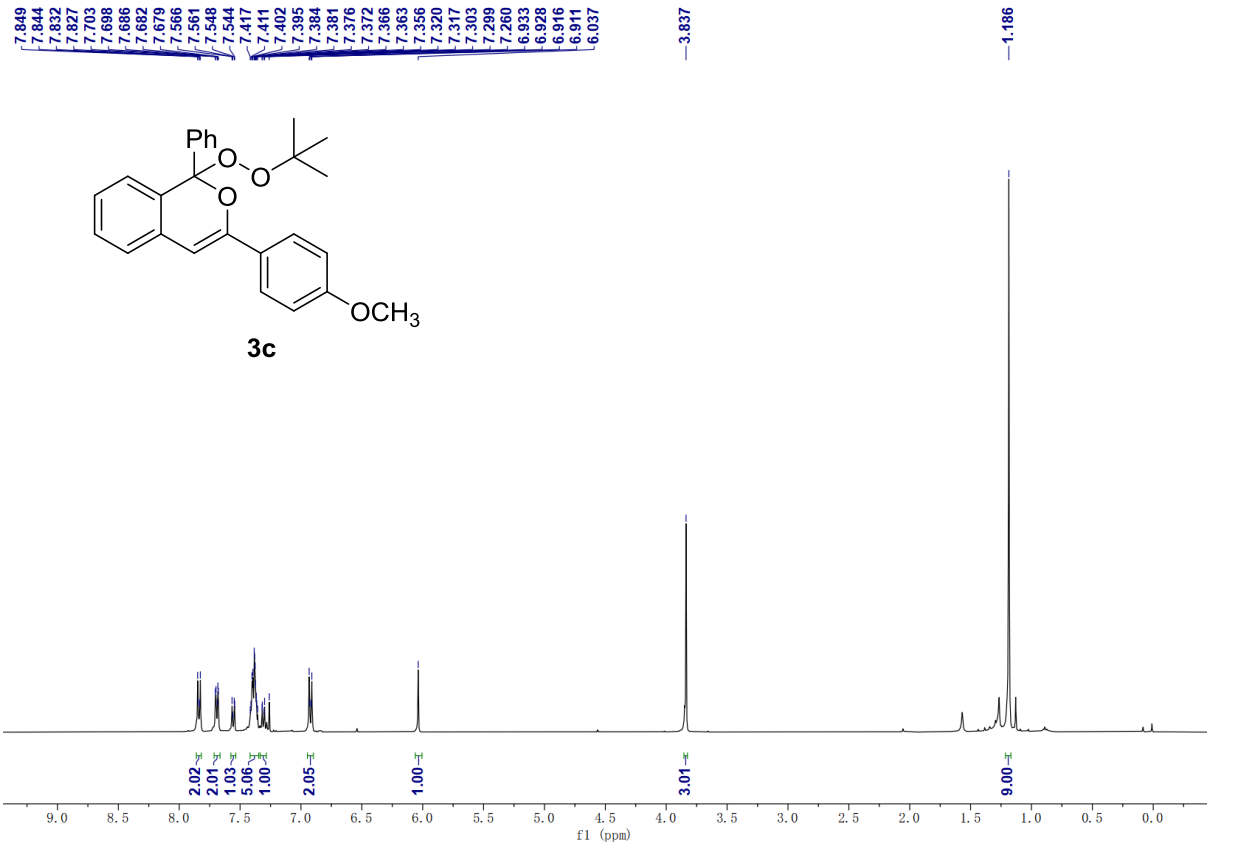
3a

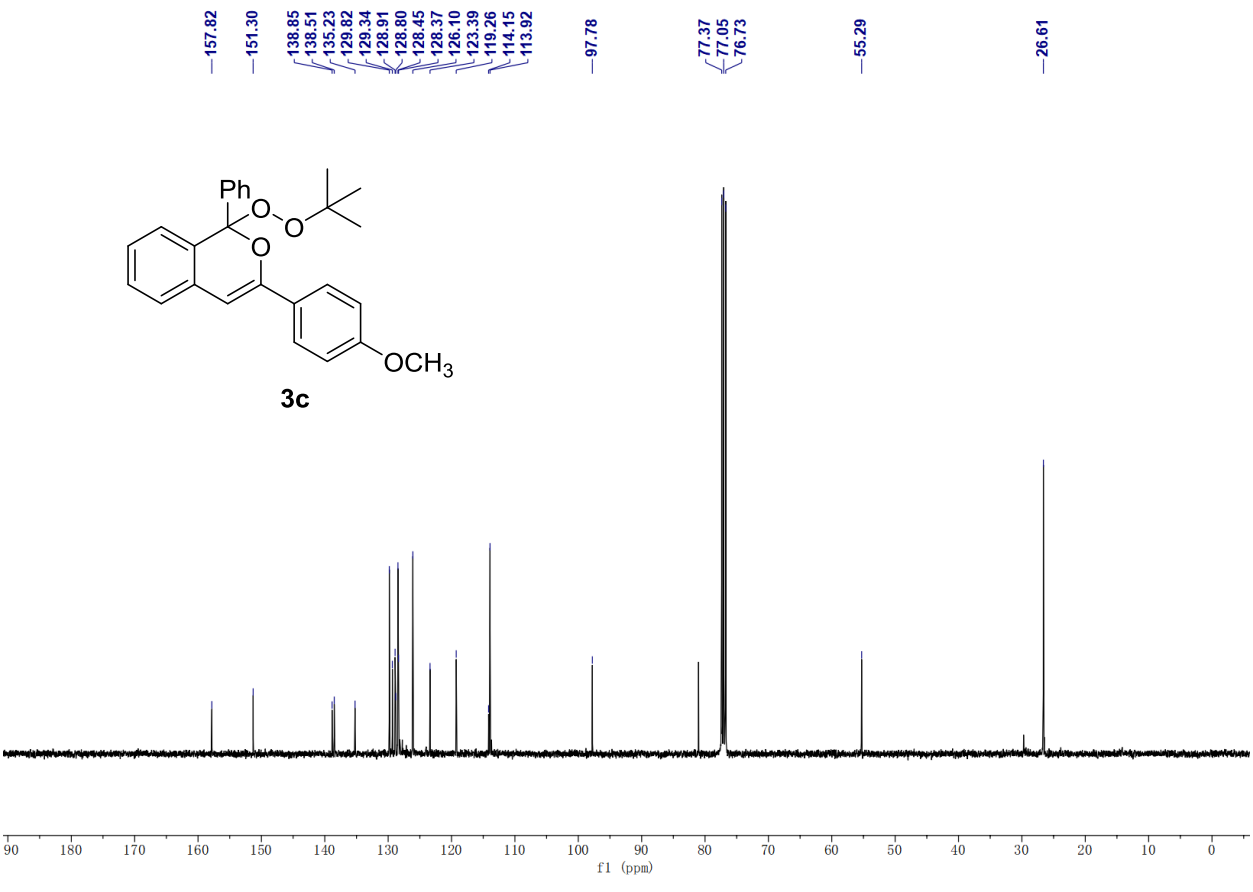

7.834
7.816
7.733
7.716
7.602
7.583
7.438
7.422
7.417
7.413
7.408
7.405
7.398
7.394
7.388
7.377
7.348
7.330
7.260
7.217
7.199
6.087
2.390
1.220
Ph
O
O
O
2.06
2.00
1.08
5.08
1.17
2.06
1.00
3.02
9.03
f1 (ppm)

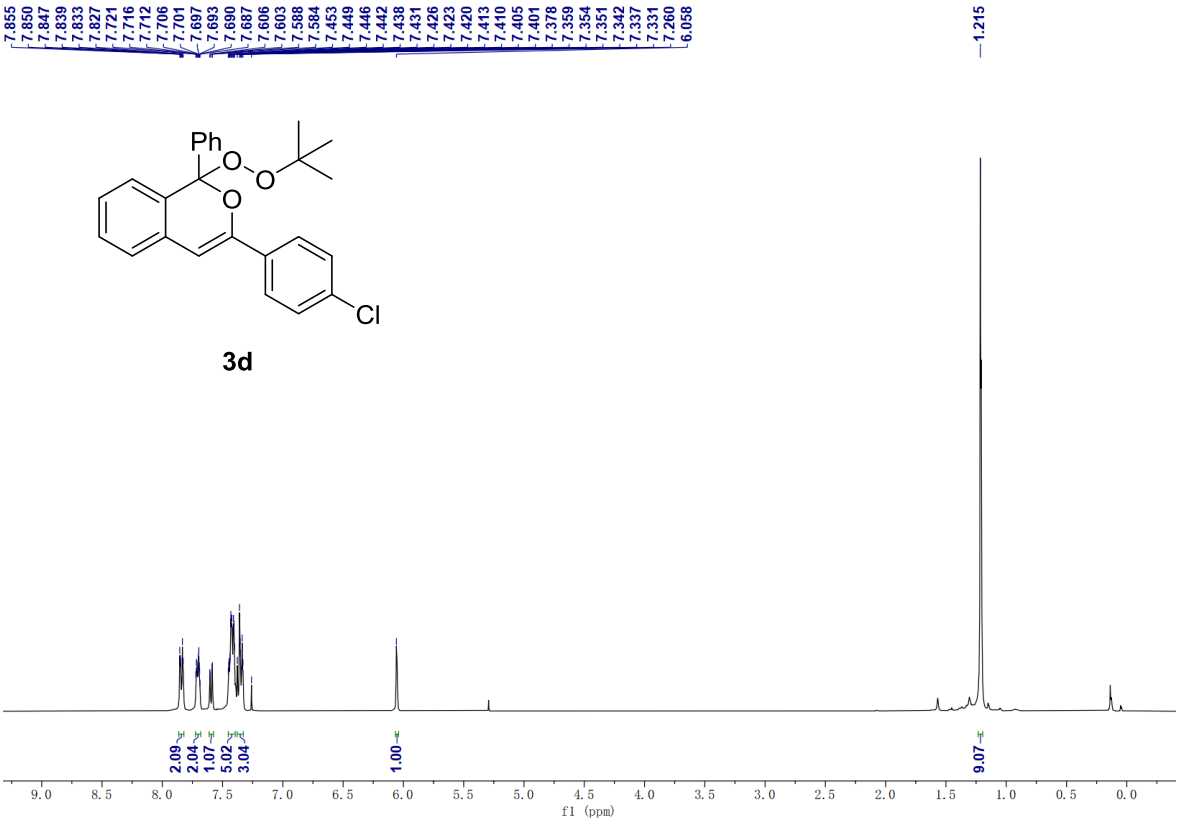
3b

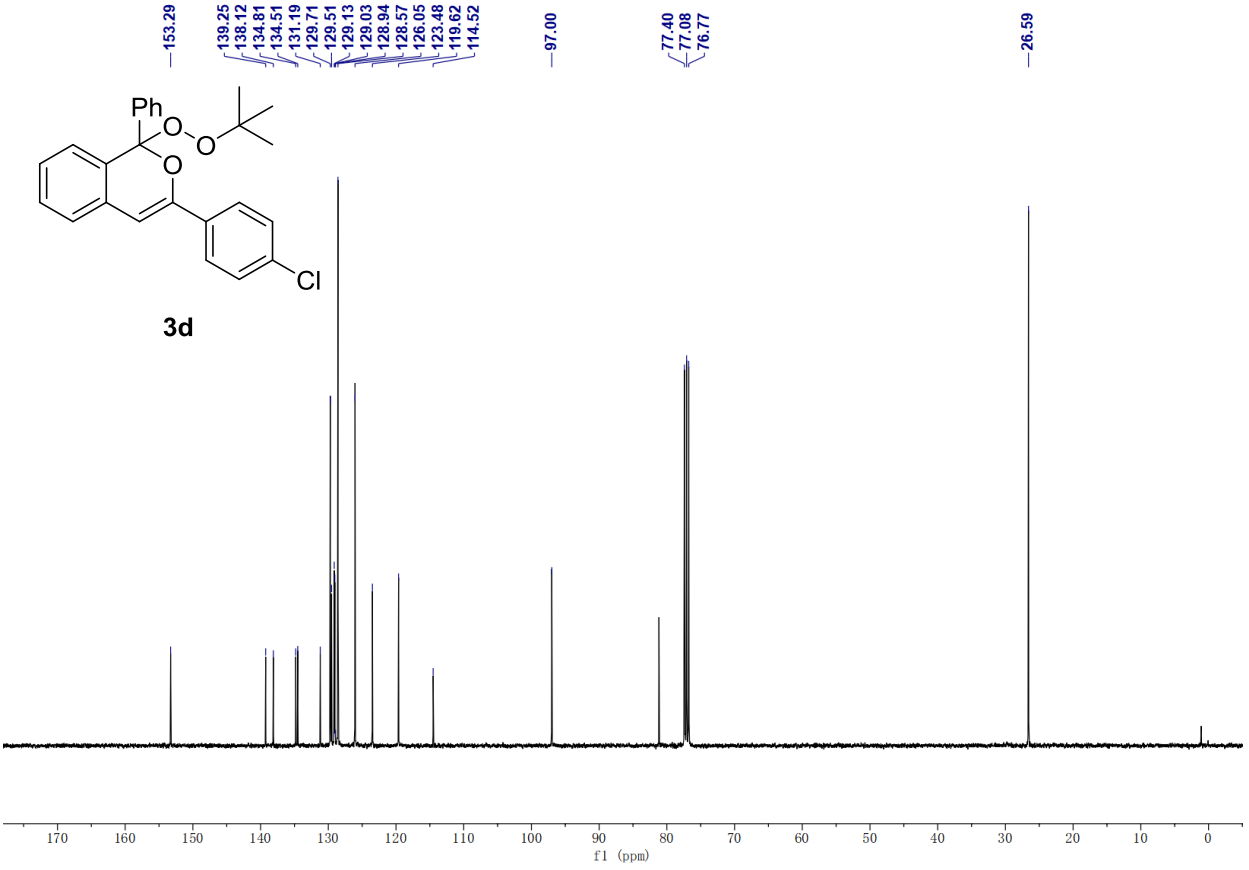

152.23
139.10
138.48
135.64
135.18
133.15
129.41
129.24
128.99
128.61
128.56
128.52
126.13
123.41
119.49
114.30
98.18
81.10
77.42
77.31
77.11
76.79
26.66
21.36
Ph
O
O
O
f1 (ppm)

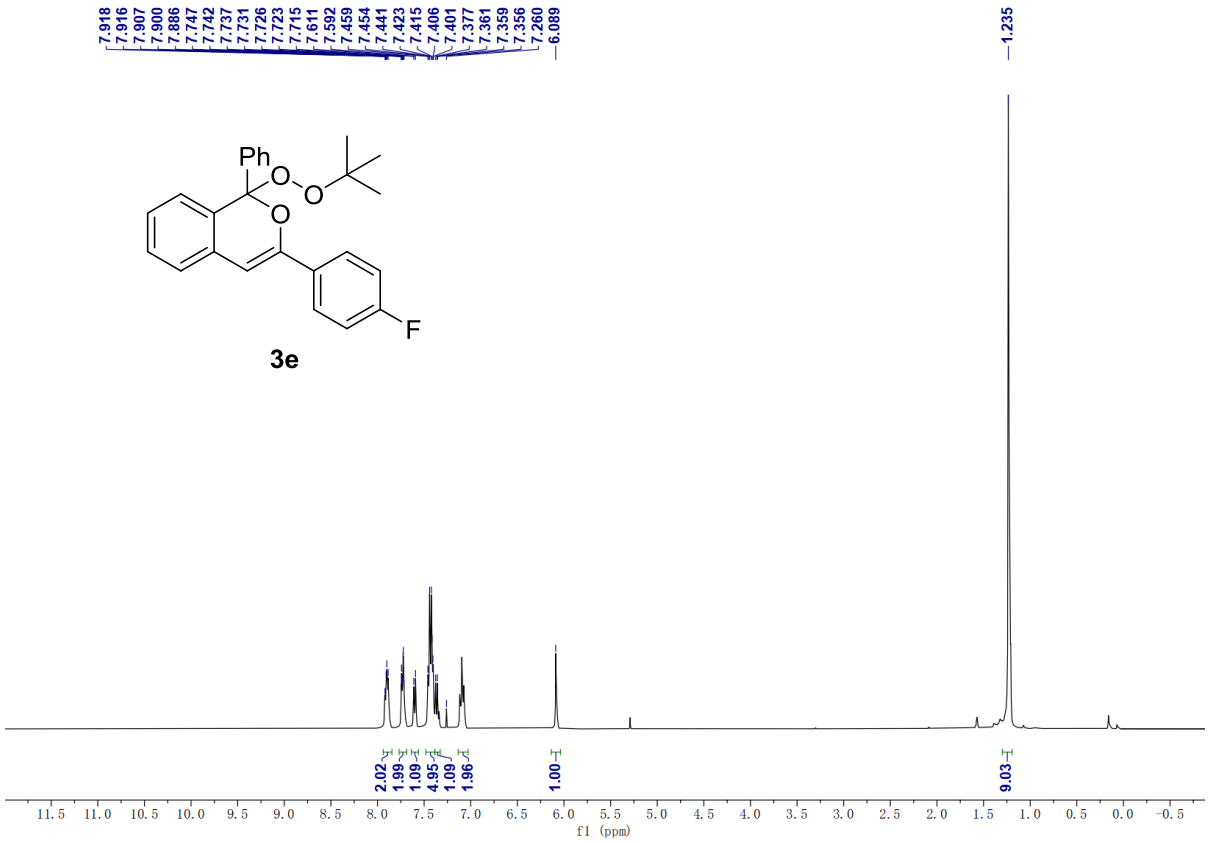
3b

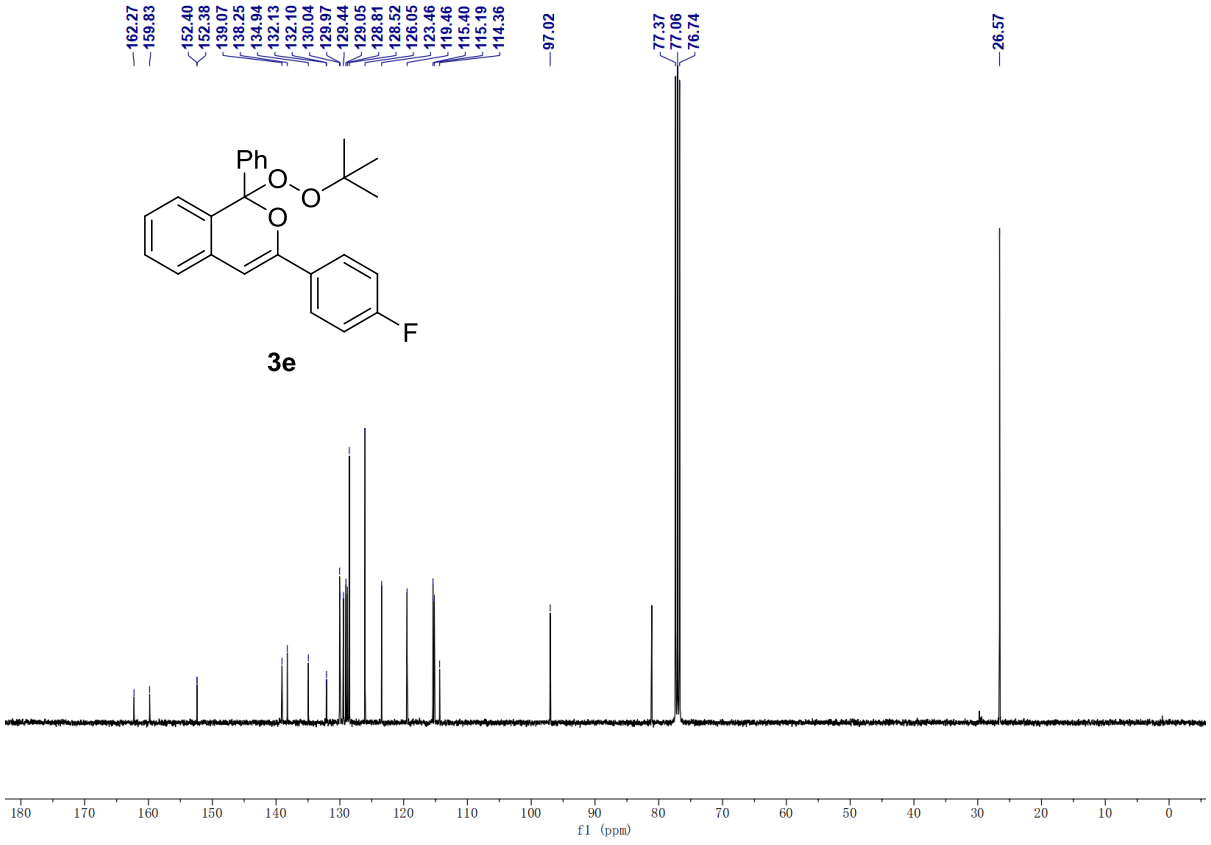

7.849
7.844
7.832
7.827
7.703
7.698
7.686
7.682
7.679
7.566
7.561
7.548
7.544
7.417
7.411
7.402
7.395
7.384
7.381
7.376
7.372
7.366
7.363
7.356
7.320
7.317
7.303
7.299
7.260
6.933
6.928
6.916
6.911
6.037
3.837
1.186
Ph
O
O
O
OCH3
3c
2.02
2.01
1.03
5.06
1.00
2.05
1.00
3.01
9.00
f1 (ppm)

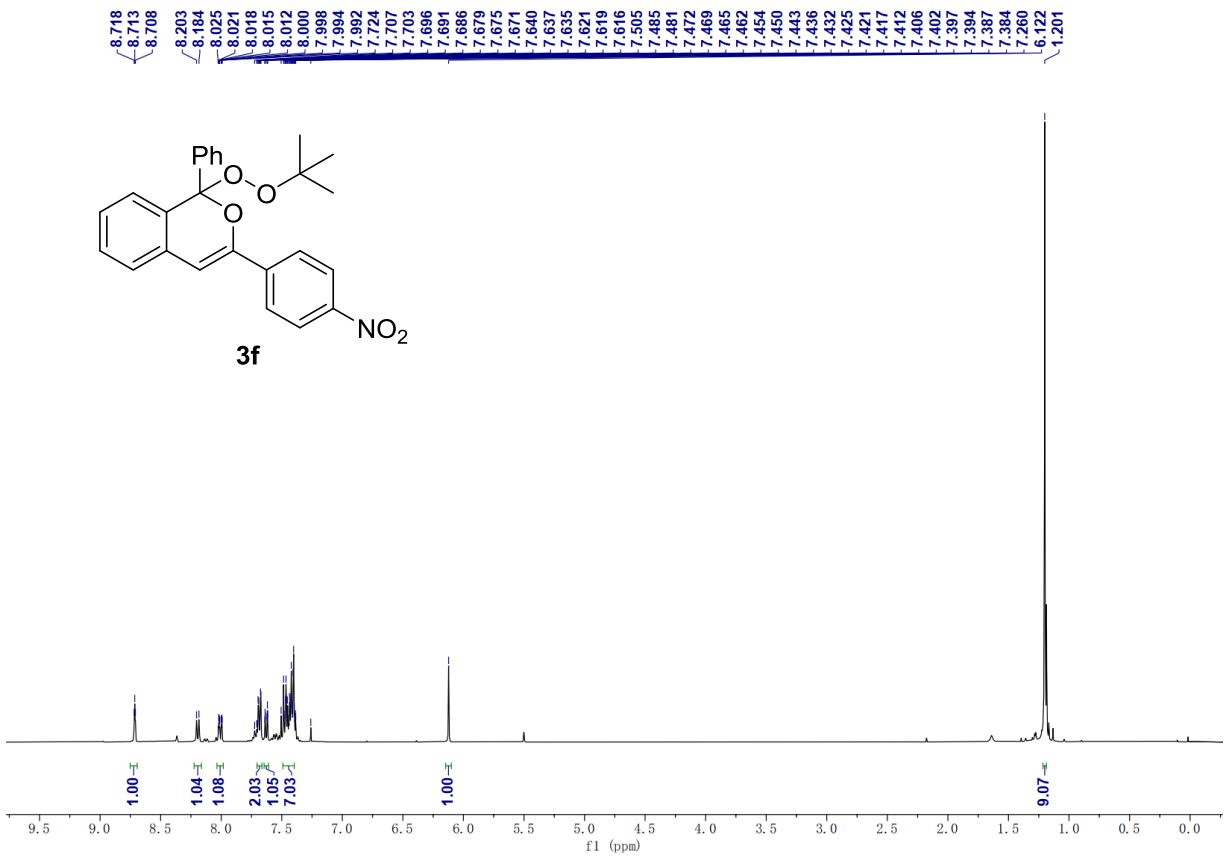

157.82
151.30
138.85
138.51
135.23
129.82
129.34
128.91
128.80
128.45
128.37
126.10
123.39
119.26
114.15
113.92
97.78
77.37
77.05
76.73
55.29
26.61
Ph
O
O
O
OCH3
3c
f1 (ppm)

