ATRA-like alkylation-peroxidation of alkenes with trichloromethyl derivatives by the combination of tBuOOH and NEt_3

Cui Chen[a], Hua Tan[a], Bifu Liu[b] Yue Chaochao[a], and Weibing Liu[a,*]

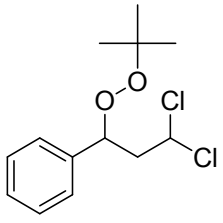
[a] College of Chemical Engineering, Guangdong University of Petrochemical Technology, 2 Guandu Road, Maoming 525000, P. R. China; Email address: lwb409@gdupt.edu.cn

[b] School of Chemistry and Material Engineering, Huizhou University, Huizhou 516007, China; Email address: liubf@hzu.edu.cn

General Information. All the reactions were carried out at room temperature for 12 h in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard; δ values are given in ppm, and coupling constants (*J*) in Hz. Mass spectra were obtained from high resolution ESI mass spectrometer.

Typical procedure: 1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (2a). A mixture of styrene (**1a**) (208 mg, 2.0 mmol), $CHCl_3$ (0.5 mL), TBHP (774 mg, 6.0 mmol, 70% in water), and Et_3N (2.0 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 12 h at room temperature. The mixture was purified by column chromatography on silica gel to afford product **2a** with PE as the eluent.

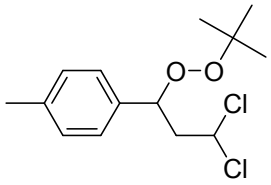
1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (2a)



Yield: 76% (420 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (m, 5H), 5.84 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.13 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.87 (m, 1H), 2.52 (m, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 139.0, 128.5, 128.3, 126.9, 82.3, 80.7, 70.4, 49.4, 26.4; HRMS (ESI):

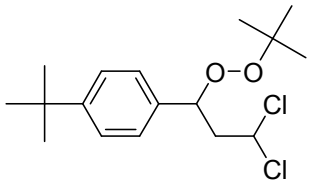
calcd for $C_{13}H_{18}Cl_2NaO_2$: [M+Na$^+$] 299.0576, found 299.0579.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-methylbenzene (2b)



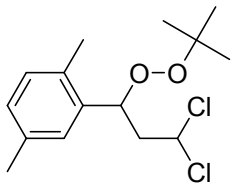
Yield: 81% (470 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.87 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.15 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.95 (m, 1H), 2.54 (m, 1H), 2.41 (s, 3H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 138.2, 135.9, 129.2, 126.9, 82.3, 80.6, 70.6, 49.4, 26.4, 21.2; HRMS (ESI): calcd for $C_{14}H_{20}Cl_2NaO_2$: [M+Na$^+$] 313.0733, found 313.0735.

1-*tert*-butyl-4-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (2c)



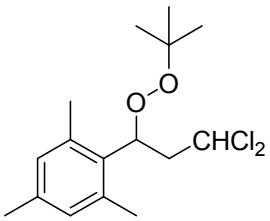
Yield: 82% (544 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.85 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.13 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.91 (m, 1H), 2.55 (m, 1H), 1.35 (s, 9H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 151.3, 135.7, 126.6, 125.5, 82.3, 80.7, 70.7, 49.5, 34.6, 31.3, 26.4; HRMS (ESI): calcd for $C_{17}H_{26}Cl_2NaO_2$: [M+Na$^+$] 355.1202, found 355.1201.

2-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-1,4-dimethylbenzene (2d)



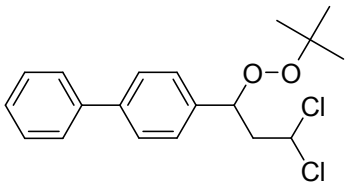
Yield: 77% (468 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.22 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.02 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.45 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.85 (m, 1H), 2.55 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.0, 135.6, 132.2, 130.5, 128.8, 126.9, 80.6, 78.9, 70.9, 49.4, 26.5, 21.1, 18.7; HRMS (ESI): calcd for $C_{15}H_{22}Cl_2NaO_2$: [M+Na$^+$] 327.0889, found 327.0885.

2-(1-(tert-butylperoxy)-3,3-dichloropropyl)-1,3,5-trimethylbenzene (2e)



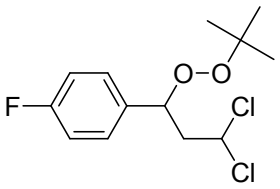
Yield: 83% (529 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 6.88 (s, 2H), 6.10 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 5.66 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 3.07 (m, 1H), 2.52 (m, 1H), 2.45 (s, 6H), 2.31 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.3, 132.3, 80.5, 19.8, 71.4, 48.3, 26.5, 20.8, 20.7; HRMS (ESI): calcd for $C_{16}H_{24}Cl_2NaO_2$: [M+Na$^+$] 341.1046, found 341.1055.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-phenylbenzene (2f)



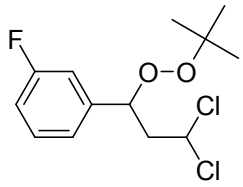
Yield: 81% (570 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.61 (d, J = 7.6 Hz, 4H), 7.45 (m, 4H), 7.37 (t, J = 7.6 Hz, 1H), 5.88 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 5.19 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 2.91 (m, 1H), 2.57 (m, 1H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 141.3, 140.6, 138.0, 128.8, 127.4, 127.4, 127.3, 127.1, 82.1, 80.8, 70.4, 49.4, 26.4; HRMS (ESI): calcd for $C_{19}H_{22}Cl_2NaO_2$: [M+Na$^+$] 375.0889, found 375.0893.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-fluorobenzene (2g)



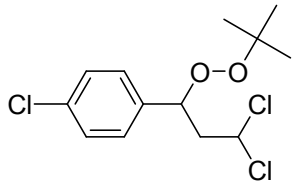
Yield: 80% (470 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.33 (dd, J = 5.6 Hz, J = 8.0 Hz, 2H), 7.06 (t, J = 8.0 Hz, 2H), 5.84 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 5.11 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H), 2.82 (m, 1H), 2.48 (m, 1H), 1.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 162.6 (d, $^{1}J_{C\text{-}F}$ = 241.0 Hz), 134.9 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 128.5 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 81.6, 80.7, 70.2, 49.3, 26.4; HRMS (ESI): calcd for $C_{13}H_{17}Cl_2FNaO_2$: [M+Na$^+$] 317.0482, found 317.0486.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-3-fluorobenzene (2h)



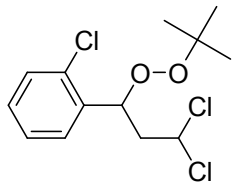
Yield: 82% (482 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.33 (m, 1H), 7.09 (m, 3H), 5.85 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.12 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.79 (m, 1H), 2.49 (m, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 162.9 (d, $^{1}J_{C\text{-}F}$ = 245.0 Hz), 142.0 (d, $^{4}J_{C\text{-}F}$ = 6.7 Hz), 130.1 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 122.3 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 113.7 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 81.6, 80.9, 70.0, 49.3, 26.4; HRMS (ESI): calcd for $C_{13}H_{17}Cl_2FNaO_2$: [M+Na$^+$] 317.0482, found 317.0484.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-chlorobenzene (2i)



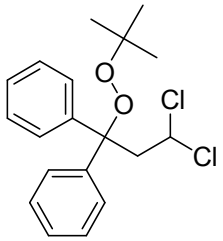
Yield: 78% (484 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.85 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.12 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.80 (m, 1H), 2.45 (m, 1H), 1.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.8, 134.1, 128.7, 128.2, 81.5, 80.8, 70.1, 49.2, 26.4; HRMS (ESI): calcd for $C_{13}H_{17}Cl_3NaO_2$: [M+Na$^+$] 333.0186, found 333.0189.

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-2-chlorobenzene (2j)



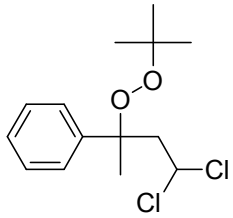
Yield: 74% 459 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 6.04 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 5.65 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 2.62 (m, 2H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.3, 132.2, 129.5, 129.0, 127.7, 127.0, 81.0, 78.8, 70.1, 48.4, 26.4; HRMS (ESI): calcd for $C_{13}H_{17}Cl_3NaO_2$: [M+Na$^+$] 333.0186, found 333.0182.

1-(*tert*-butylperoxy)-3,3-dichloro-1,1-diphenylpropane (2k)



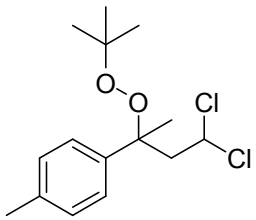
Yield: 84% (591 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.35 (m, 10H), 5.96 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 3.67 (d, *J* = 8.4 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 143.1, 127.9, 127.4, 126.8, 85.1, 76.8, 69.6, 50.5, 26.6; HRMS (ESI): calcd for $C_{19}H_{22}Cl_2NaO_2$: [M+Na$^+$] 375.0889, found 375.0888.

1-(2-(*tert*-butylperoxy)-4,4-dichlorobutan-2-yl)benzene (2l)



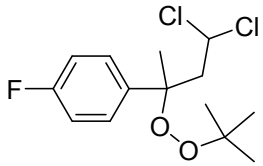
Yield: 79% (458 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 5.78 (t, *J* = 6.0 Hz, 1H), 2.98 (m, 2H), 1.71 (s, 3H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 143.4, 128.1, 127.2, 125.4, 82.3, 79.5, 69.5, 53.5, 26.6, 25.2; HRMS (ESI): calcd for $C_{14}H_{20}Cl_2NaO_2$: [M+Na$^+$] 313.0733, found 313.0731.

1-(2-(tert-butylperoxy)-4,4-dichlorobutan-2-yl)-4-methylbenzene (2m)



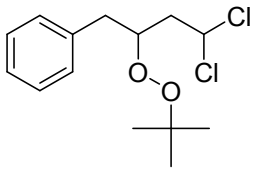
Yield: 74% (451 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.77 (t, *J* = 6.0 Hz, 1H), 2.98 (m, 2H), 2.38 (s, 3H), 1.71 (s, 3H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 140.4, 136.9, 128.8, 125.4, 82.2, 19.4, 69.7, 53.6, 26.6, 25.1, 21.0; HRMS (ESI): calcd for $C_{15}H_{22}Cl_2NaO_2$: [M+Na$^+$] 327.0889, found 327.0881.

1-(2-(tert-butylperoxy)-4,4-dichlorobutan-2-yl)-4-fluorobenzene (2n)



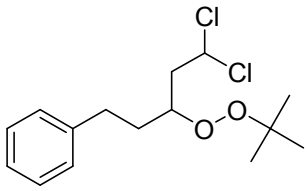
Yield: 81% (501 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.43 (m, 2H), 7.04 (t, J = 8.0 Hz, 2H), 5.75 (t, J = 6.0 Hz, 1H), 2.93 (m, 2H), 1.68 (s, 3H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ161.9 (d, $^{1}J_{C\text{-}F}$ = 244.4 Hz), 139.2 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 127.2 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 114.9 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 82.0, 79.6, 69.3, 53.6, 26.6, 25.2; HRMS (ESI): calcd for $C_{14}H_{19}Cl_2FNaO_2$: [M+Na$^+$] 331.0638, found 331.0694.

1-(2-(*tert*-butylperoxy)-4,4-dichlorobutyl)benzene (2o)



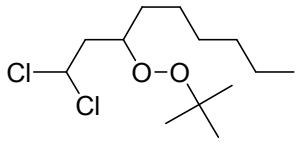
Yield: 77% (447 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.28 (m, 5H), 6.03 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 4.43 (m, 1H), 3.05 (dd, J = 14.0 Hz, J = 6.0 Hz, 1H), 2.81 (dd, J = 14.0 Hz, J = 6.0 Hz, 1H), 2.48 (m, 1H), 2.35 (m, 1H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.2, 129.5, 128.4, 126.5, 80.8, 80.6, 71.1, 47.6, 39.0, 26.3; HRMS (ESI): calcd for $C_{14}H_{20}Cl_2NaO_2$: [M+Na$^+$] 313.0733, found 313.0730.

1-(3-(*tert*-butylperoxy)-5,5-dichloropentyl)benzene (2p)



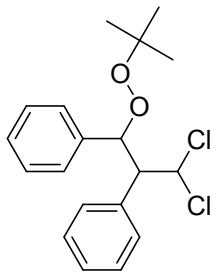
Yield: 78% (474 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.28 (m, 5H), 6.07 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 4.21 (m, 1H), 2.74 (m, 3H), 2.34 (m, 1H), 2.04 (m, 1H), 1.82 (m, 1H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 141.5, 128.4, 128.3, 125.9, 80.1, 79.4, 71.3, 48.3, 34.4, 31.7, 26.4; HRMS (ESI): calcd for $C_{15}H_{22}Cl_2NaO_2$: [M+Na$^+$] 327.0889, found 327.0883.

3-(*tert*-butylperoxy)-1,1-dichlorononane (2q)



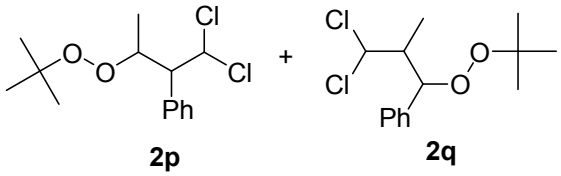
Yield: 80% (455 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 6.07 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 4.14 (m, 1H), 2.54 (m, 3H), 2.33 (m, 1H), 1.70 (m, 1H), 1.41 (m, 3H), 1.29 (m, 6H), 1.24 (s, 9H), 0.89 (t, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 80.2, 80.1, 71.6, 48.7, 32.7, 31.7, 29.2, 26.4, 25.4, 22.5, 14.0; HRMS (ESI): calcd for $C_{13}H_{26}Cl_2NaO_2$: [M+Na$^+$] 307.1202, found 307.1202.

1-(*tert*-butylperoxy)-3,3-dichloro-1,2-diphenylpropane (2r)



Yield: 71% (500 mg); Orange oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.19 (s, 5H), 7.14 (s, 5H), 6.52 (d, J = 4.0 Hz, 1H), 5.42 (d, J = 9.6 Hz, 1H), 3.80 (dd, J = 10.0 Hz, J = 10.0 Hz, 1H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 137.9, 133.5, 130.9, 128.1, 127.9, 127.8, 127.7, 127.5, 85.2, 80.6, 73.7, 58.8, 26.5; HRMS (ESI): calcd for $C_{19}H_{22}Cl_2NaO_2$: [M+Na$^+$] 375.0889, found 375.0883.

1-(3-(tert-butylperoxy)-1,1-dichlorobutan-2-yl)benzene (2s) and 1-(1-(tert-butylperoxy)-3,3-dichloro-2-methylpropyl)benzene (2t)

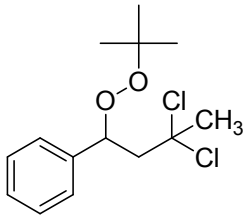


2p **2q**

2p : 2q = 3 : 2

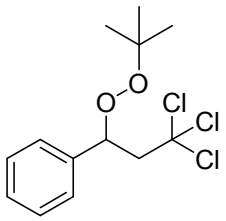
Yield: 76% (441 mg); Pale yellow oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.35 (m, 5H), 6.43 (d, J = 1.6 Hz, 0.4H), 5.49 (d, J = 4.4 Hz, 0.6H), 4.93 (d, J = 7.6 Hz, 0.6H), 4.72 (d, J = 10.0 Hz, 0.4H), 2.57 (m, 0.4H), 2.45 (m, 0.6H), 1.38 (d, J = 6.8 Hz, 1.8H), 1.20 (s, 5.4H), 1.16 (s, 3.6H), 0.92 (d, J = 6.8 Hz, 1.2H),; ^{13}C NMR ($CDCl_3$, 100 Hz) δ 139.1, 138.8, 128.4, 128.2, 128.2, 128.1, 127.7, 127.1, 86.6, 86.0, 80.5, 80.5, 77.3, 77.0, 76.7, 76.1, 75.8, 49.5, 48.0, 26.4, 10.5, 10.1; HRMS (ESI): calcd for $C_{14}H_{20}Cl_2NaO_2$: [M+Na$^+$] 313.0733, found 313.0730.

1-(1-(tert-butylperoxy)-3,3-dichlorobutyl)benzene (2u)



Yield: 63% (366 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.36 (m, 5H), 5.28 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 2.94 (dd, *J* = 14.0 Hz, *J* = 6.0 Hz, 1H), 2.71 (dd, *J* = 14.0 Hz, *J* = 6.0 Hz, 1H), 2.23 (s, 3H), 1.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 140.9, 128.3, 128.0, 127.1, 88.4, 82.8, 80.1, 54.4, 37.8, 26.6; HRMS (ESI): calcd for $C_{14}H_{20}Cl_2NaO_2$: [M+Na$^+$] 313.0733, found 313.0736.

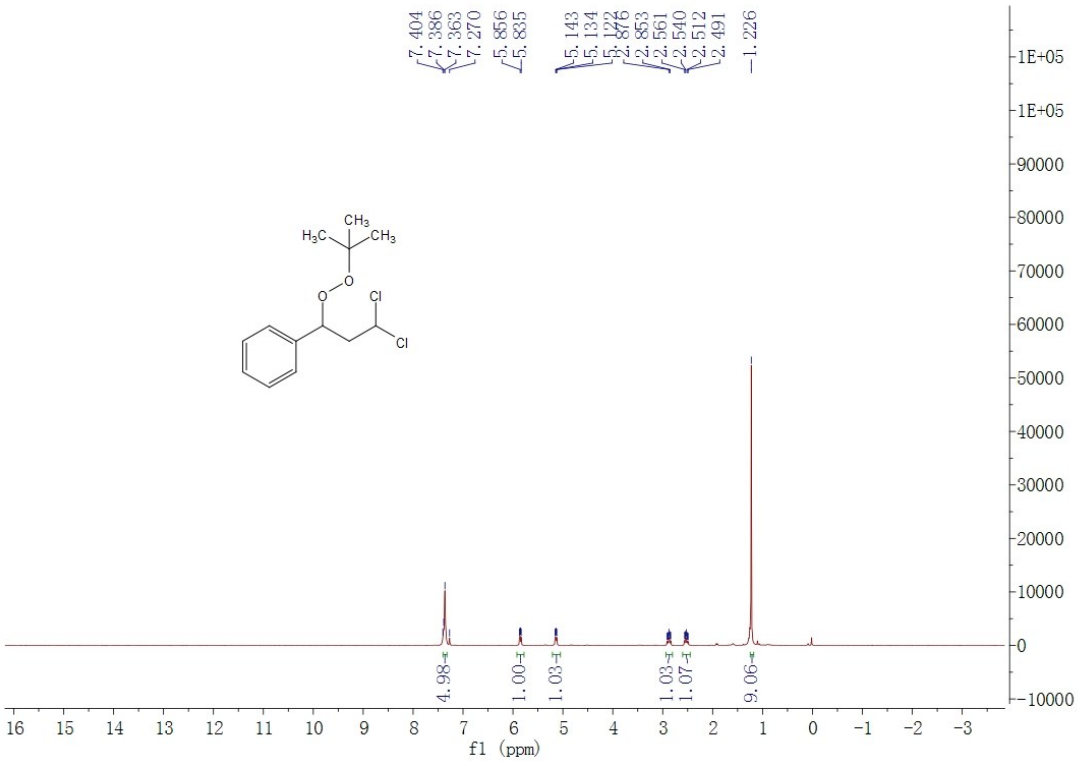
1-(1-(tert-butylperoxy)-3,3,3-trichloropropyl)benzene (2v)

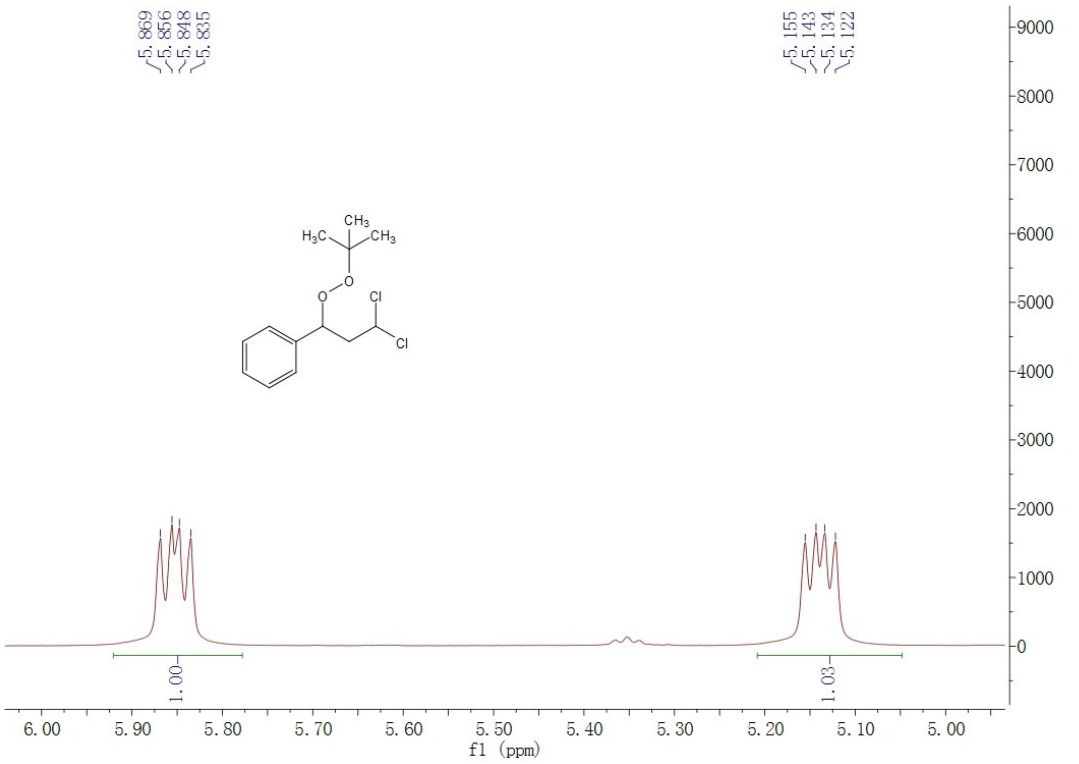


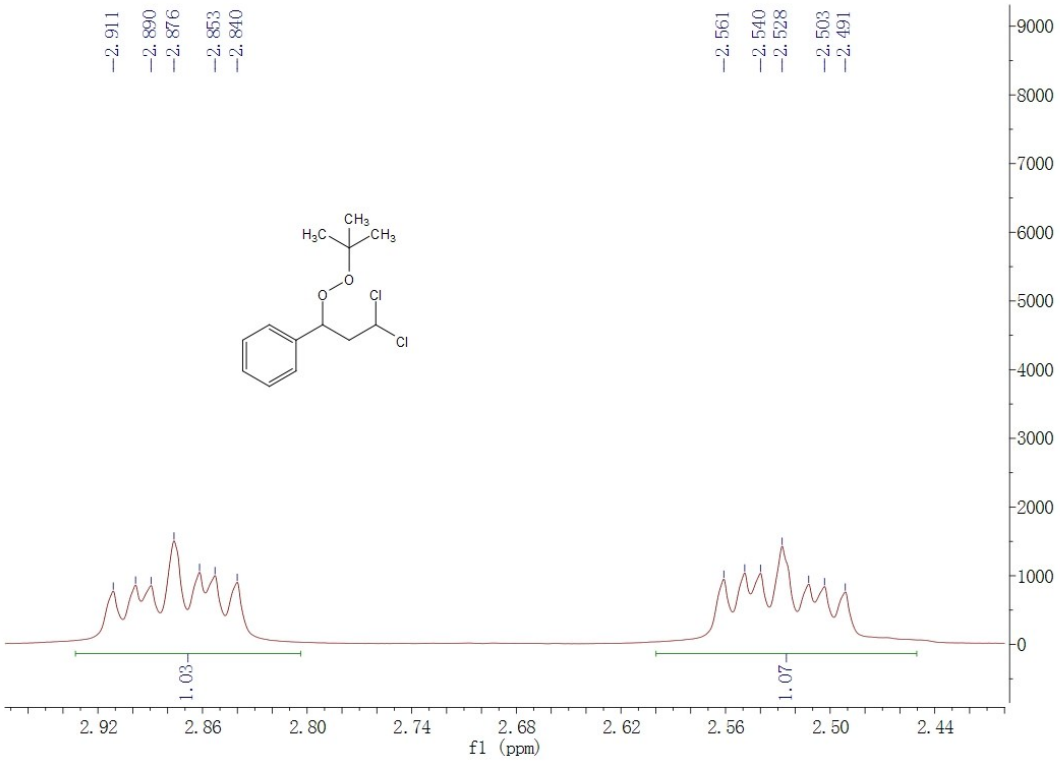
Yield: 85% (528 mg); Colorless oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.40 (m, 5H), 5.38 (t, *J* = 5.6 Hz, 1H), 3.48 (dd, *J* = 10.0 Hz, *J* = 6.0 Hz, 1H), 3.16 (dd, *J* = 10.0 Hz, *J* = 6.0 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 139.7, 128.5, 128.3, 127.4, 96.8, 83.0, 59.0, 26.5; HRMS (ESI): calcd for C13H17Cl3NaO2: [M+Na$^+$] 333.0186, found 333.0194.