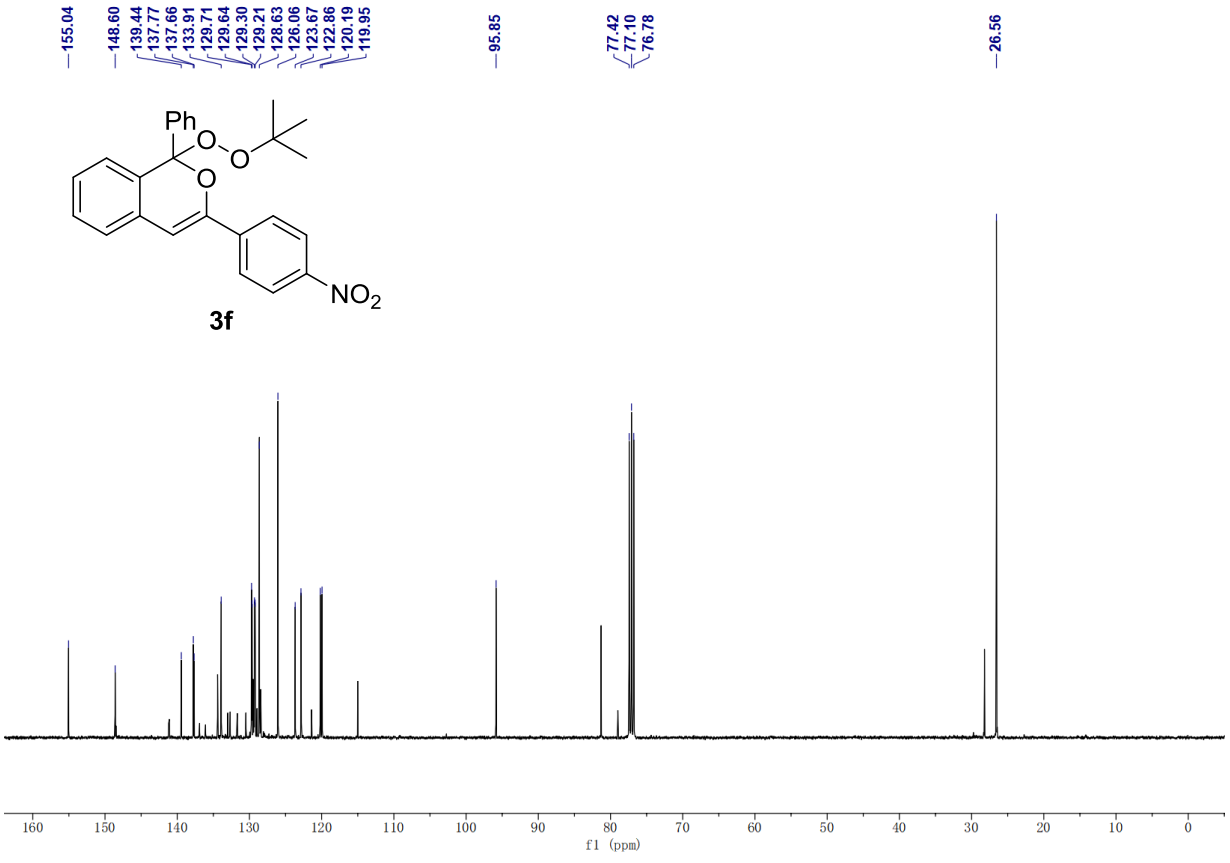

7.855
7.850
7.847
7.839
7.833
7.827
7.721
7.716
7.712
7.706
7.701
7.697
7.693
7.690
7.687
7.606
7.603
7.588
7.584
7.453
7.449
7.446
7.442
7.438
7.431
7.426
7.423
7.420
7.413
7.410
7.405
7.401
7.378
7.359
7.354
7.351
7.342
7.337
7.331
7.260
6.058
1.215
Ph
O
O
O
Cl
3d
2.09
2.04
1.07
5.02
3.04
1.00
9.07
f1 (ppm)

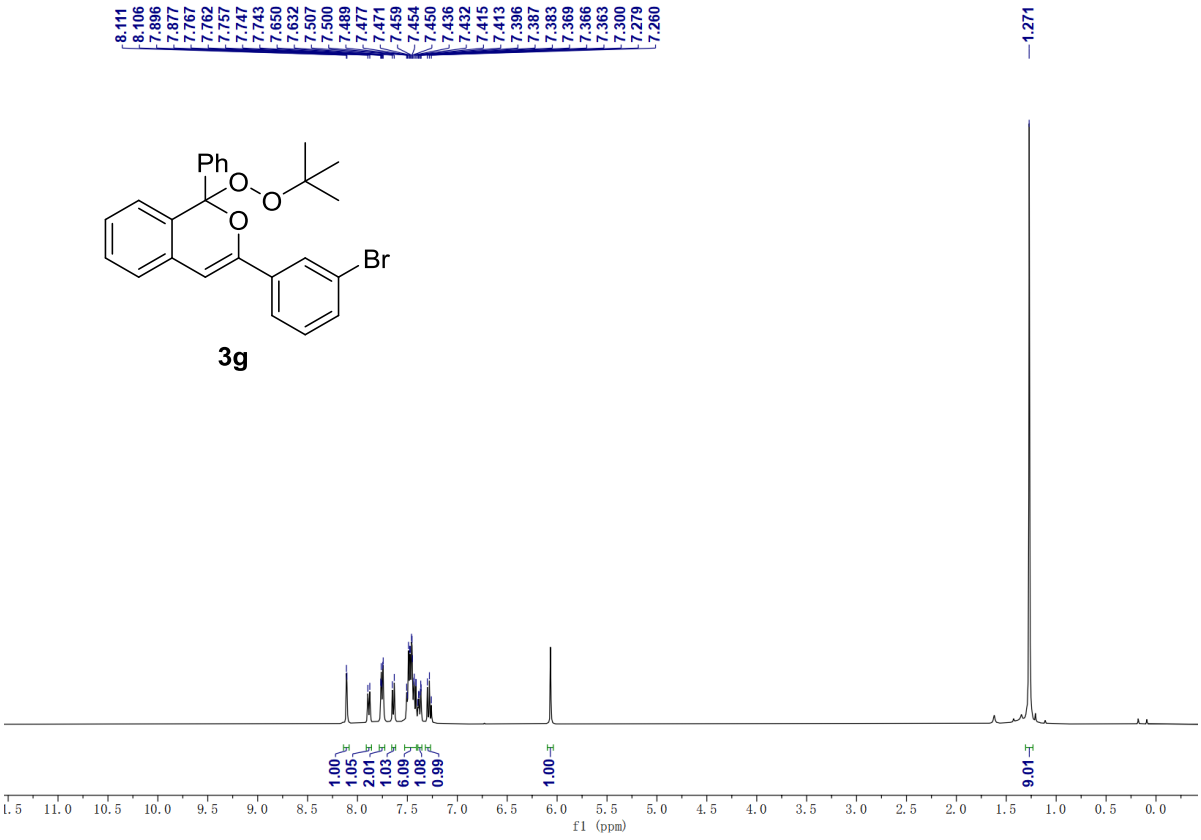

153.29
139.25
138.12
134.81
134.51
131.19
129.71
129.51
129.13
129.03
128.94
128.57
126.05
123.48
119.62
114.52
97.00
77.40
77.08
76.77
26.59
Ph
O
O
O
Cl
3d
f1 (ppm)

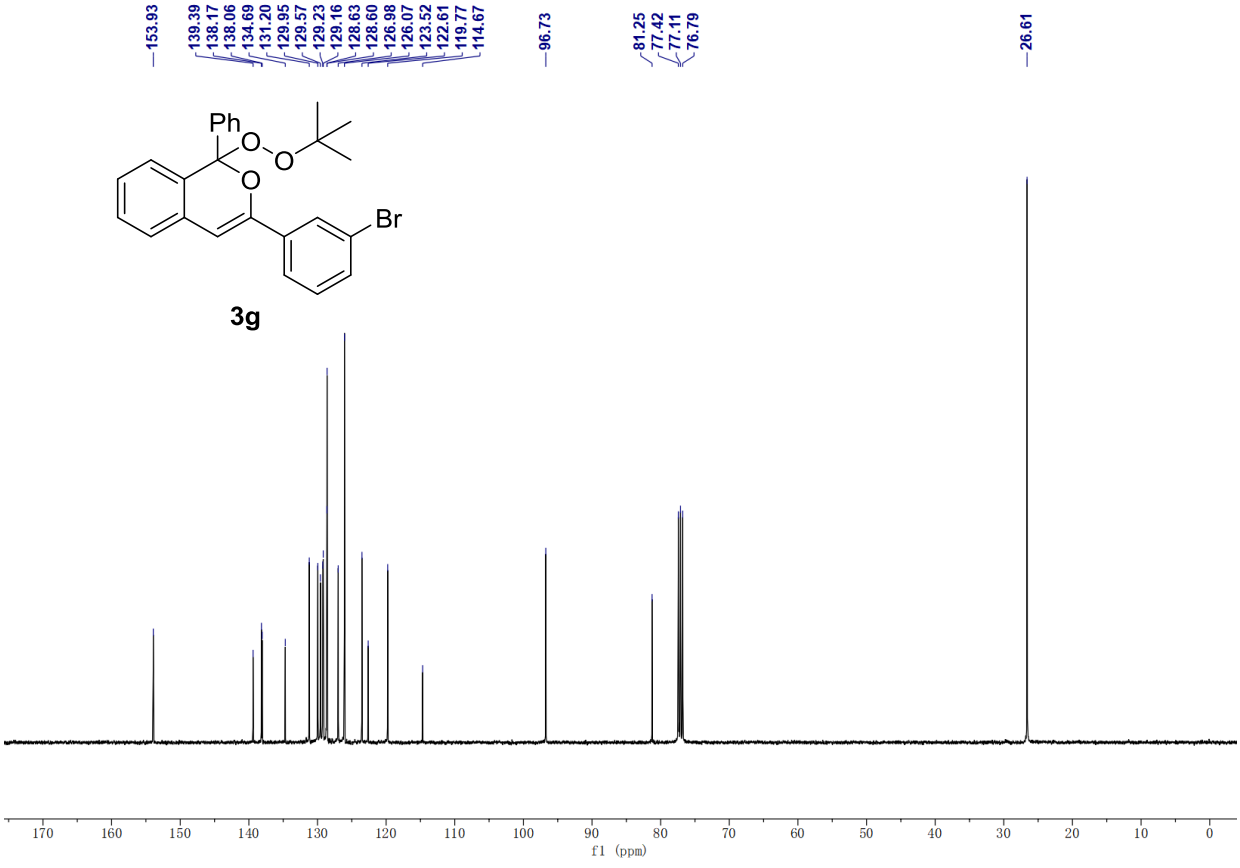

7.918
7.916
7.907
7.900
7.886
7.747
7.742
7.737
7.731
7.726
7.723
7.715
7.611
7.592
7.459
7.454
7.441
7.423
7.415
7.406
7.401
7.377
7.361
7.359
7.356
7.260
6.089
1.235
Ph
O
O
O
F
3e
2.02
1.99
1.09
4.95
1.09
1.96
1.00
9.03
f1 (ppm)

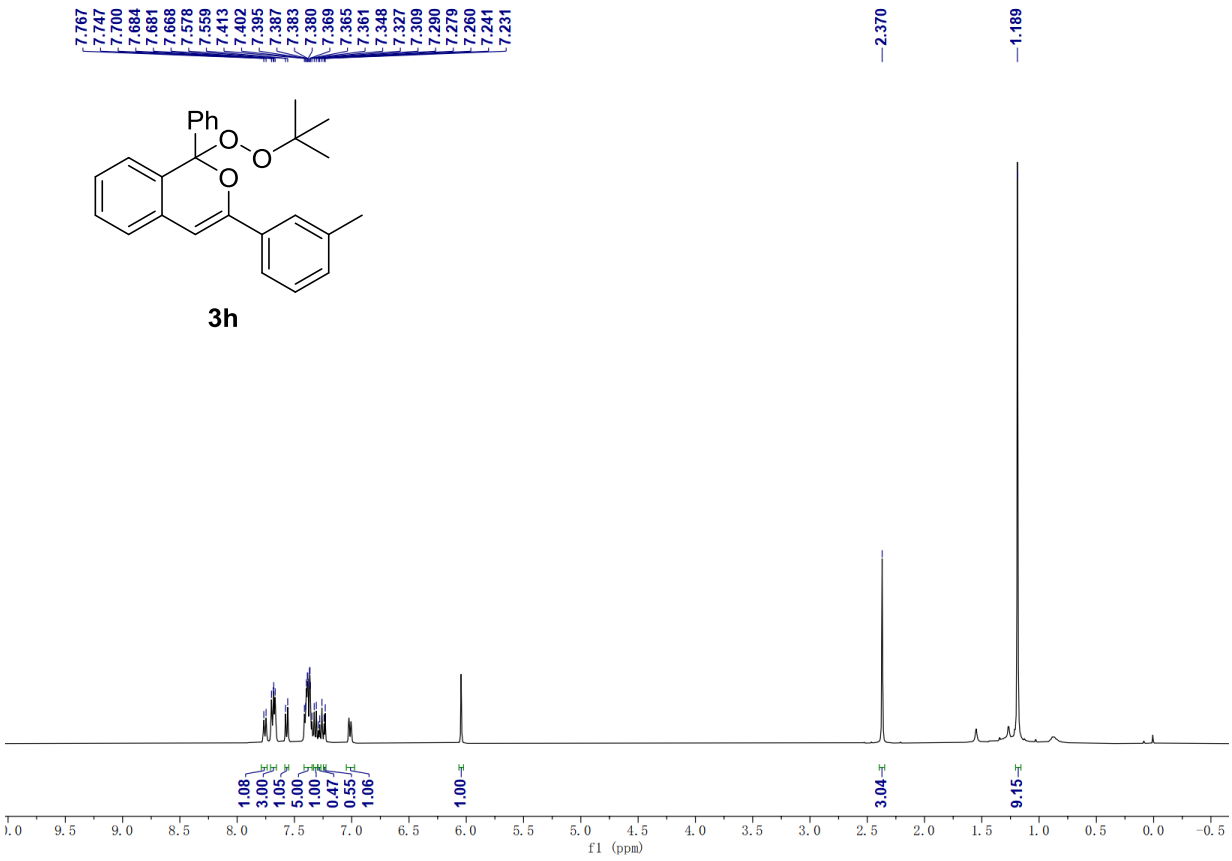

162.27
159.83
152.40
152.38
139.07
138.25
134.94
132.13
132.10
130.04
129.97
129.44
129.05
128.81
128.52
126.05
123.46
119.46
115.40
115.19
114.36
97.02
77.37
77.06
76.74
26.57
Ph
O
O
O
F
3e
f1 (ppm)


8.718
8.713
8.708
8.203
8.184
8.025
8.021
8.018
8.015
8.012
8.000
7.998
7.994
7.992
7.724
7.707
7.703
7.696
7.691
7.686
7.679
7.675
7.671
7.640
7.637
7.635
7.621
7.619
7.616
7.505
7.485
7.481
7.472
7.469
7.465
7.462
7.454
7.450
7.443
7.436
7.432
7.425
7.421
7.417
7.412
7.406
7.402
7.397
7.394
7.387
7.384
7.260
6.122
1.201
Ph
O
O
O
NO2
3f
1.00
1.04
1.08
2.03
1.05
7.03
1.00
9.07
f1 (ppm)

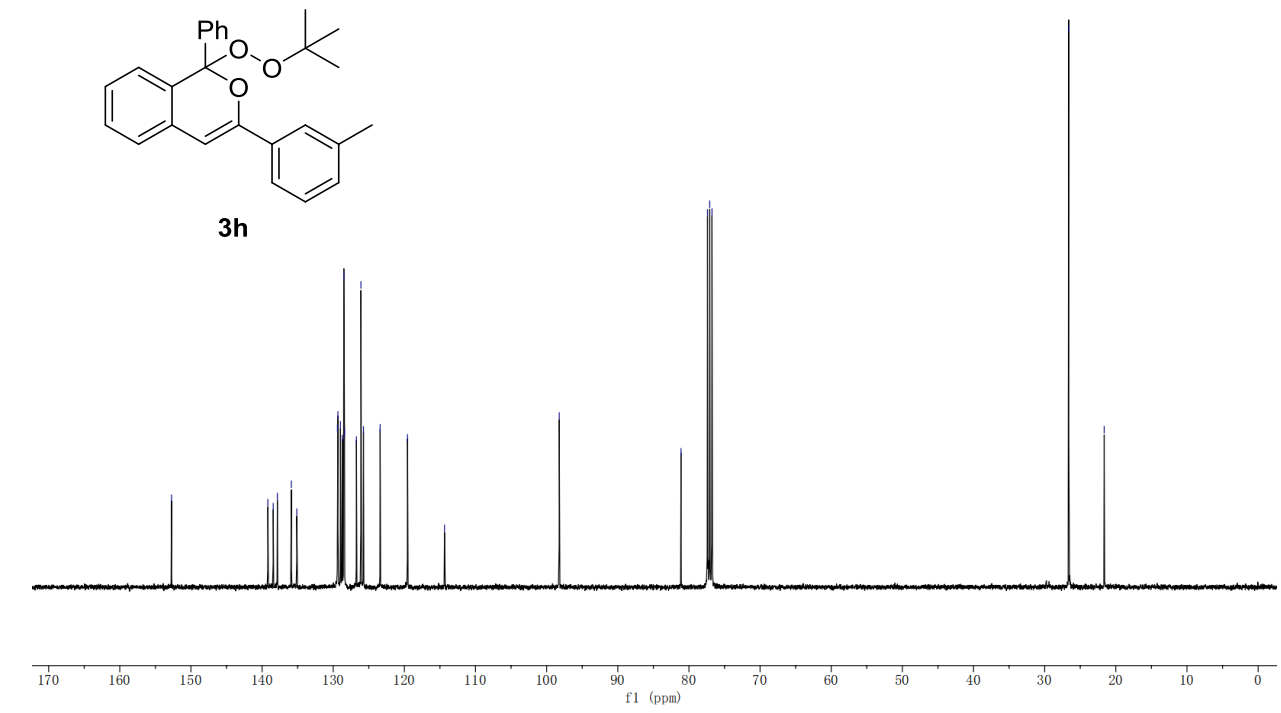

155.04
148.60
139.44
137.77
137.66
133.91
129.71
129.64
129.30
129.21
128.63
126.06
123.67
122.86
120.19
119.95
95.85
77.42
77.10
76.78
26.56
Ph
O
O
O
NO2
3f
f1 (ppm)


8.111
8.106
7.896
7.877
7.767
7.762
7.757
7.747
7.743
7.650
7.632
7.507
7.500
7.489
7.477
7.471
7.459
7.454
7.450
7.436
7.432
7.415
7.413
7.396
7.387
7.383
7.369
7.366
7.363
7.300
7.279
7.260
1.271
Ph
O
O
O
Br
3g
1.00
1.05
2.01
1.03
6.09
1.08
0.99
1.00
9.01
f1 (ppm)

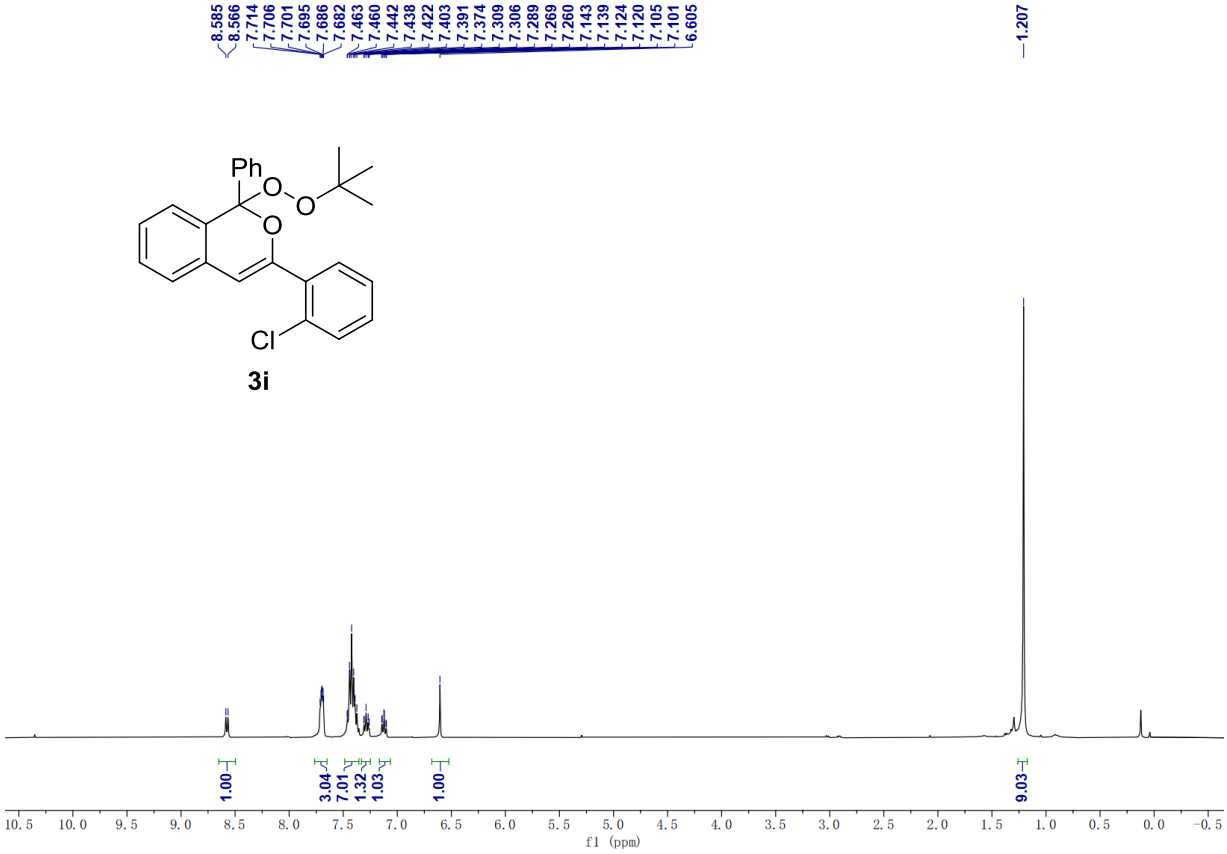

153.93
139.39
138.17
138.06
134.69
131.20
129.95
129.57
129.23
129.16
128.63
128.60
126.98
126.07
123.52
122.61
119.77
114.67
96.73
81.25
77.42
77.11
76.79
26.61
Ph
O
O
O
Br
3g
f1 (ppm)


7.767
7.747
7.700
7.684
7.681
7.668
7.578
7.559
7.413
7.402
7.395
7.387
7.383
7.380
7.369
7.365
7.361
7.348
7.327
7.309
7.290
7.279
7.260
7.241
7.231
2.370
1.189
Ph
O
O
O
1.08
3.00
1.05
5.00
1.00
0.47
0.55
1.06
1.00
3.04
9.15
f1 (ppm)

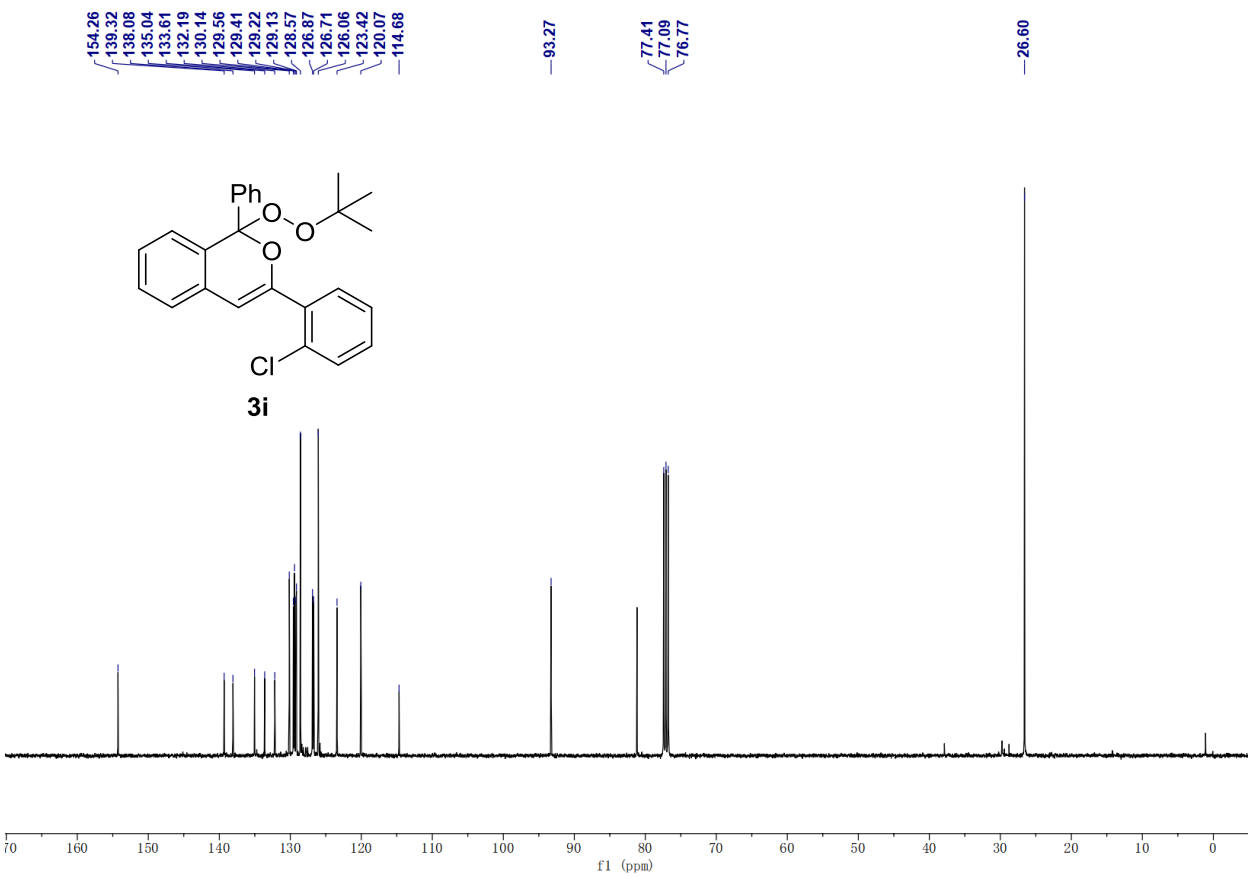
3h


152.73
139.19
138.43
137.85
135.88
135.12
129.41
129.34
128.98
128.73
128.51
128.41
126.74
126.10
125.74
123.40
119.56
114.36
98.23
81.11
77.39
77.08
76.76
26.62
21.63
Ph
O
O
O
f1 (ppm)

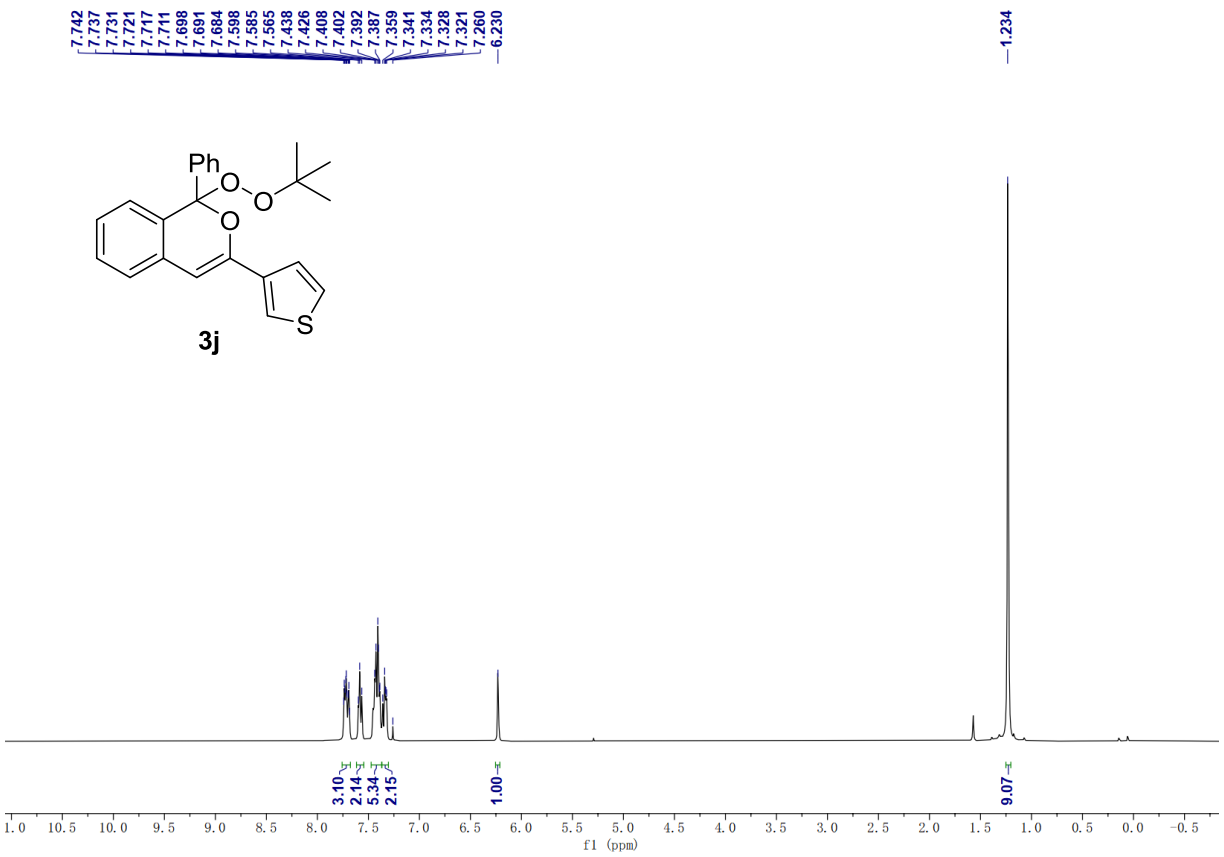
3h

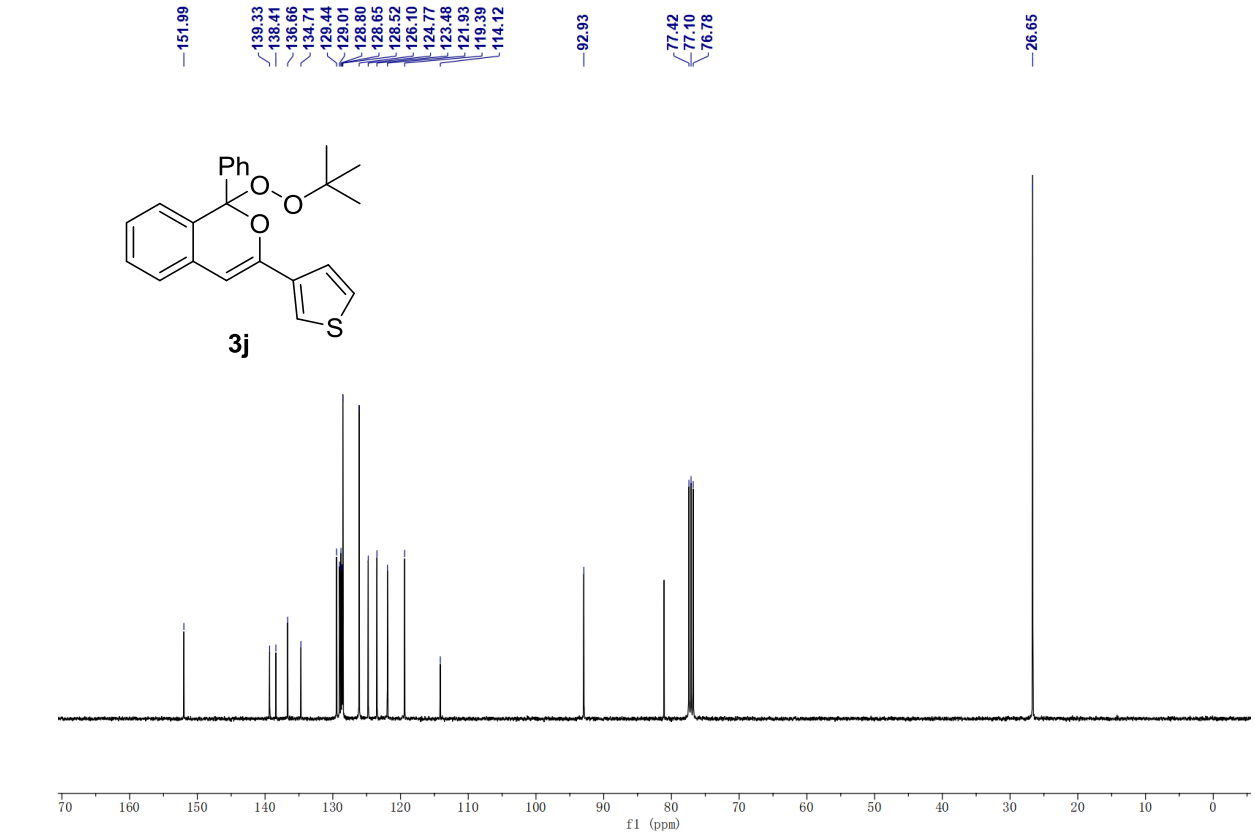

8.585
8.566
7.714
7.706
7.701
7.695
7.686
7.682
7.463
7.460
7.442
7.438
7.422
7.403
7.391
7.374
7.309
7.306
7.289
7.269
7.260
7.143
7.139
7.124
7.120
7.105
7.101
6.605
1.207
Ph
O
O
O
Cl
1.00
3.04
7.01
1.32
1.03
1.00
9.03
f1 (ppm)

3i

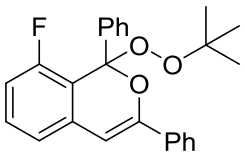

154.26
139.32
138.08
135.04
133.61
132.19
130.14
129.56
129.41
129.22
129.13
128.57
126.87
126.71
126.06
123.42
120.07
114.68
93.27
77.41
77.09
76.77
26.60
Ph
O
O
O
Cl
f1 (ppm)

3i


7.742
7.737
7.731
7.721
7.717
7.711
7.698
7.691
7.684
7.598
7.585
7.565
7.438
7.426
7.408
7.402
7.392
7.387
7.359
7.341
7.334
7.328
7.321
7.260
6.230
1.234
Ph
O
O
O
S
3j
3.10
2.14
5.34
2.15
1.00
9.07
f1 (ppm)


151.99
139.33
138.41
136.66
134.71
129.44
129.01
128.80
128.65
128.52
126.10
124.77
123.48
121.93
119.39
114.12
92.93
77.42
77.10
76.78
26.65
Ph
O
O
O
S
3j
f1 (ppm)

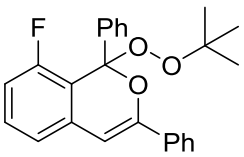

7.888
7.868
7.685
7.680
7.675
7.665
7.660
7.656
7.529
7.524
7.511
7.507
7.463
7.450
7.446
7.441
7.428
7.416
7.410
7.395
7.377
7.357
7.260
7.238
7.219
7.201
6.073
1.201


F
Ph
O
O
O
Ph

3m

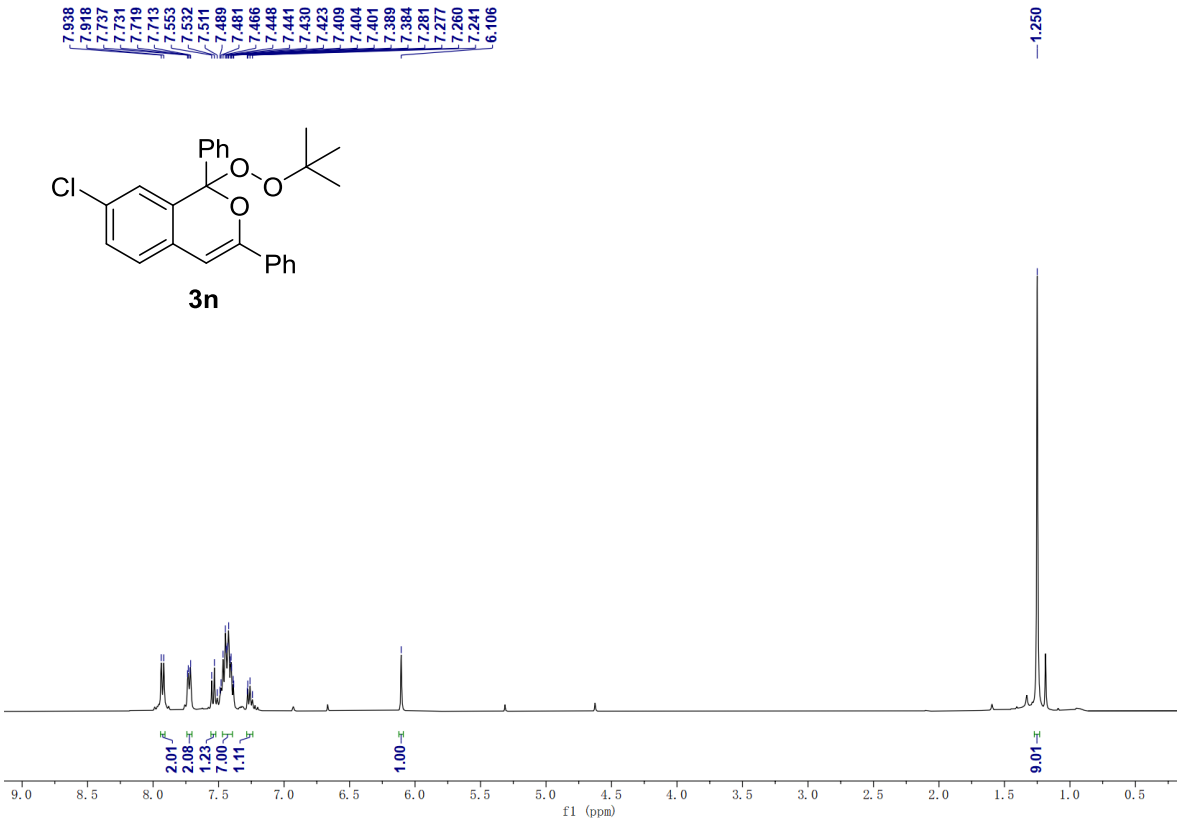
2.05
2.02
1.02
1.00
6.01
1.01
1.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.78
156.27
152.05
138.48
138.43
137.00
135.55
131.80
131.73
129.29
128.69
128.50
128.34
126.58
126.56
126.17
125.60
125.44
115.79
115.58
115.38
115.34
114.17
113.98
98.92
81.24
77.37
77.05
76.74
26.54

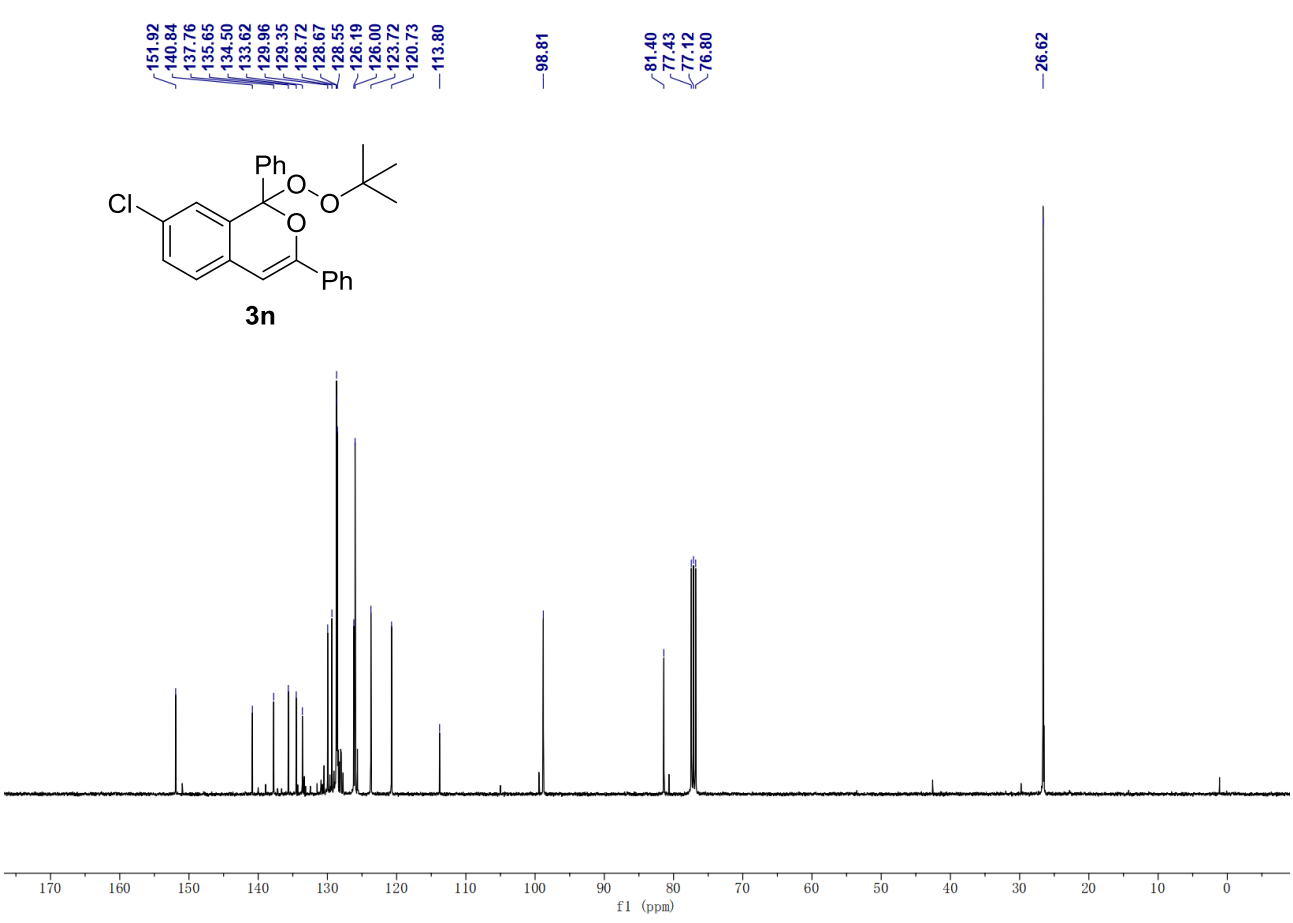

F
Ph
O
O
O
Ph

3m

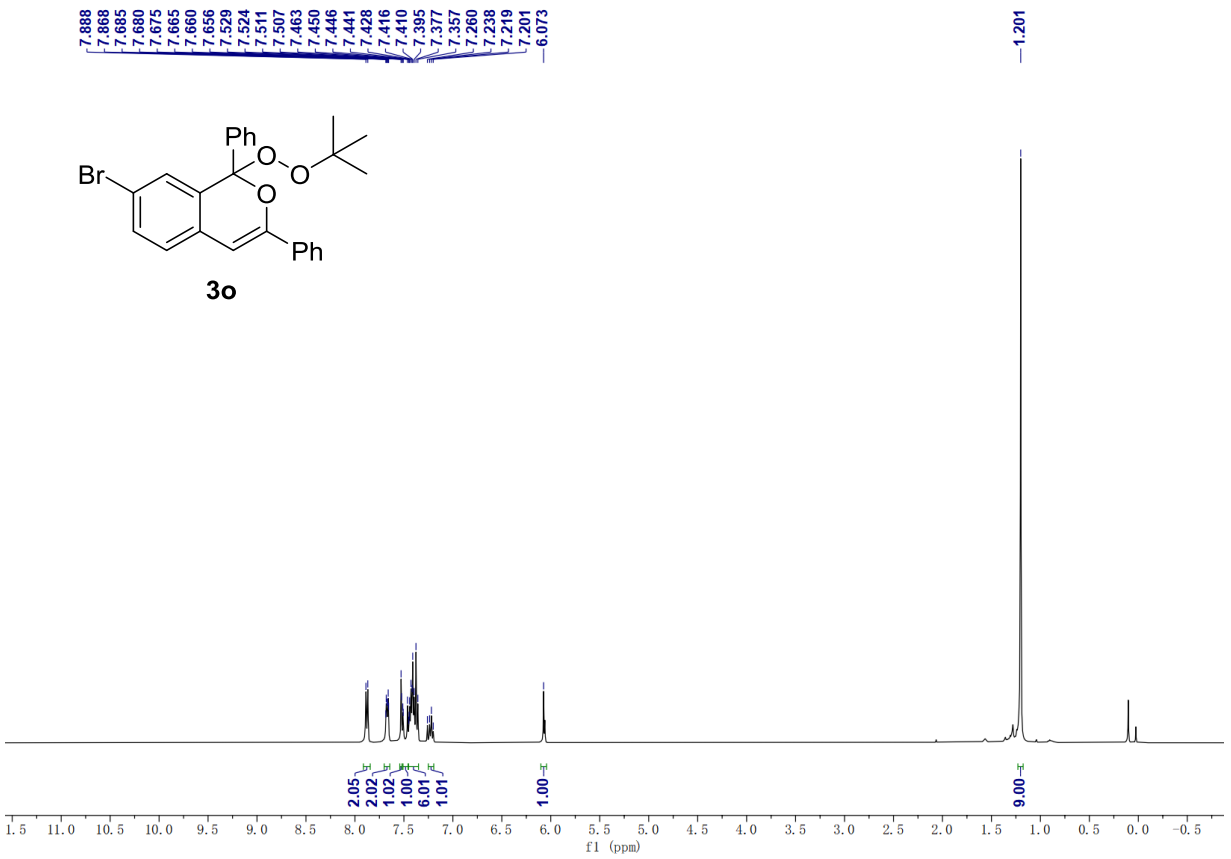
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

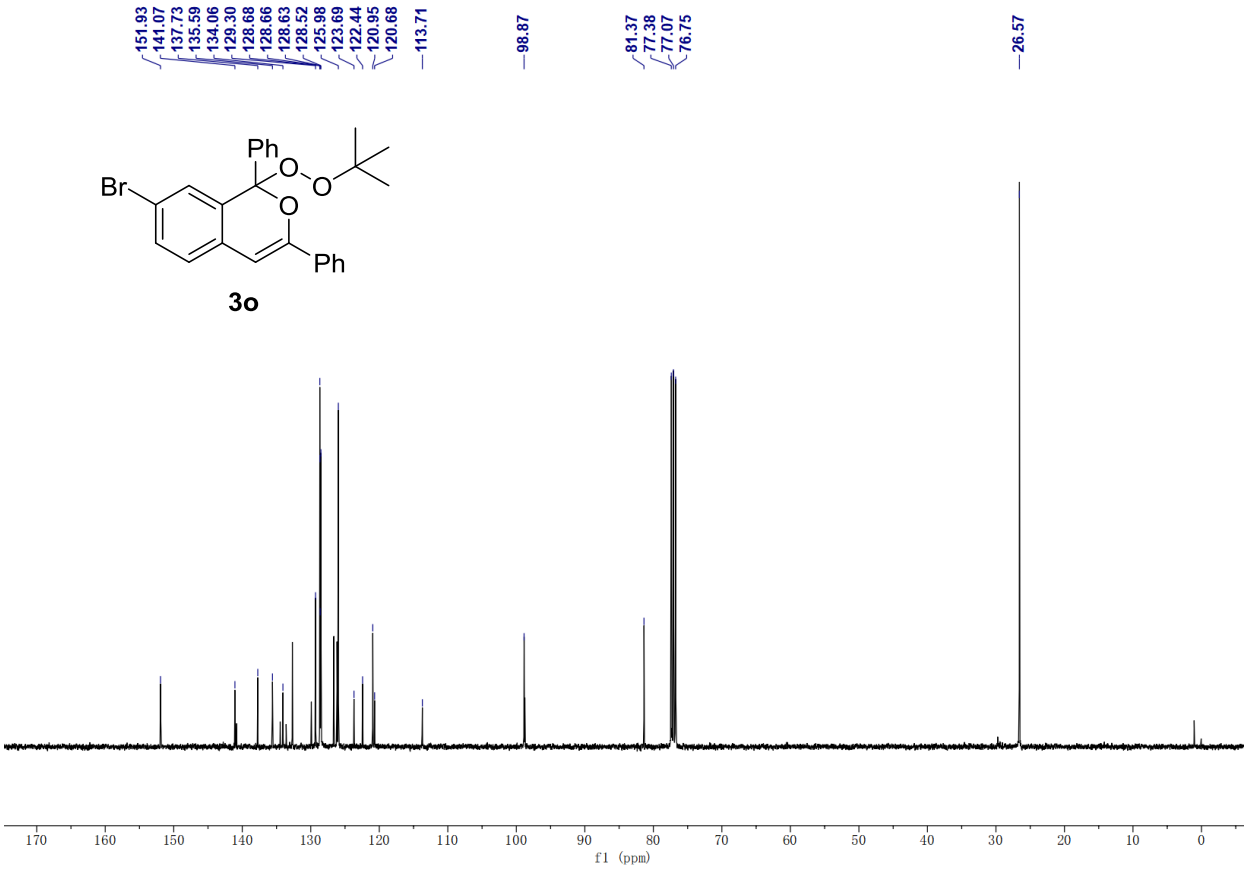

7.938
7.918
7.737
7.731
7.719
7.713
7.553
7.532
7.511
7.489
7.481
7.466
7.448
7.441
7.430
7.423
7.409
7.404
7.401
7.389
7.384
7.281
7.277
7.260
7.241
6.106
1.250
Ph
O
O
Cl
O
Ph
2.01
2.08
1.23
7.00
1.11
1.00
9.01
f1 (ppm)