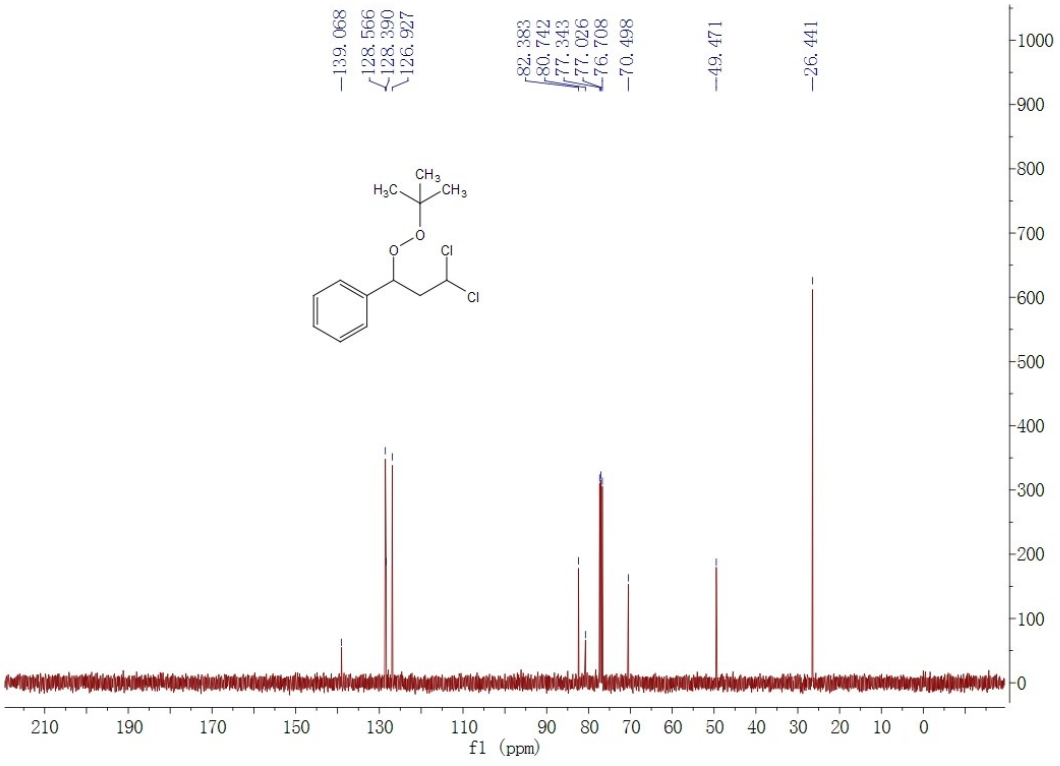
NMR spectra

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (2a)

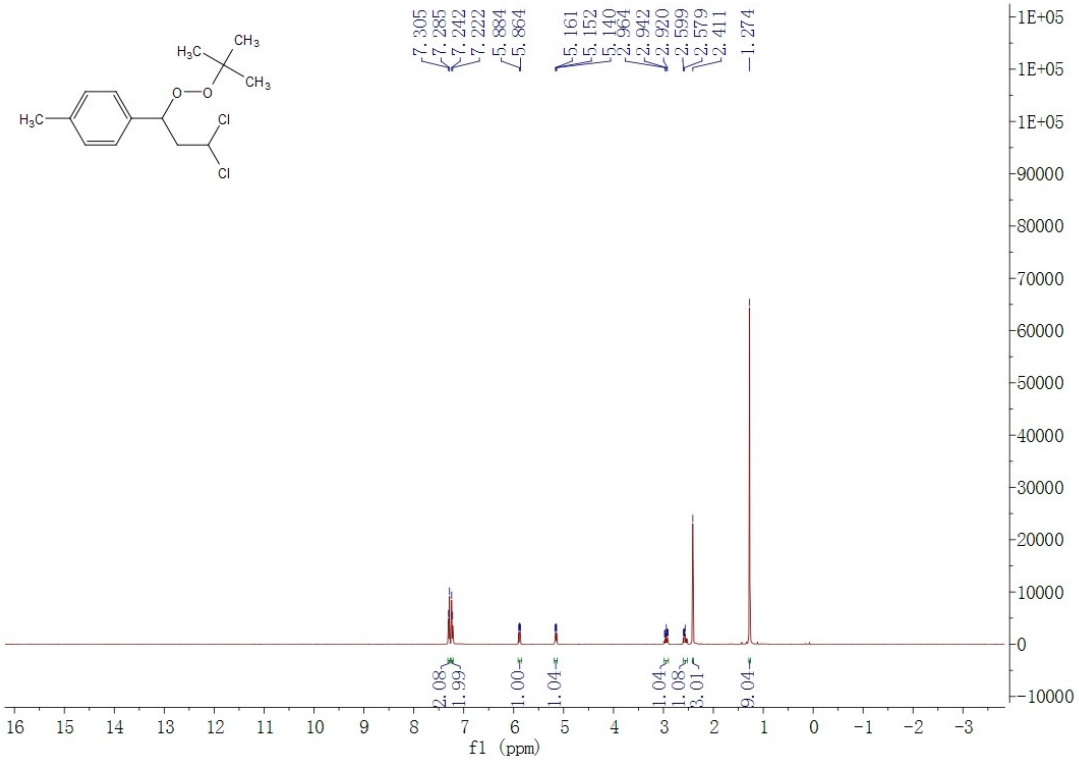


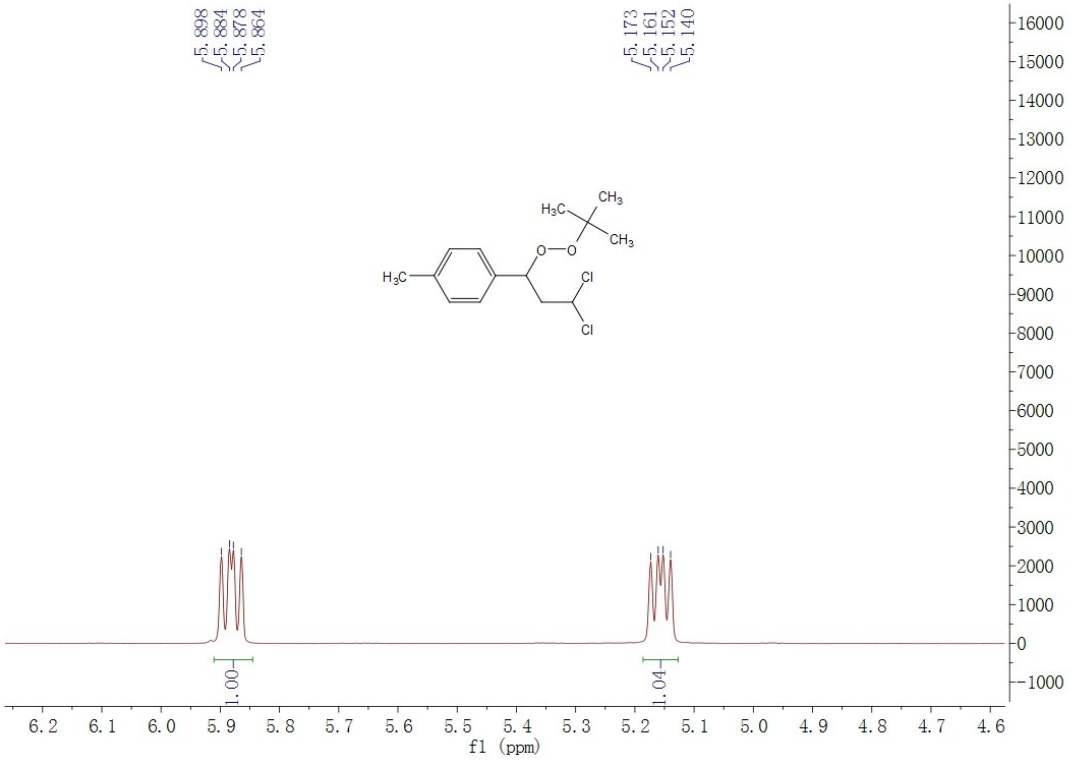


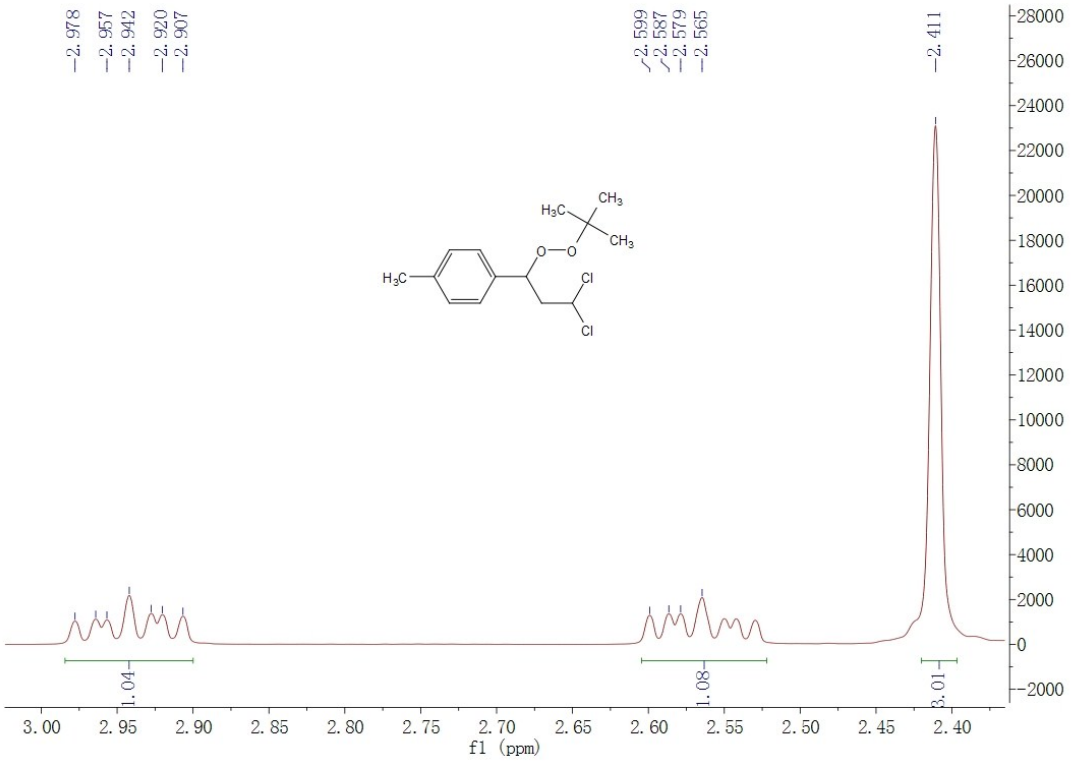

2.911
2.890
2.876
2.853
2.840
2.561
2.540
2.528
2.503
2.491
1.03
1.07
f1 (ppm)

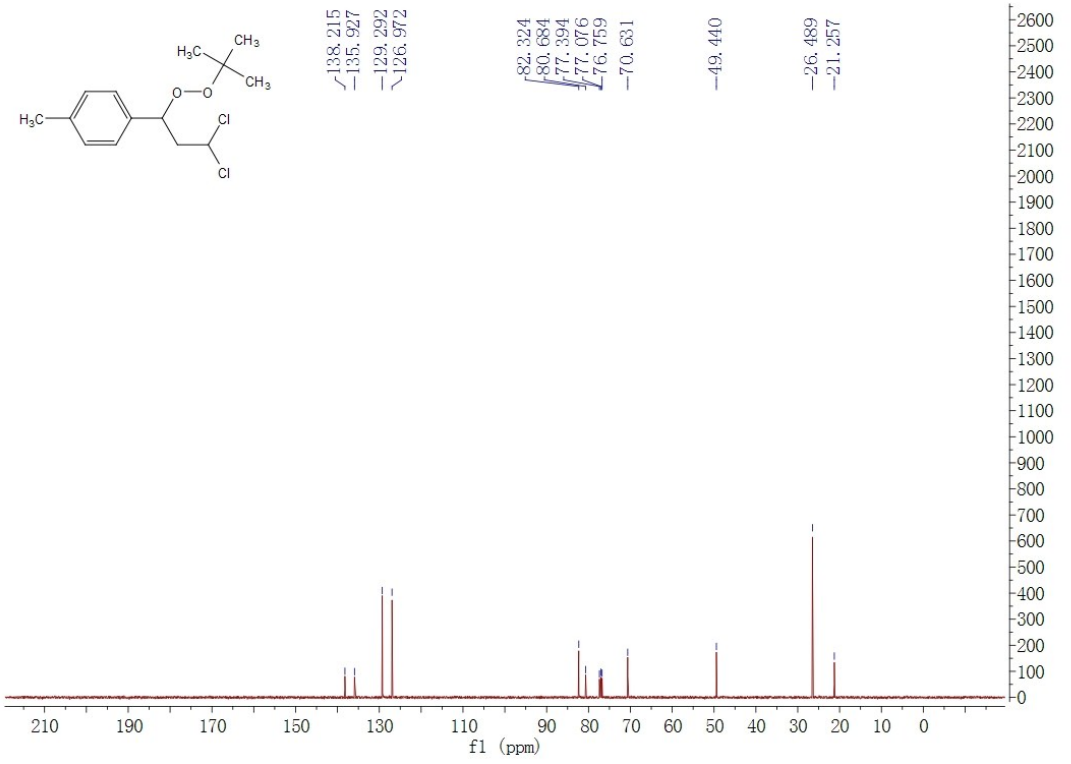

139.068
128.566
128.390
126.927
82.383
80.742
77.343
77.026
76.708
70.498
49.471
26.441
f1 (ppm)

1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-methylbenzene (2b)

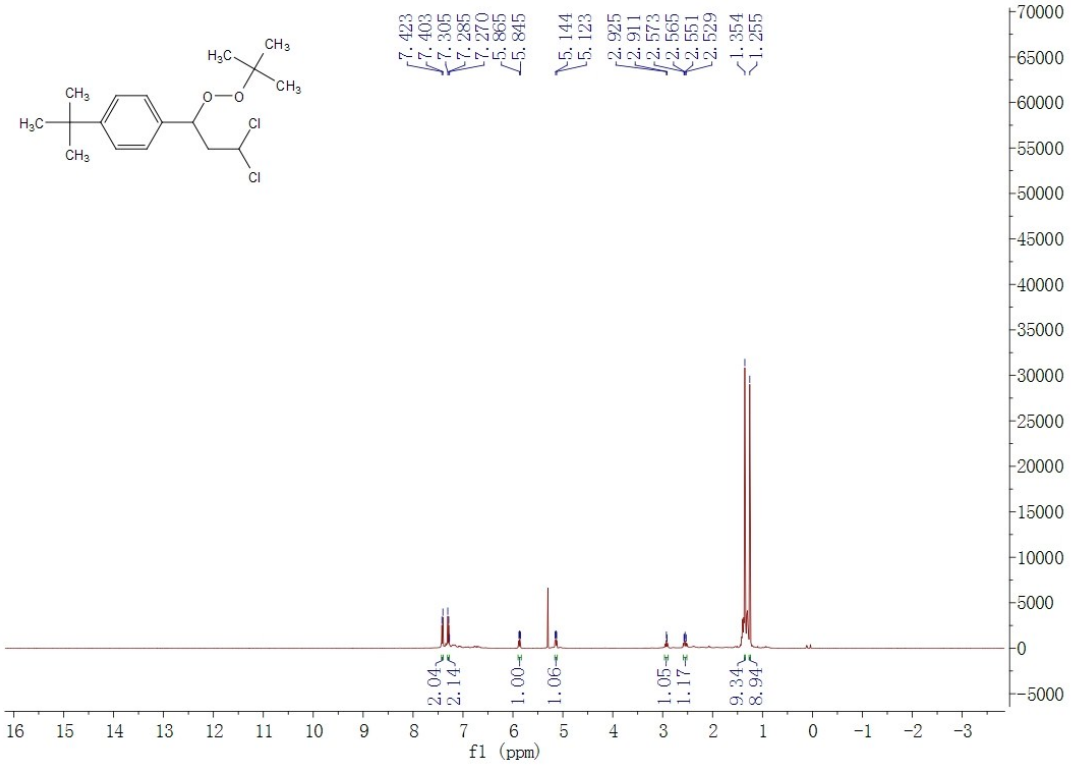


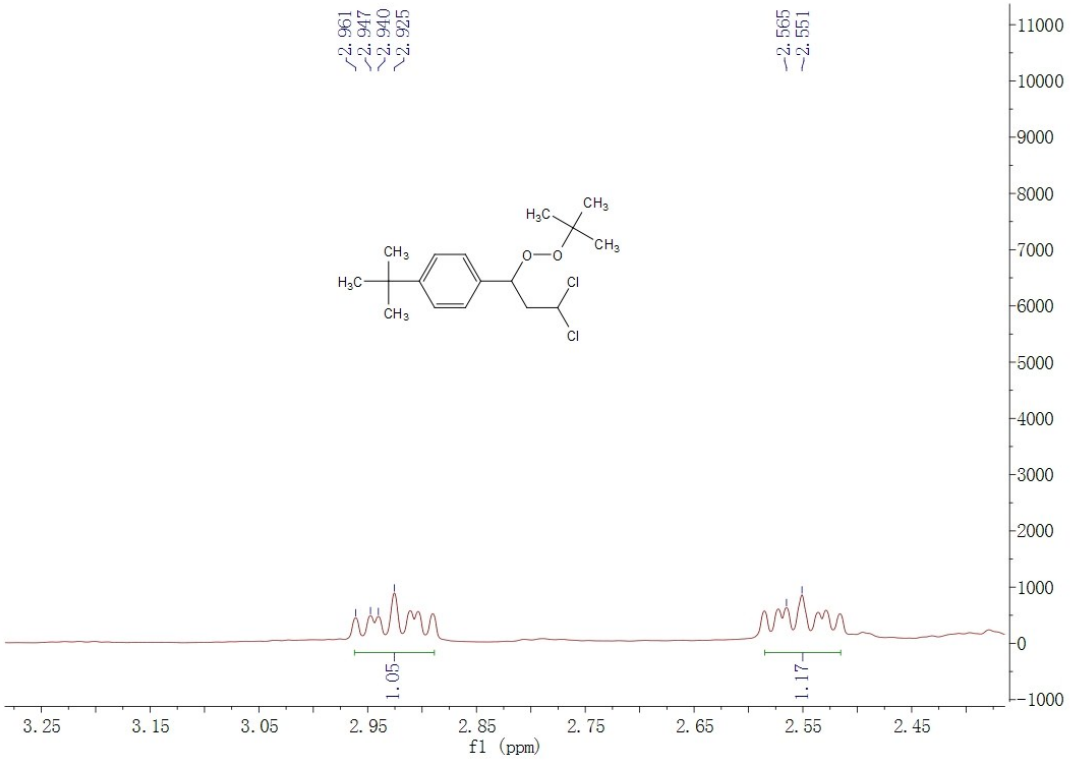


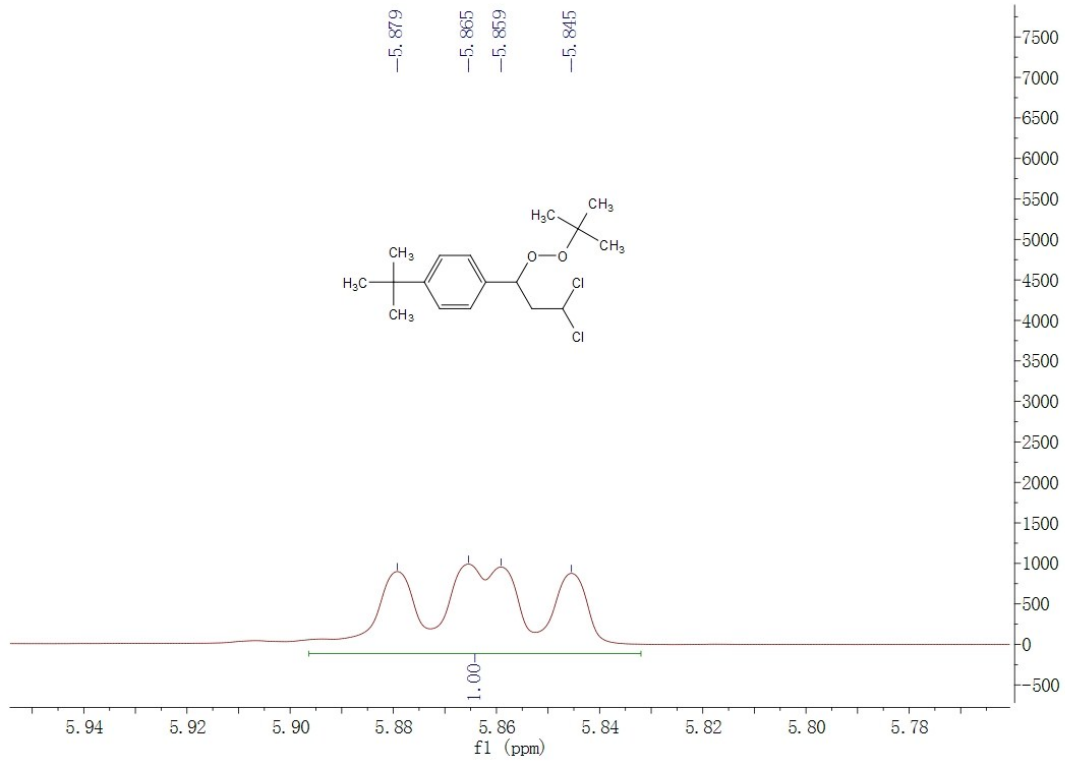

2.978
2.957
2.942
2.920
2.907
2.599
2.587
2.579
2.565
2.411
1.04
1.08
3.01
f1 (ppm)

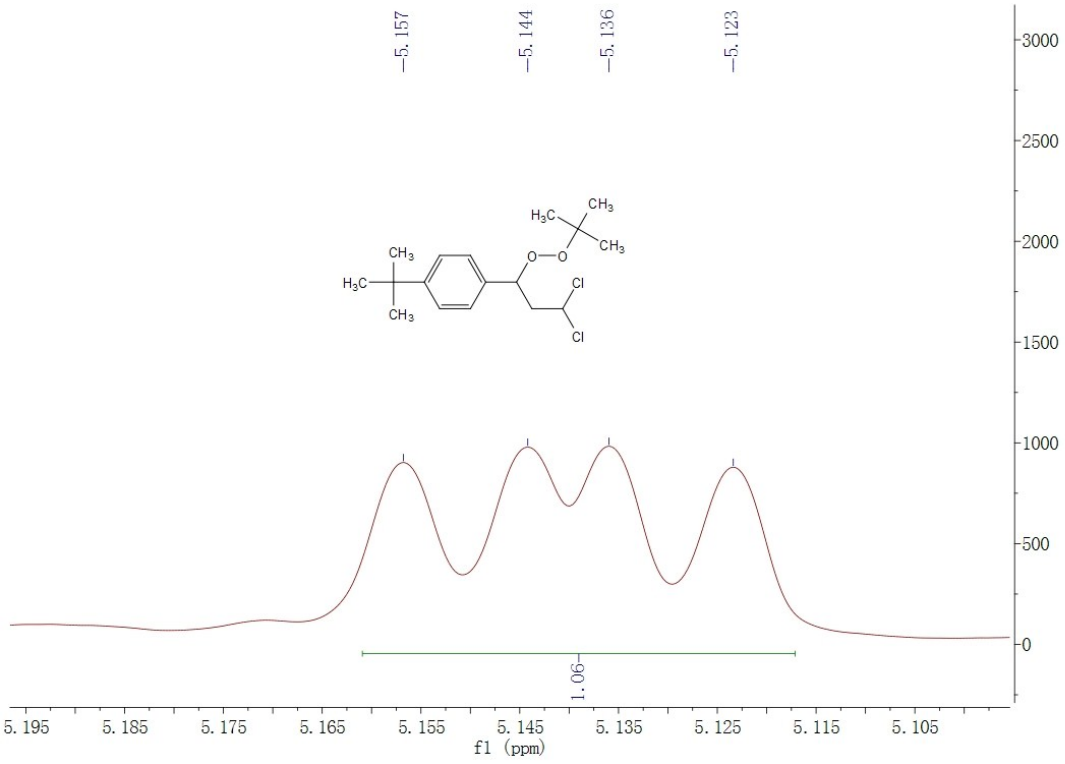

138.215
135.927
129.292
126.972
82.324
80.684
77.394
77.076
76.759
70.631
49.440
26.489
21.257
f1 (ppm)

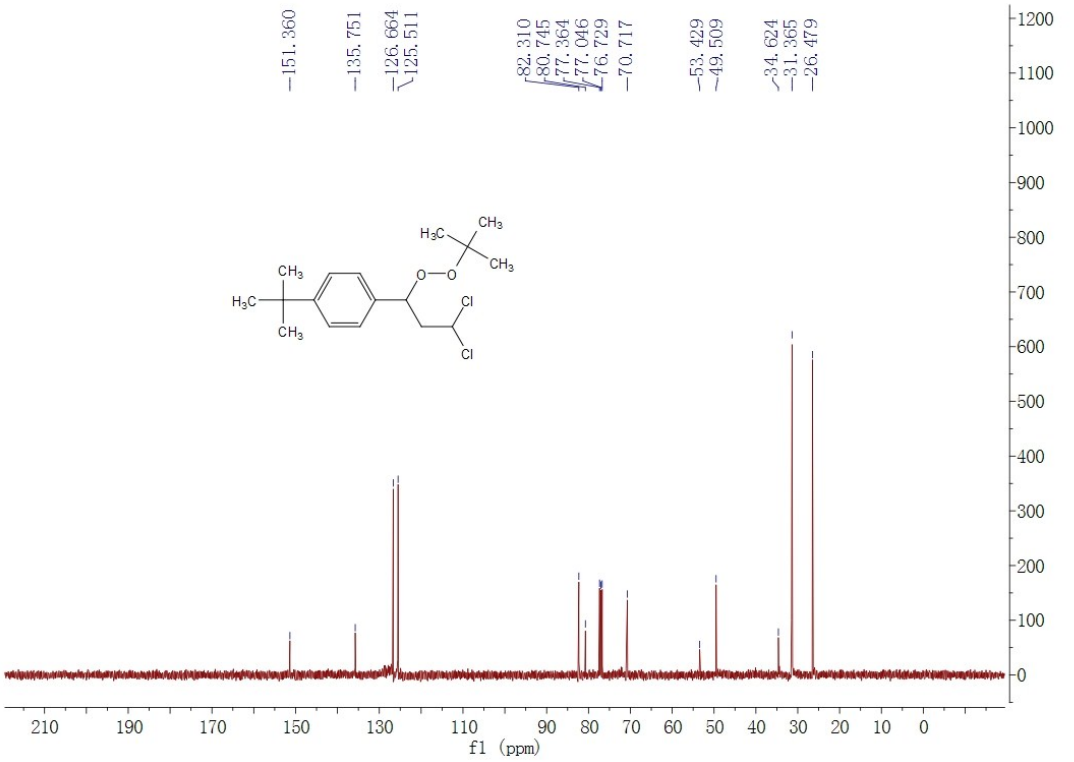
1-*tert*-butyl-4-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)benzene (2c)



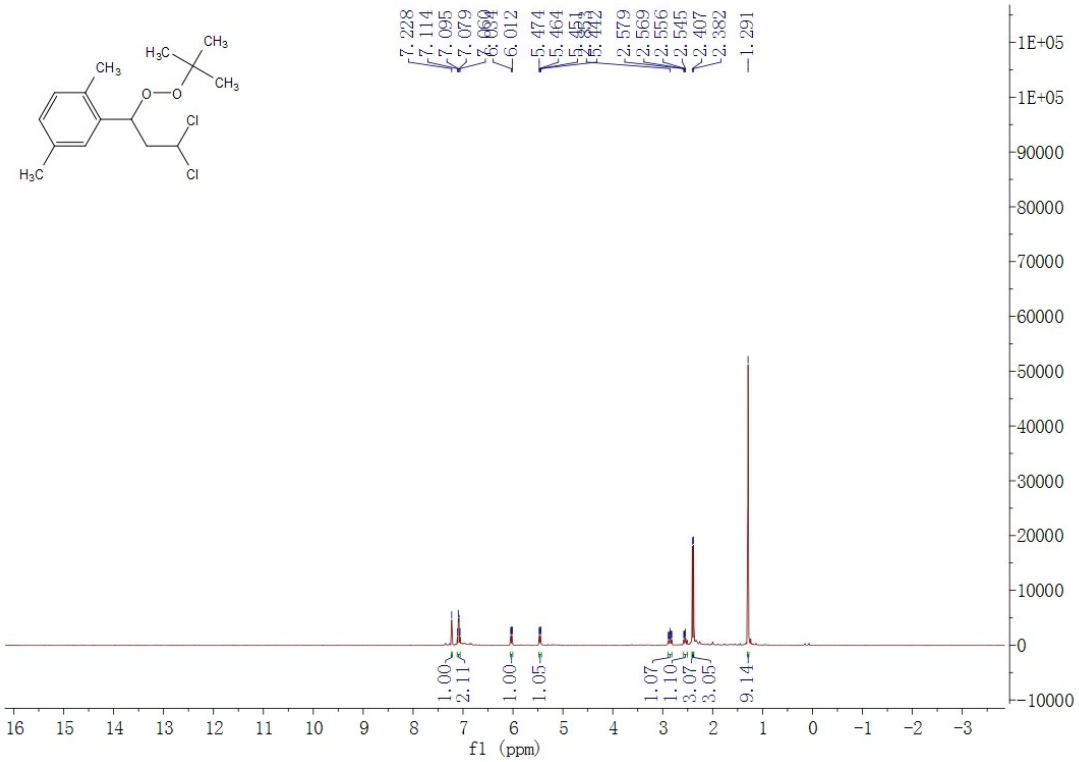


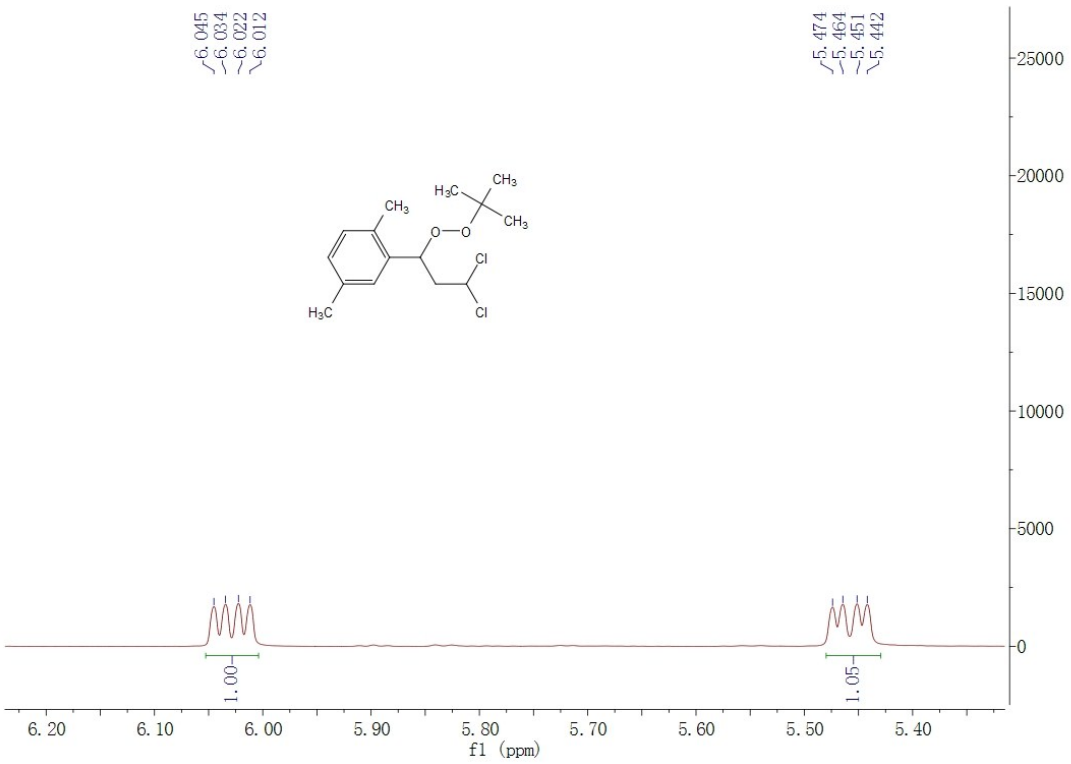

5.879
5.865
5.859
5.845
CH3
H3C
CH3
O
O
CH3
H3C
CH3
Cl
Cl
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1.00
5.94
5.92
5.90
5.88
5.86
5.84
5.82
5.80
5.78
f1 (ppm)

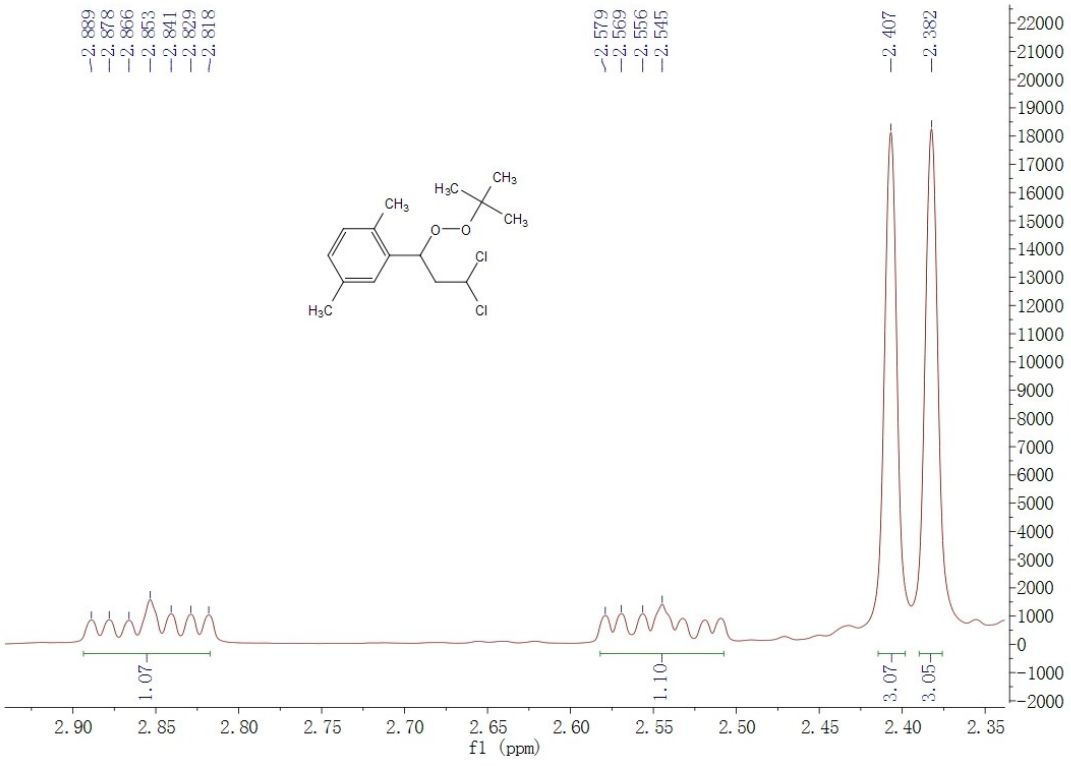

5.157
5.144
5.136
5.123
CH3
H3C
CH3
O
O
CH3
H3C
CH3
Cl
Cl
3000
2500
2000
1500
1000
500
0
1.06
5.195
5.185
5.175
5.165
5.155
5.145
5.135
5.125
5.115
5.105
f1 (ppm)

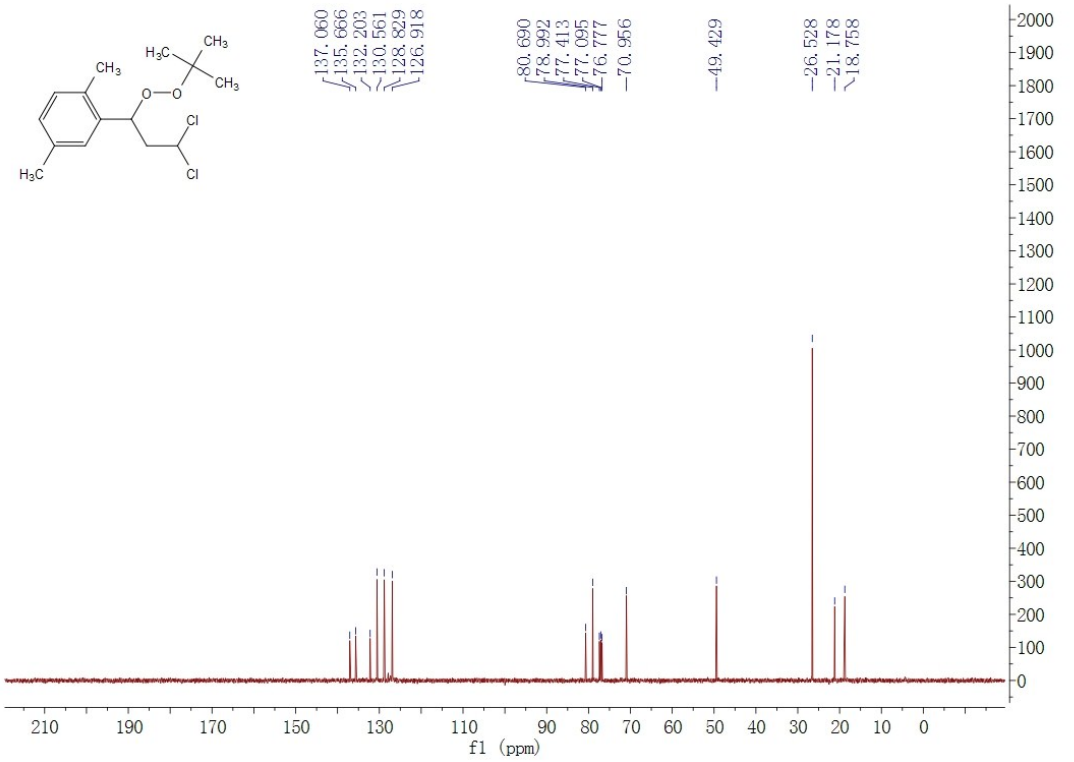


2-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-1,4-dimethylbenzene (2d)

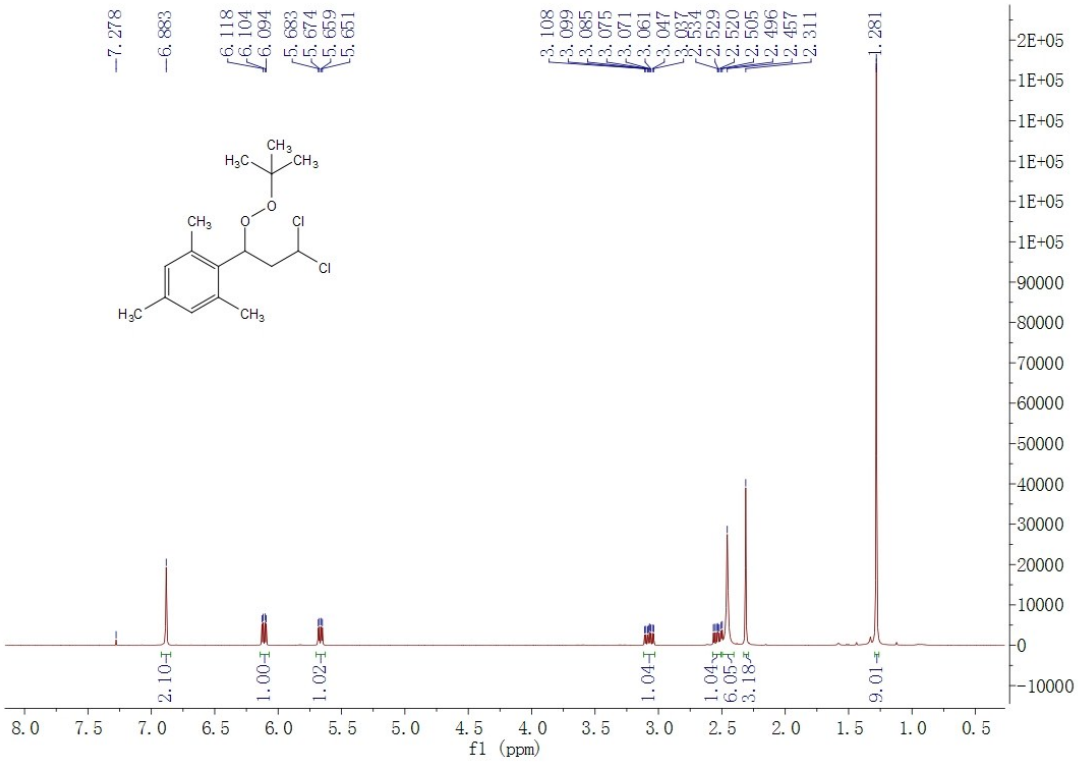


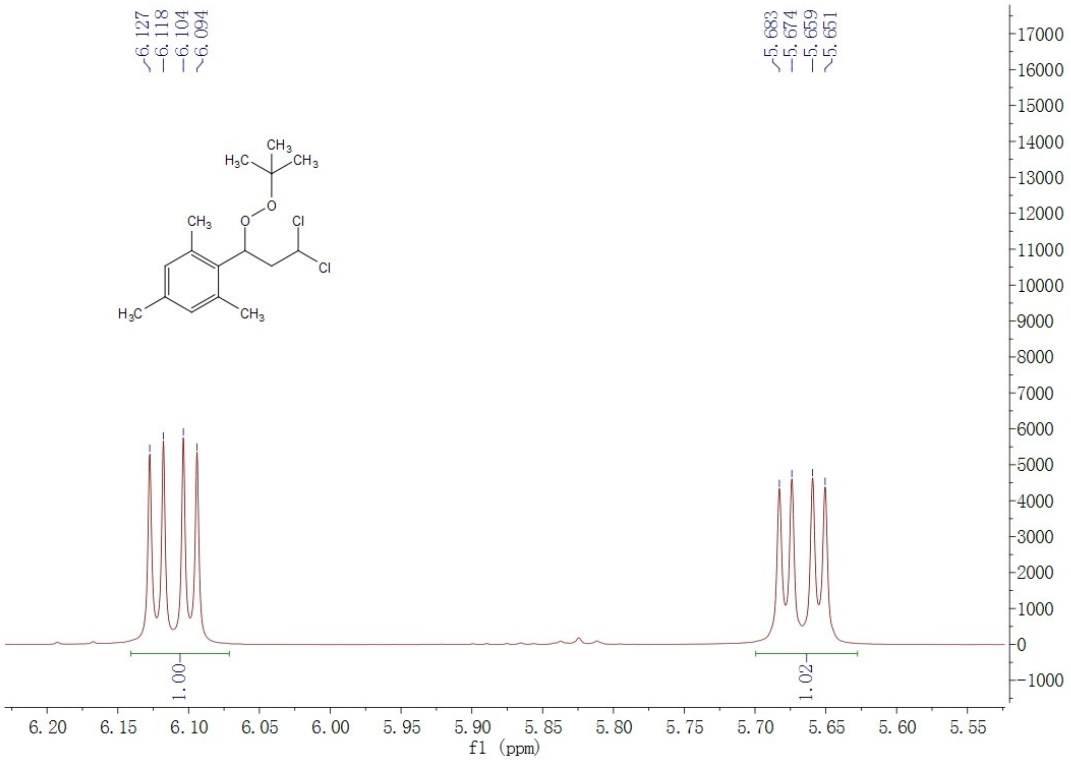

6.045
6.034
6.022
6.012
5.474
5.464
5.451
5.442
CH3
H3C
CH3
O
O
CH3
Cl
Cl
H3C
25000
20000
15000
10000
5000
0
1.00
1.05
6.20
6.10
6.00
5.90
5.80
5.70
5.60
5.50
5.40
f1 (ppm)

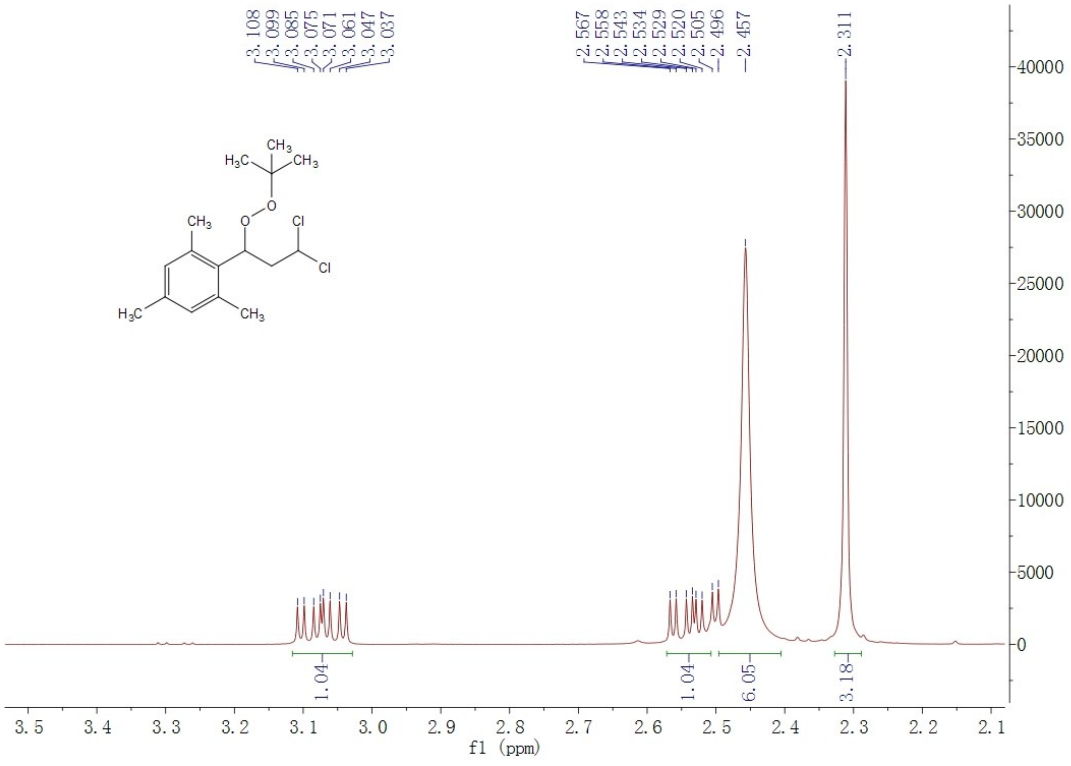

2.889
2.878
2.866
2.853
2.841
2.829
2.818
2.579
2.569
2.556
2.545
2.407
2.382
CH3
H3C
CH3
O
O
CH3
Cl
Cl
H3C
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
1.07
1.10
3.07
3.05
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
f1 (ppm)

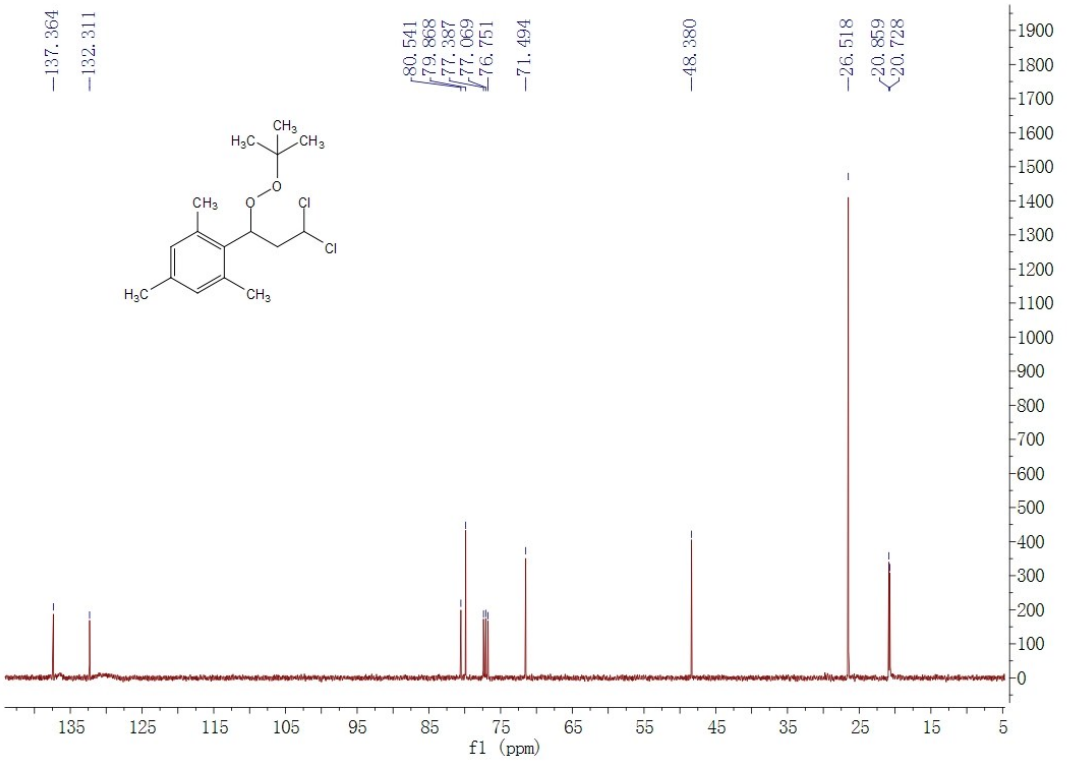


2-(1-(tert-butylperoxy)-3,3-dichloropropyl)-1,3,5-trimethylbenzene (2e)

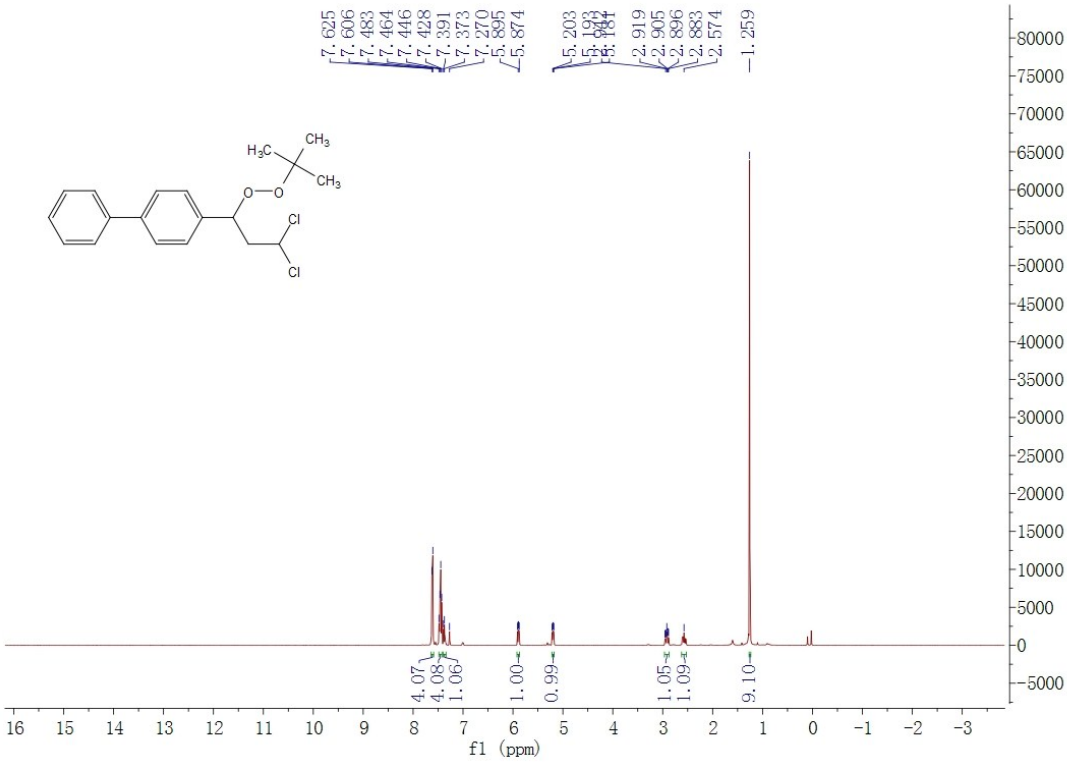


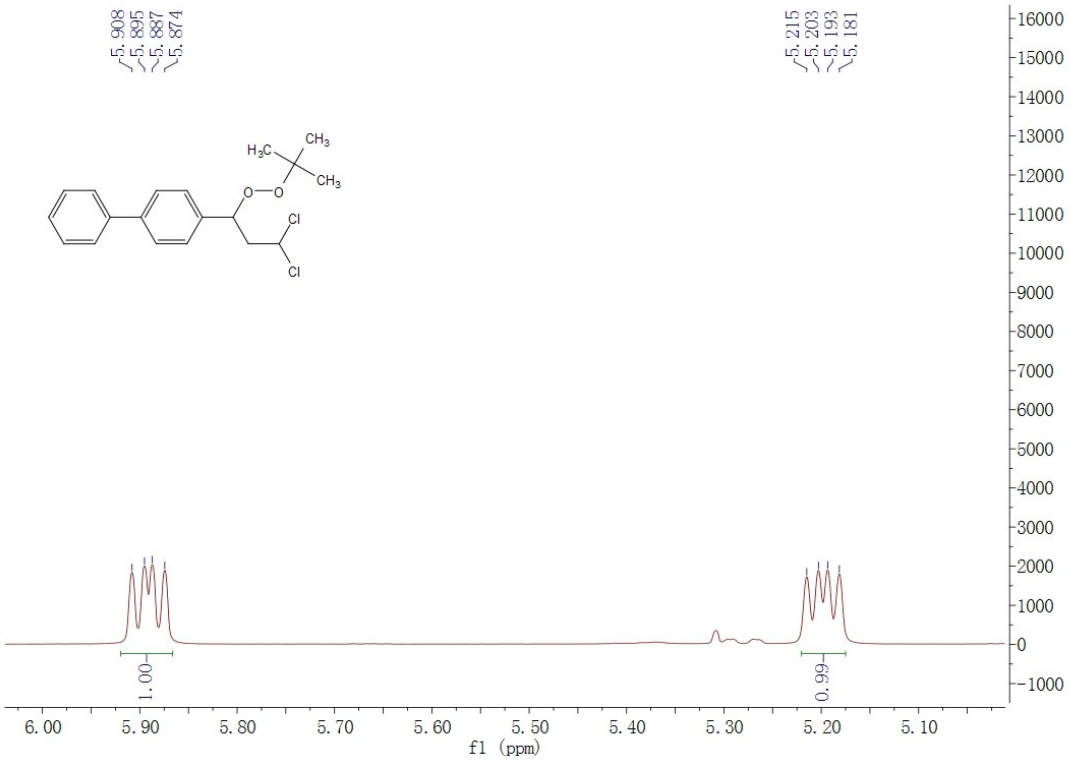

6.127
6.118
6.104
6.094
5.683
5.674
5.659
5.651
1.00
1.02
f1 (ppm)

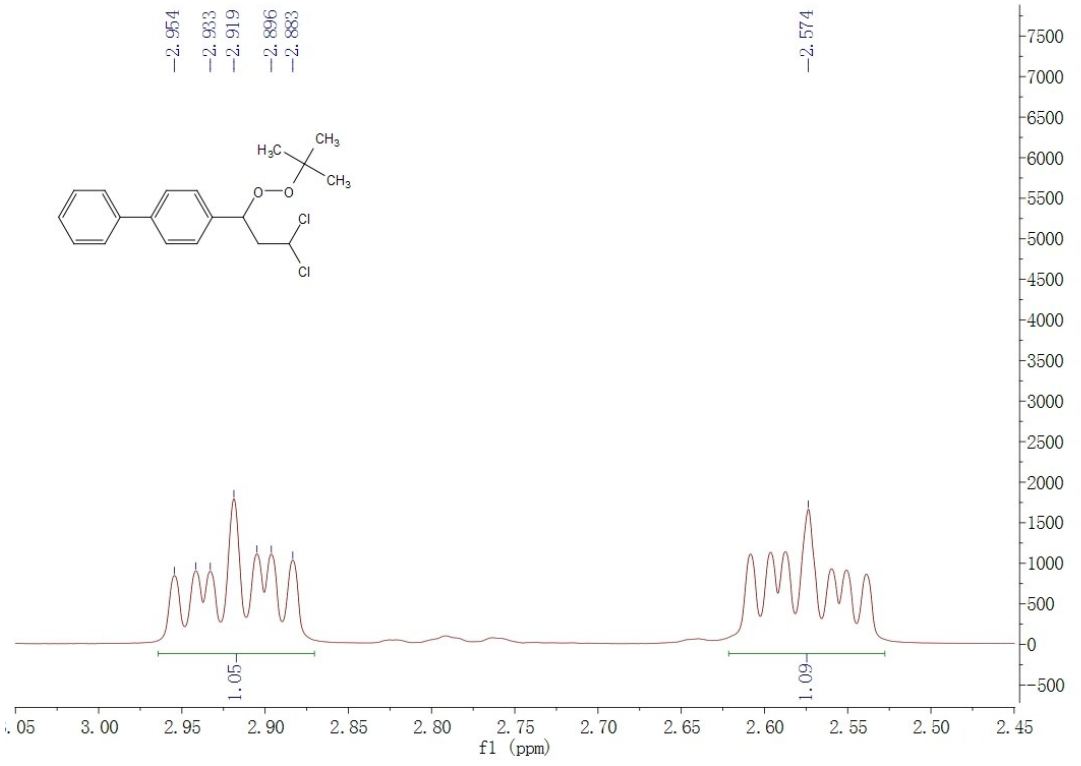

3.108
3.099
3.085
3.075
3.071
3.061
3.047
3.037
2.567
2.558
2.543
2.534
2.529
2.520
2.505
2.496
2.457
2.311
1.04
1.04
6.05
3.18
f1 (ppm)

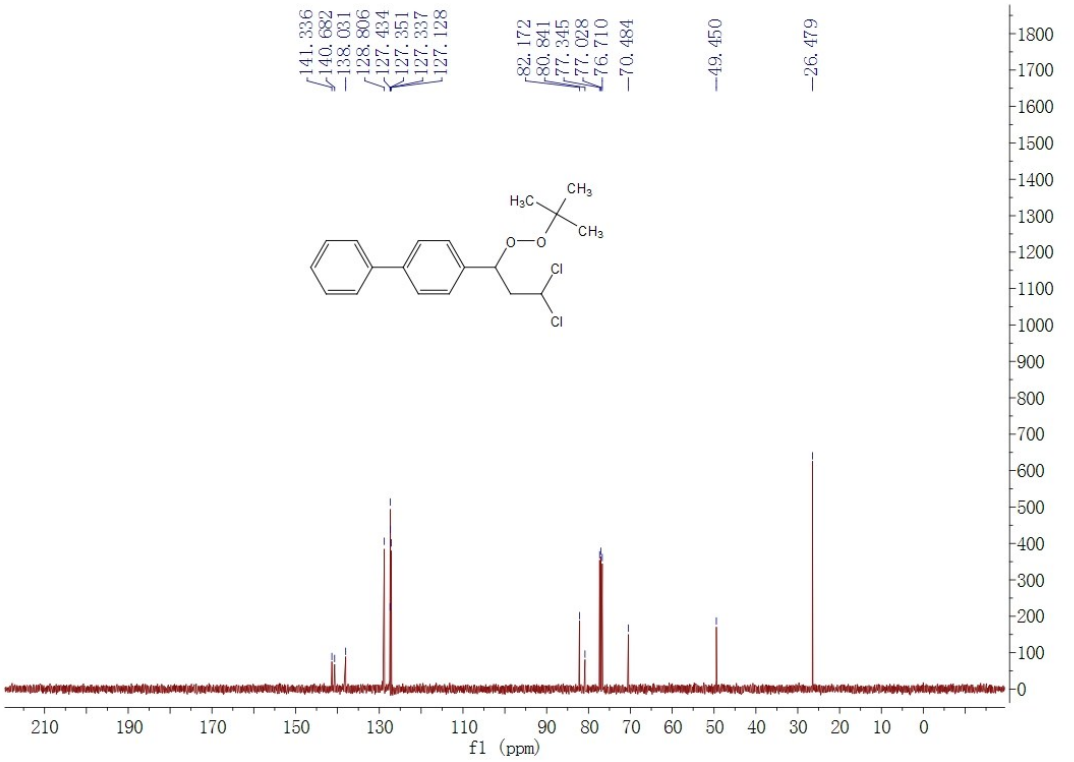


1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-phenylbenzene (2f)