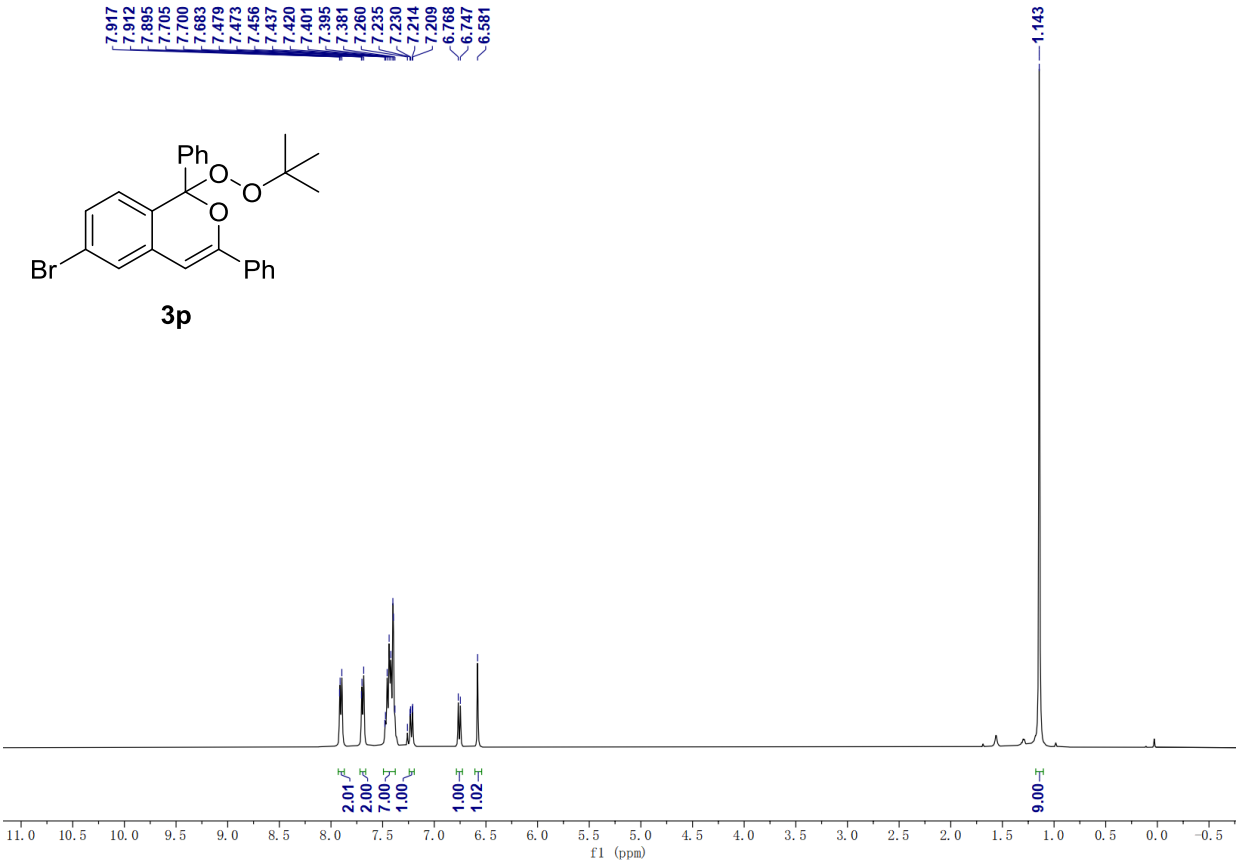
3n


151.92
140.84
137.76
135.65
134.50
133.62
129.96
129.35
128.72
128.67
128.55
126.19
126.00
123.72
120.73
113.80
98.81
81.40
77.43
77.12
76.80
26.62
Ph
O
O
Cl
O
Ph
f1 (ppm)

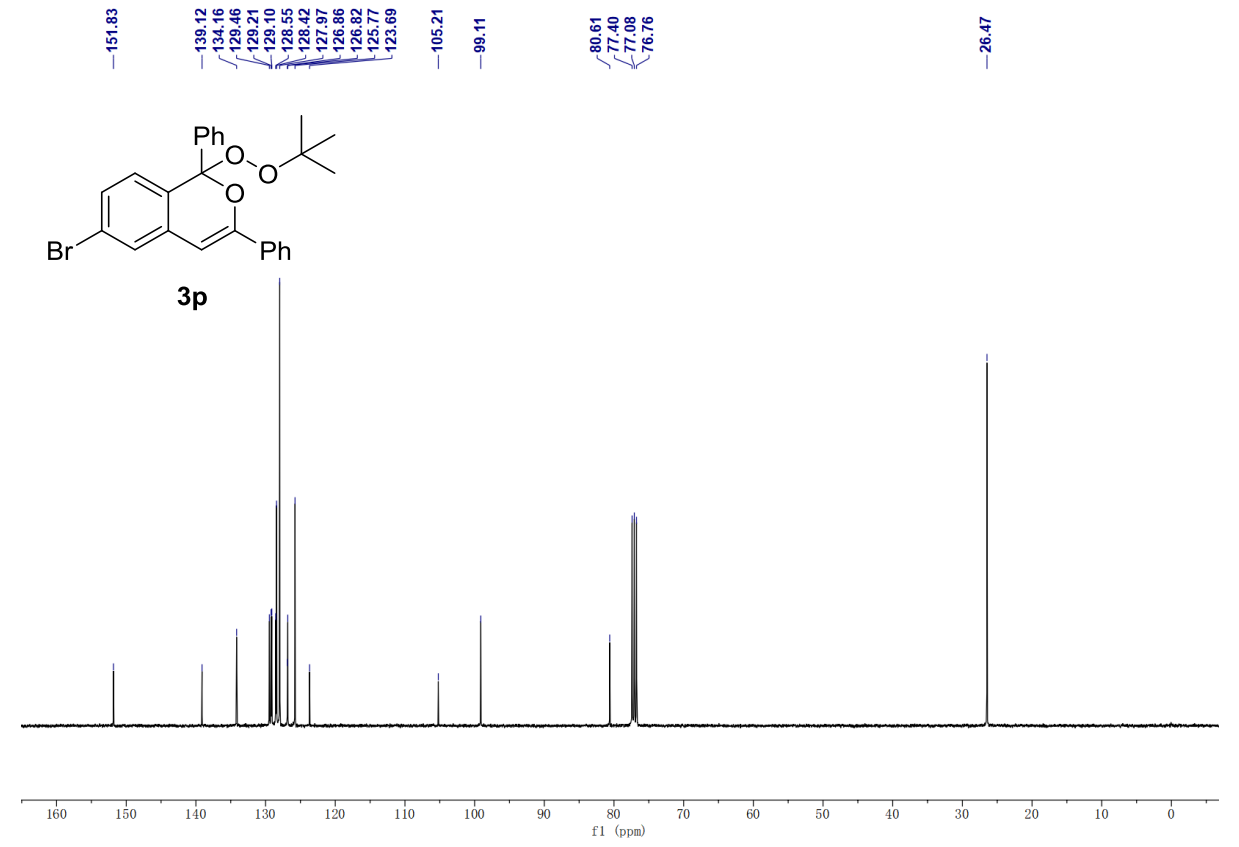
3n


7.888
7.868
7.685
7.680
7.675
7.665
7.660
7.656
7.529
7.524
7.511
7.507
7.463
7.450
7.446
7.441
7.428
7.416
7.410
7.395
7.377
7.357
7.260
7.238
7.219
7.201
6.073
1.201
Ph
O
O
Br
O
Ph
3o
2.05
2.02
1.02
1.00
6.01
1.01
1.00
9.00
f1 (ppm)

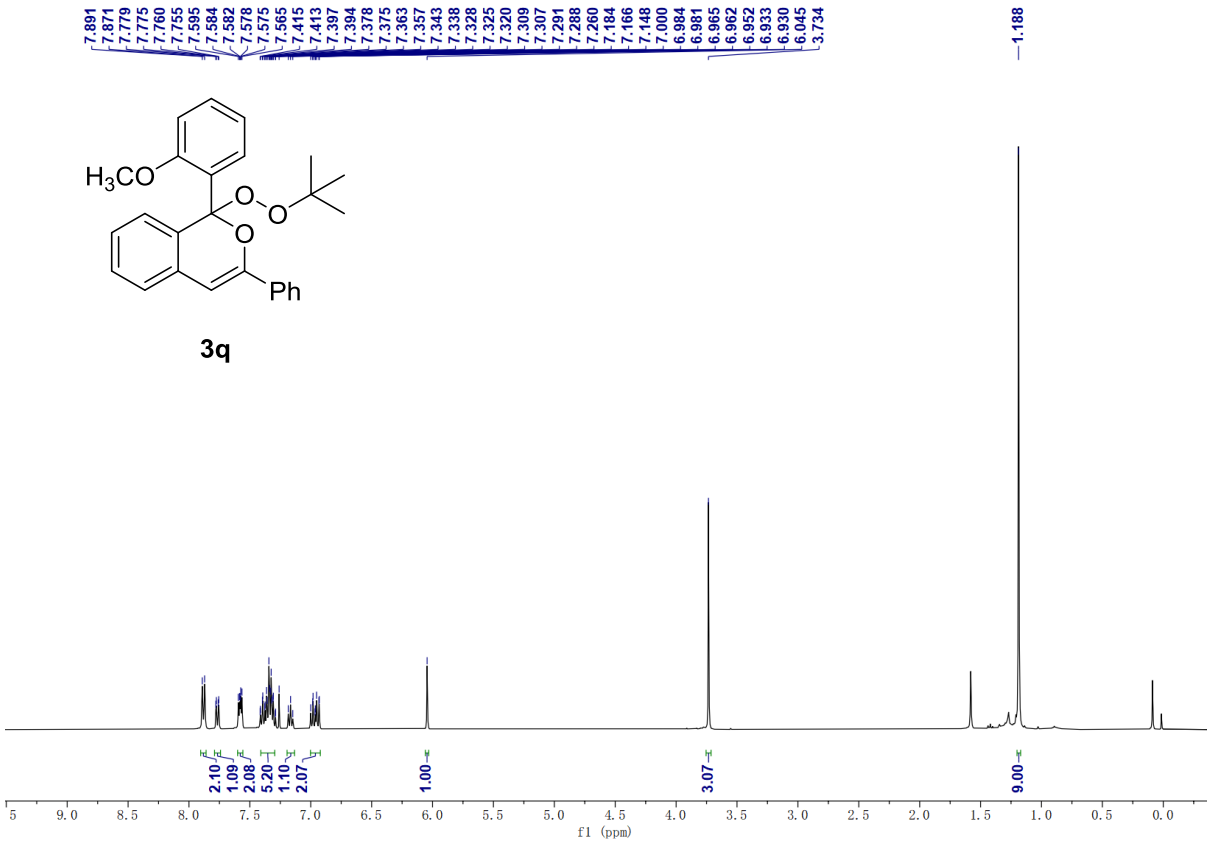

151.93
141.07
137.73
135.59
134.06
129.30
128.68
128.66
128.63
128.52
125.98
123.69
122.44
120.95
120.68
113.71
98.87
81.37
77.38
77.07
76.75
26.57
Ph
O
O
Br
O
Ph
3o
f1 (ppm)


7.917
7.912
7.895
7.705
7.700
7.683
7.479
7.473
7.456
7.437
7.420
7.401
7.395
7.381
7.260
7.235
7.230
7.214
7.209
6.768
6.747
6.581
1.143
Ph
O
O
O
Br
Ph
2.01
2.00
7.00
1.00
1.00
1.02
9.00
f1 (ppm)

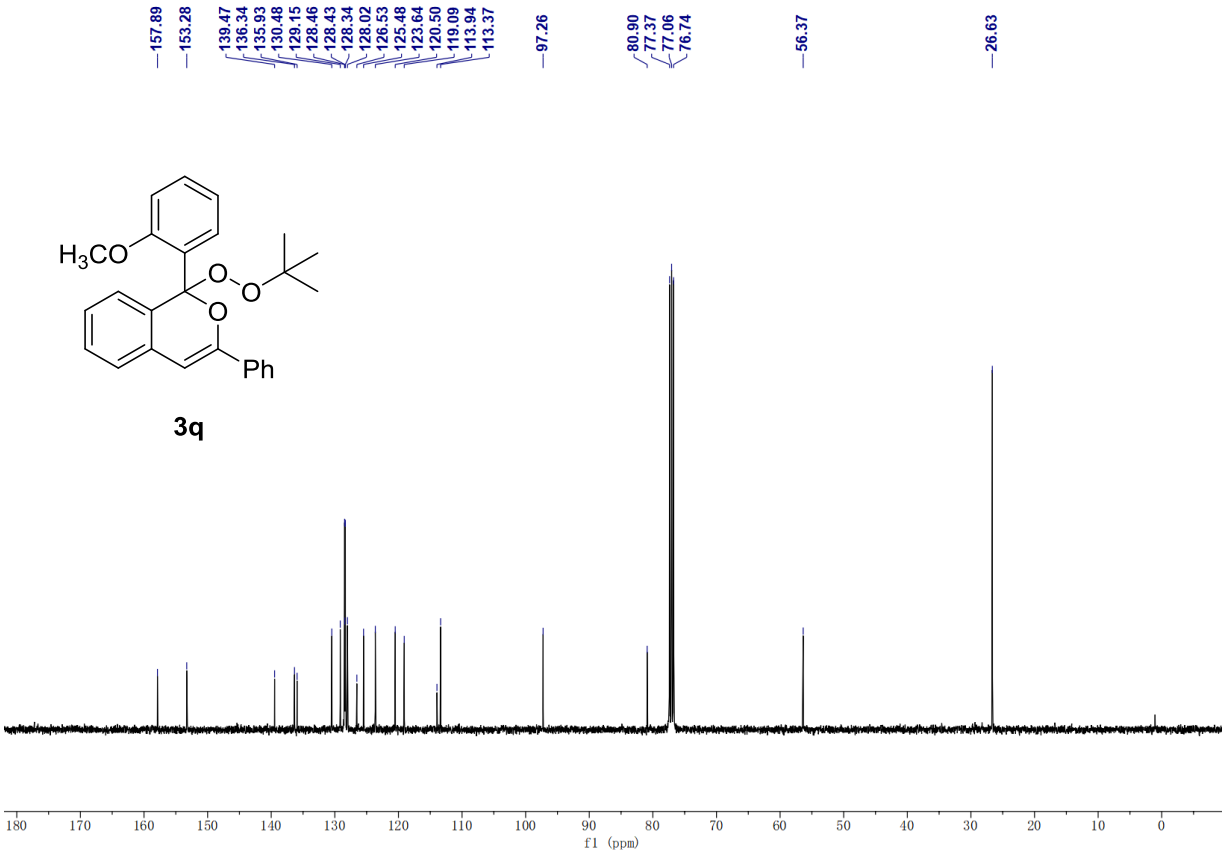
3p


151.83
139.12
134.16
129.46
129.21
129.10
128.55
128.42
127.97
126.86
126.82
125.77
123.69
105.21
99.11
80.61
77.40
77.08
76.76
26.47
Ph
O
O
O
Br
Ph
f1 (ppm)

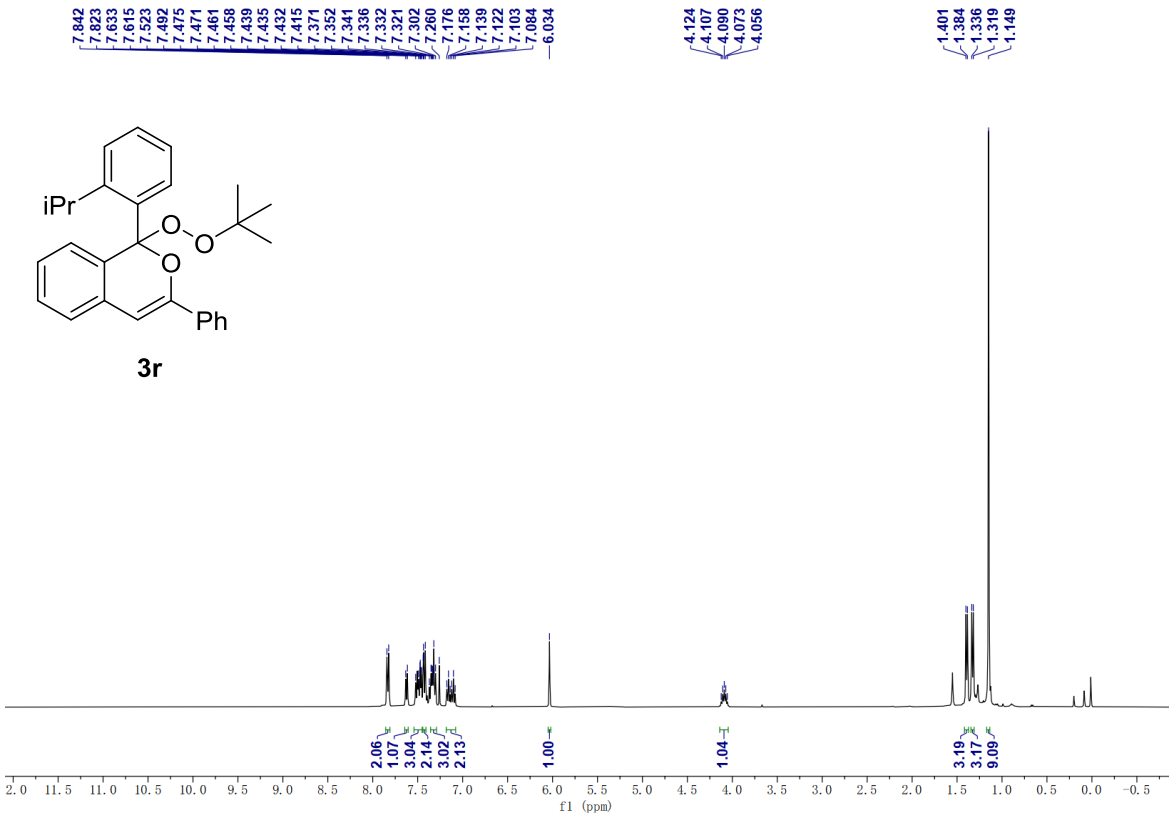
3p

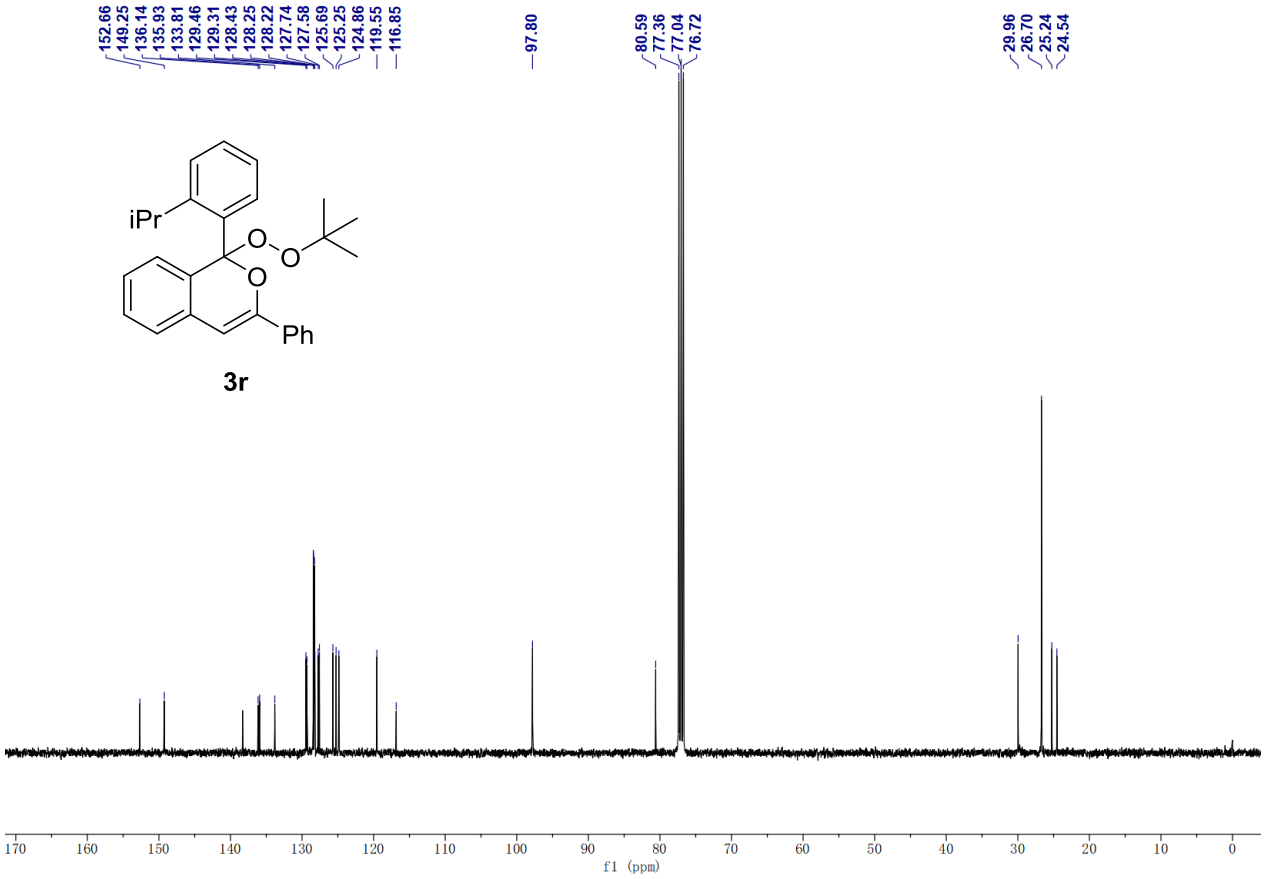

7.891
7.871
7.779
7.775
7.760
7.755
7.595
7.584
7.582
7.578
7.575
7.565
7.415
7.413
7.397
7.394
7.378
7.375
7.363
7.357
7.343
7.338
7.328
7.325
7.320
7.309
7.307
7.291
7.288
7.260
7.184
7.166
7.148
7.000
6.984
6.981
6.965
6.962
6.952
6.933
6.930
6.045
3.734
1.188
H3CO
O
O
O
Ph
2.10
1.09
2.08
5.20
1.10
2.07
1.00
3.07
9.00
f1 (ppm)