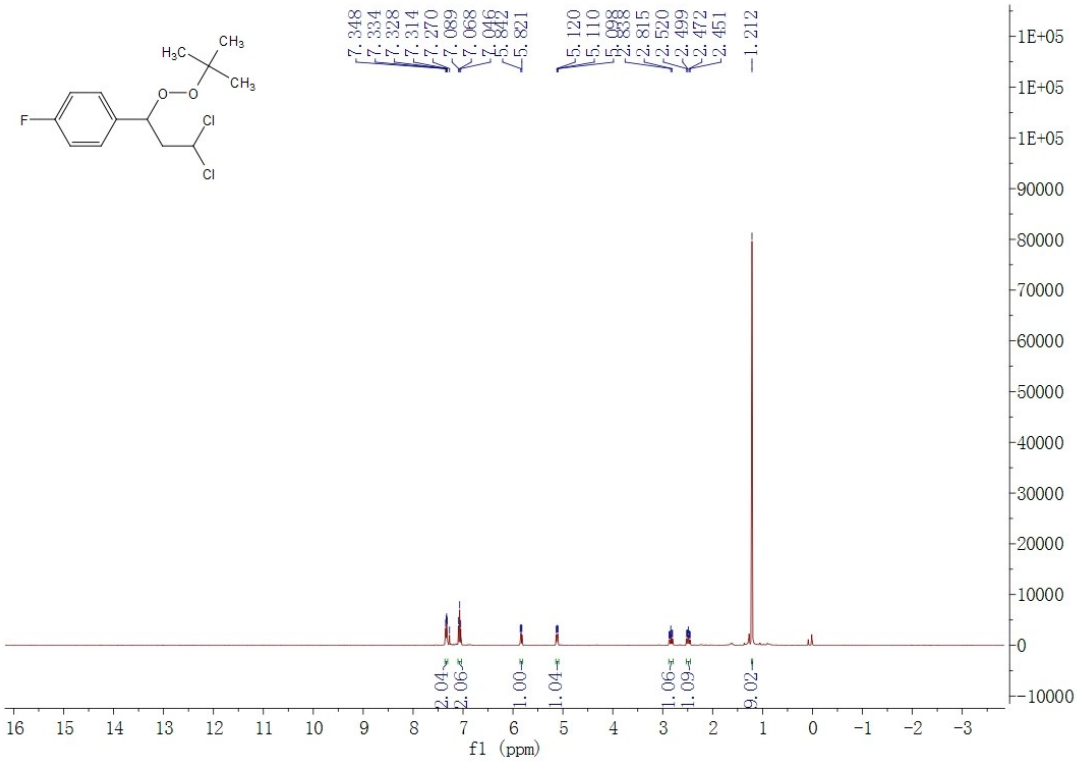


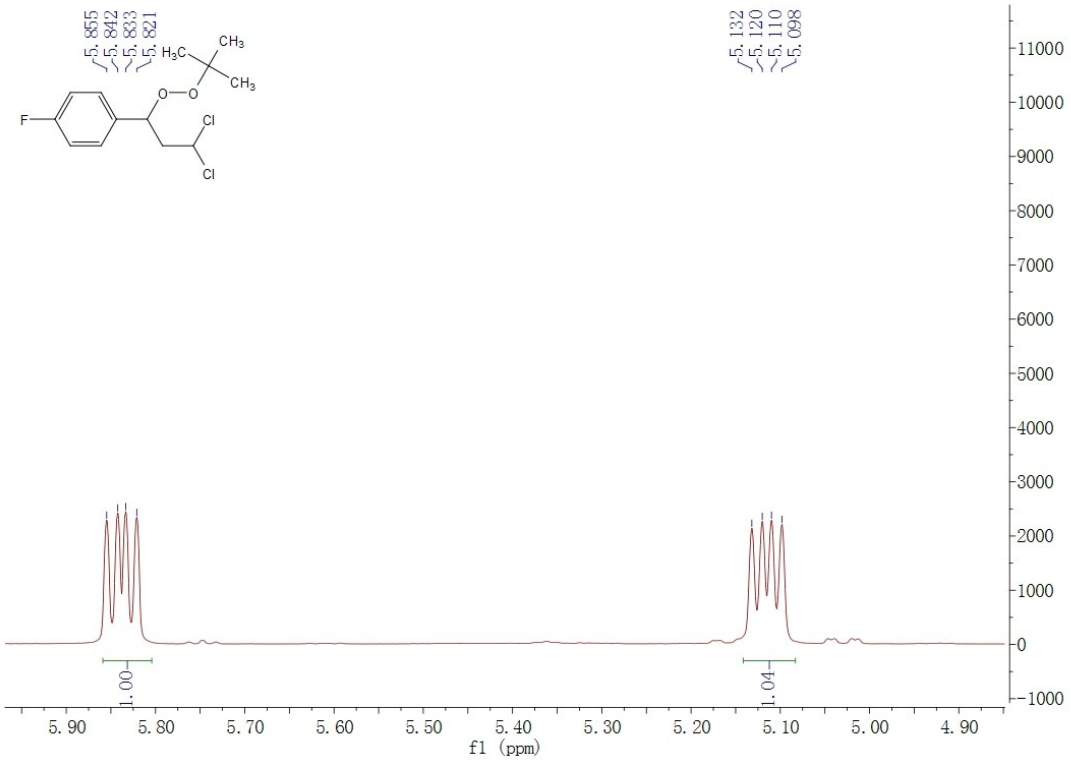

5.908
5.895
5.887
5.874
5.215
5.203
5.193
5.181
H3C
CH3
CH3
O
O
Cl
Cl
1.00
0.99
f1 (ppm)

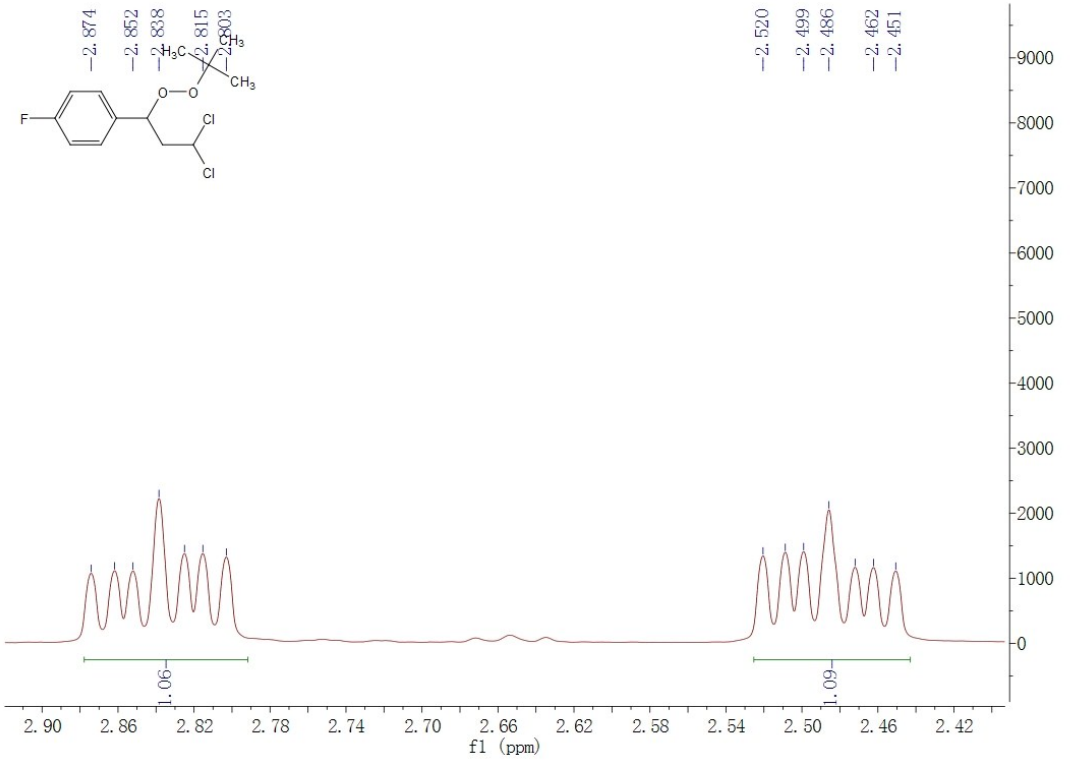

2.954
2.933
2.919
2.896
2.883
2.574
H3C
CH3
CH3
O
O
Cl
Cl
1.05
1.09
f1 (ppm)

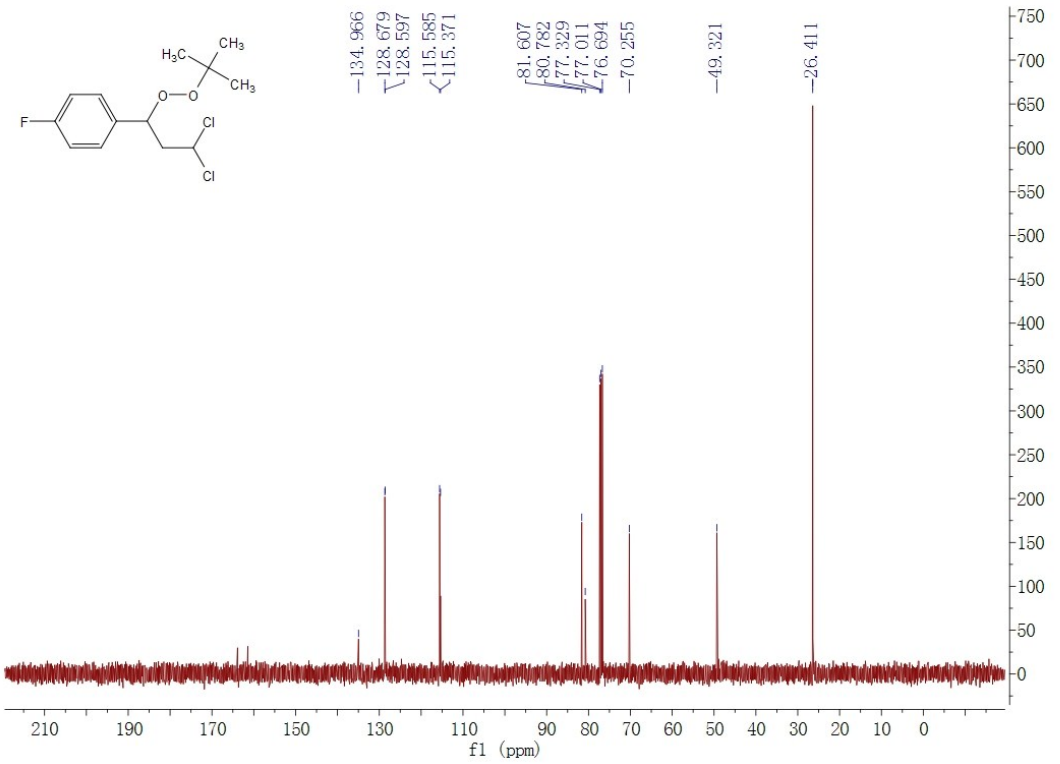


1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-fluorobenzene (2g)

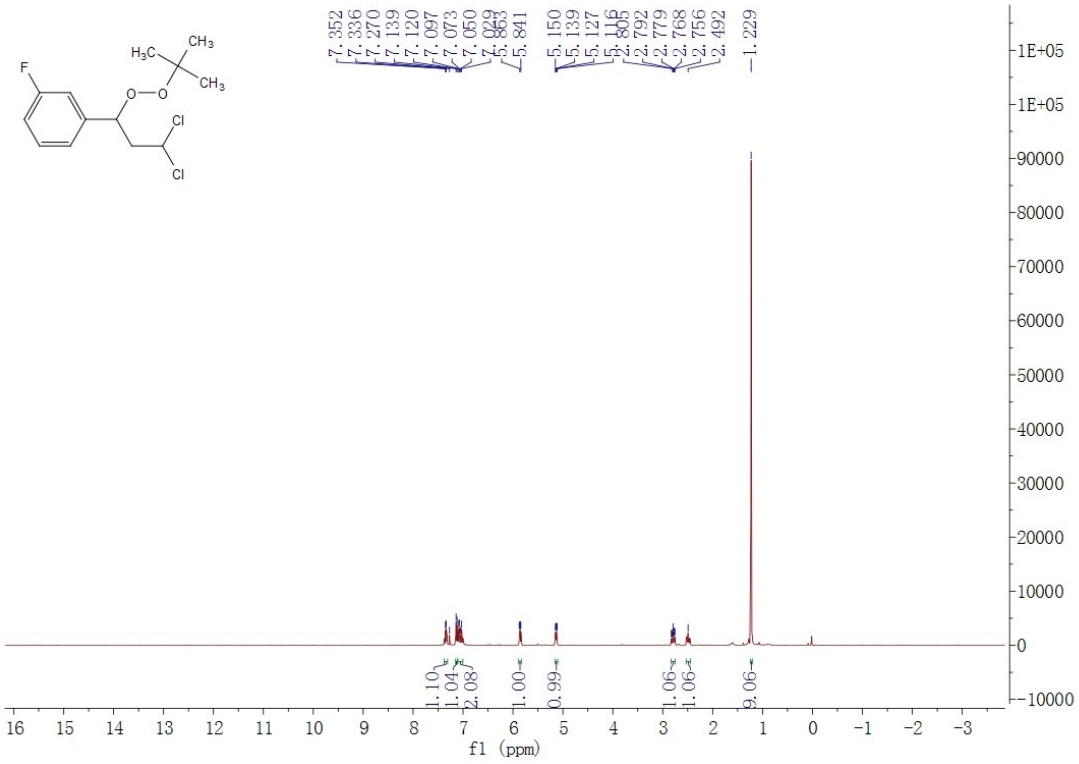


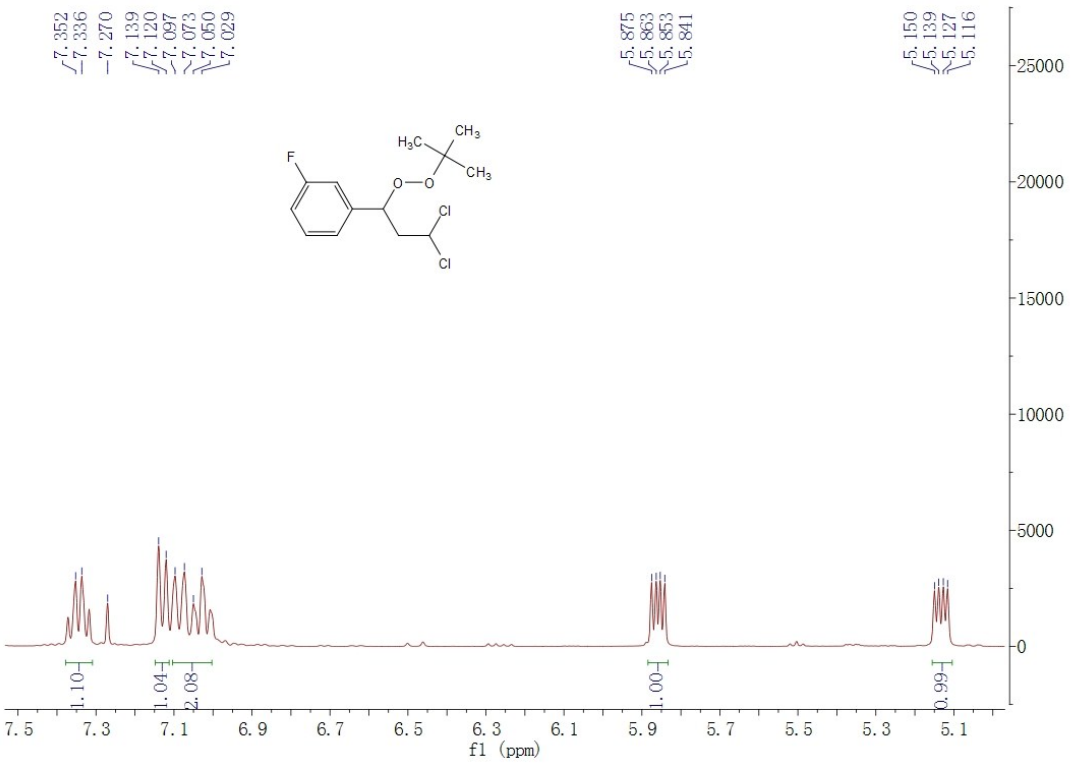

5.855
5.842
5.833
5.821
5.132
5.120
5.110
5.098
CH3
H3C
CH3
O
O
F
Cl
Cl
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.04
5.90
5.80
5.70
5.60
5.50
5.40
5.30
5.20
5.10
5.00
4.90
f1 (ppm)

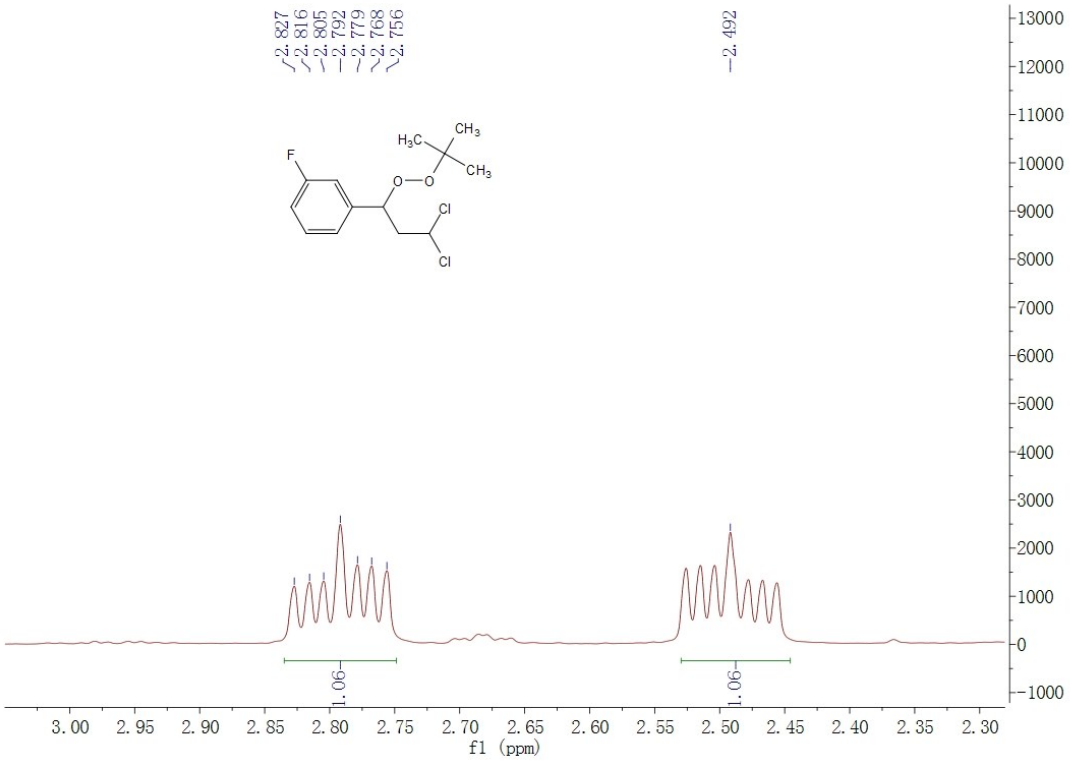

2.874
2.852
2.838
2.815
2.803
2.520
2.499
2.486
2.462
2.451
CH3
H3C
CH3
O
O
F
Cl
Cl
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.06
1.09
2.90
2.86
2.82
2.78
2.74
2.70
2.66
2.62
2.58
2.54
2.50
2.46
2.42
f1 (ppm)

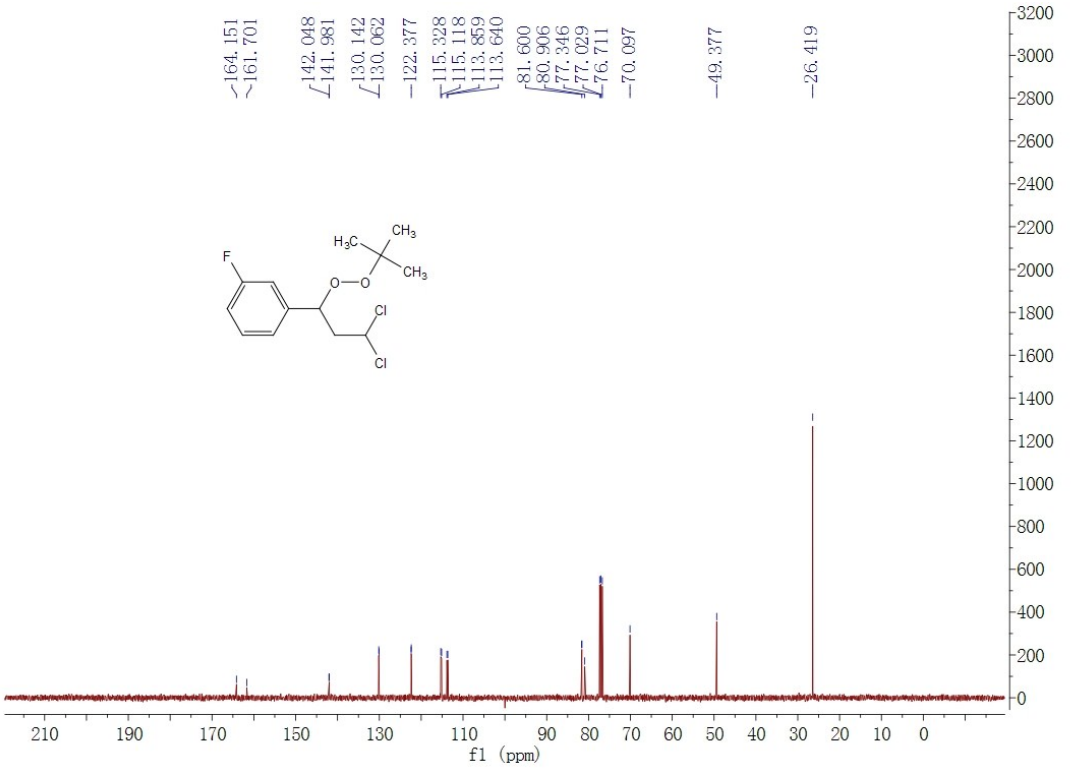


1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-3-fluorobenzene (2h)

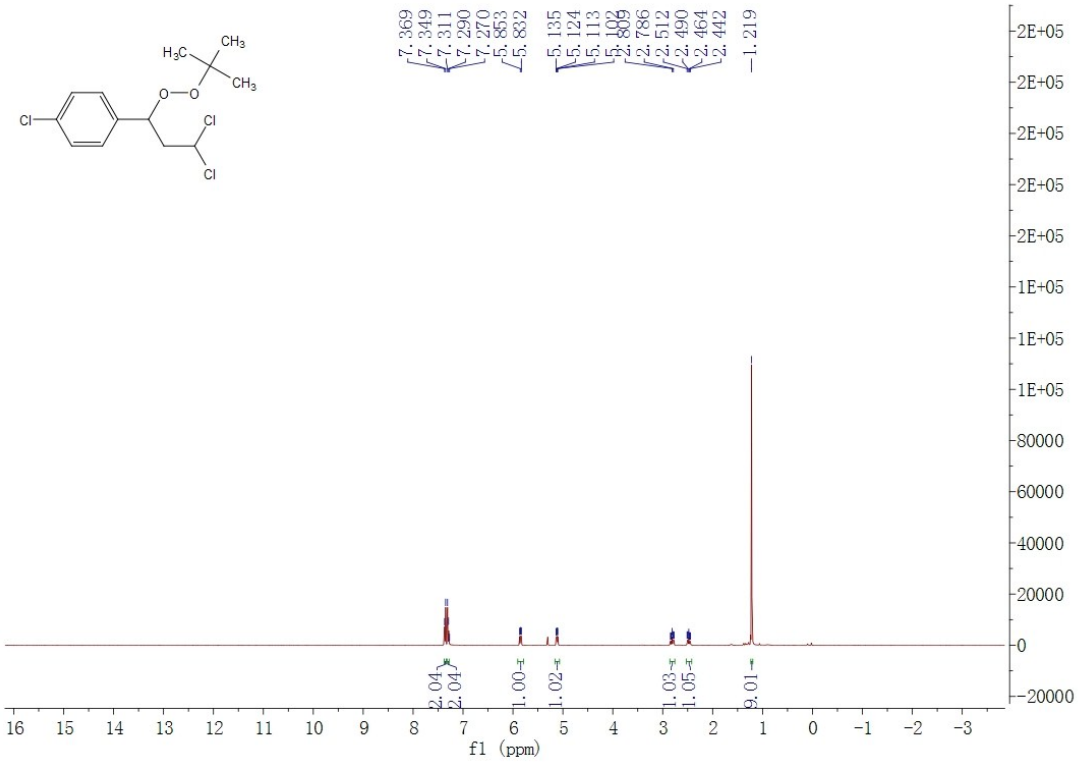


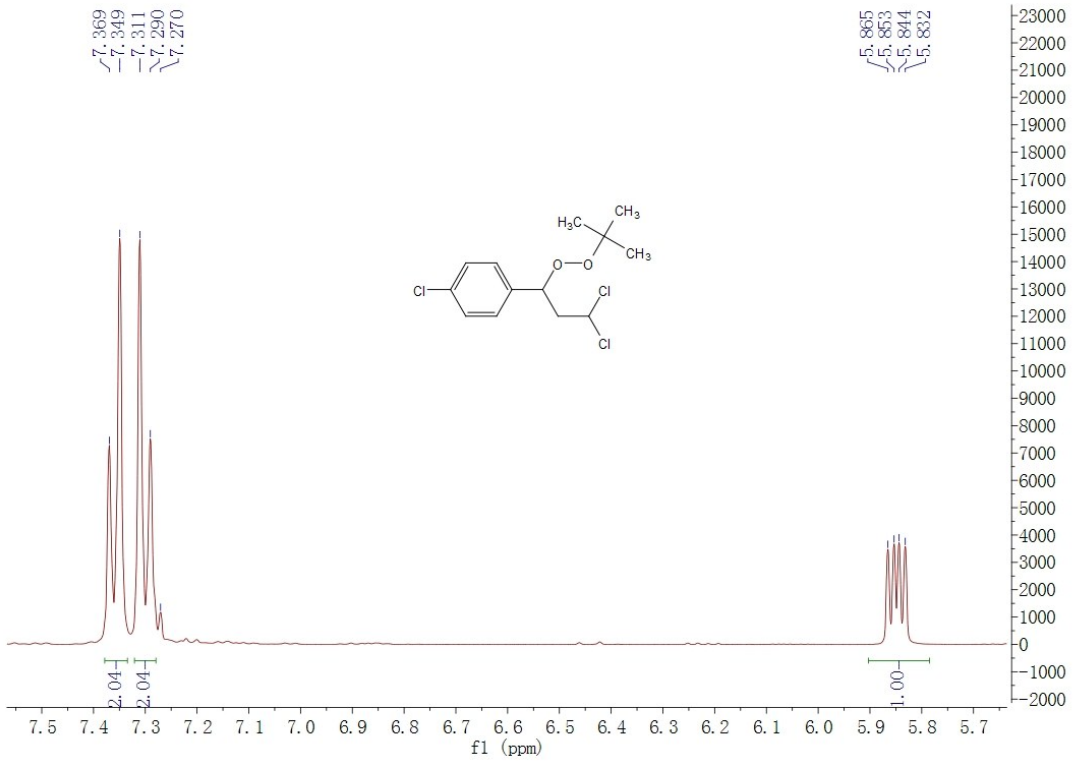

7.352
7.336
7.270
7.139
7.120
7.097
7.073
7.050
7.029
5.875
5.863
5.853
5.841
5.150
5.139
5.127
5.116
F
H3C
CH3
CH3
O
O
Cl
Cl
25000
20000
15000
10000
5000
0
1.10
1.04
2.08
1.00
0.99
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
f1 (ppm)

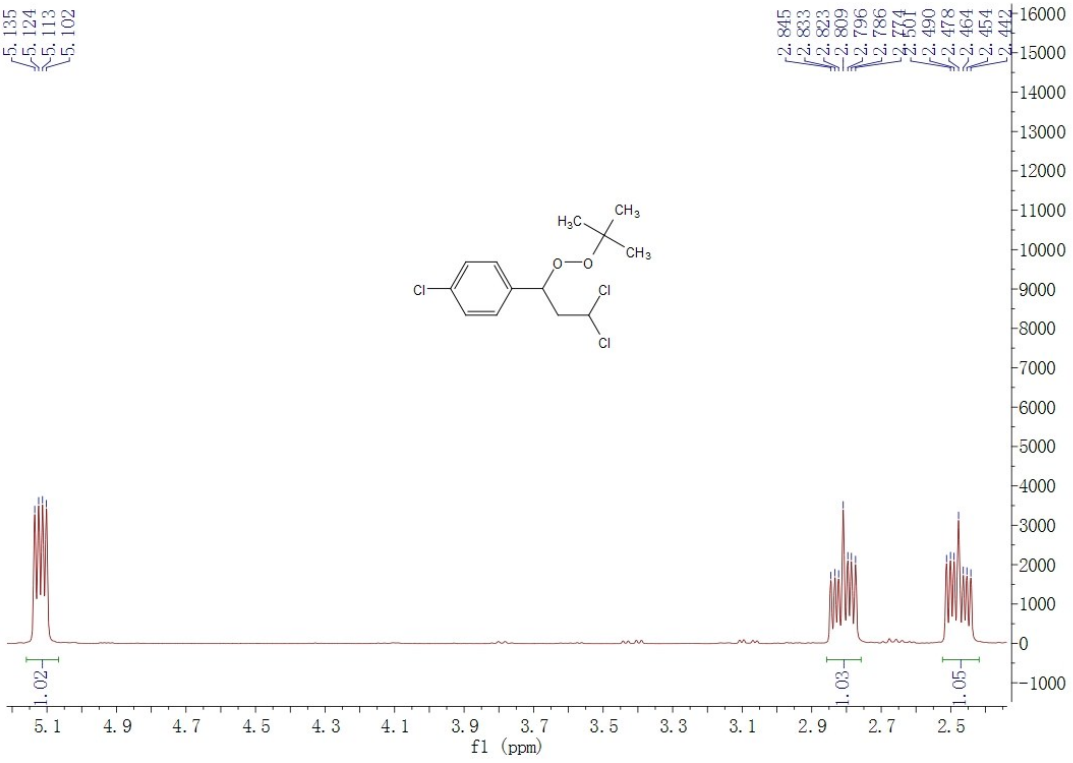

2.827
2.816
2.805
2.792
2.779
2.768
2.756
2.492
F
H3C
CH3
CH3
O
O
Cl
Cl
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.06
1.06
3.00
2.95
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
f1 (ppm)

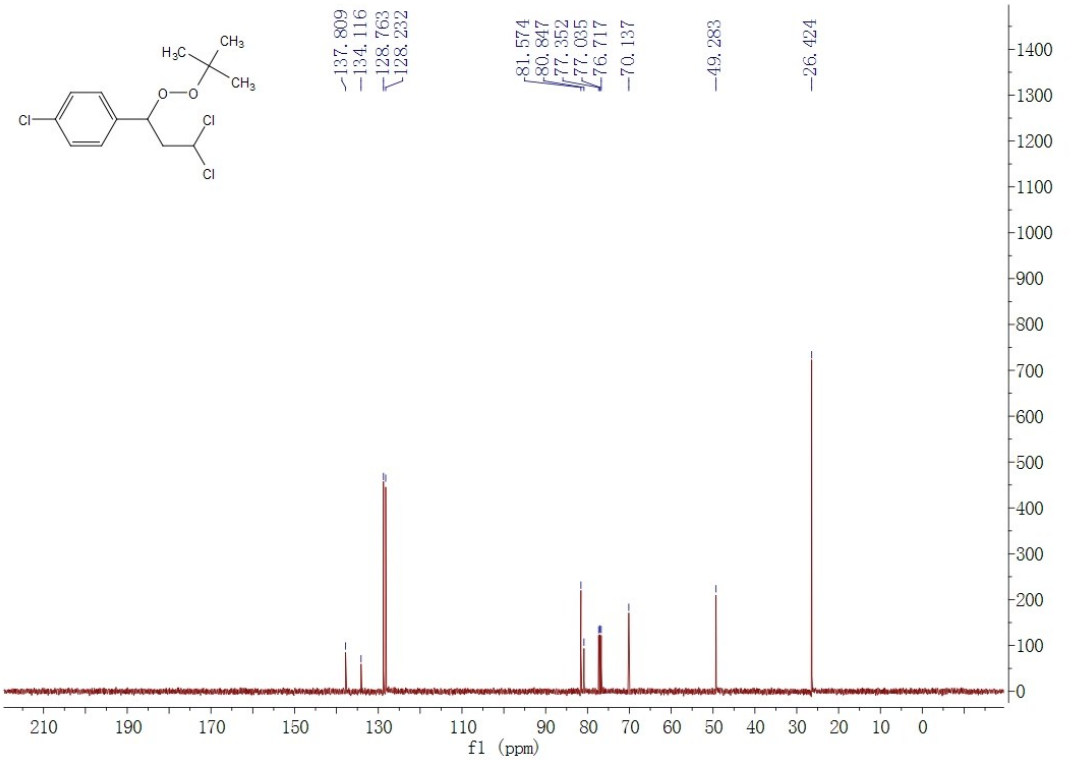


1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-4-chlorobenzene (2i)

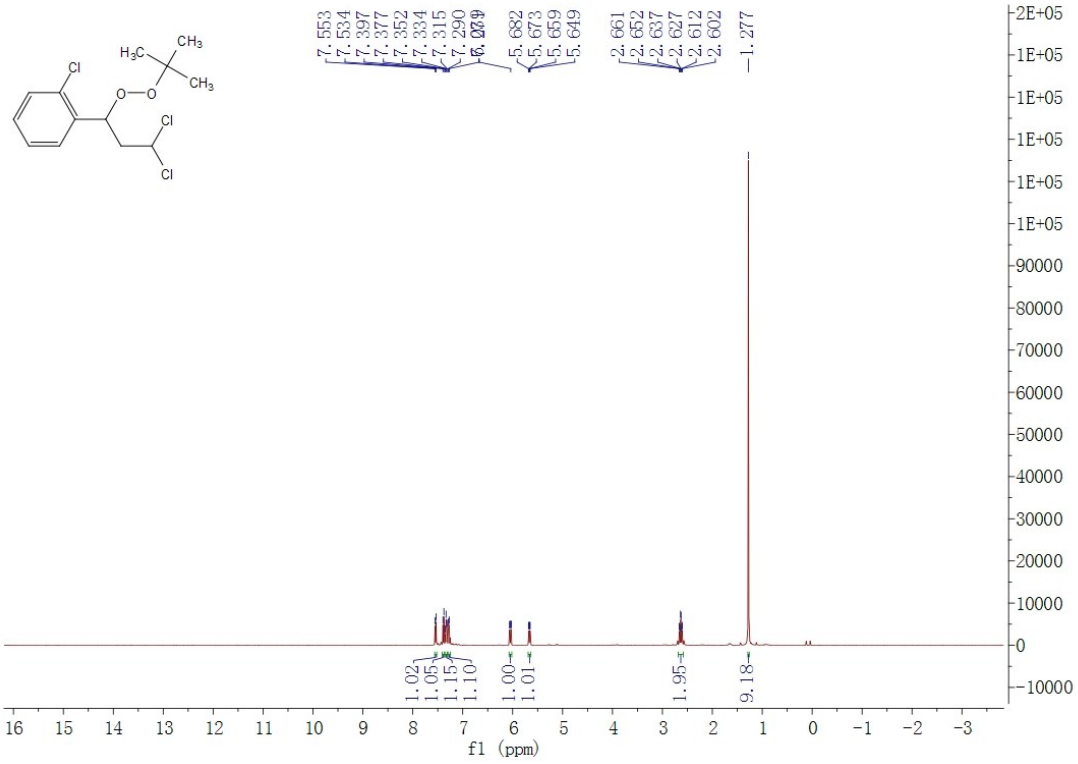


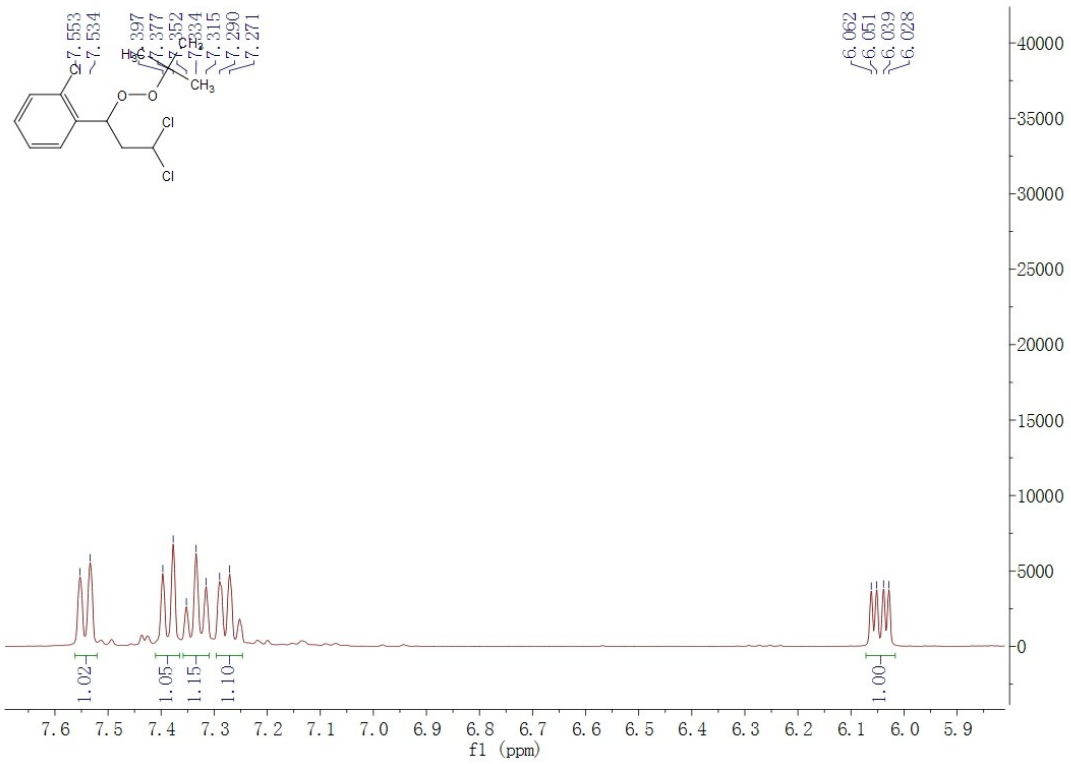

7.369
7.349
7.311
7.290
7.270
5.865
5.853
5.844
5.832
H3C
CH3
CH3
O
O
Cl
Cl
Cl
2.04
2.04
1.00
f1 (ppm)

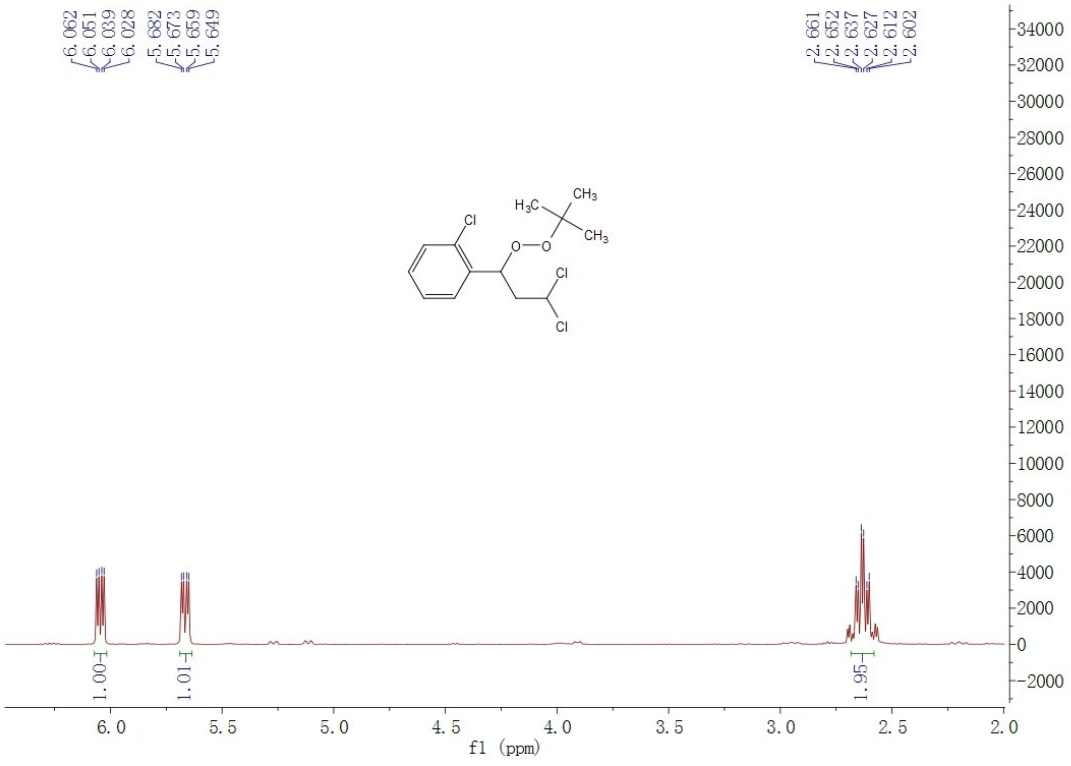

5.135
5.124
5.113
5.102
H3C
CH3
CH3
O
O
Cl
Cl
Cl
1.02
1.03
1.05
f1 (ppm)

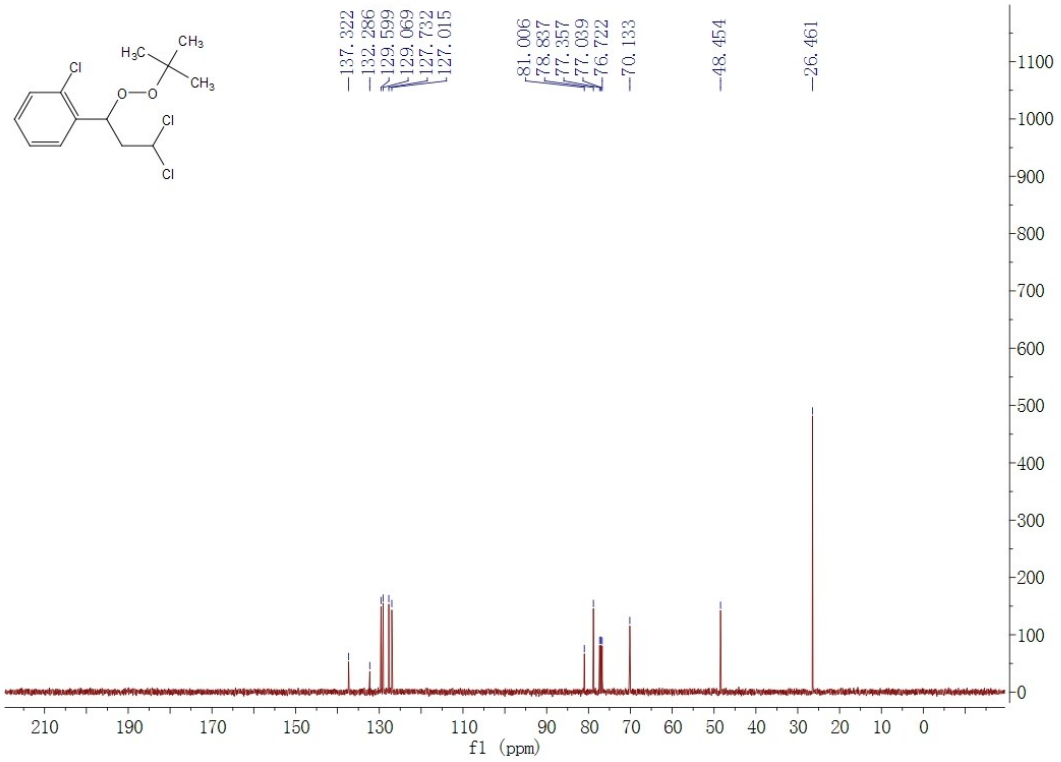


1-(1-(*tert*-butylperoxy)-3,3-dichloropropyl)-2-chlorobenzene (2j)

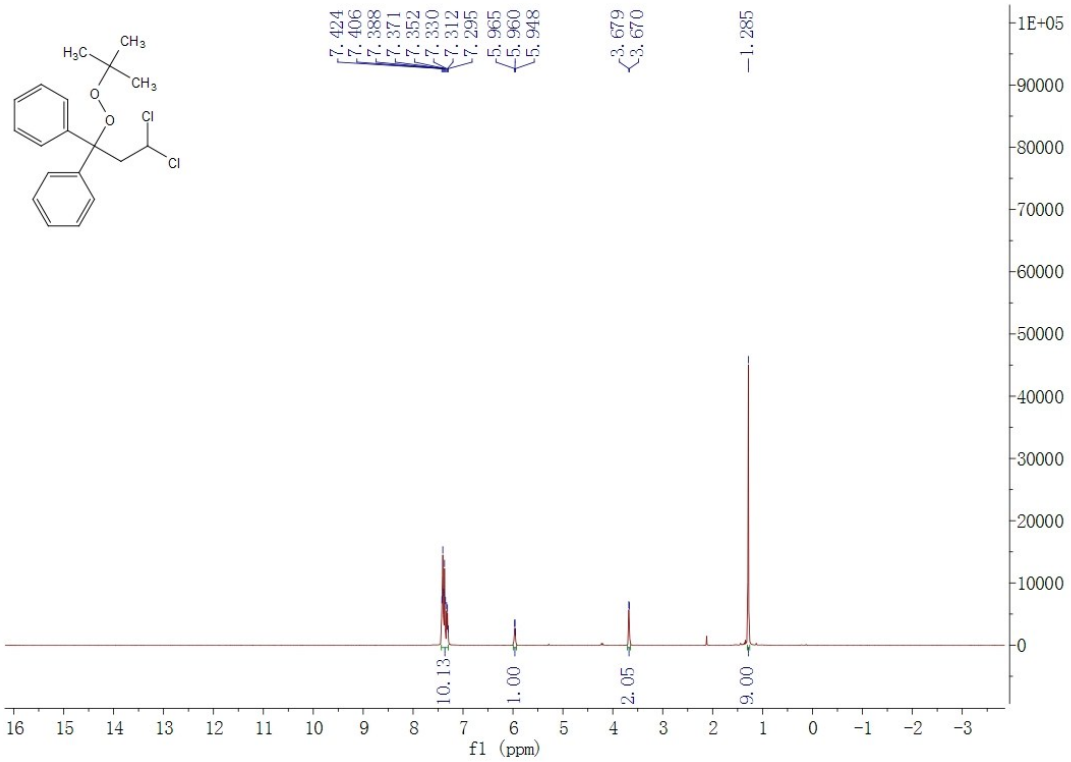


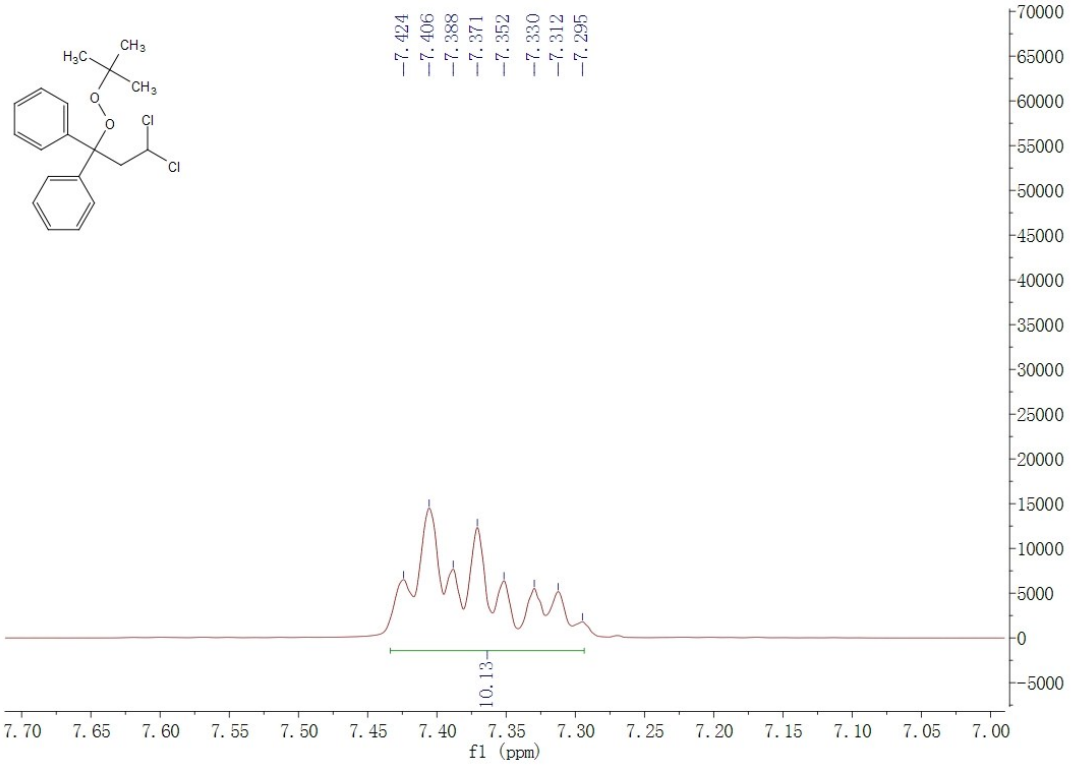

7.553
7.534
7.397
7.377
7.352
7.334
7.315
7.290
7.271
6.062
6.051
6.039
6.028
Cl
Cl
1.02
1.05
1.15
1.10
1.00
f1 (ppm)

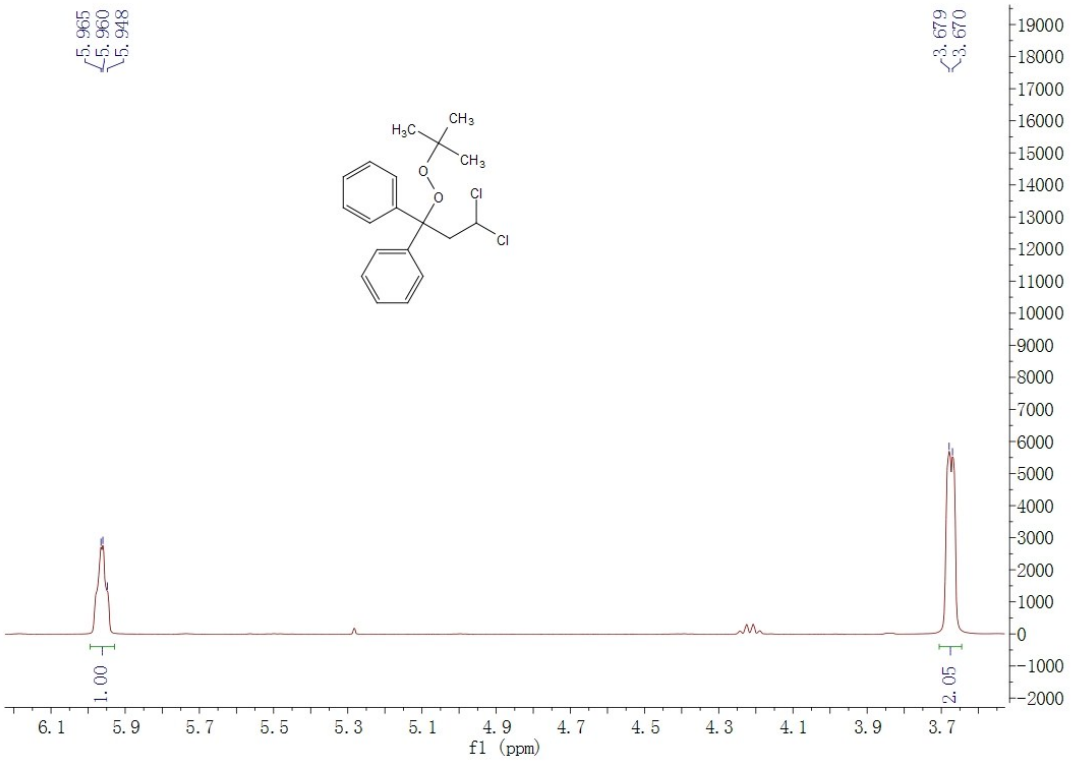

6.062
6.051
6.039
6.028
5.682
5.673
5.659
5.649
2.661
2.652
2.637
2.627
2.612
2.602
Cl
Cl
1.00
1.01
1.95
f1 (ppm)

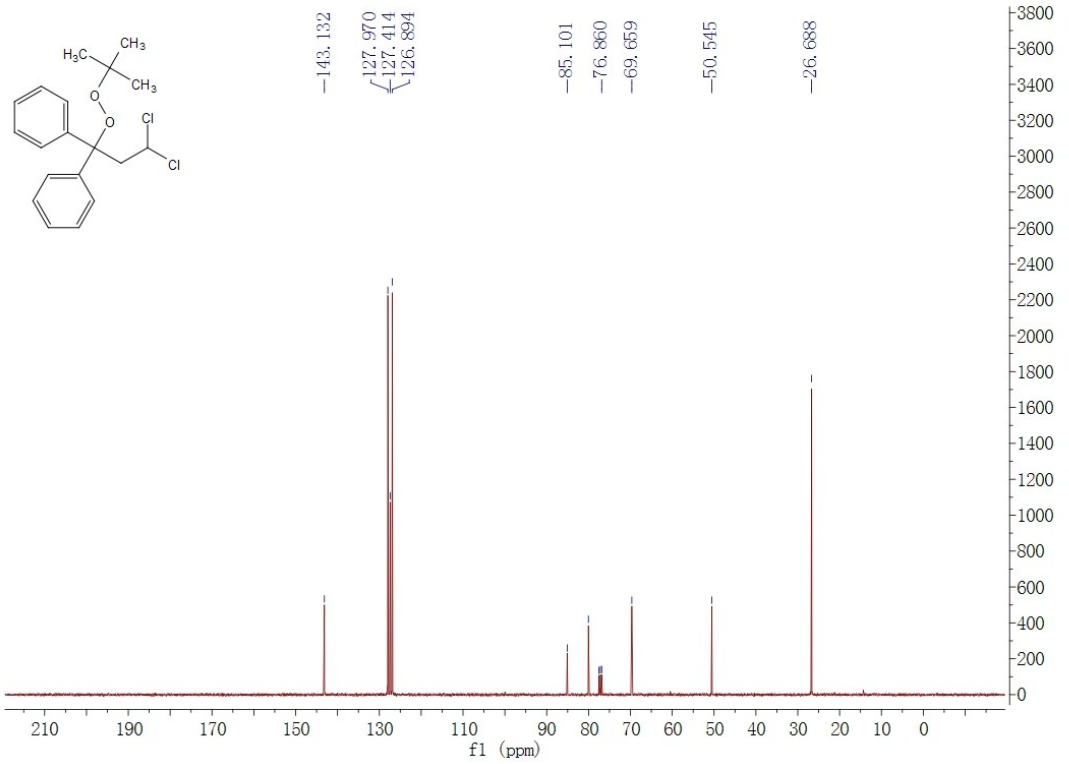


1-(*tert*-butylperoxy)-3,3-dichloro-1,1-diphenylpropane (2k)

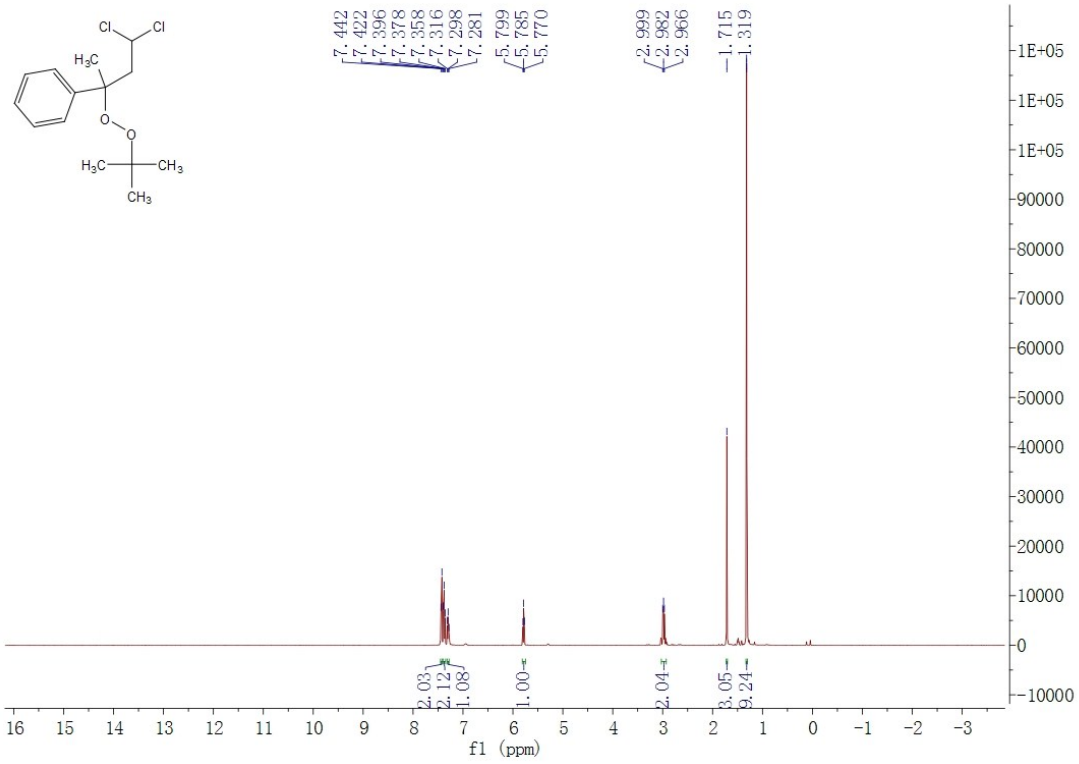


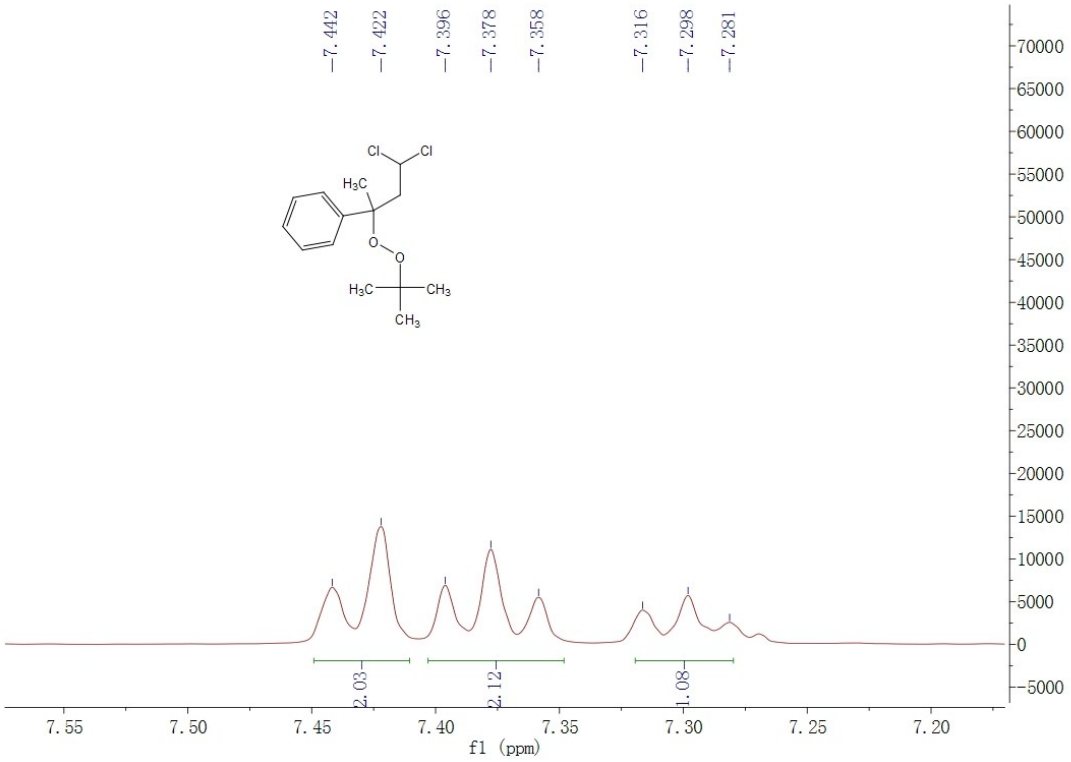

7.424
7.406
7.388
7.371
7.352
7.330
7.312
7.295
10.13
f1 (ppm)