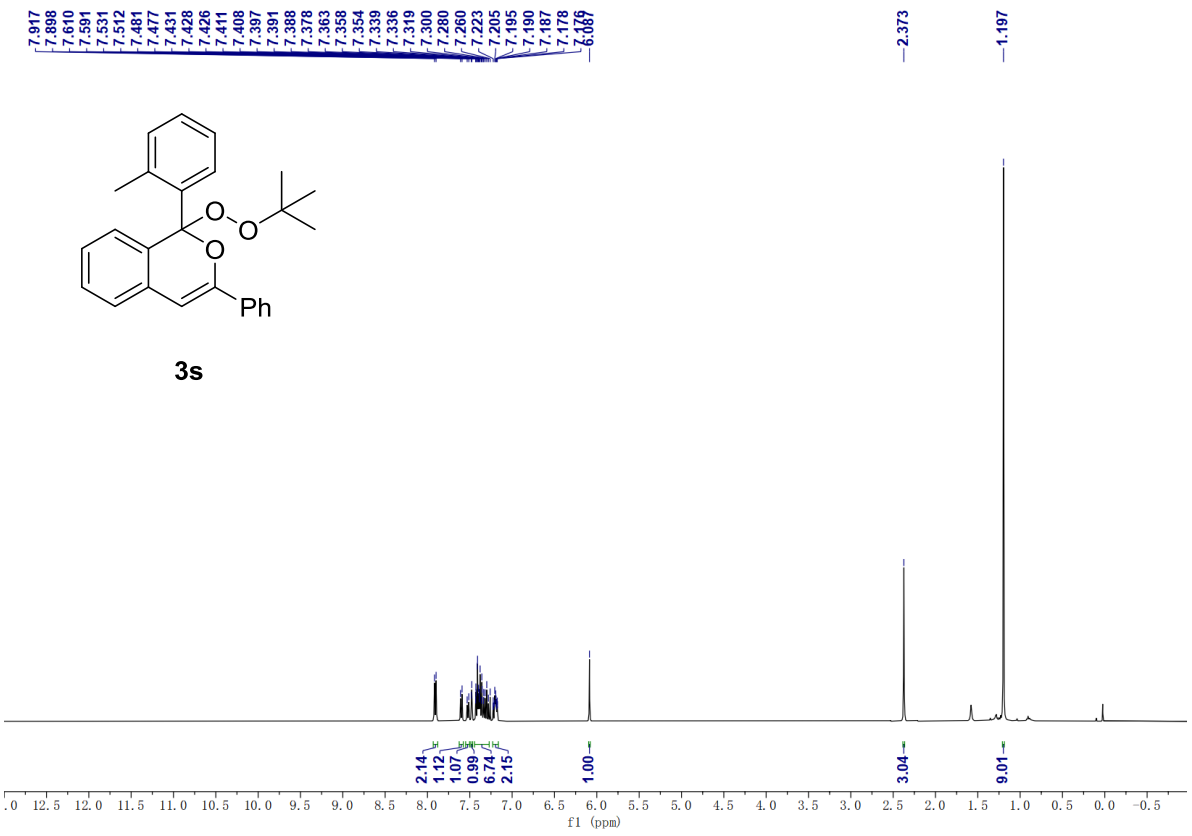
3q


157.89
153.28
139.47
136.34
135.93
130.48
129.15
128.46
128.43
128.34
128.02
126.53
125.48
123.64
120.50
119.09
113.94
113.37
97.26
80.90
77.37
77.06
76.74
56.37
26.63
H3CO
O
O
O
Ph
f1 (ppm)

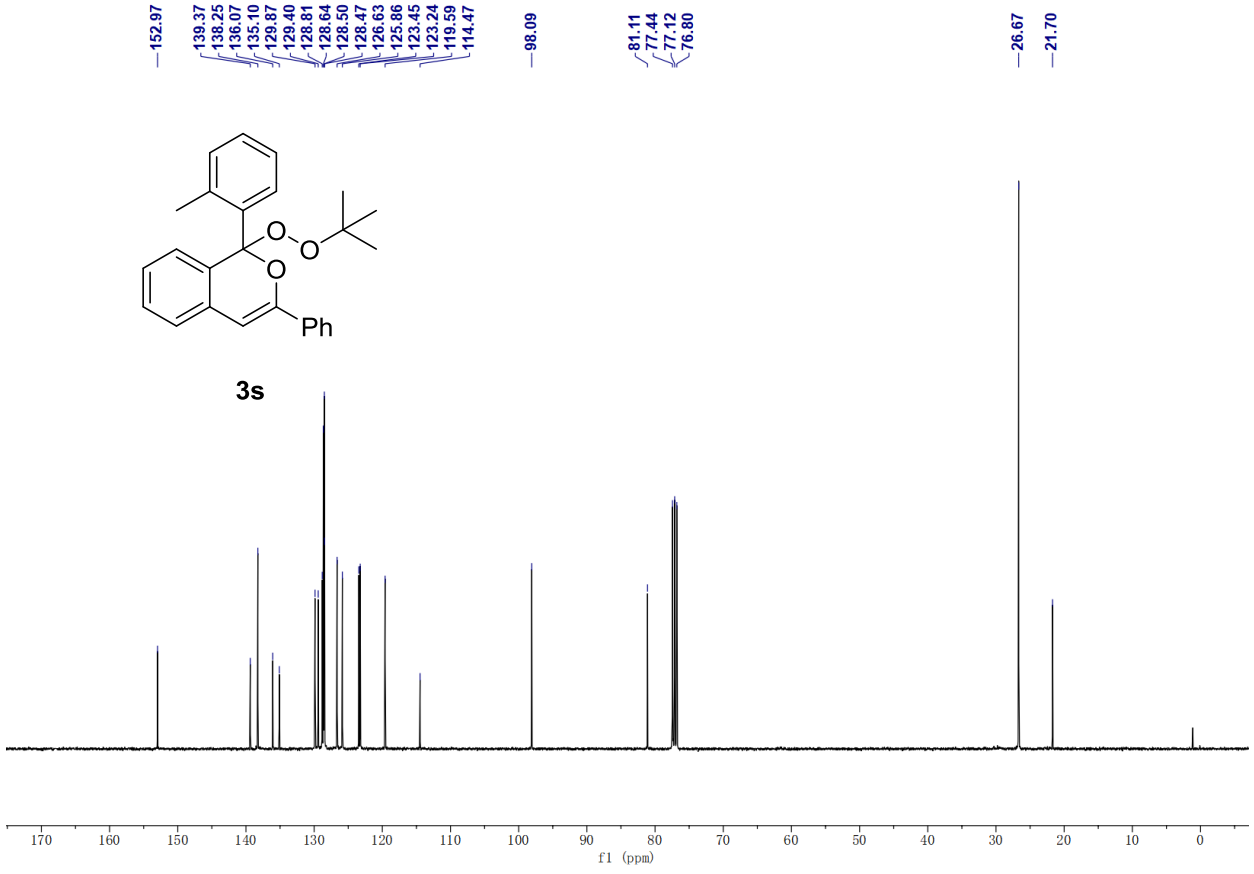
3q


7.842
7.823
7.633
7.615
7.523
7.492
7.475
7.471
7.461
7.458
7.439
7.435
7.432
7.415
7.371
7.352
7.341
7.336
7.332
7.321
7.302
7.260
7.176
7.158
7.139
7.122
7.103
7.084
6.034
4.124
4.107
4.090
4.073
4.056
1.401
1.384
1.336
1.319
1.149
iPr
O
O
O
Ph
3r
2.06
1.07
3.04
2.14
3.02
2.13
1.00
1.04
3.19
3.17
9.09
f1 (ppm)

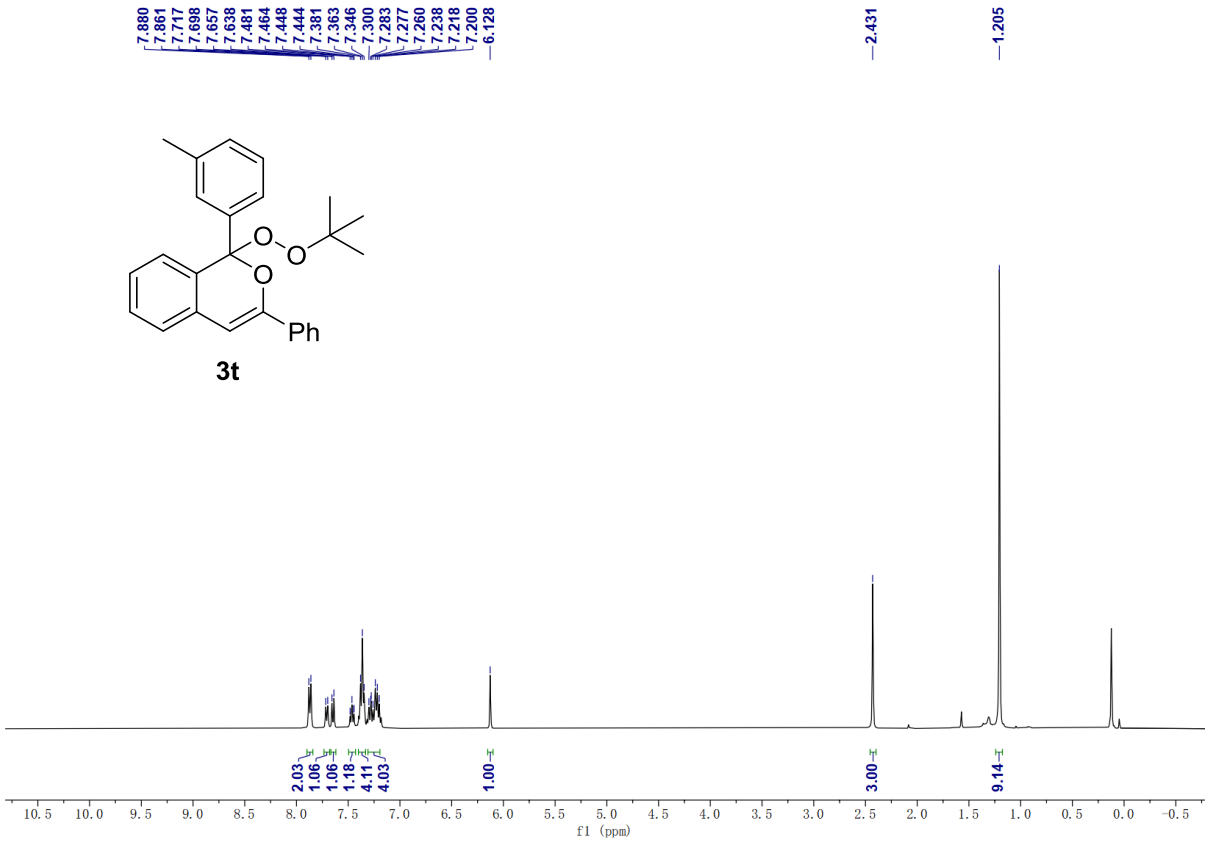

152.66
149.25
136.14
135.93
133.81
129.46
129.31
128.43
128.25
128.22
127.74
127.58
125.69
125.25
124.86
119.55
116.85
97.80
80.59
77.36
77.04
76.72
29.96
26.70
25.24
24.54
iPr
O
O
O
Ph
3r
f1 (ppm)

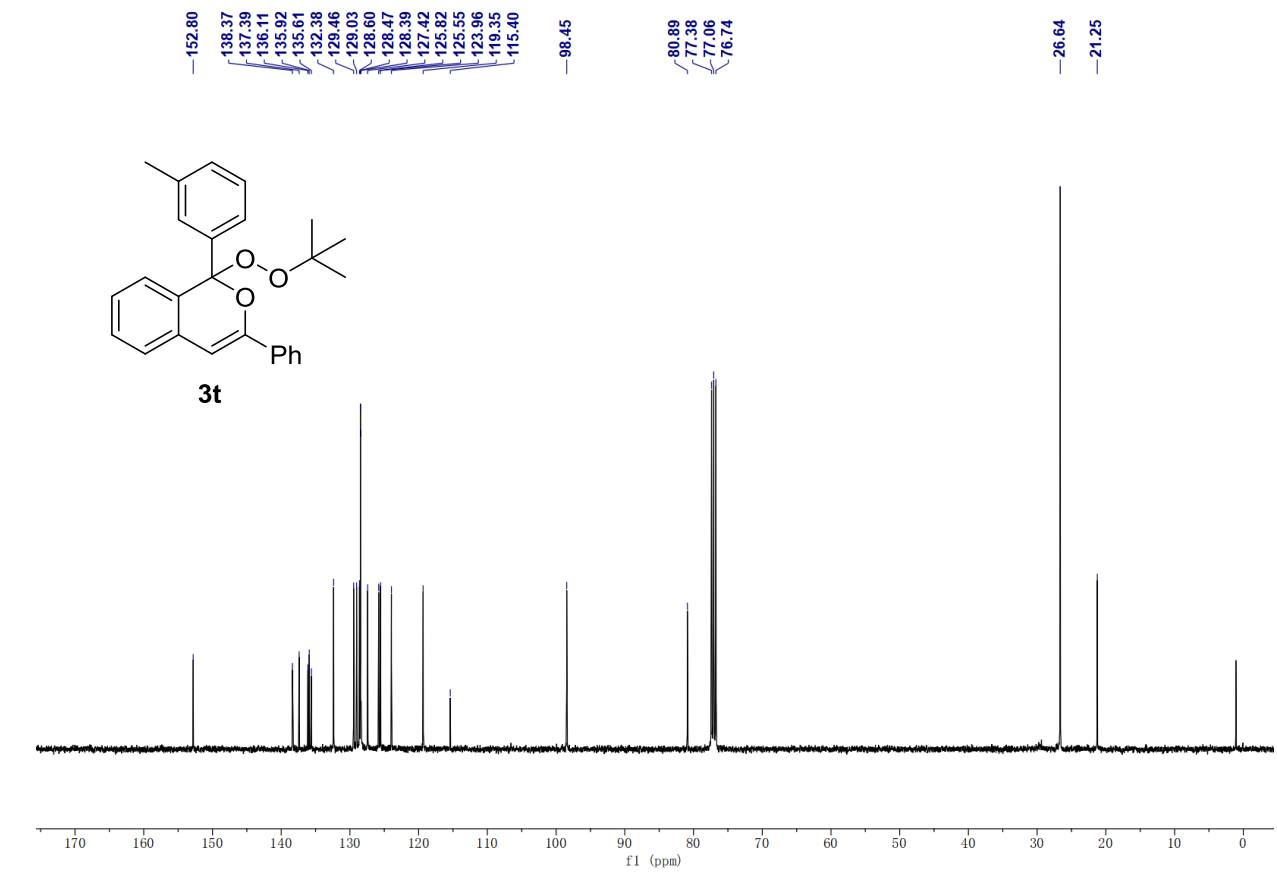

7.917
7.898
7.610
7.591
7.531
7.512
7.481
7.477
7.431
7.428
7.426
7.411
7.408
7.397
7.391
7.388
7.378
7.363
7.358
7.354
7.339
7.336
7.319
7.300
7.280
7.260
7.223
7.205
7.195
7.190
7.187
7.178
6.087
2.373
1.197
O
O
O
Ph
2.14
1.12
1.07
0.99
6.74
2.15
1.00
3.04
9.01
f1 (ppm)

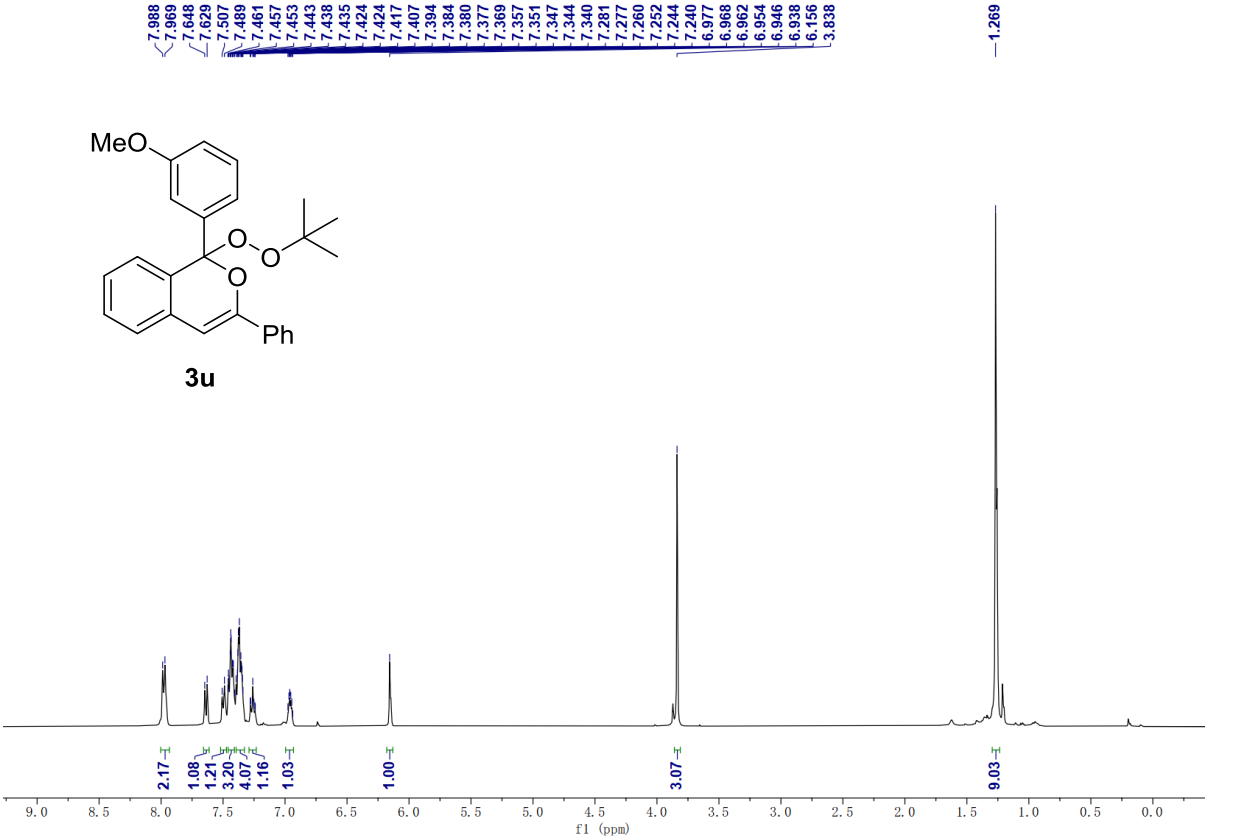
3s

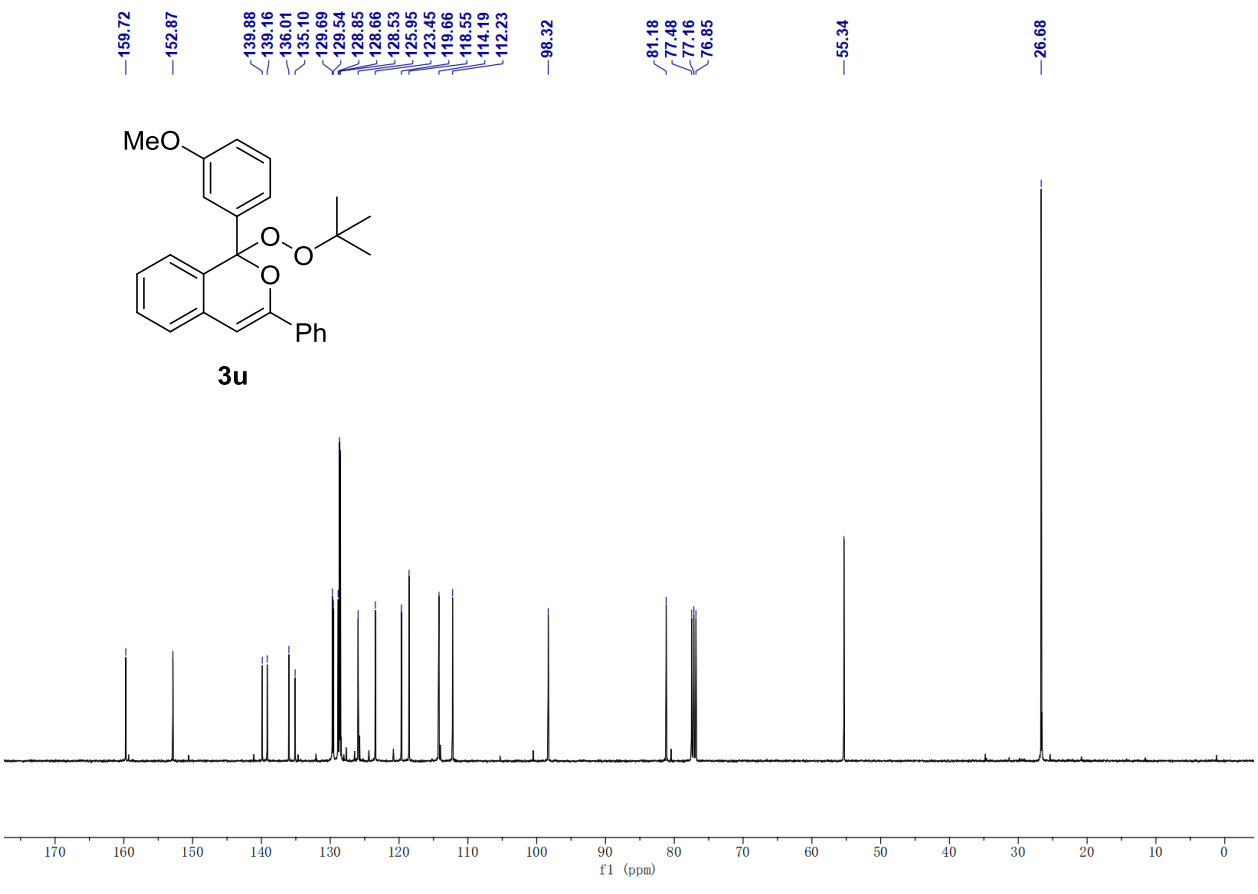

152.97
139.37
138.25
136.07
135.10
129.87
129.40
128.81
128.64
128.50
128.47
126.63
125.86
123.45
123.24
119.59
114.47
98.09
81.11
77.44
77.12
76.80
26.67
21.70
O
O
O
Ph
f1 (ppm)

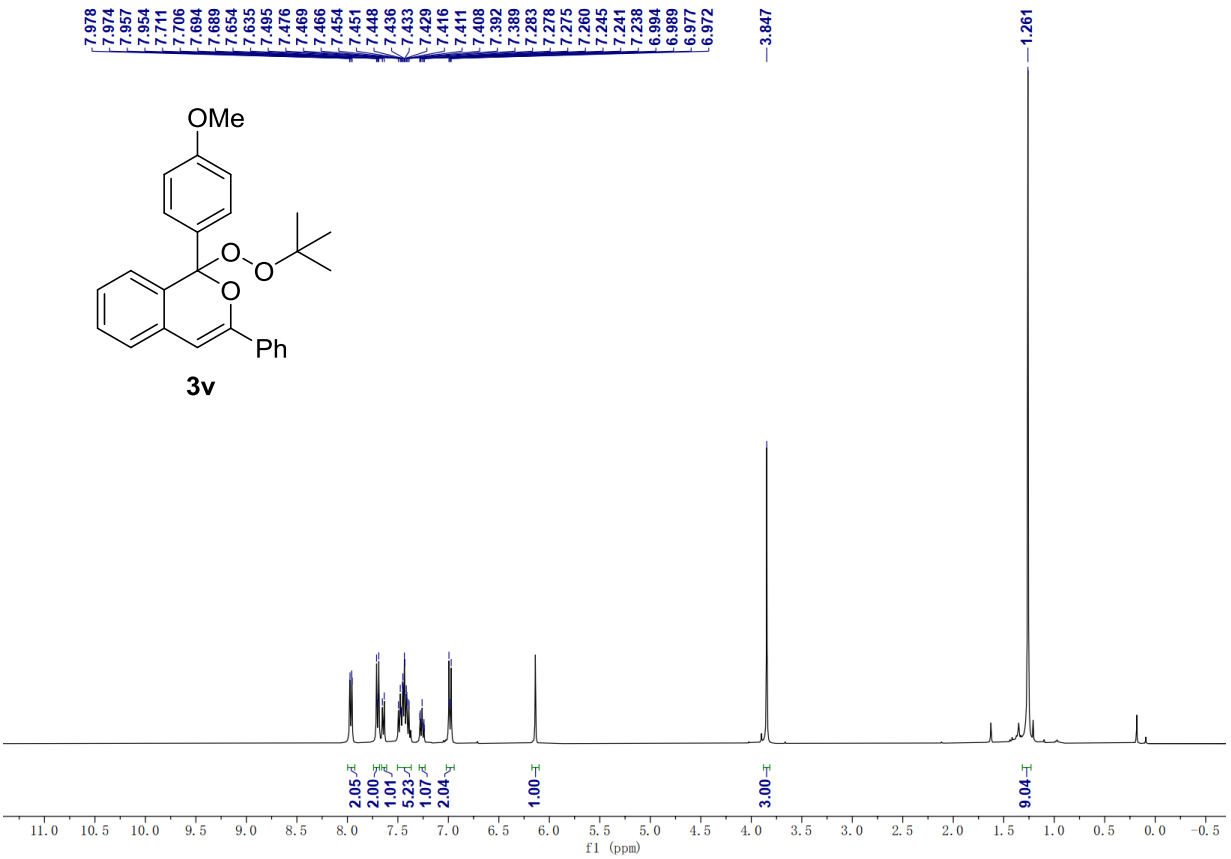
3s

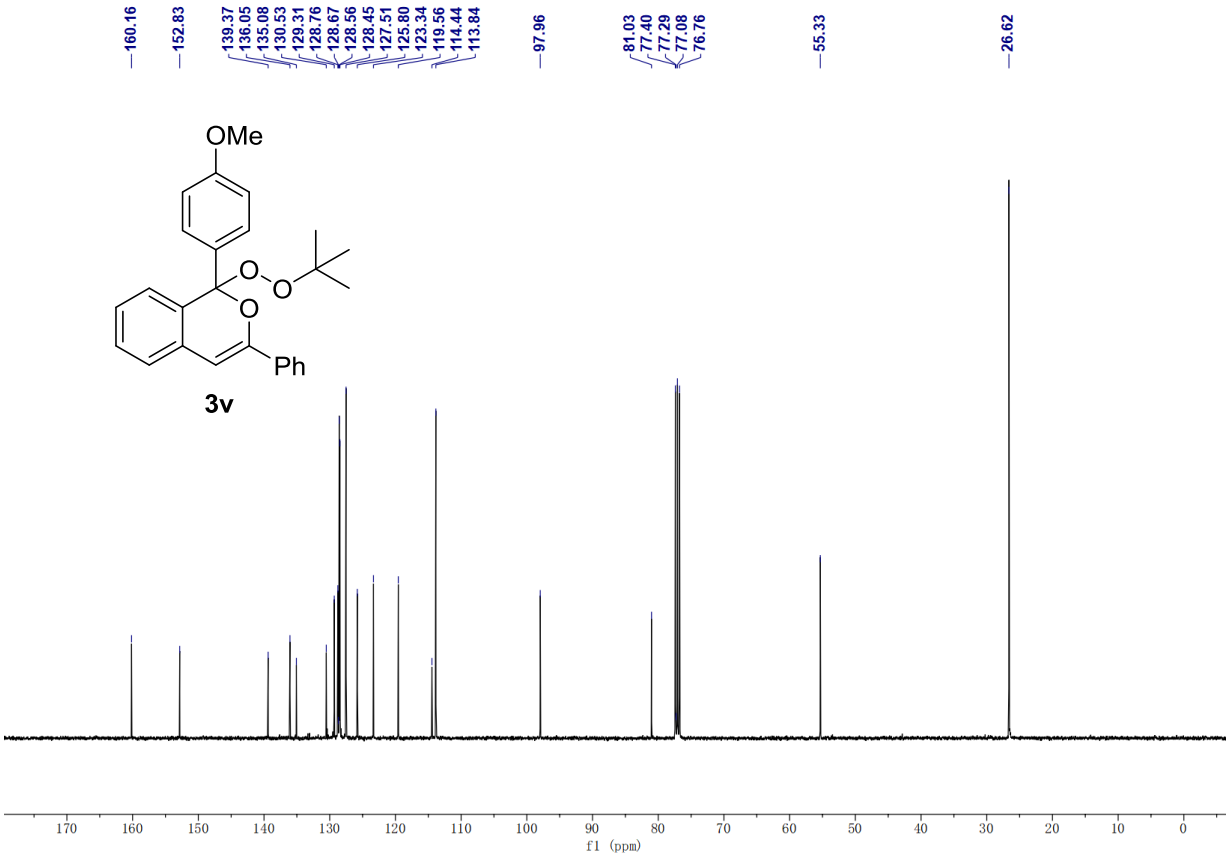

7.880
7.861
7.717
7.698
7.657
7.638
7.481
7.464
7.448
7.444
7.381
7.363
7.346
7.300
7.283
7.277
7.260
7.238
7.218
7.200
6.128
2.431
1.205
O
O
O
Ph
3t
2.03
1.06
1.06
1.18
4.11
4.03
1.00
3.00
9.14
f1 (ppm)