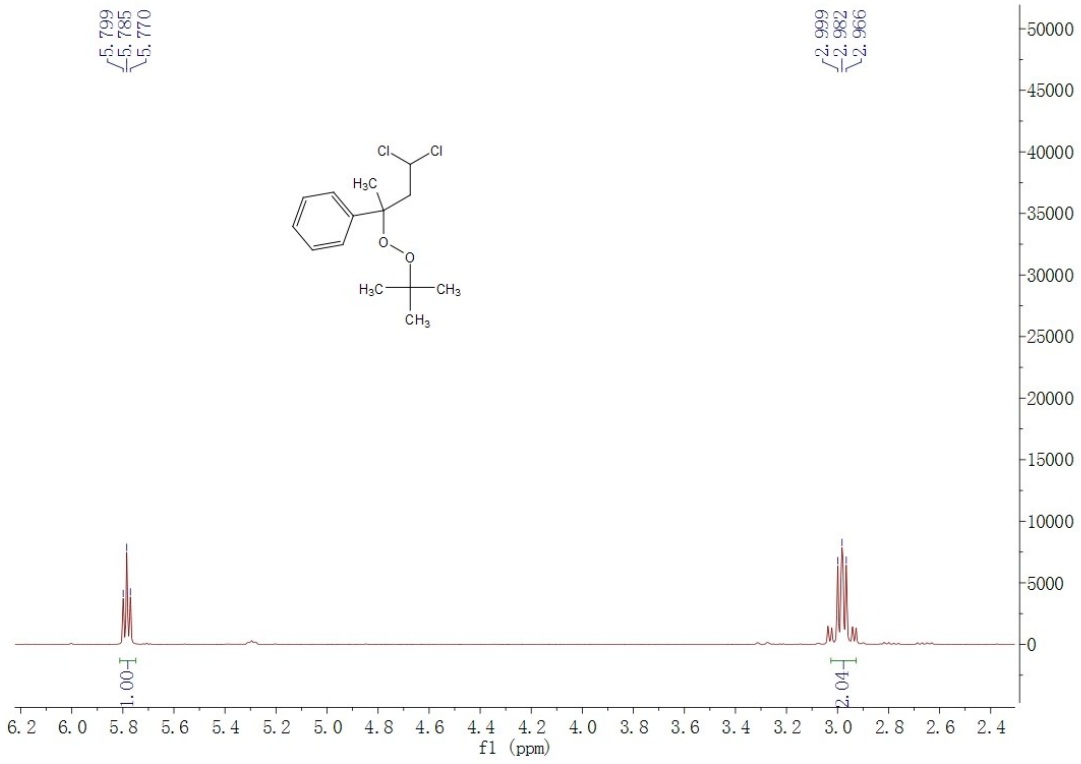

5.965
5.960
5.948
3.679
3.670
1.00
2.05
f1 (ppm)

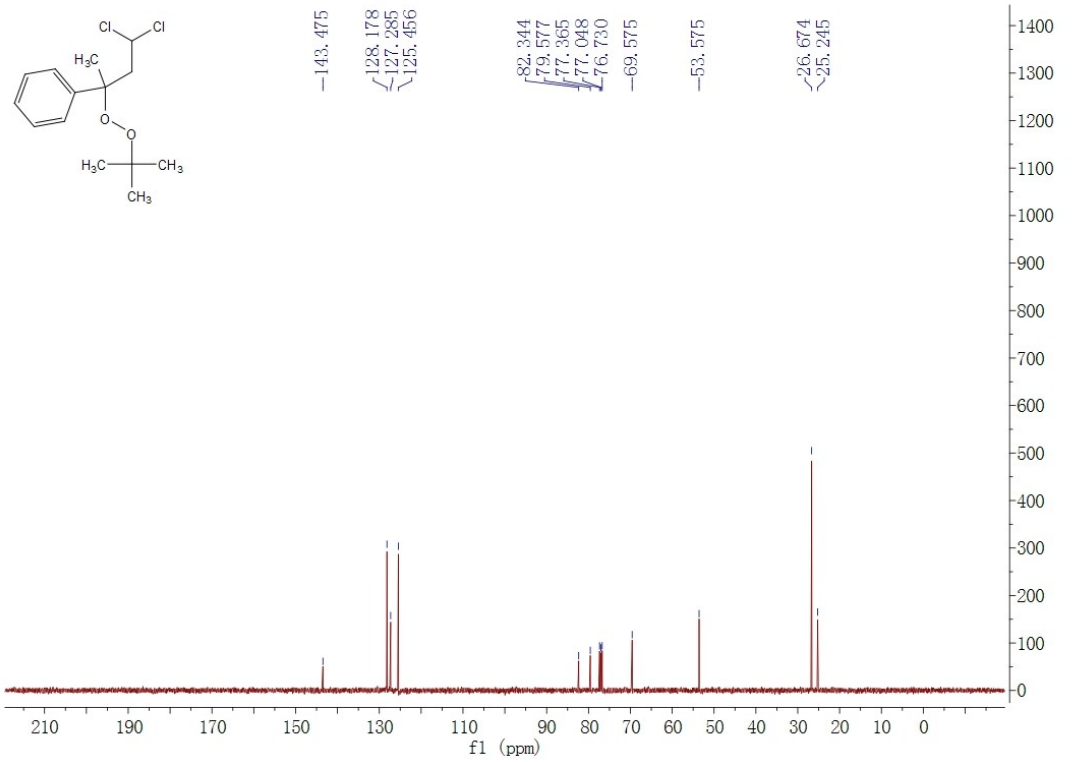


1-(2-(*tert*-butylperoxy)-4,4-dichlorobutan-2-yl)benzene (2l)

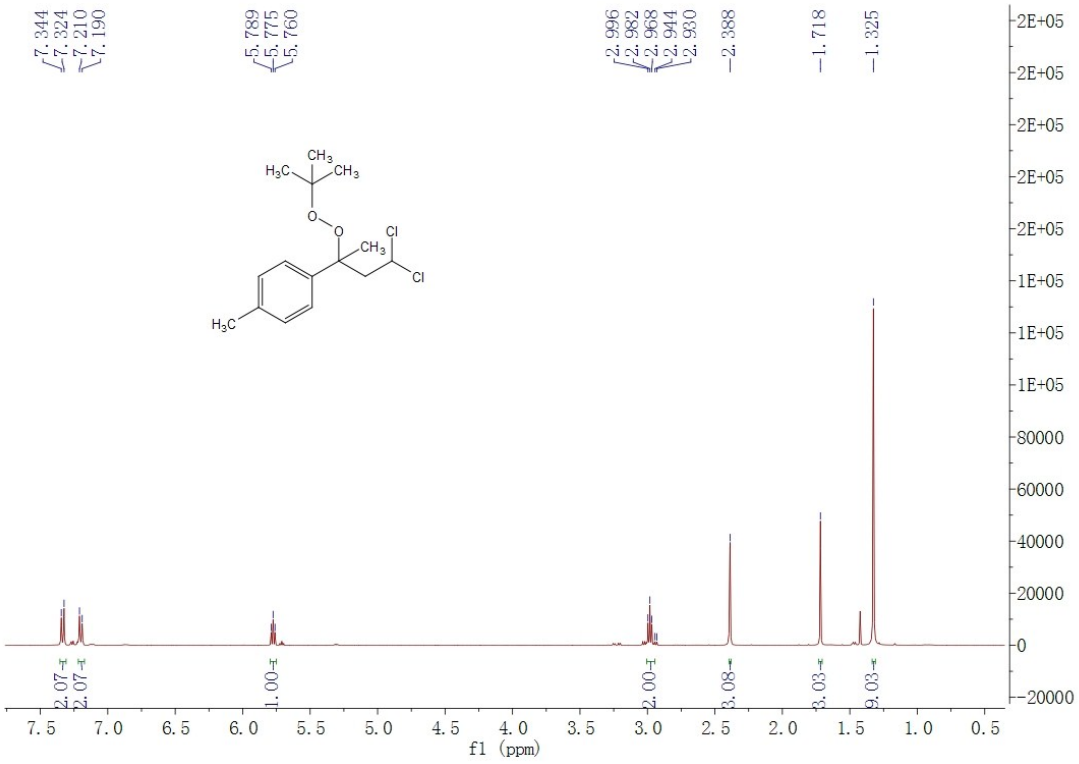


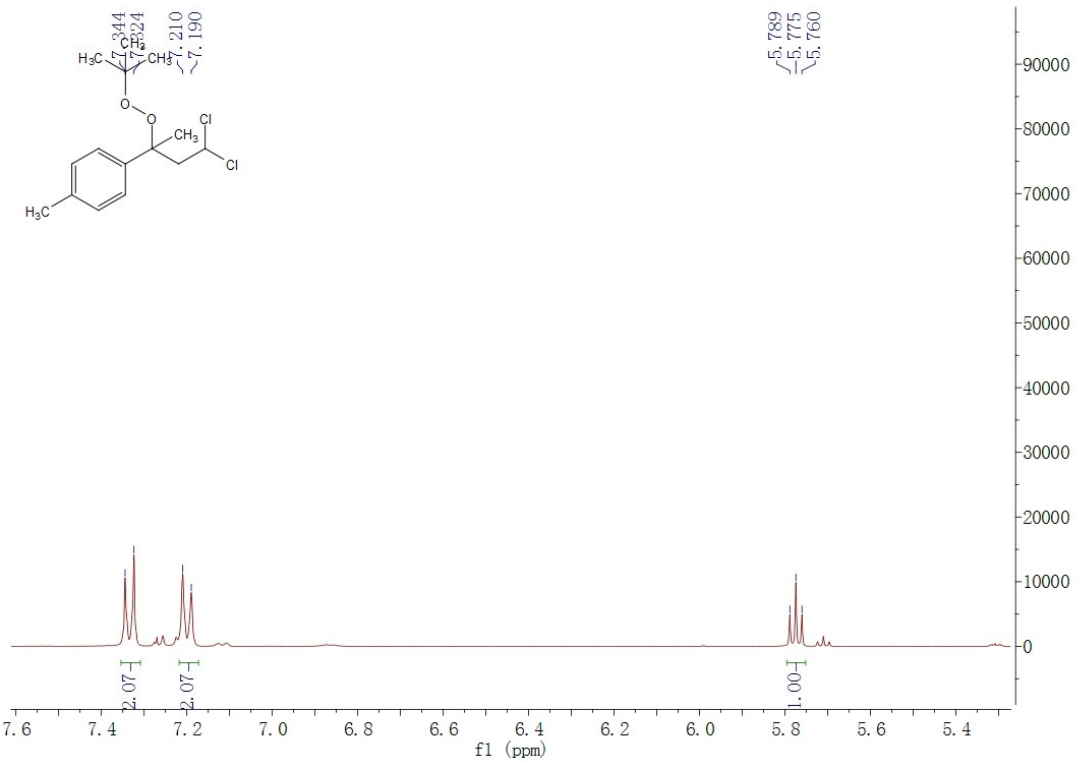

7.442
7.422
7.396
7.378
7.358
7.316
7.298
7.281
Cl
Cl
H3C
O
O
H3C
CH3
CH3
2.03
2.12
1.08
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)

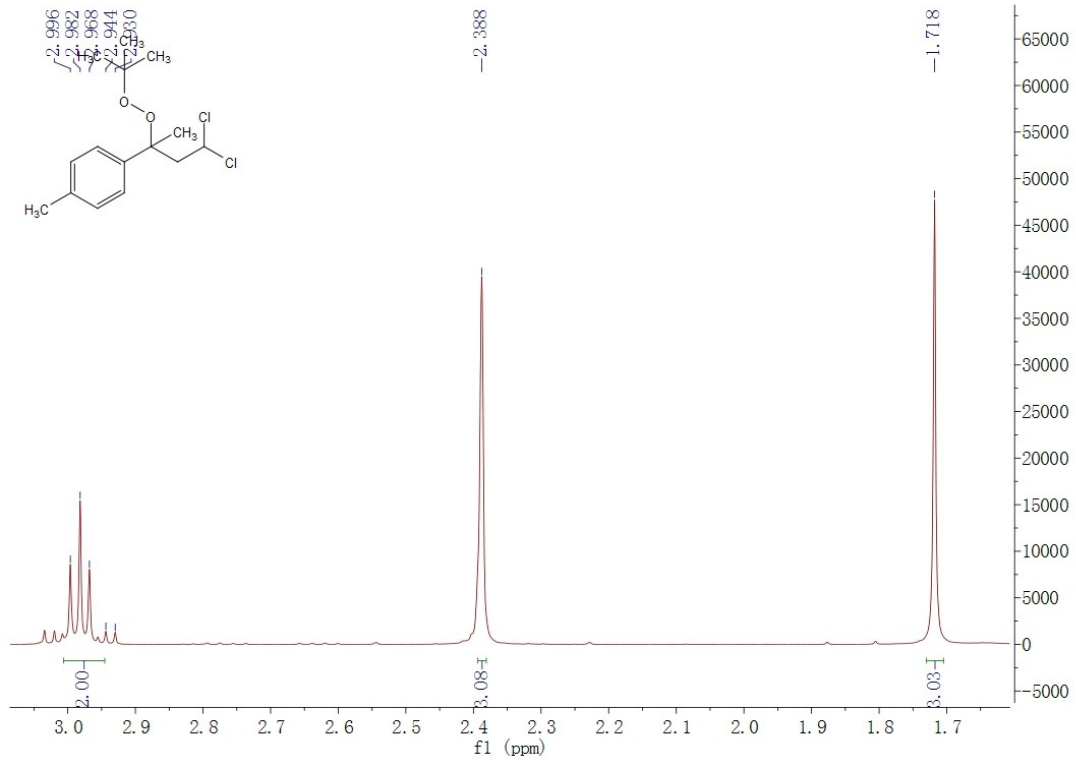

5.799
5.785
5.770
2.999
2.982
2.966
Cl
Cl
H3C
O
O
H3C
CH3
CH3
1.00
2.04
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
f1 (ppm)

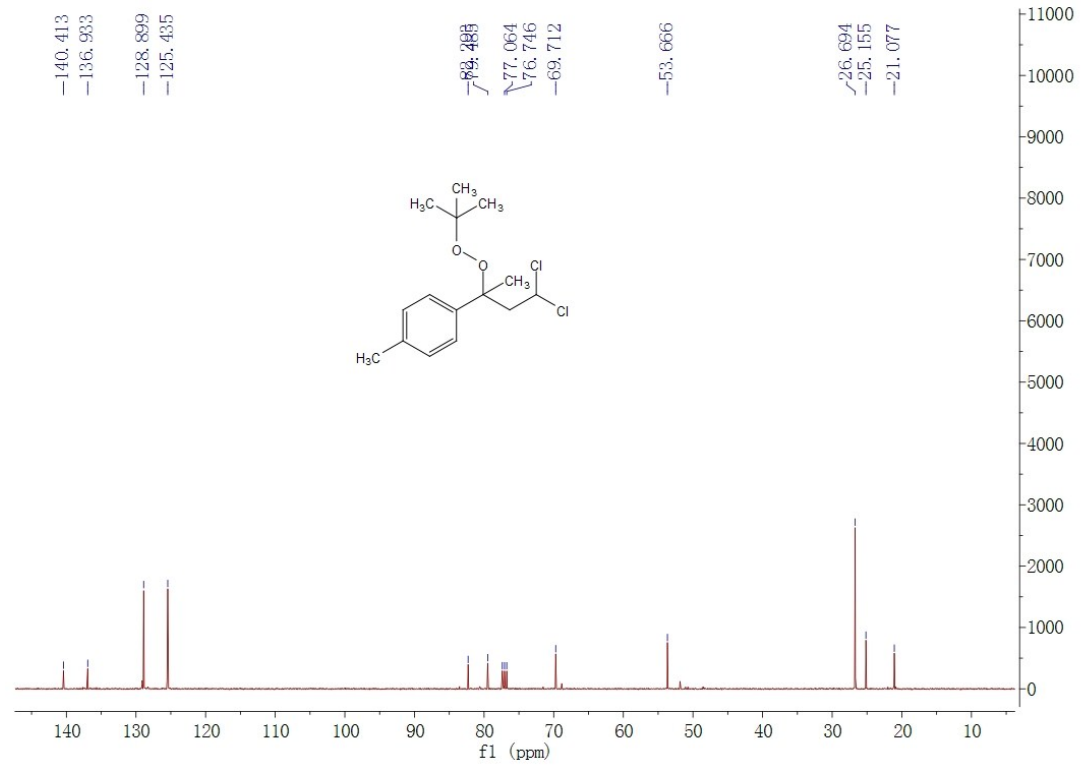


1-(2-(tert-butylperoxy)-4,4-dichlorobutan-2-yl)-4-methylbenzene (2m)

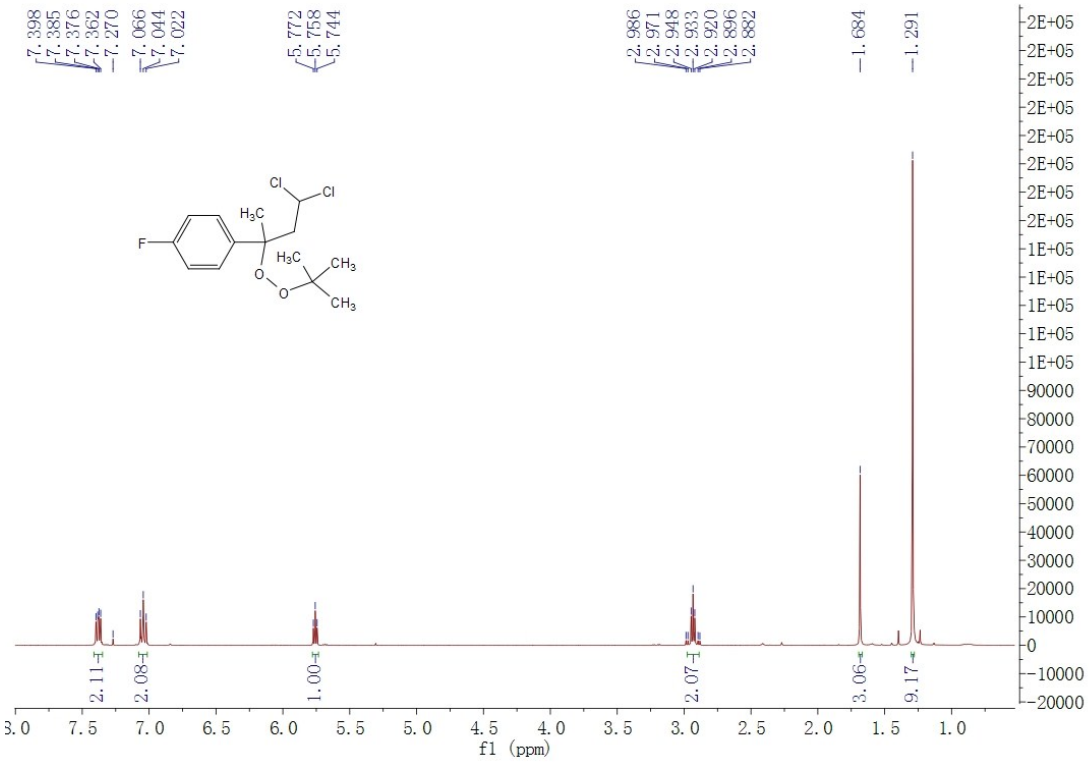


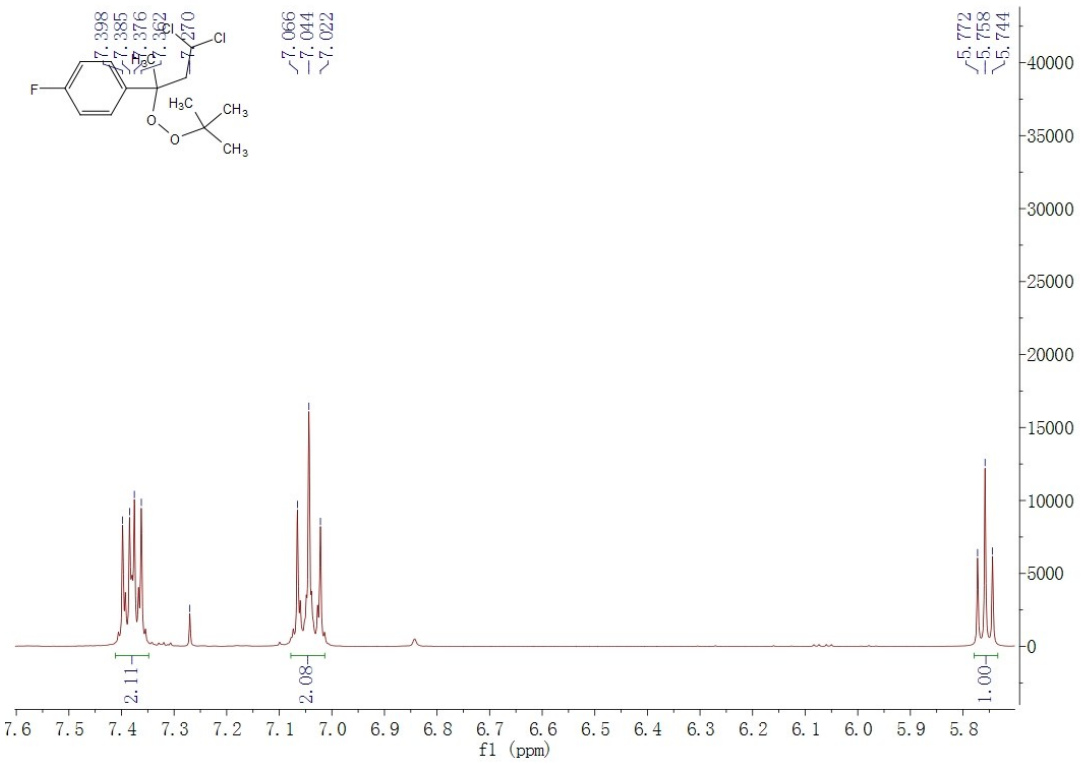

7.344
7.324
7.210
7.190
5.789
5.775
5.760
2.07
2.07
1.00
f1 (ppm)

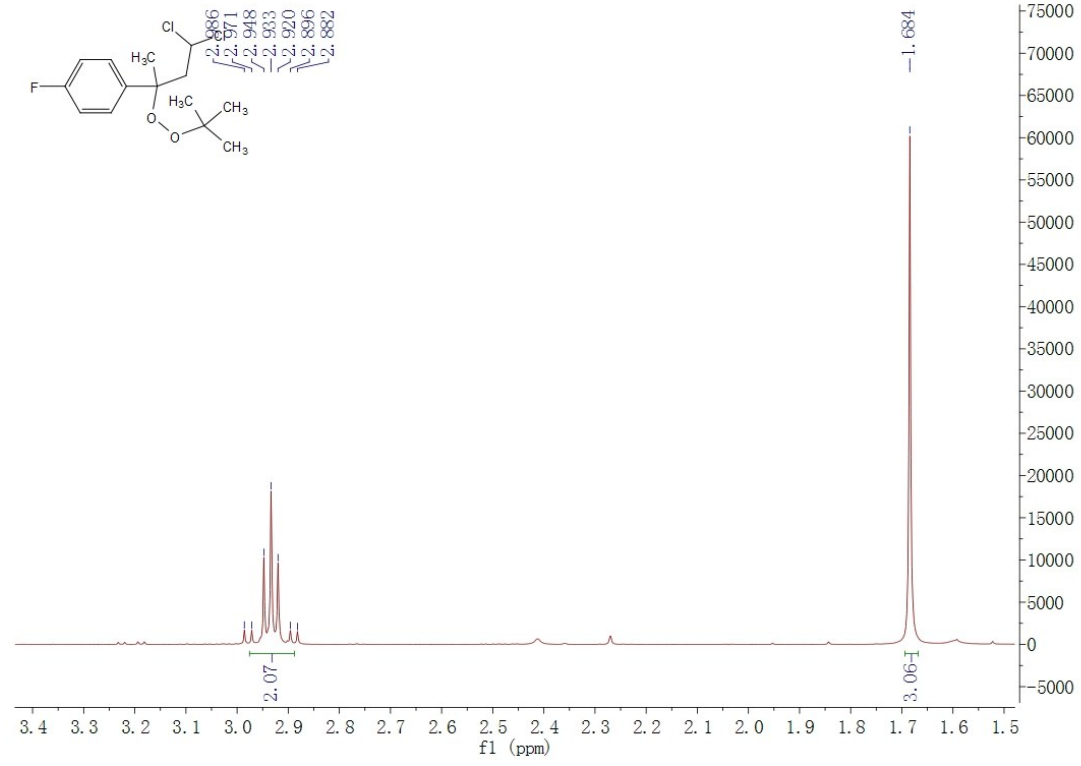

2.996
2.982
2.968
2.944
2.930
2.388
1.718
2.00
3.08
3.03
f1 (ppm)

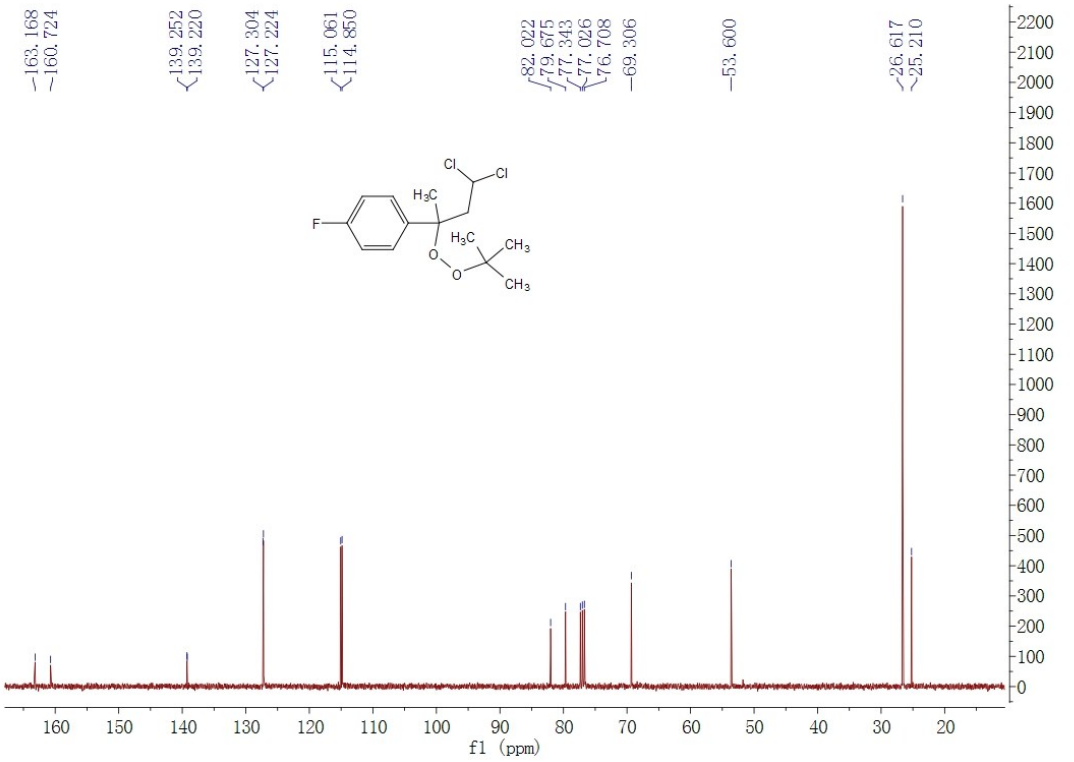


1-(2-(tert-butylperoxy)-4,4-dichlorobutan-2-yl)-4-fluorobenzene (2n)