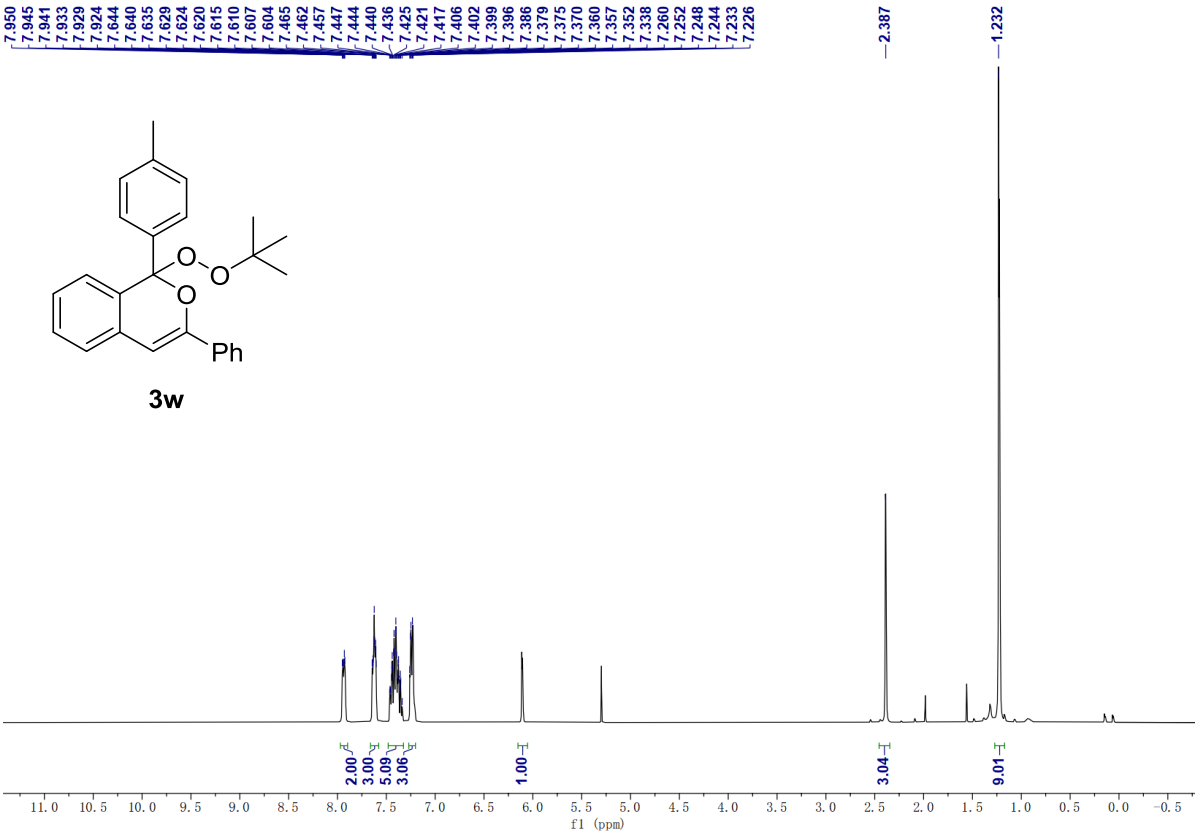

152.80
138.37
137.39
136.11
135.92
135.61
132.38
129.46
129.03
128.60
128.47
128.39
127.42
125.82
125.55
123.96
119.35
115.40
98.45
80.89
77.38
77.06
76.74
26.64
21.25
O
O
O
Ph
3t
f1 (ppm)

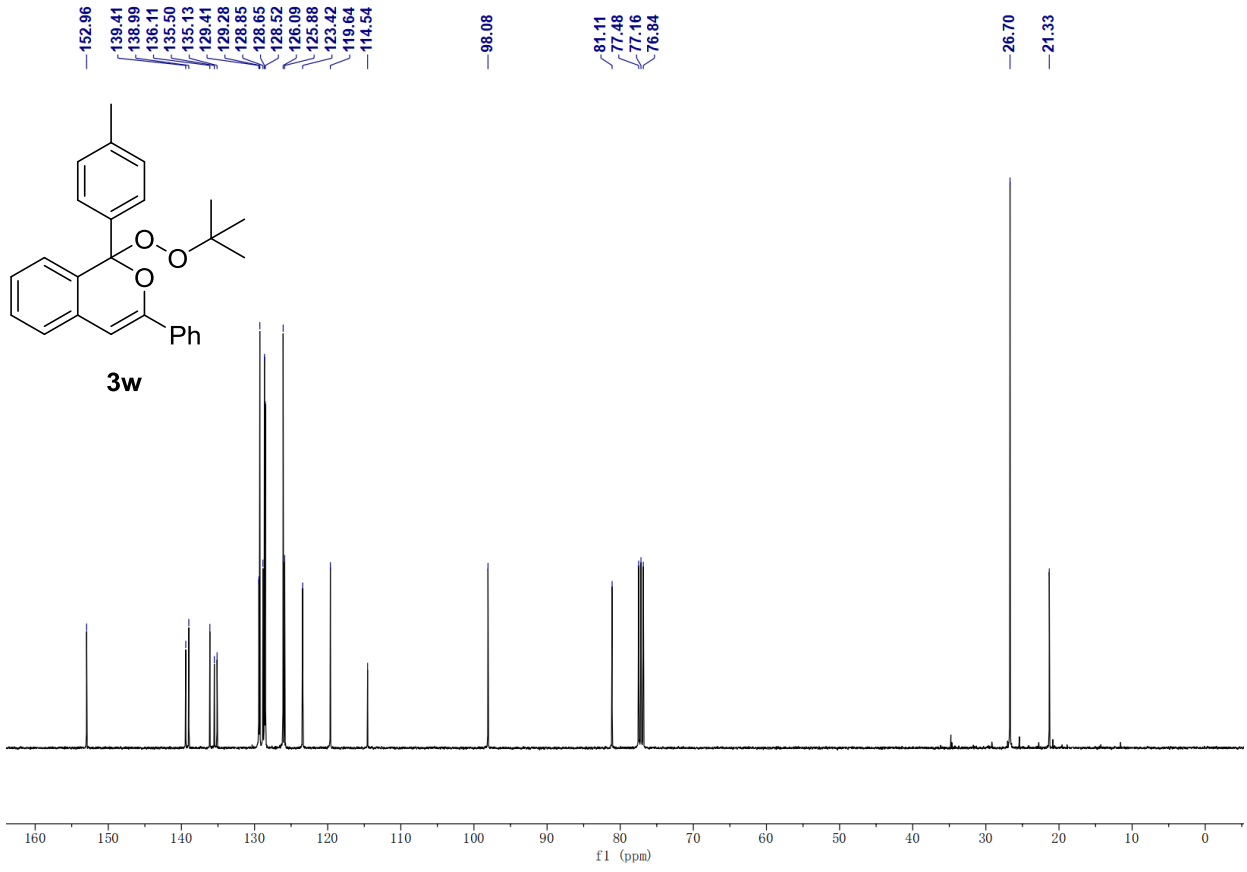

7.988
7.969
7.648
7.629
7.507
7.489
7.461
7.457
7.453
7.443
7.438
7.435
7.424
7.424
7.417
7.407
7.394
7.384
7.380
7.377
7.369
7.357
7.351
7.347
7.344
7.340
7.281
7.277
7.260
7.252
7.244
7.240
6.977
6.968
6.962
6.954
6.946
6.938
6.156
3.838
1.269
MeO
O
O
O
Ph
3u
2.17
1.08
1.21
3.20
4.07
1.16
1.03
1.00
3.07
9.03
f1 (ppm)

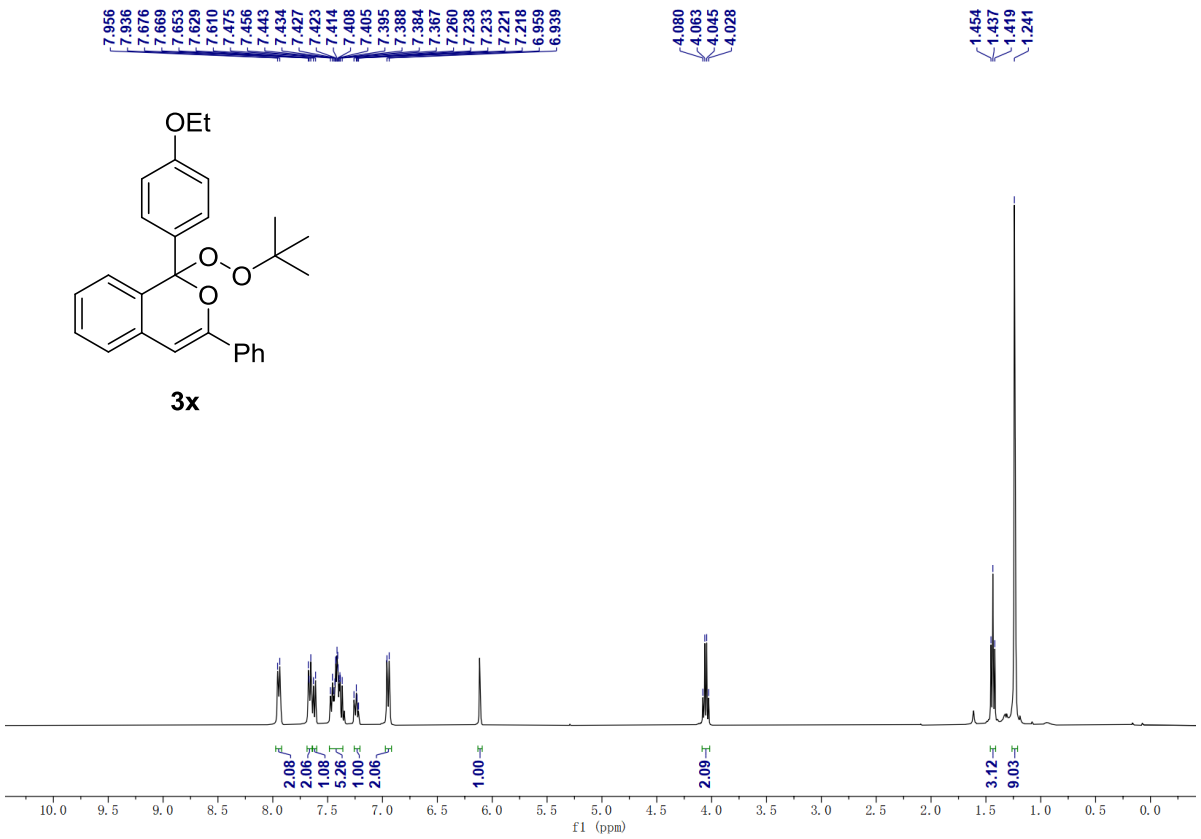

159.72
152.87
139.88
139.16
136.01
135.10
129.69
129.54
128.85
128.66
128.53
125.95
123.45
119.66
118.55
114.19
112.23
98.32
81.18
77.48
77.16
76.85
55.34
26.68
MeO
O
O
O
Ph
3u
f1 (ppm)

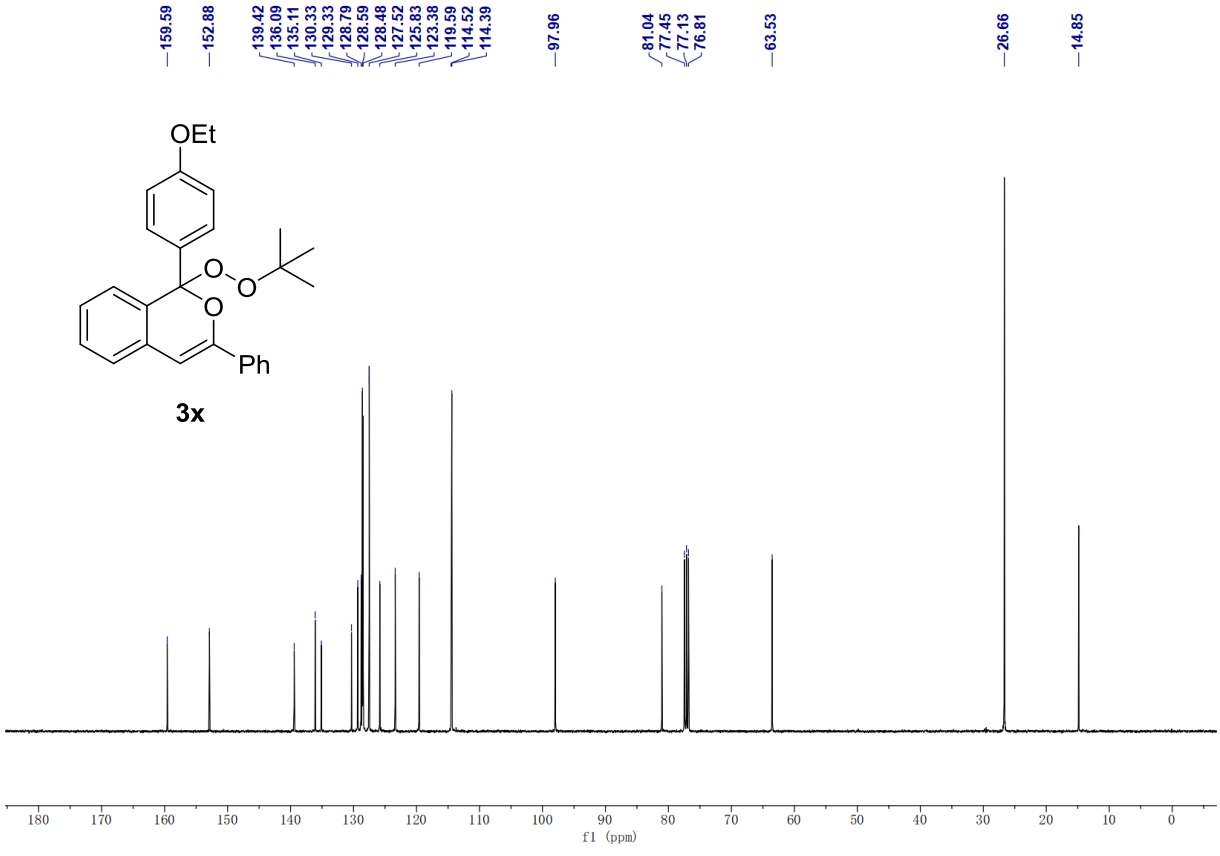

7.978
7.974
7.957
7.954
7.711
7.706
7.694
7.689
7.654
7.635
7.495
7.476
7.469
7.466
7.454
7.451
7.448
7.436
7.433
7.429
7.416
7.411
7.408
7.392
7.389
7.283
7.278
7.275
7.260
7.245
7.241
7.238
6.994
6.989
6.977
6.972
3.847
1.261
OMe
O
O
O
Ph
3v
2.05
2.00
1.01
5.23
1.07
2.04
1.00
3.00
9.04
f1 (ppm)

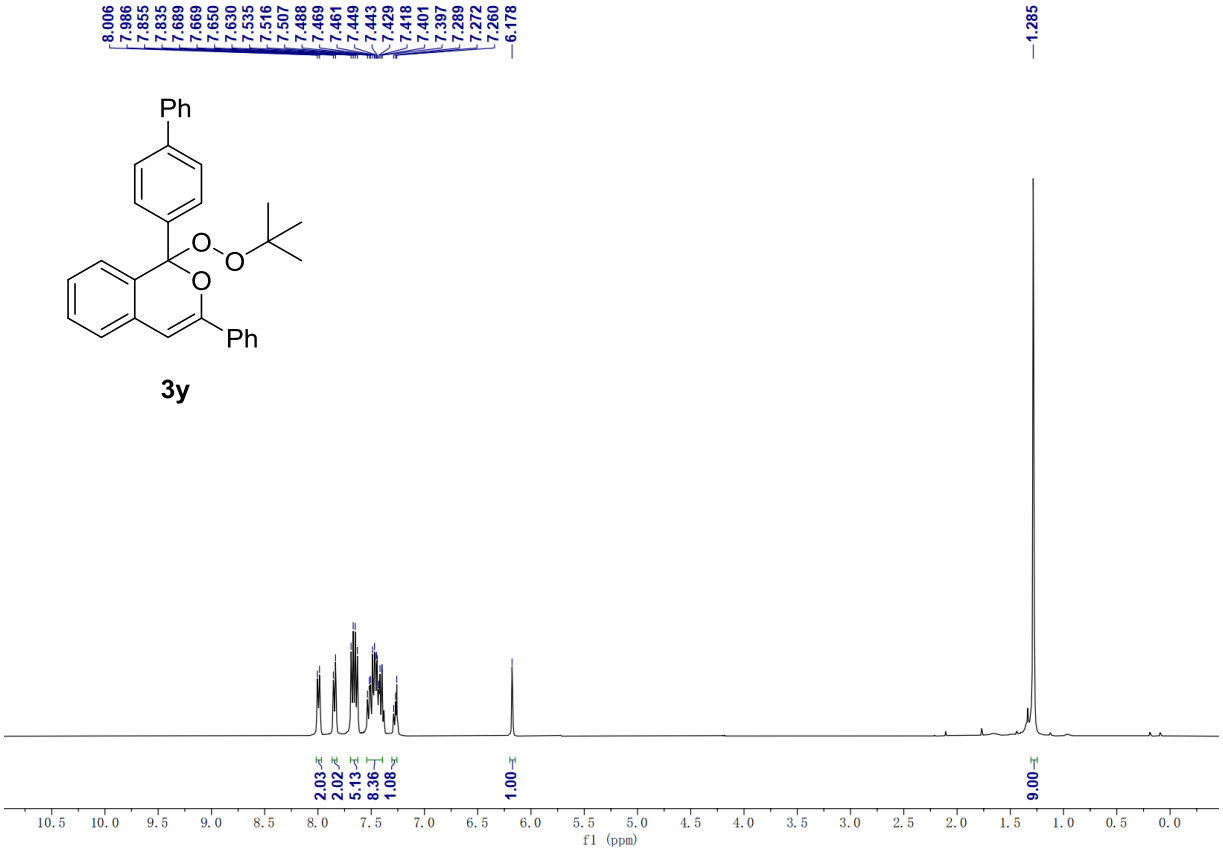

160.16
152.83
139.37
136.05
135.08
130.53
129.31
128.76
128.67
128.56
128.45
127.51
125.80
123.34
119.56
114.44
113.84
97.96
81.03
77.40
77.29
77.08
76.76
55.33
26.62
OMe
O
O
O
Ph
3v
f1 (ppm)


7.950
7.945
7.941
7.933
7.929
7.924
7.644
7.640
7.635
7.629
7.624
7.620
7.615
7.610
7.607
7.604
7.465
7.462
7.457
7.447
7.444
7.440
7.436
7.425
7.421
7.417
7.406
7.402
7.399
7.396
7.386
7.379
7.375
7.370
7.360
7.357
7.352
7.338
7.260
7.252
7.248
7.244
7.233
7.226
2.387
1.232
O
O
O
Ph
3w
2.00
3.00
5.09
3.06
1.00
3.04
9.01
f1 (ppm)

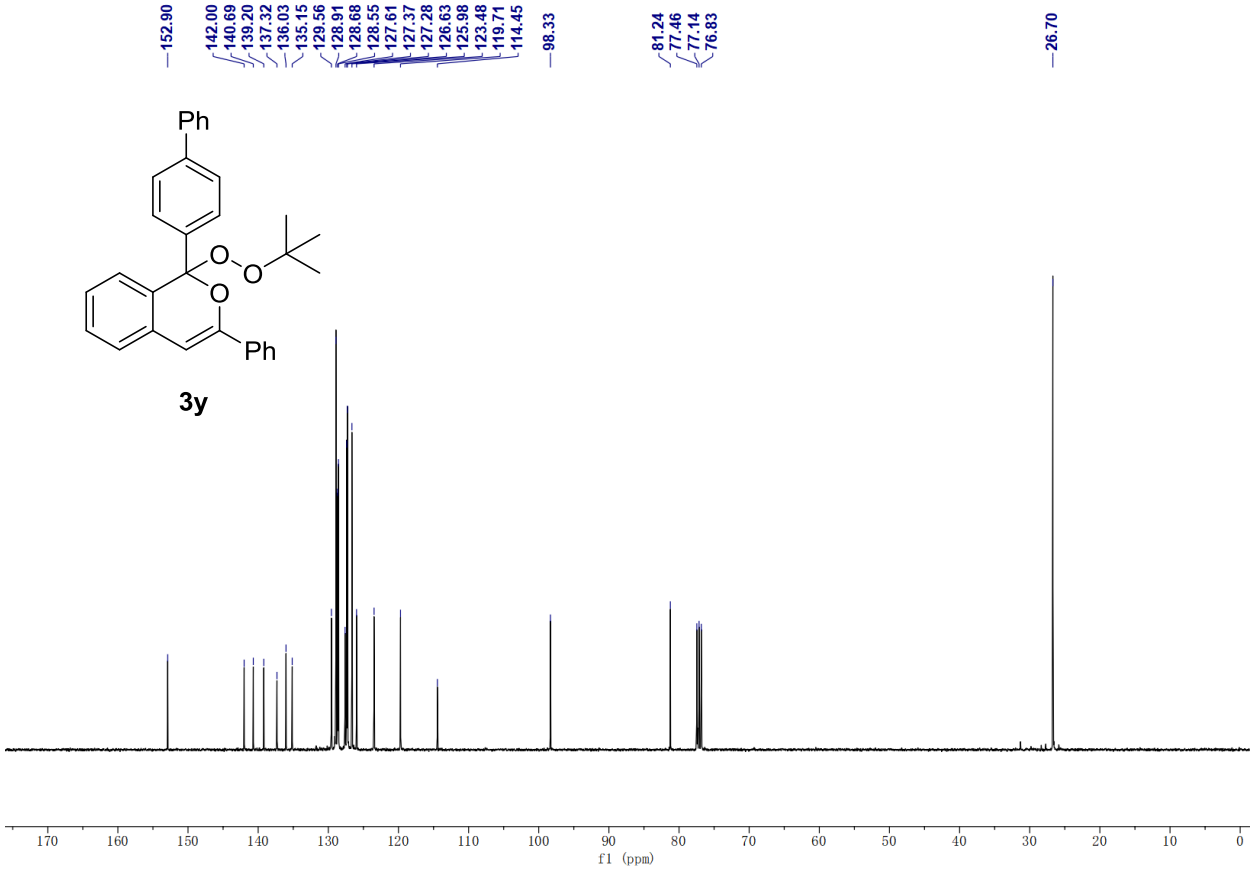

152.96
139.41
138.99
136.11
135.50
135.13
129.41
129.28
128.85
128.65
128.52
126.09
125.88
123.42
119.64
114.54
98.08
81.11
77.48
77.16
76.84
26.70
21.33
O
O
O
Ph
3w
f1 (ppm)