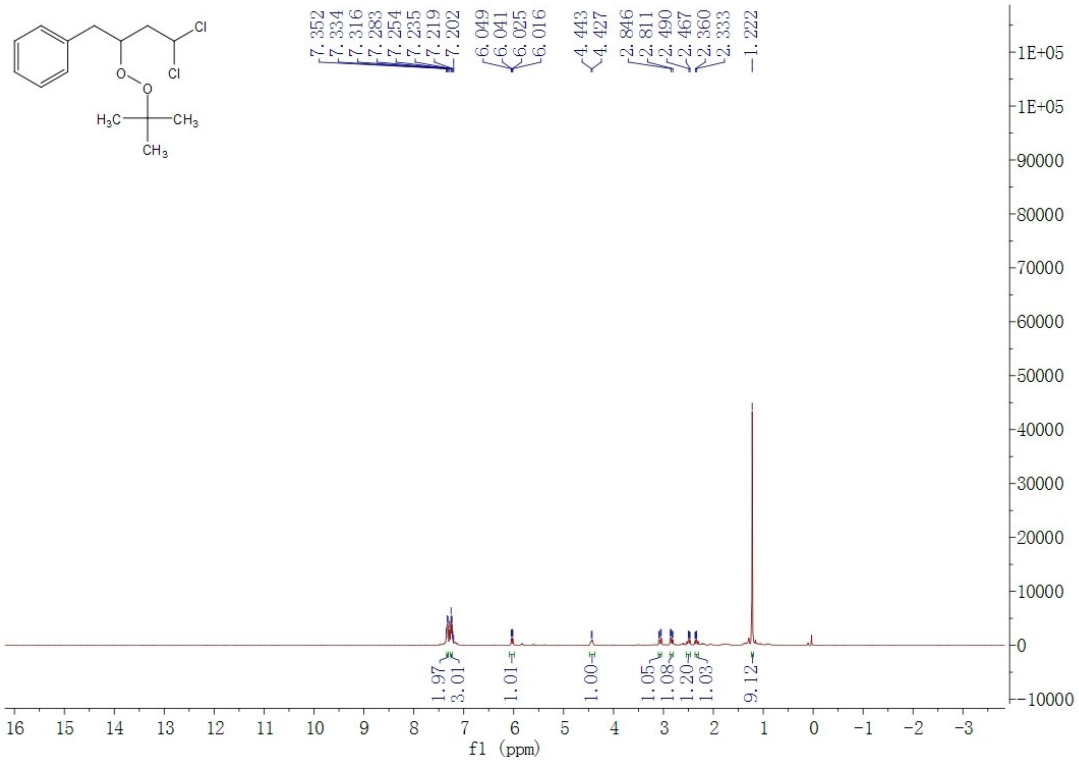


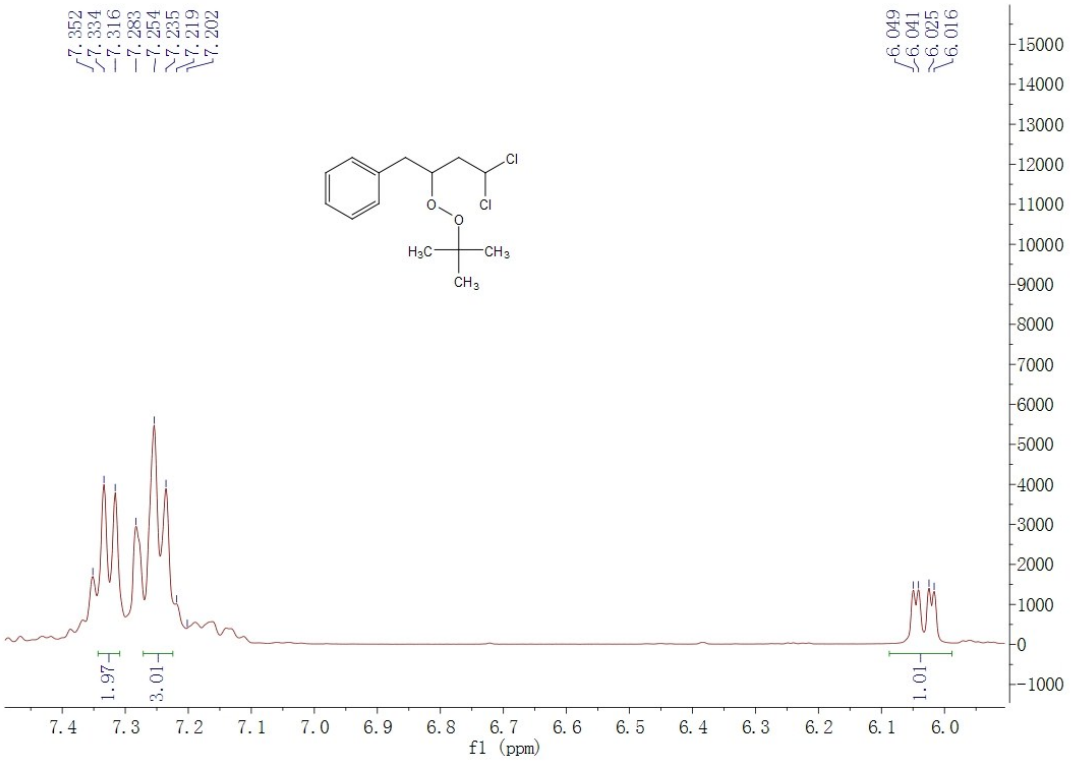

7.398
7.385
7.376
7.362
7.270
7.066
7.044
7.022
5.772
5.758
5.744
F
Cl
H3C
CH3
O
O
CH3
2.11
2.08
1.00
f1 (ppm)

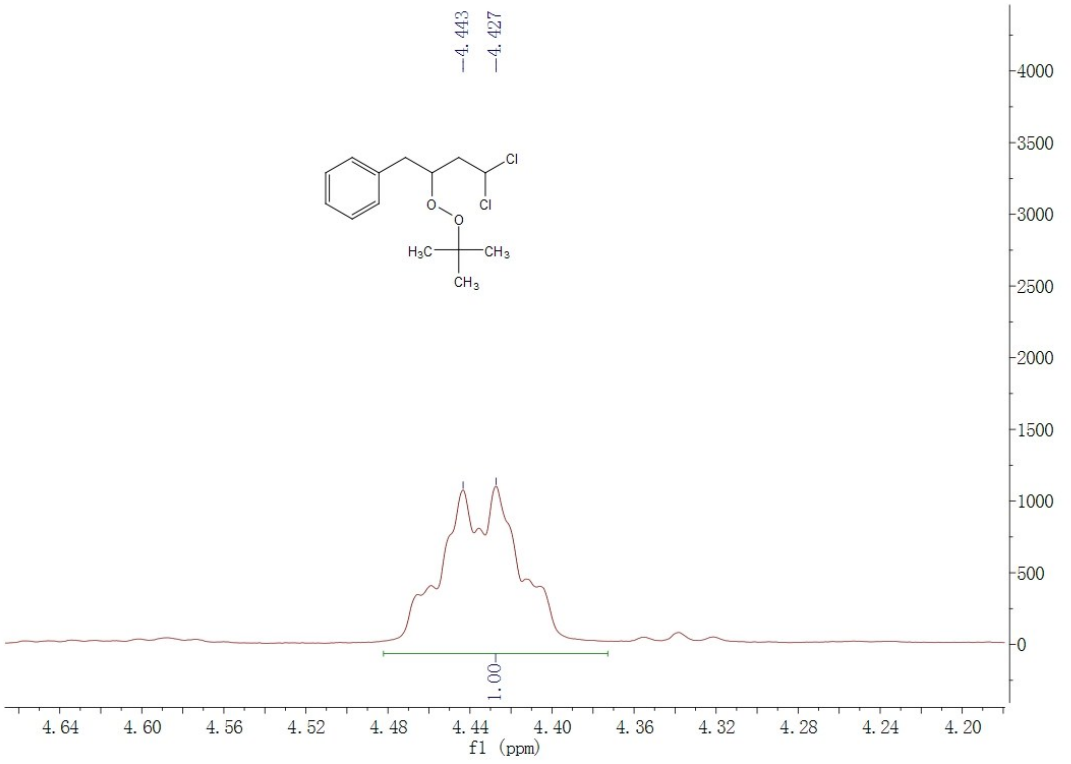

2.886
2.871
2.948
2.933
2.920
2.896
2.882
1.684
F
Cl
H3C
H3C
CH3
O
O
CH3
2.07
3.06
f1 (ppm)

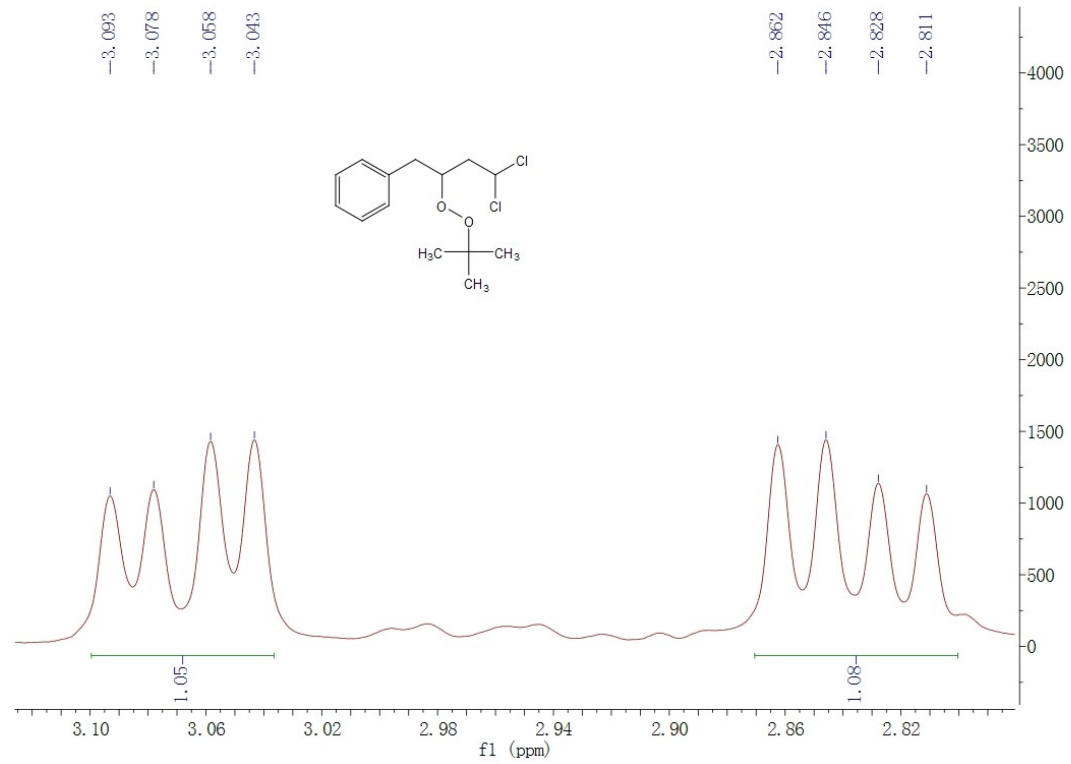


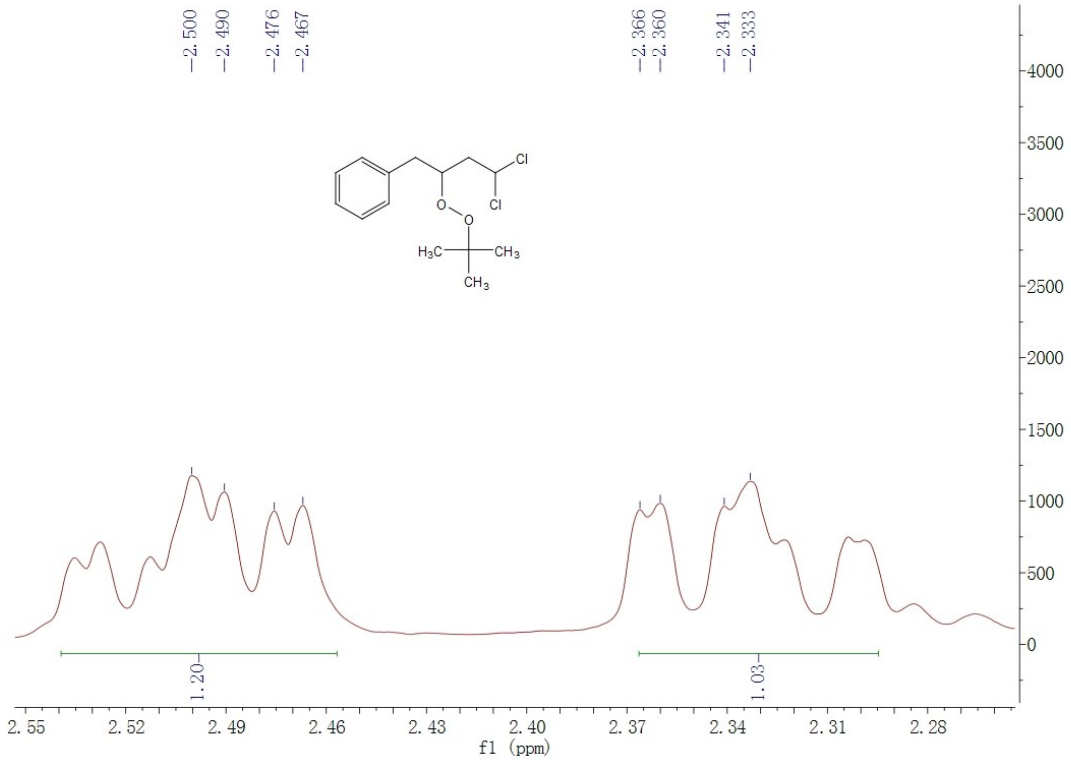
1-(2-(*tert*-butylperoxy)-4,4-dichlorobutyl)benzene (2o)

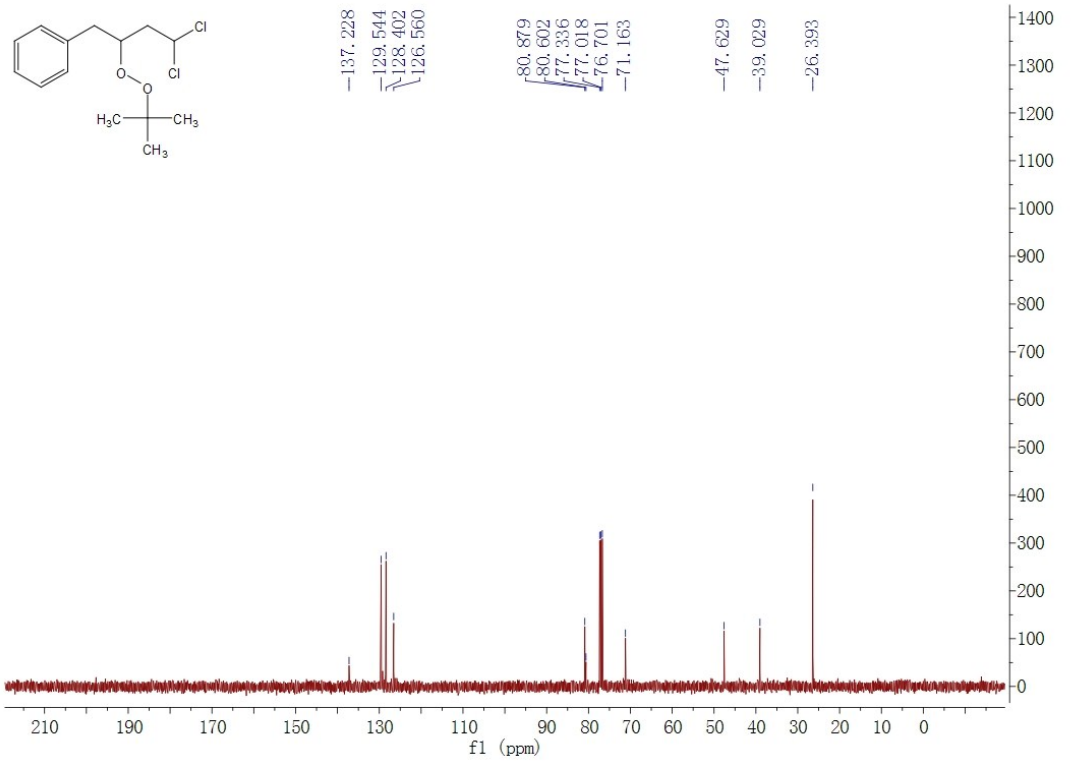



7.352
7.334
7.316
7.283
7.254
7.235
7.219
7.202
6.049
6.041
6.025
6.016
Cl
Cl
O
O
H3C
CH3
CH3
1.97
3.01
1.01
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)

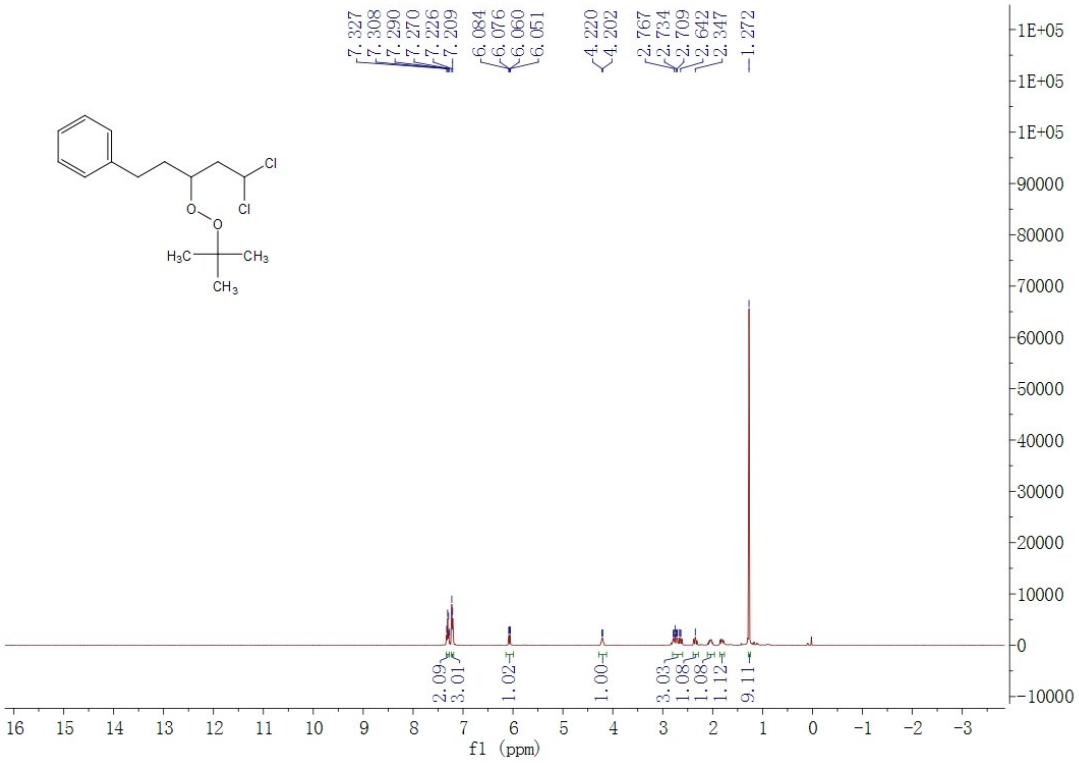

4.443
4.427
Cl
Cl
O
O
H3C
CH3
CH3
1.00
4.64
4.60
4.56
4.52
4.48
4.44
4.40
4.36
4.32
4.28
4.24
4.20
f1 (ppm)

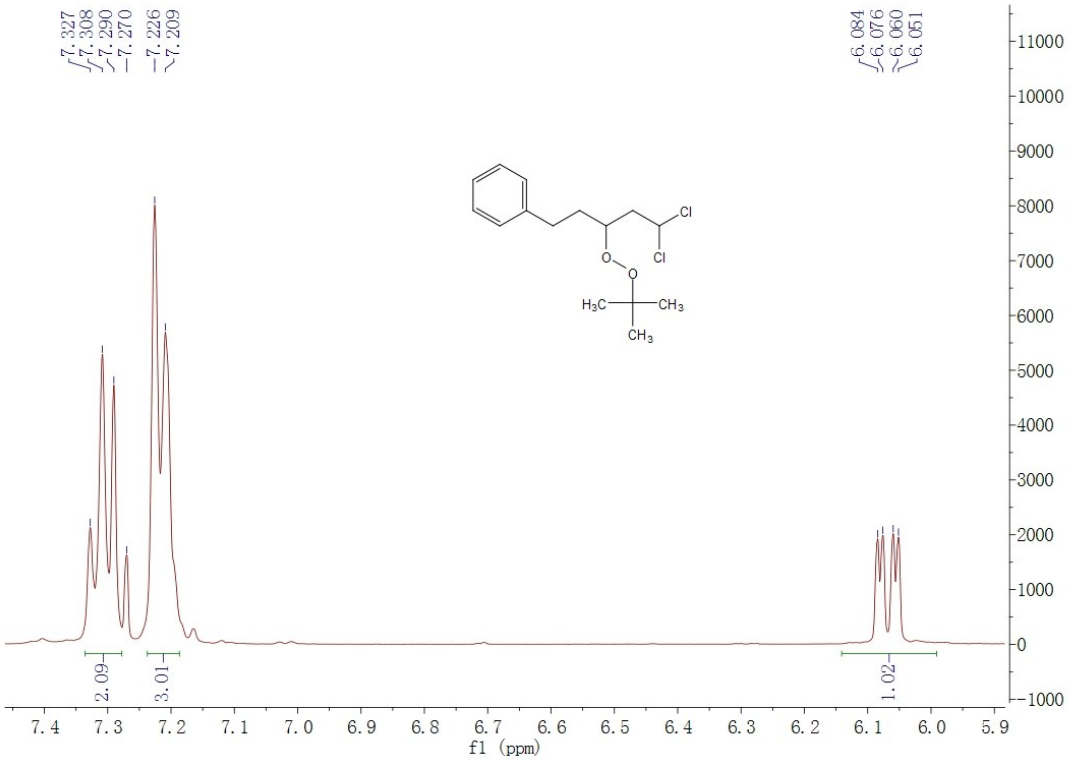

3.093
3.078
3.058
3.043
2.862
2.846
2.828
2.811
Cl
Cl
O
O
H3C
CH3
CH3
4000
3500
3000
2500
2000
1500
1000
500
0
1.05
1.08
3.10
3.06
3.02
2.98
2.94
2.90
2.86
2.82
f1 (ppm)

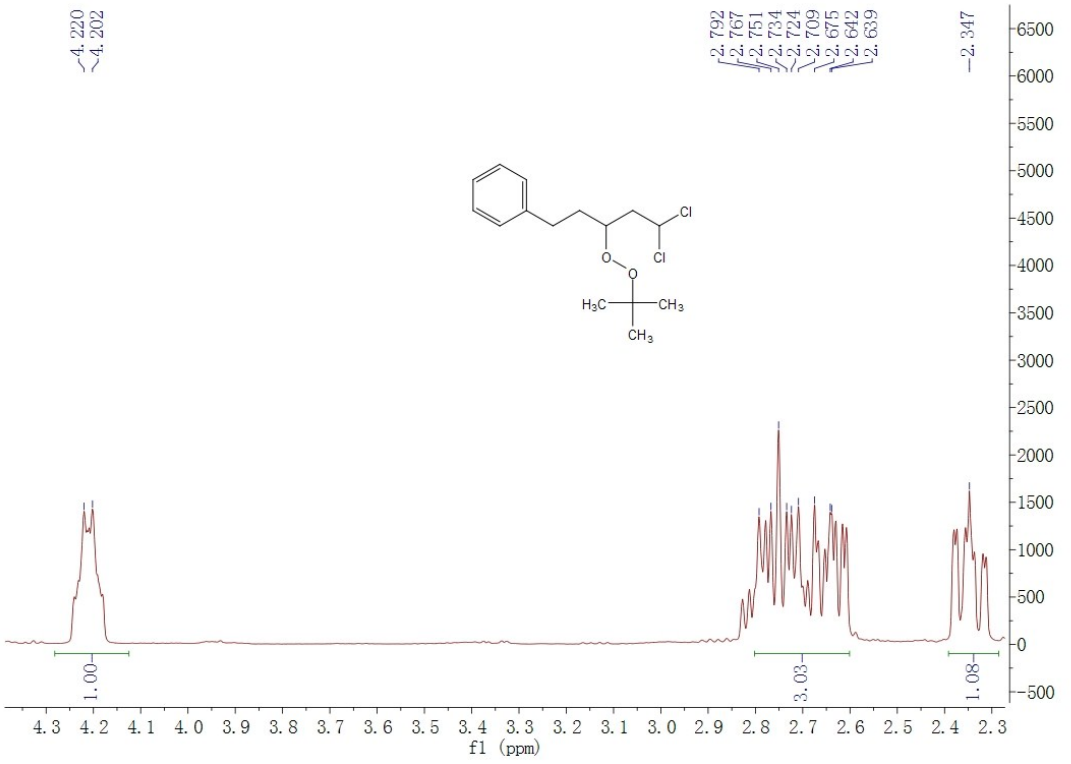

2.500
2.490
2.476
2.467
2.366
2.360
2.341
2.333
Cl
Cl
O
O
H3C
CH3
CH3
4000
3500
3000
2500
2000
1500
1000
500
0
1.20
1.03
2.55
2.52
2.49
2.46
2.43
2.40
2.37
2.34
2.31
2.28
f1 (ppm)

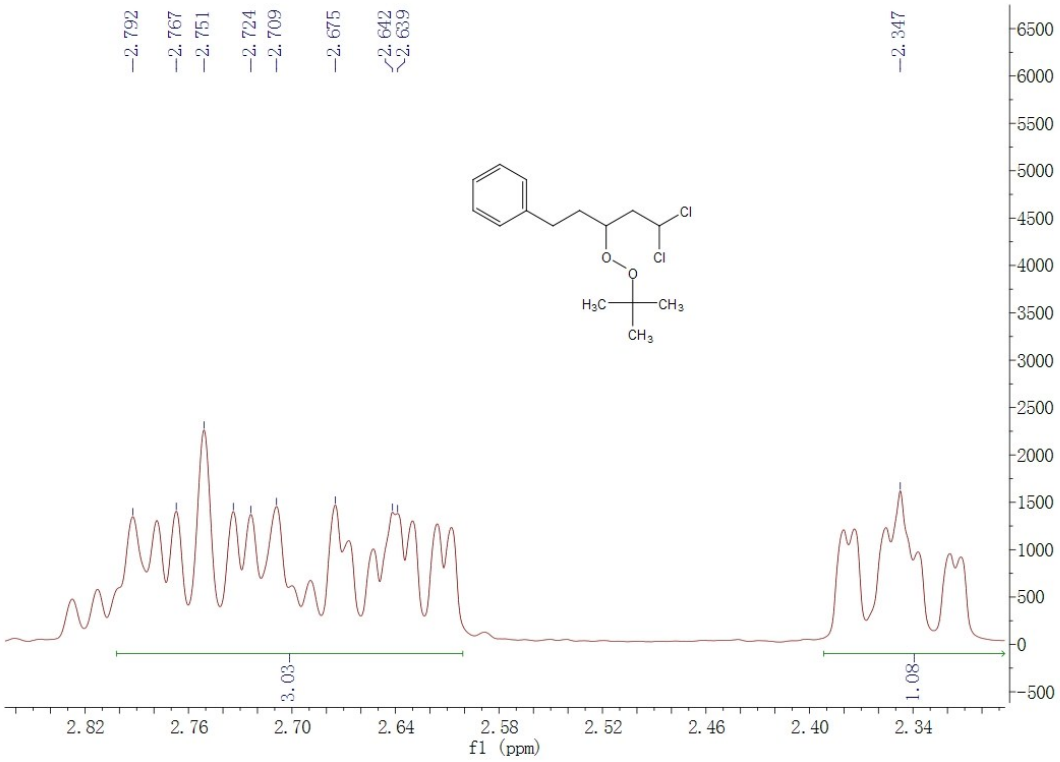


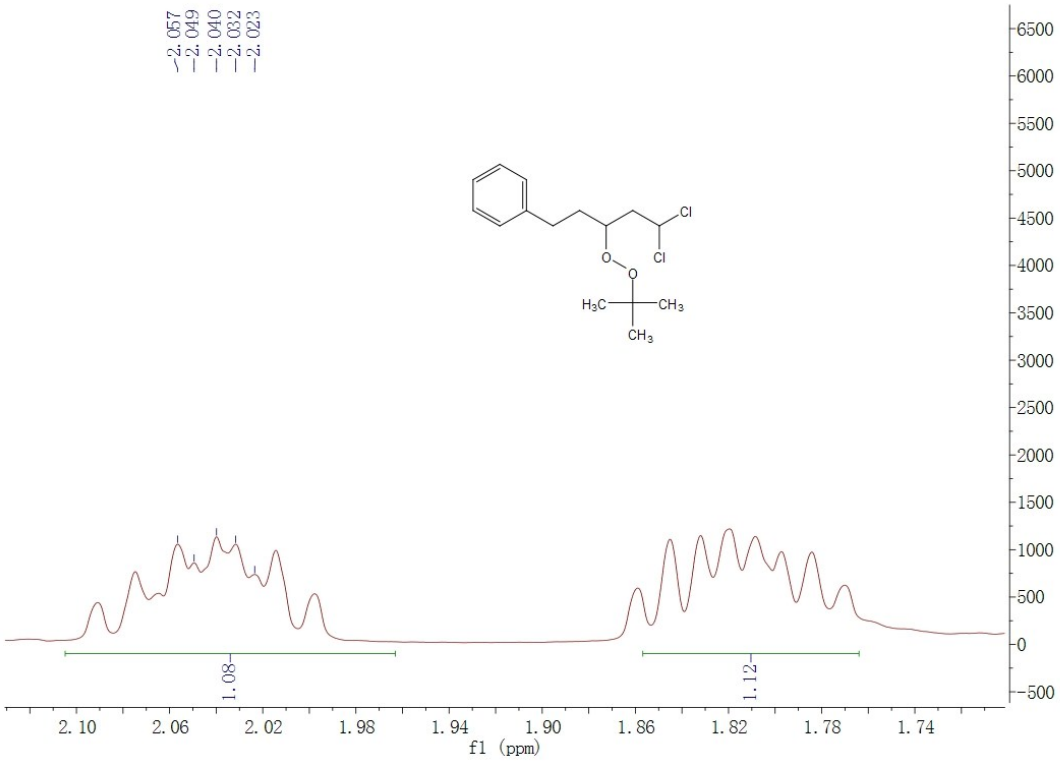
1-(3-(*tert*-butylperoxy)-5,5-dichloropentyl)benzene (2p)