7.956
7.936
7.676
7.669
7.653
7.629
7.610
7.475
7.456
7.443
7.434
7.427
7.423
7.414
7.408
7.405
7.395
7.388
7.384
7.367
7.260
7.238
7.233
7.221
7.218
6.959
6.939
4.080
4.063
4.045
4.028
1.454
1.437
1.419
1.241
OEt
O
O
O
Ph
3x
2.08
2.06
1.08
5.26
1.00
2.06
1.00
2.09
3.12
9.03
f1 (ppm)

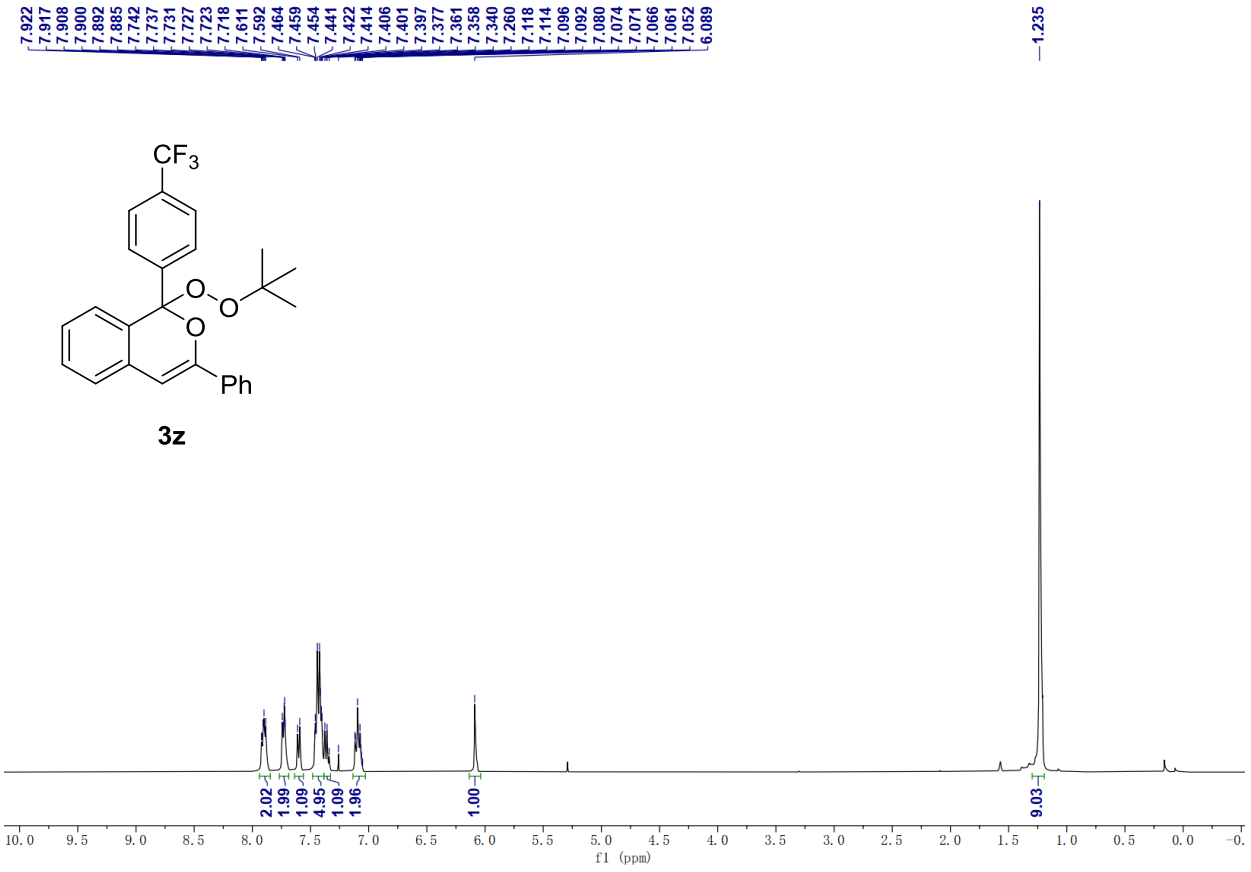

159.59
152.88
139.42
136.09
135.11
130.33
129.33
128.79
128.59
128.48
127.52
125.83
123.38
119.59
114.52
114.39
97.96
81.04
77.45
77.13
76.81
63.53
26.66
14.85
OEt
O
O
O
Ph
3x
f1 (ppm)


8.006
7.986
7.855
7.835
7.689
7.669
7.650
7.630
7.535
7.516
7.507
7.488
7.469
7.461
7.449
7.443
7.429
7.418
7.401
7.397
7.289
7.272
7.260
6.178
1.285
Ph
O
O
O
Ph
2.03
2.02
5.13
8.36
1.08
1.00
9.00
f1 (ppm)

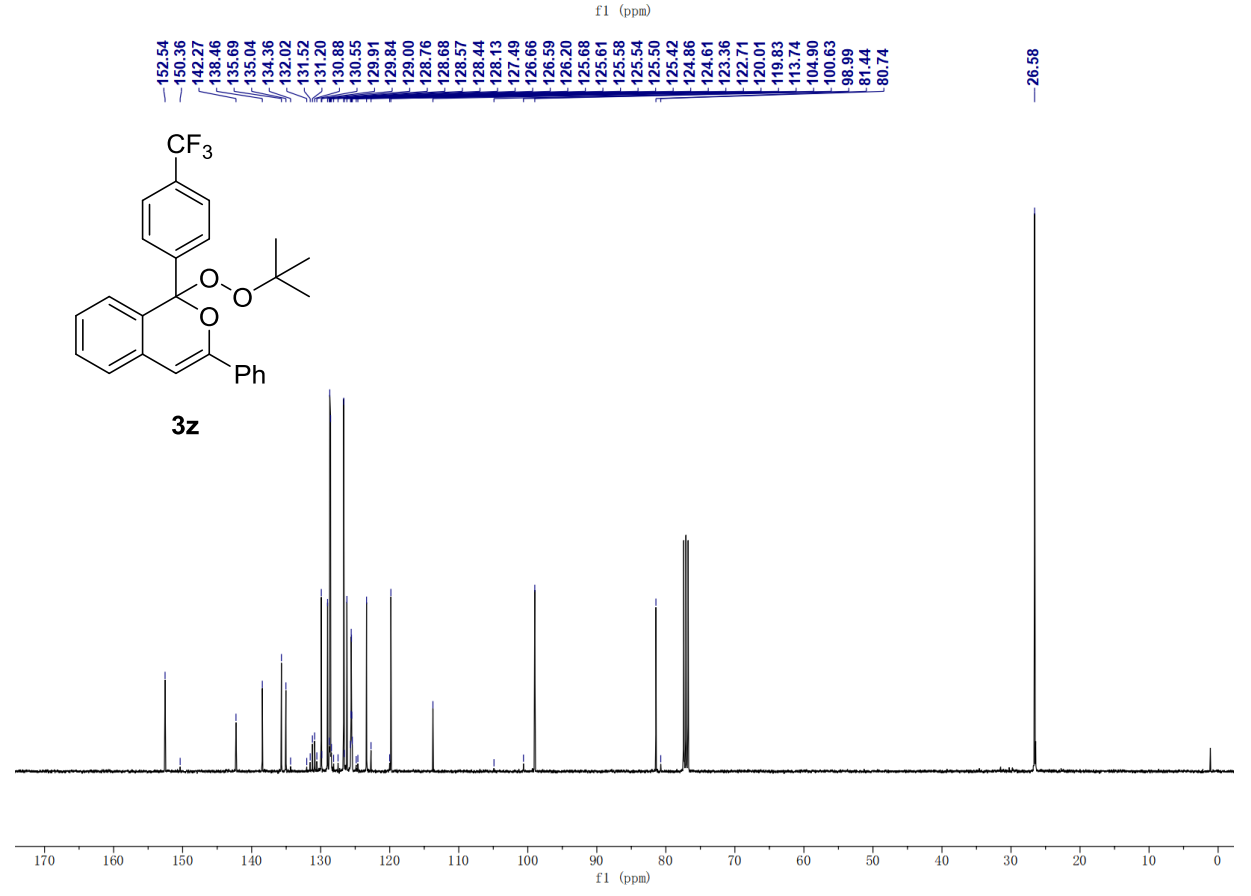
3y


152.90
142.00
140.69
139.20
137.32
136.03
135.15
129.56
128.91
128.68
128.55
127.61
127.37
127.28
126.63
125.98
123.48
119.71
114.45
98.33
81.24
77.46
77.14
76.83
26.70
Ph
O
O
O
Ph
f1 (ppm)

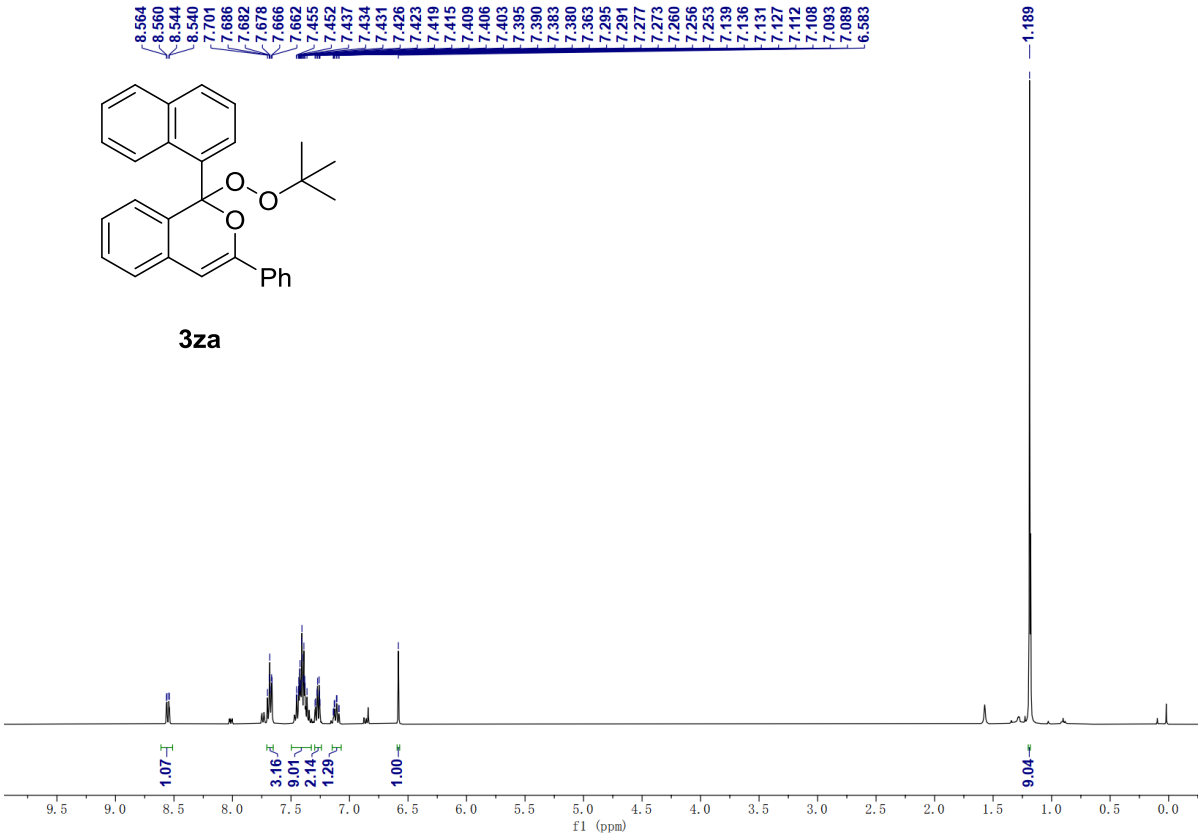
3y


7.922
7.917
7.908
7.900
7.892
7.885
7.742
7.737
7.731
7.727
7.723
7.718
7.611
7.592
7.464
7.459
7.454
7.441
7.422
7.414
7.406
7.401
7.397
7.377
7.361
7.358
7.340
7.260
7.118
7.114
7.096
7.092
7.080
7.074
7.071
7.066
7.061
7.052
6.089
1.235
CF3
O
O
O
Ph
2.02
1.99
1.09
4.95
1.09
1.96
1.00
9.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

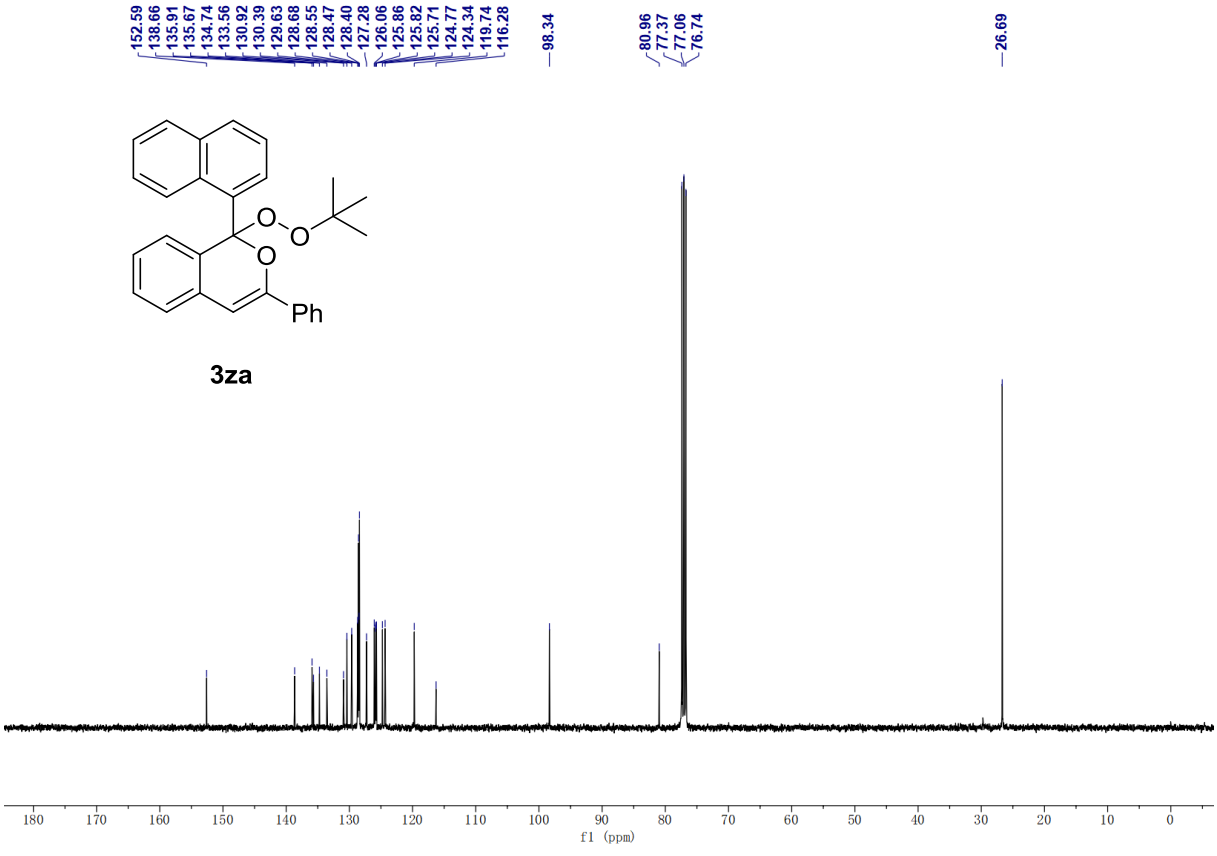
3z


152.54
150.36
142.27
138.46
135.69
135.04
134.36
132.02
131.52
131.20
130.88
130.55
129.91
129.84
129.00
128.76
128.68
128.57
128.44
128.13
127.49
126.66
126.59
126.20
125.68
125.61
125.58
125.54
125.50
125.42
124.86
124.61
123.36
122.71
120.01
119.83
113.74
104.90
100.63
98.99
81.44
80.74
26.58
CF3
O
O
O
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

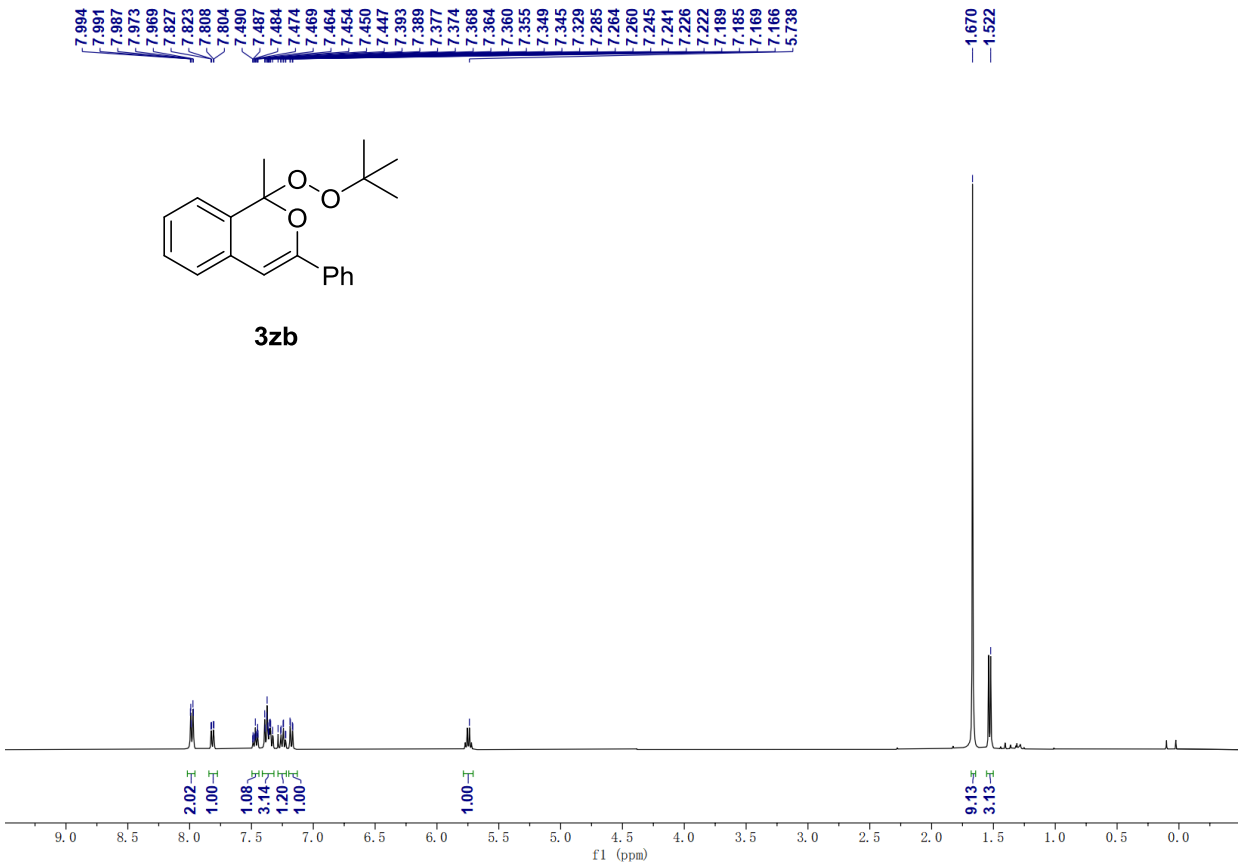
3z


8.564
8.560
8.544
8.540
7.701
7.686
7.682
7.678
7.666
7.662
7.455
7.452
7.437
7.434
7.431
7.426
7.423
7.419
7.415
7.409
7.406
7.403
7.395
7.390
7.383
7.380
7.363
7.295
7.291
7.277
7.273
7.260
7.256
7.253
7.139
7.136
7.131
7.127
7.112
7.108
7.093
7.089
6.583
1.189
O
O
O
Ph
1.07
3.16
9.01
2.14
1.29
1.00
9.04
f1 (ppm)

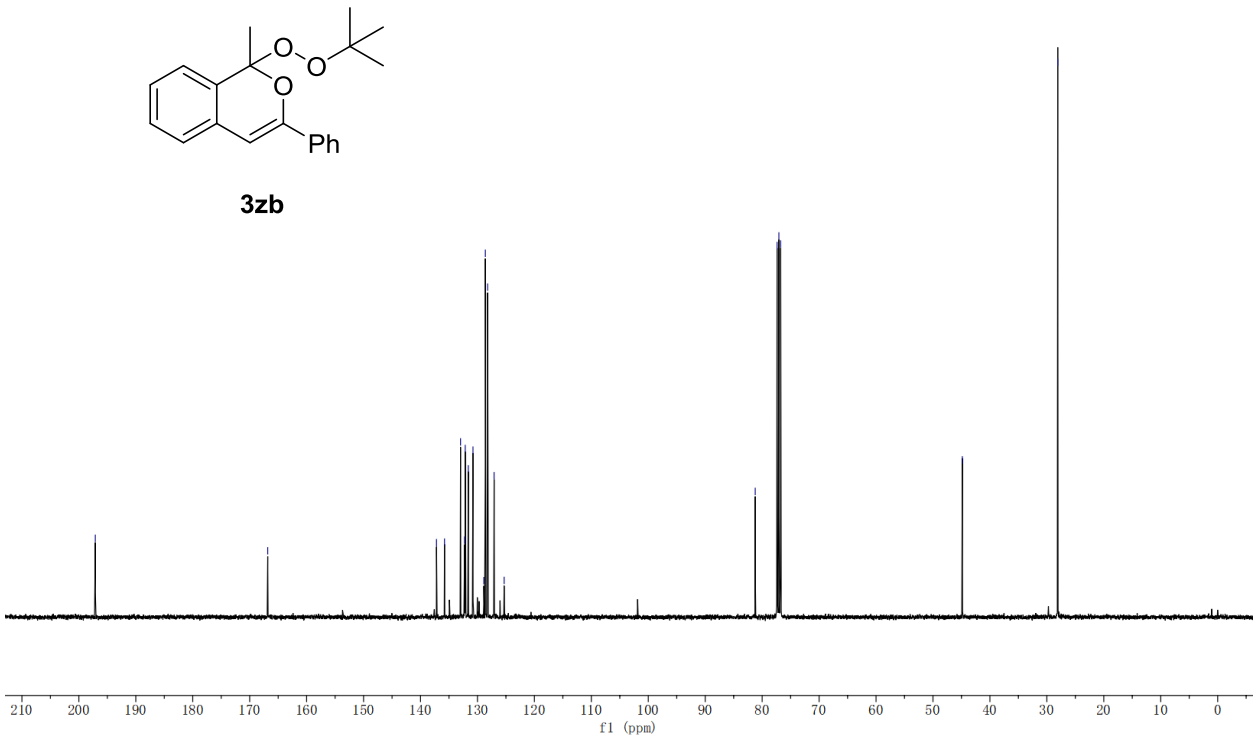
3za


152.59
138.66
135.91
135.67
134.74
133.56
130.92
130.39
129.63
128.68
128.55
128.47
128.40
127.28
126.06
125.86
125.82
125.71
124.77
124.34
119.74
116.28
98.34
80.96
77.37
77.06
76.74
26.69
O
O
O
Ph
f1 (ppm)

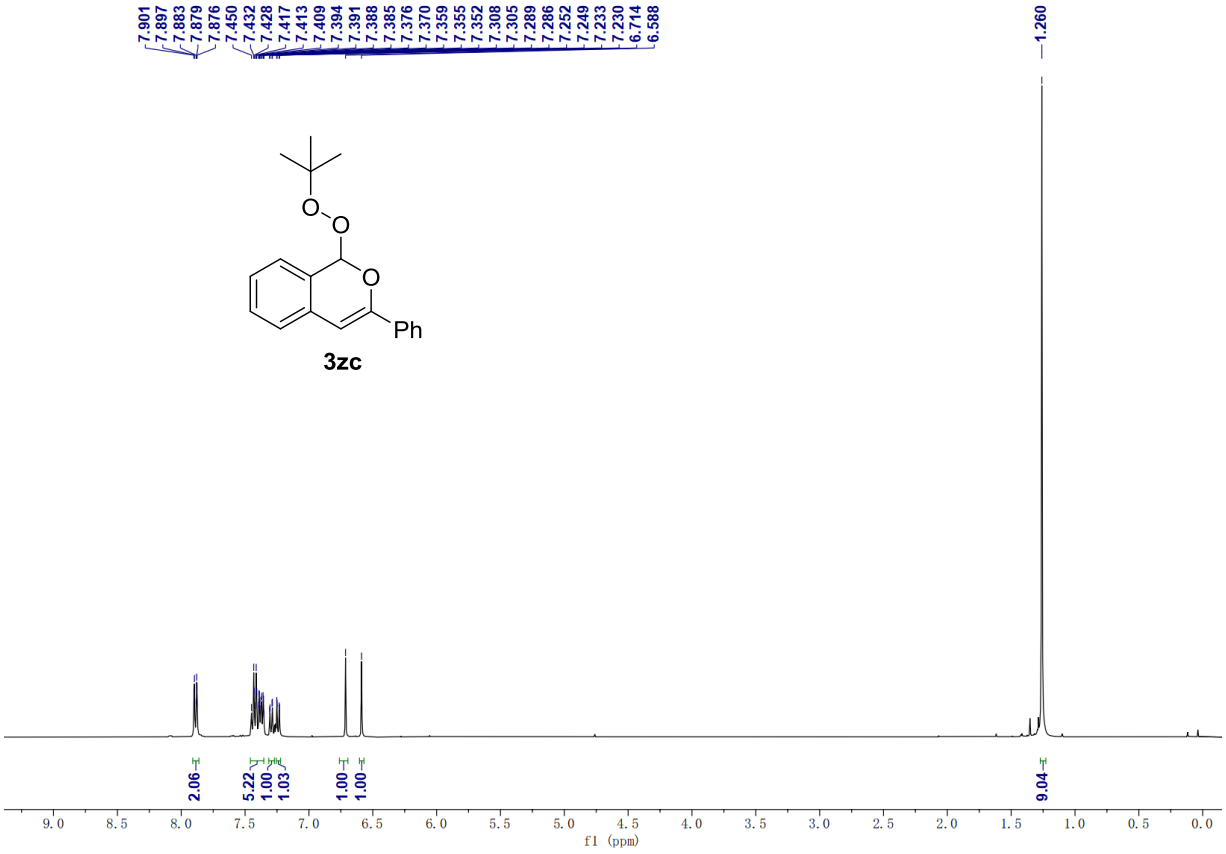
3za


7.994
7.991
7.987
7.973
7.969
7.827
7.823
7.808
7.804
7.490
7.487
7.484
7.474
7.469
7.464
7.454
7.450
7.447
7.393
7.389
7.377
7.374
7.368
7.364
7.360
7.355
7.349
7.345
7.329
7.285
7.264
7.260
7.245
7.241
7.226
7.222
7.189
7.185
7.169
7.166
5.738
1.670
1.522
O
O
O
Ph
2.02
1.00
1.08
3.14
1.20
1.00
1.00
9.13
3.13
f1 (ppm)

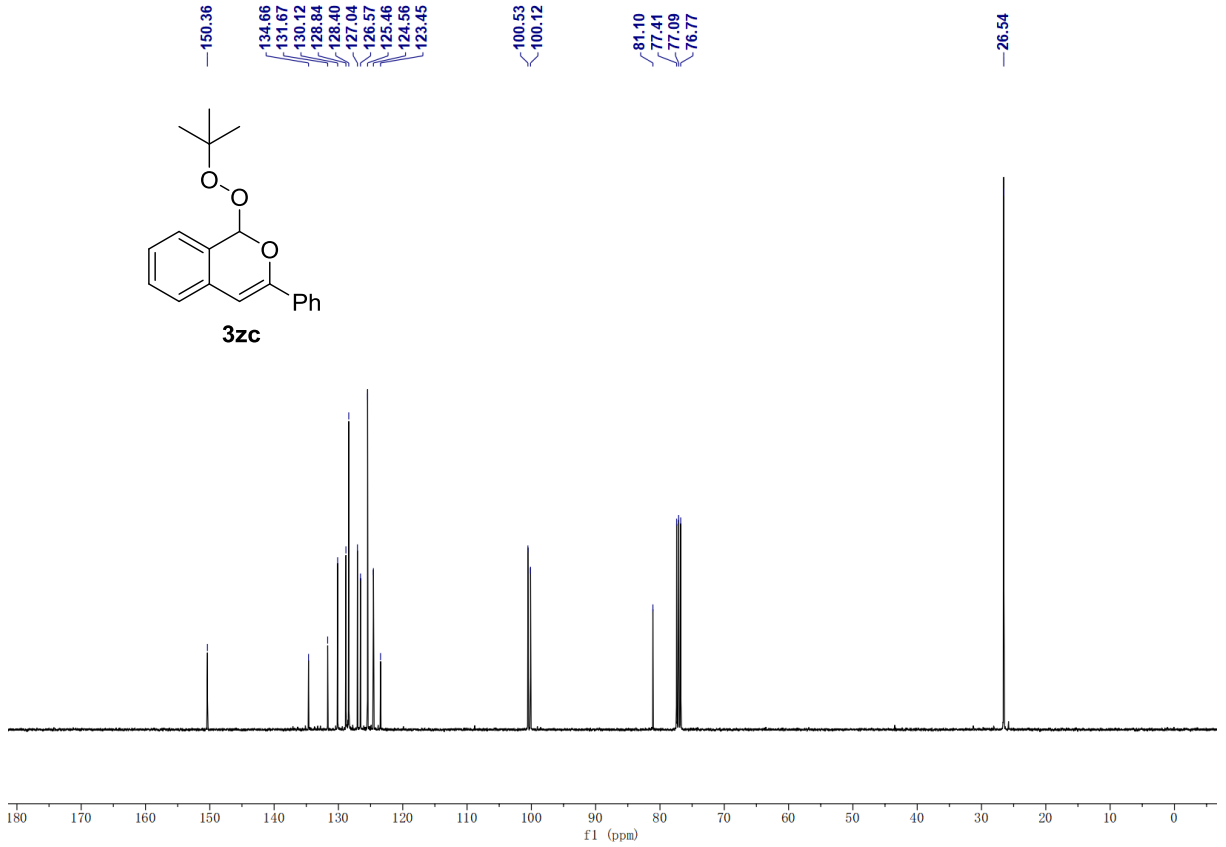
3zb


197.11
166.83
137.19
135.79
132.97
132.26
132.14
131.60
130.79
128.88
128.61
128.22
127.08
125.31
81.22
77.38
77.06
76.74
44.85
28.08
O
O
O
Ph
f1 (ppm)

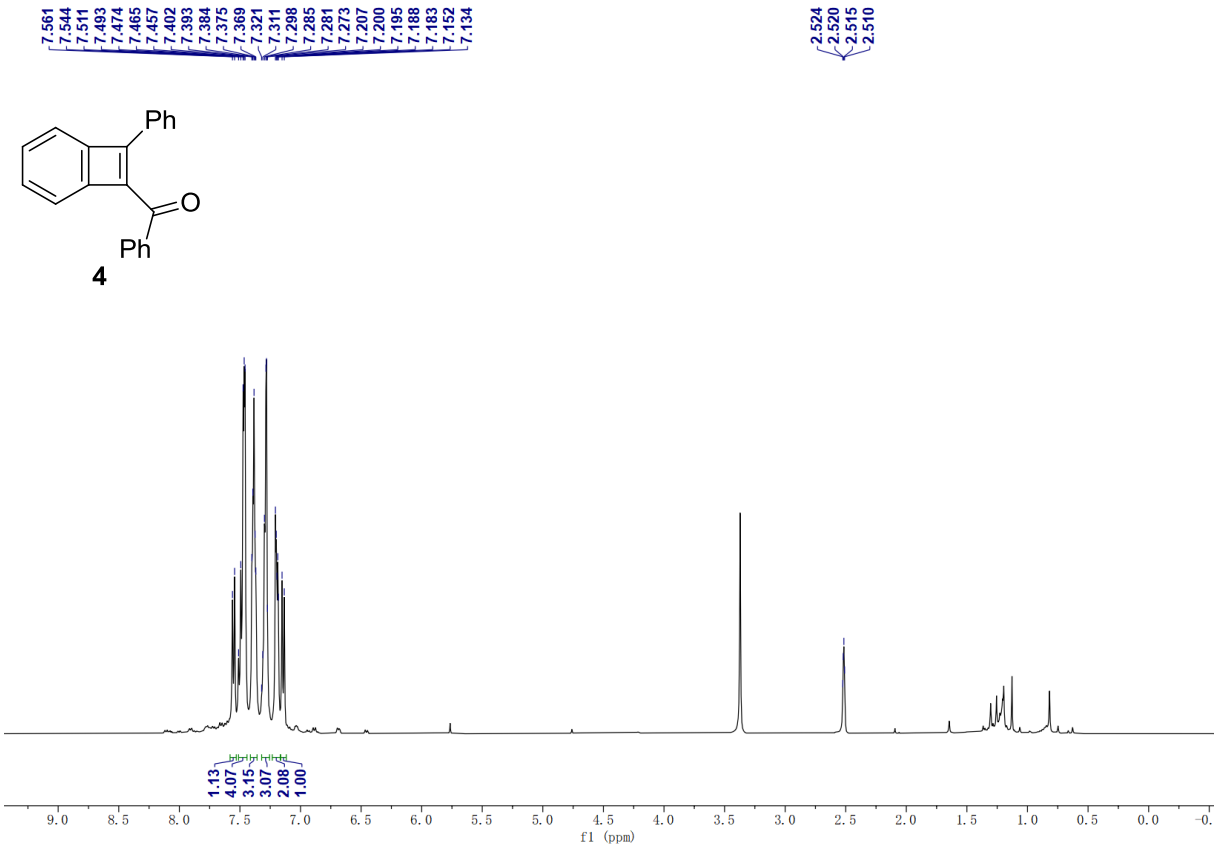
3zb

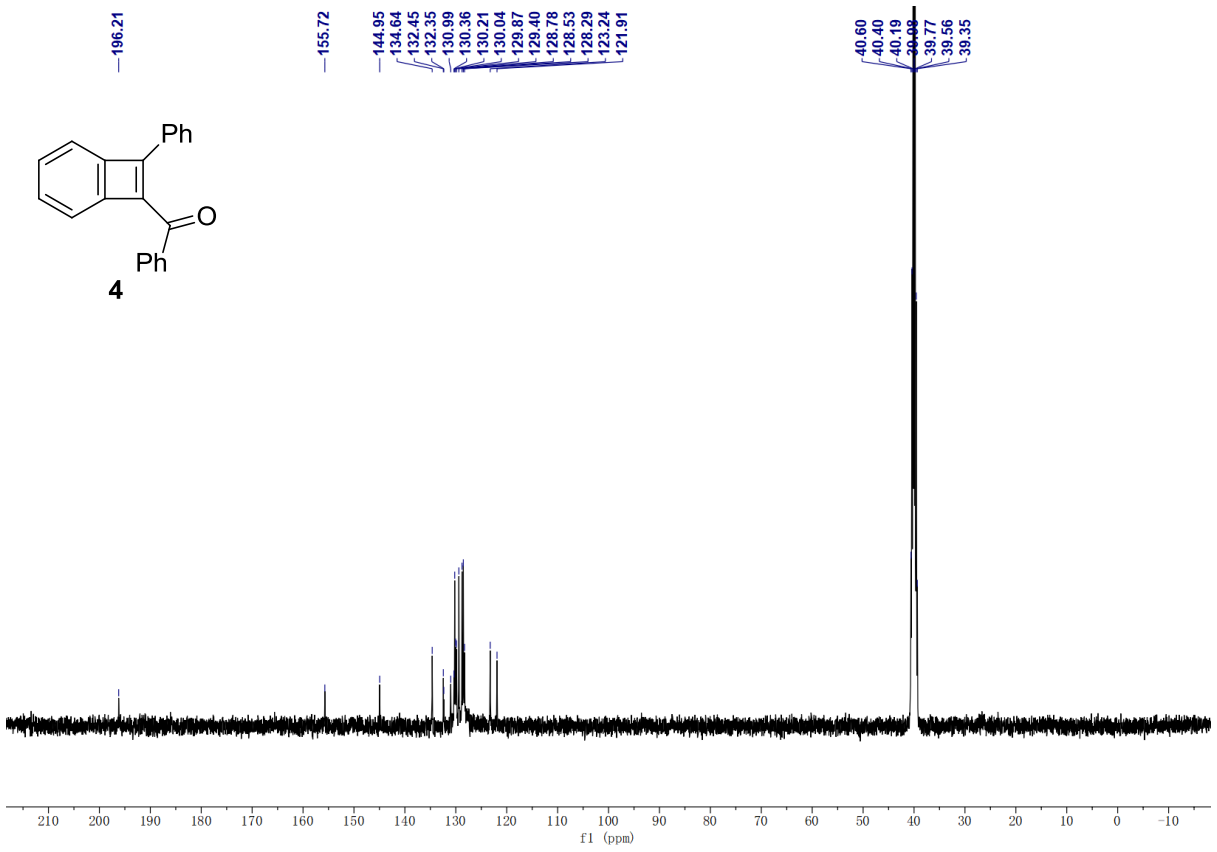

7.901
7.897
7.883
7.879
7.876
7.450
7.432
7.428
7.417
7.413
7.409
7.394
7.391
7.388
7.385
7.376
7.370
7.359
7.355
7.352
7.308
7.305
7.289
7.286
7.252
7.249
7.233
7.230
6.714
6.588
1.260
O
O
O
Ph
2.06
5.22
1.00
1.03
1.00
1.00
9.04
f1 (ppm)

3zc

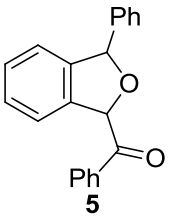

150.36
134.66
131.67
130.12
128.84
128.40
127.04
126.57
125.46
124.56
123.45
100.53
100.12
81.10
77.41
77.09
76.77
26.54
O
O
O
Ph
f1 (ppm)

3zc

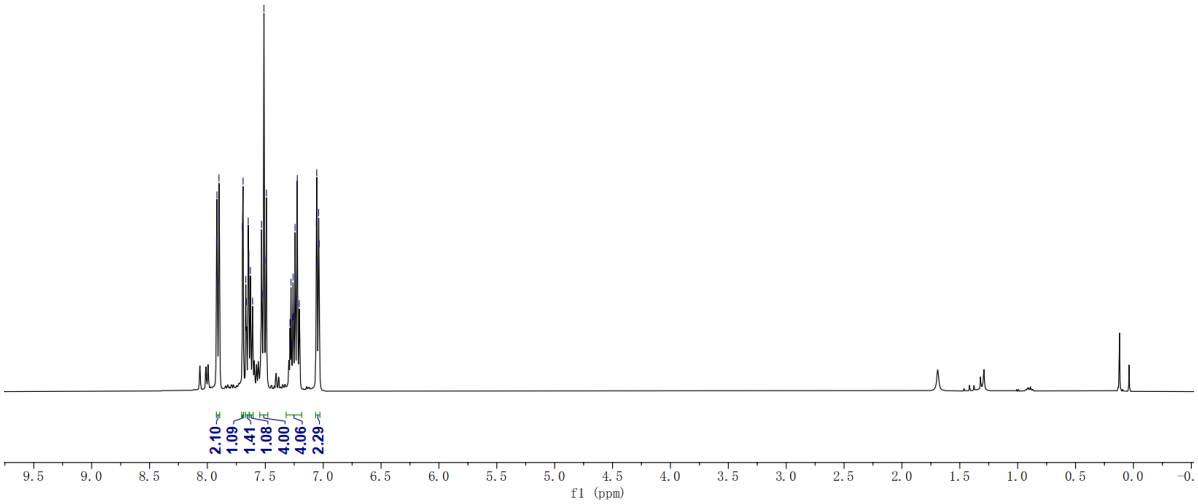

7.561
7.544
7.511
7.493
7.474
7.465
7.457
7.402
7.393
7.384
7.375
7.369
7.321
7.311
7.298
7.285
7.281
7.273
7.207
7.200
7.195
7.188
7.183
7.152
7.134
2.524
2.520
2.515
2.510
Ph
O
Ph
4
1.13
4.07
3.15
3.07
2.08
1.00
f1 (ppm)

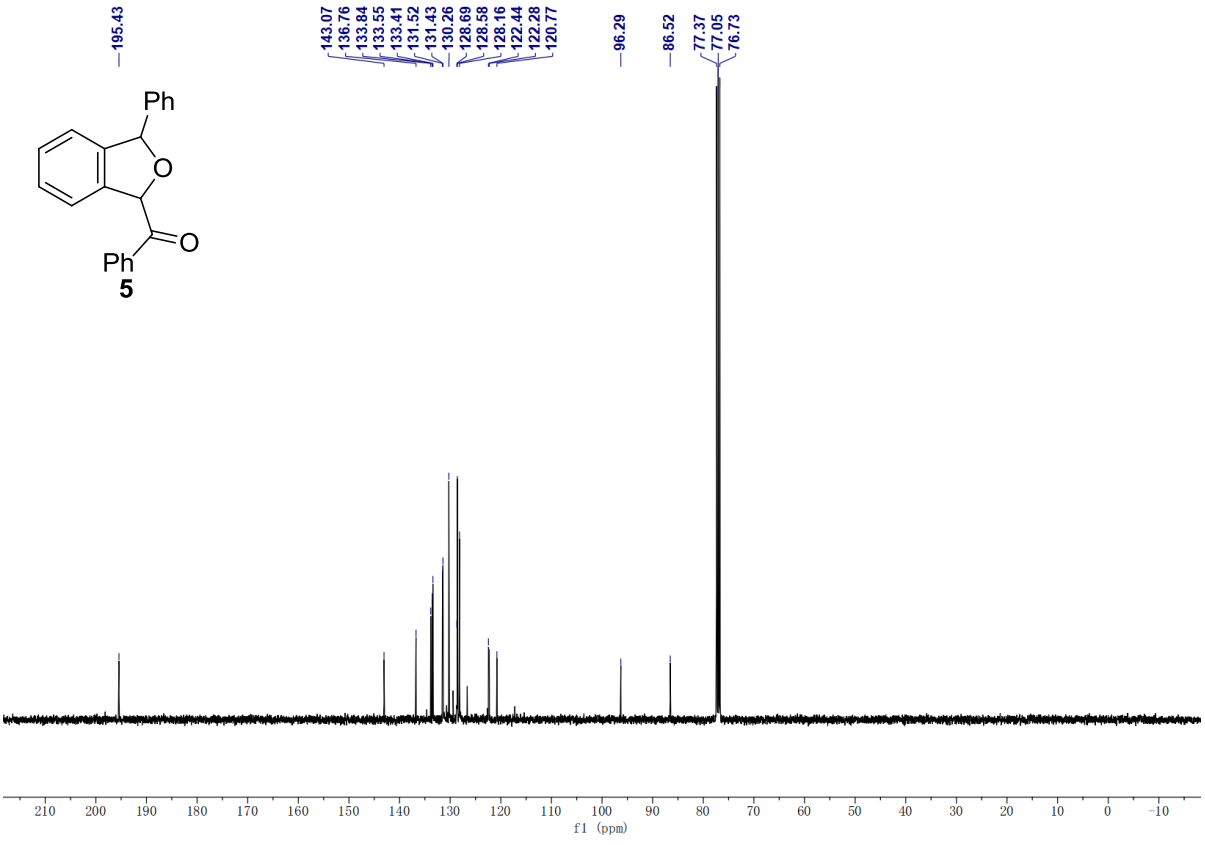

196.21
155.72
144.95
134.64
132.45
132.35
130.99
130.36
130.21
130.04
129.87
129.40
128.78
128.53
128.29
123.24
121.91
40.60
40.40
40.19
39.77
39.56
39.35
Ph
O
Ph
4
f1 (ppm)


7.921
7.918
7.914
7.900
7.896
7.697
7.692
7.668
7.663
7.648
7.643
7.629
7.610
7.532
7.528
7.512
7.494
7.490
7.287
7.278
7.271
7.264
7.260
7.256
7.243
7.239
7.228
7.224
7.207
7.059
7.056
7.052
7.039
7.034


Ph
O
O
Ph

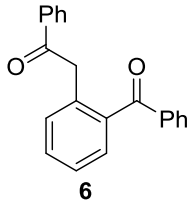
5


2.10
1.09
1.41
1.08
4.00
4.06
2.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

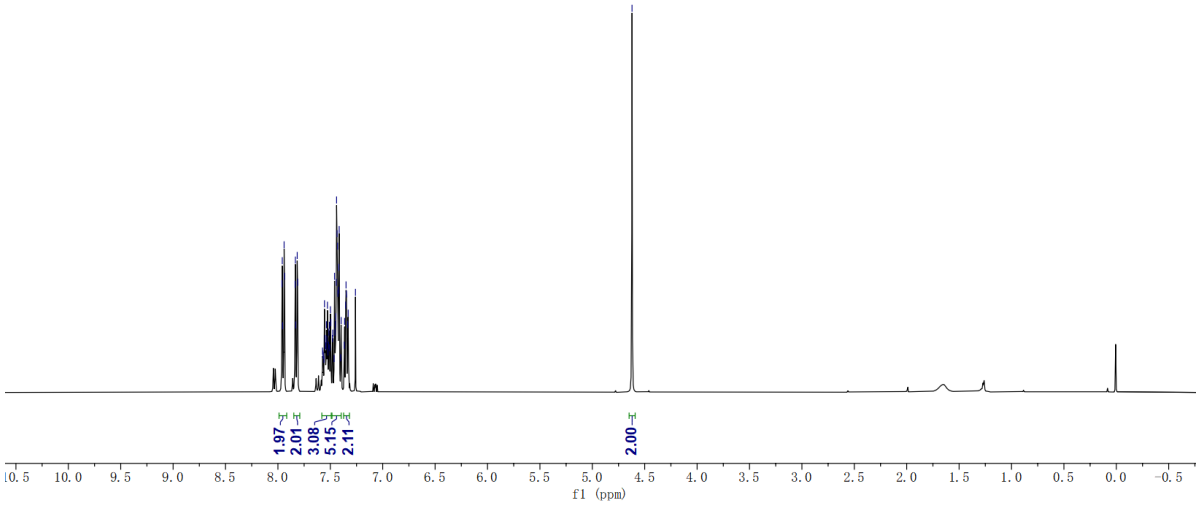

195.43
143.07
136.76
133.84
133.55
133.41
131.52
131.43
130.26
128.69
128.58
128.16
122.44
122.28
120.77
96.29
86.52
77.37
77.05
76.73
Ph
O
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5

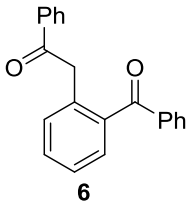

7.961
7.959
7.955
7.941
7.937
7.836
7.833
7.830
7.816
7.812
7.574
7.570
7.568
7.561
7.556
7.550
7.546
7.541
7.537
7.533
7.528
7.523
7.518
7.513
7.509
7.506
7.499
7.495
7.480
7.476
7.464
7.460
7.456
7.452
7.447
7.443
7.440
7.436
7.431
7.428
7.422
7.419
7.415
7.401
7.397
7.367
7.363
7.354
7.350
7.346
7.334
7.330
7.260
4.621


Ph
O
O
Ph

6


1.97
2.01
3.08
5.15
2.11
2.00
f1 (ppm)


198.39
197.13
138.36
137.96
136.85
134.74
133.08
132.82
132.12
130.99
130.44
130.33
128.57
128.28
126.31
77.37
77.05
76.74
43.17


Ph
O
O
Ph

6

f1 (ppm)