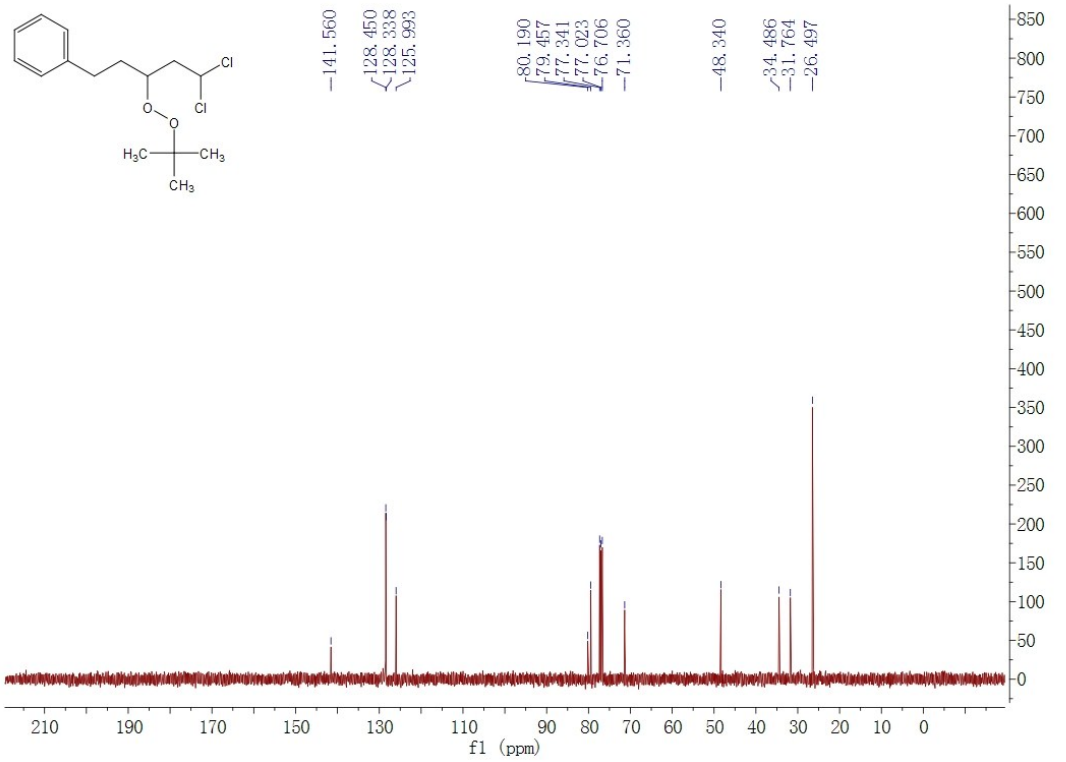



7.327
7.308
7.290
7.270
7.226
7.209
6.084
6.076
6.060
6.051
Cl
Cl
O
O
H3C
CH3
CH3
2.09
3.01
1.02
f1 (ppm)

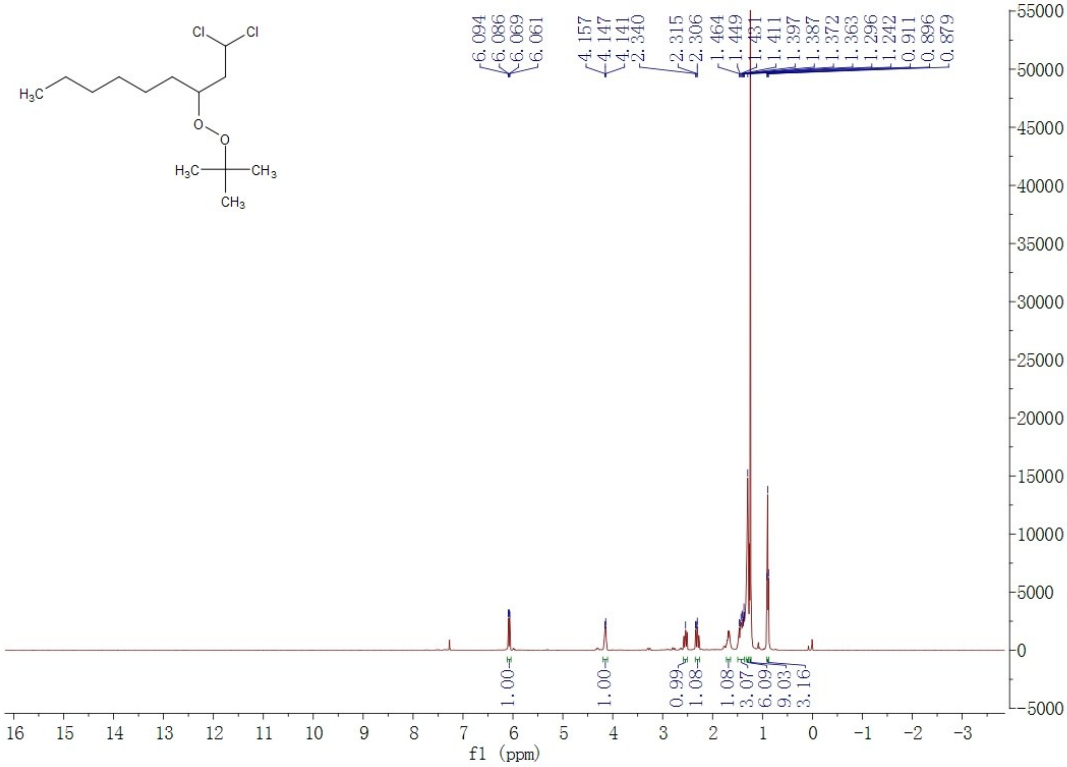

4.220
4.202
2.792
2.767
2.751
2.734
2.724
2.709
2.675
2.642
2.639
2.347
Cl
Cl
O
O
H3C
CH3
CH3
1.00
3.03
1.08
f1 (ppm)

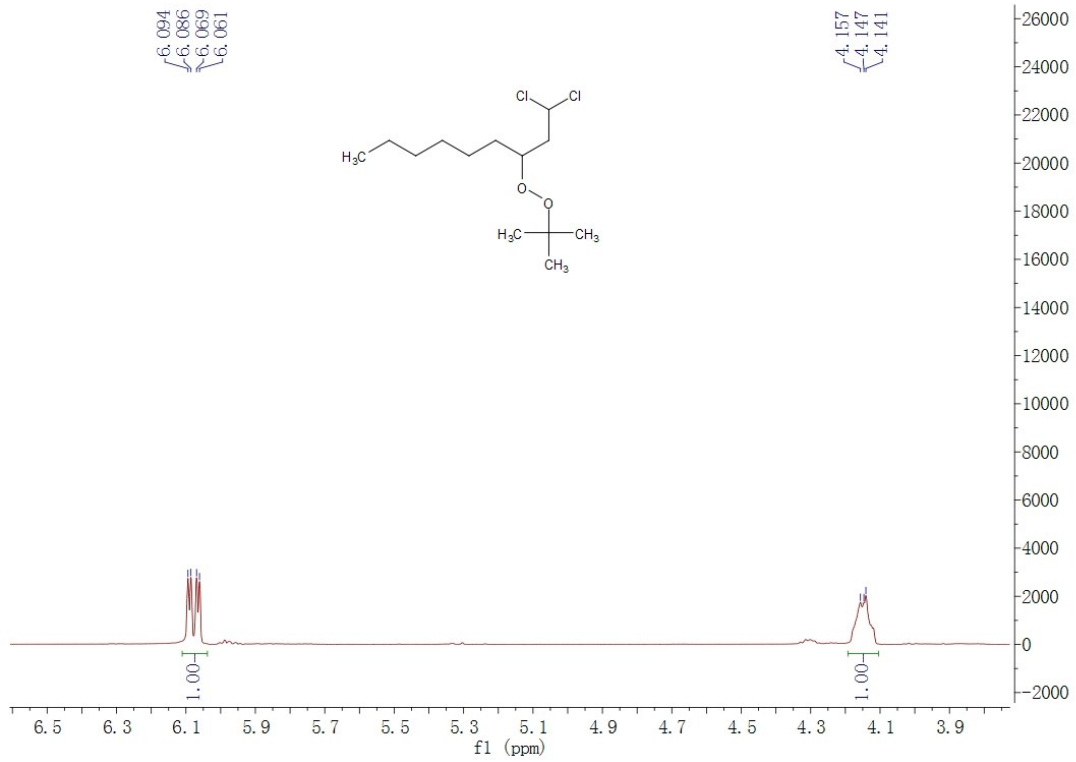

2.792
2.767
2.751
2.724
2.709
2.675
2.642
2.639
2.347
Cl
Cl
O
O
H3C
CH3
CH3
3.03
1.08
2.82
2.76
2.70
2.64
2.58
2.52
2.46
2.40
2.34
f1 (ppm)

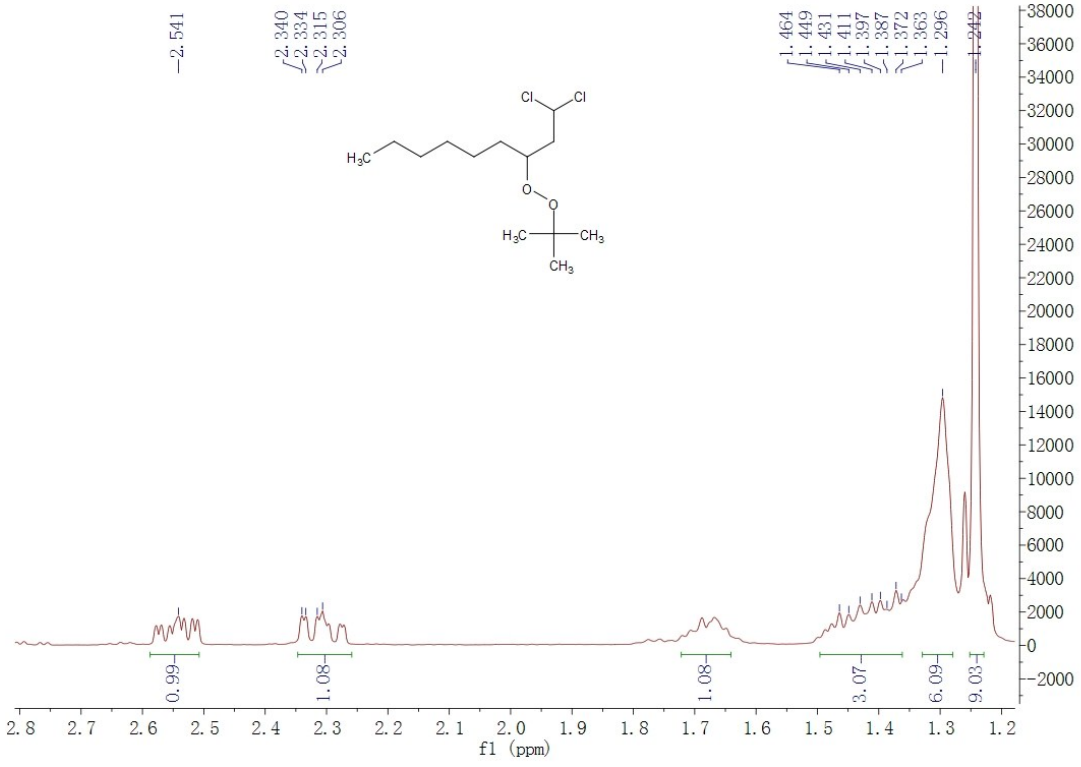

2.057
2.049
2.040
2.032
2.023
Cl
Cl
O
O
H3C
CH3
CH3
1.08
1.12
2.10
2.06
2.02
1.98
1.94
1.90
1.86
1.82
1.78
1.74
f1 (ppm)

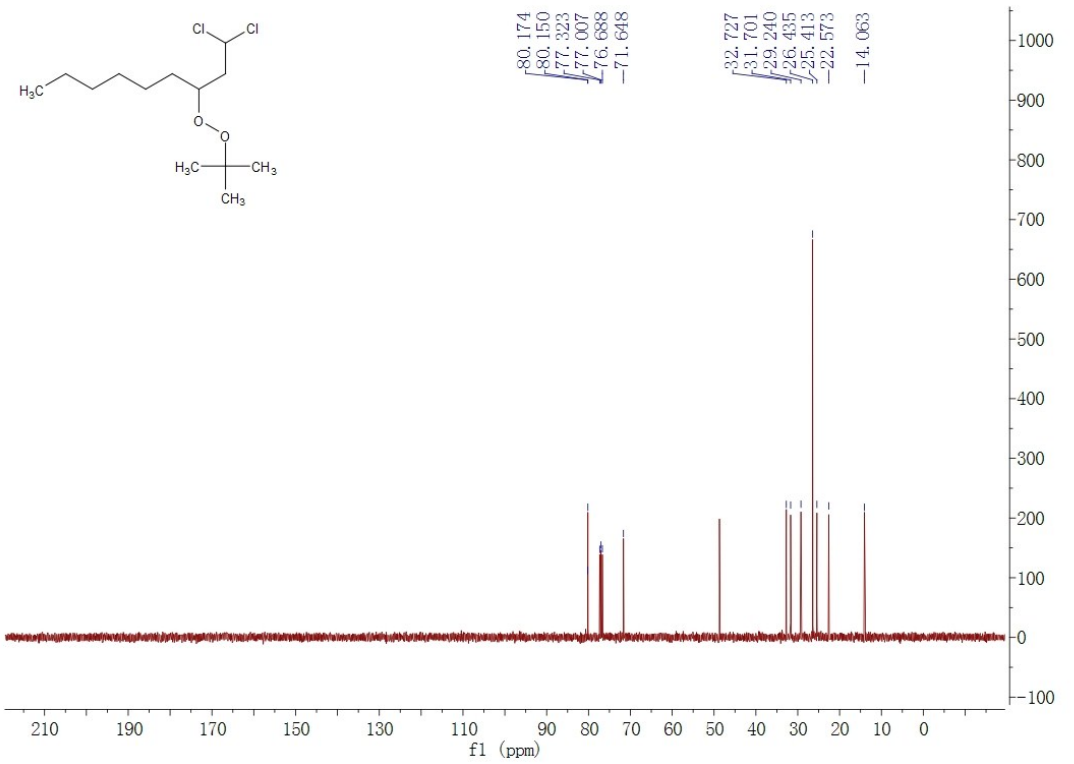


3-(*tert*-butylperoxy)-1,1-dichlorononane (2q)

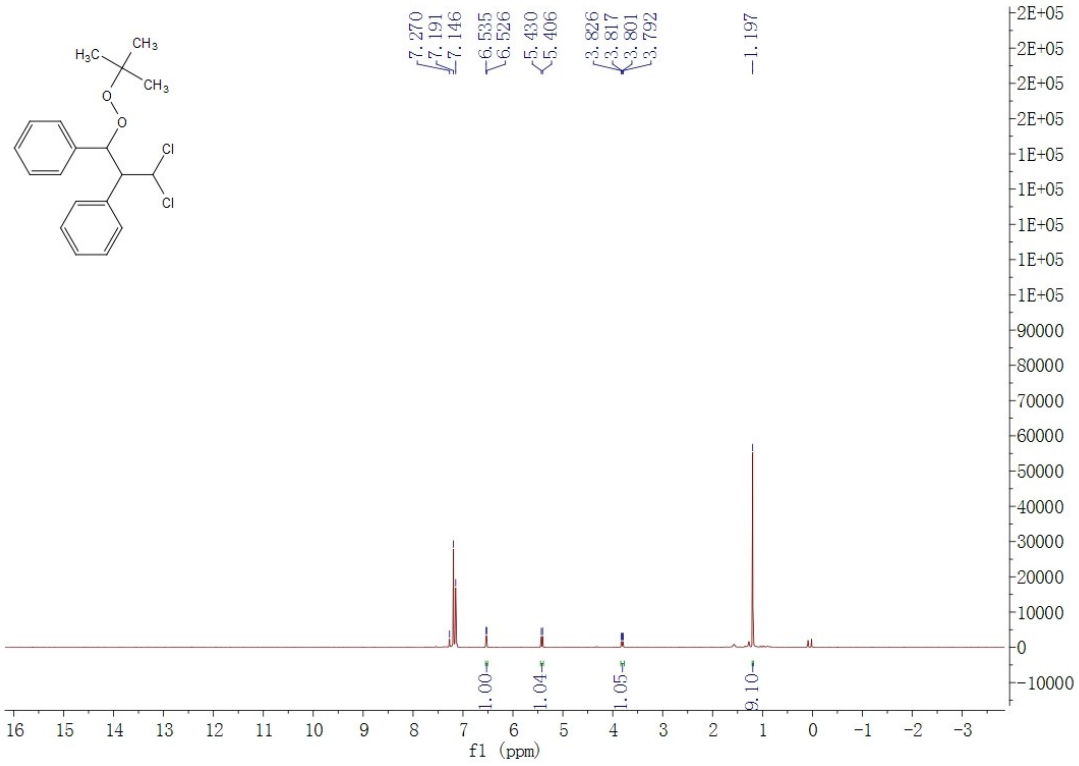


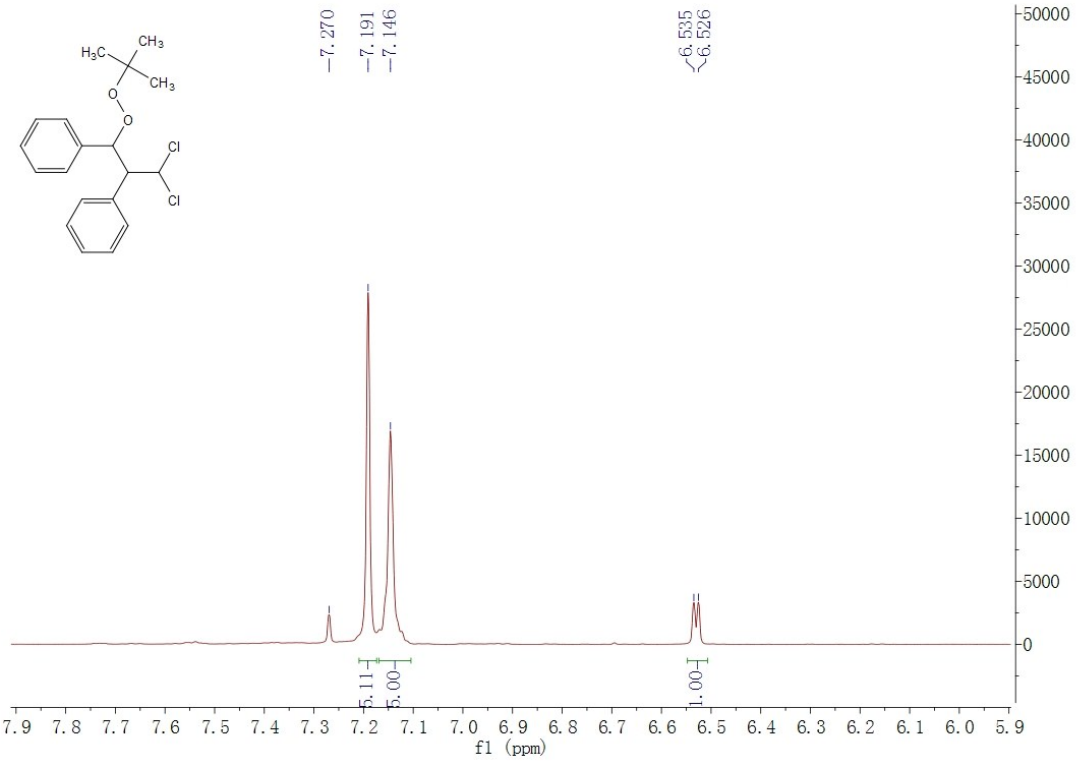

6.094
6.086
6.069
6.061
4.157
4.147
4.141
Cl
Cl
H3C
O
O
H3C
CH3
CH3
1.00
1.00
f1 (ppm)

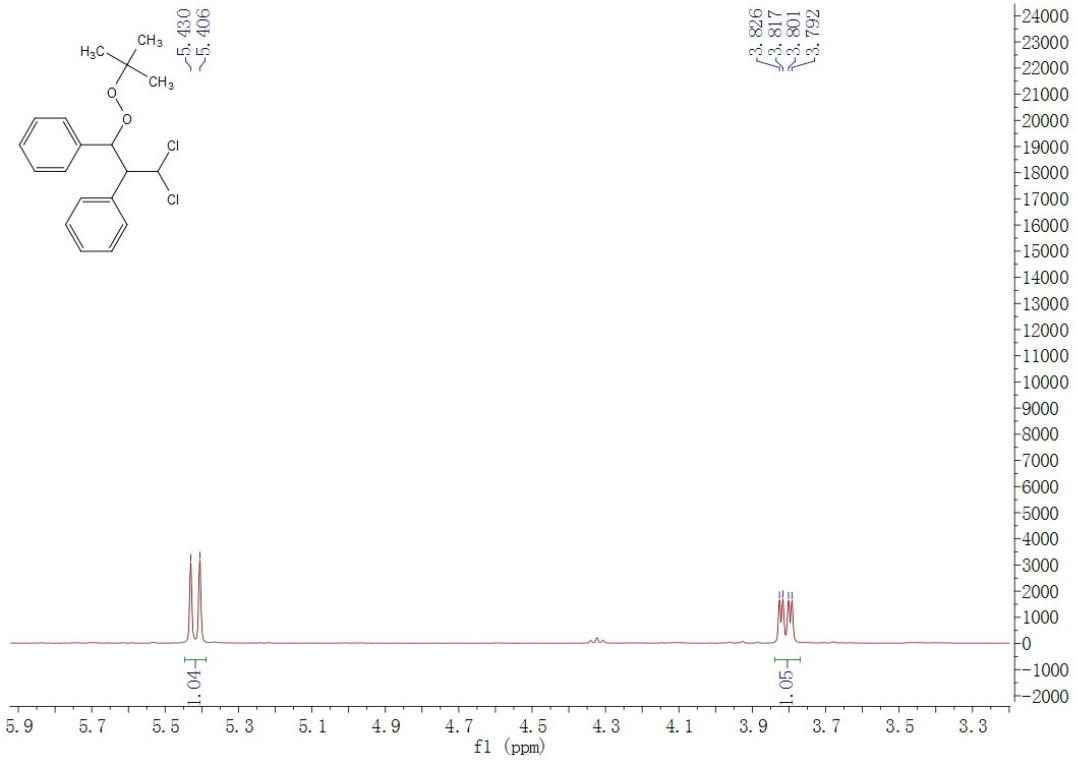

2.541
2.340
2.334
2.315
2.306
1.464
1.449
1.431
1.411
1.397
1.387
1.372
1.363
1.296
1.242
Cl
Cl
H3C
O
O
H3C
CH3
CH3
0.99
1.08
1.08
3.07
6.09
9.03
f1 (ppm)

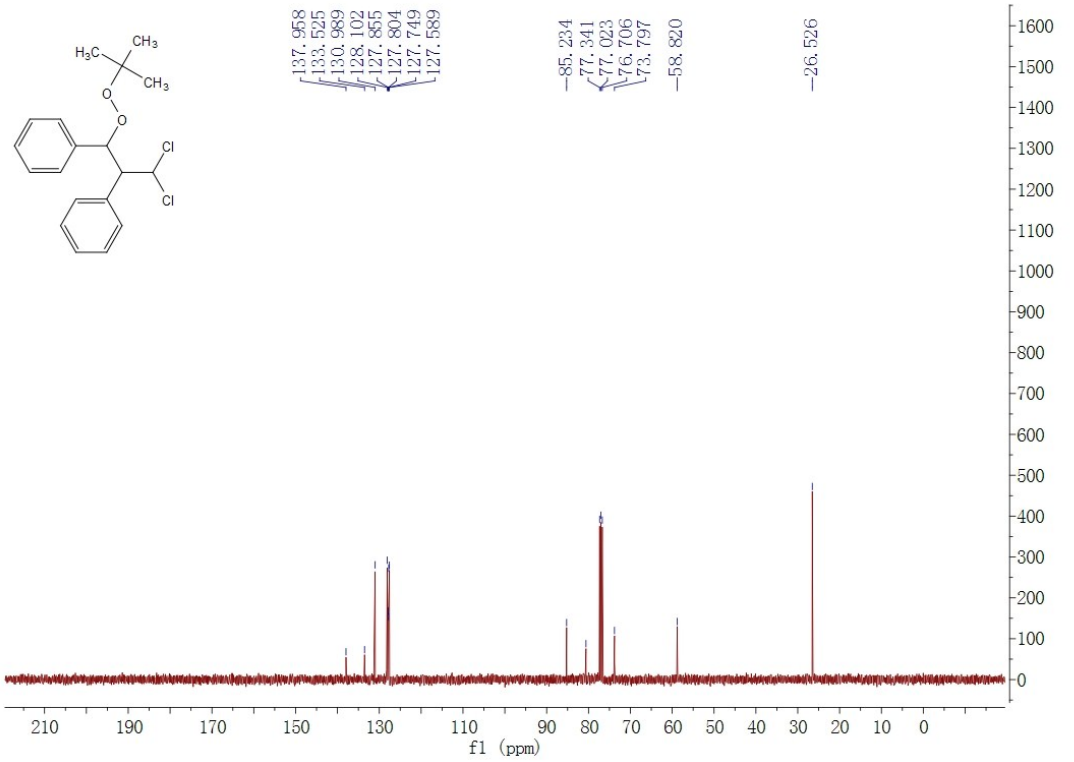


1-(*tert*-butylperoxy)-3,3-dichloro-1,2-diphenylpropane (2r)

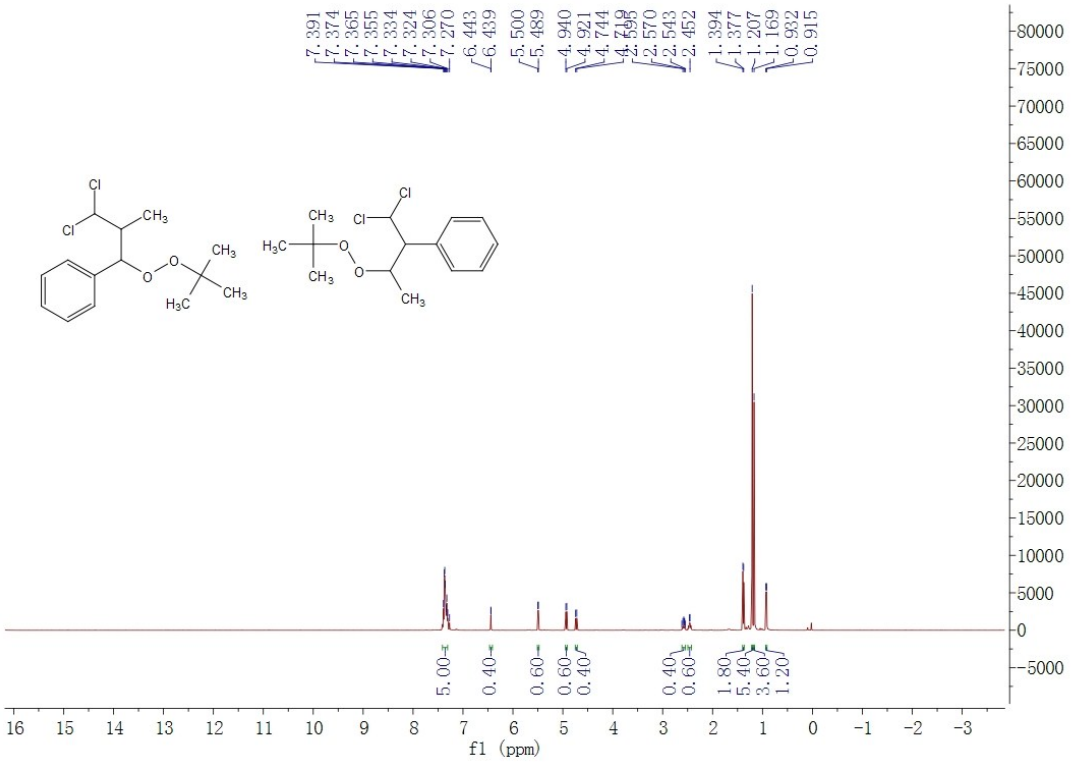


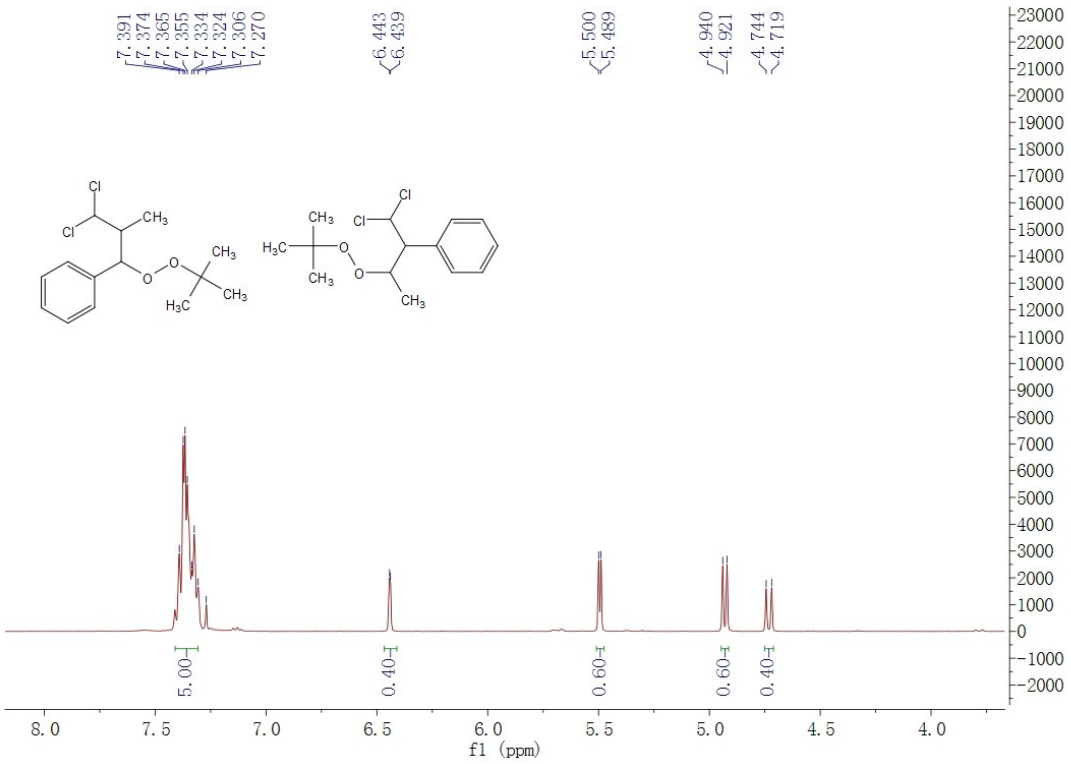

7.270
7.191
7.146
6.535
6.526
5.11
5.00
1.00
f1 (ppm)

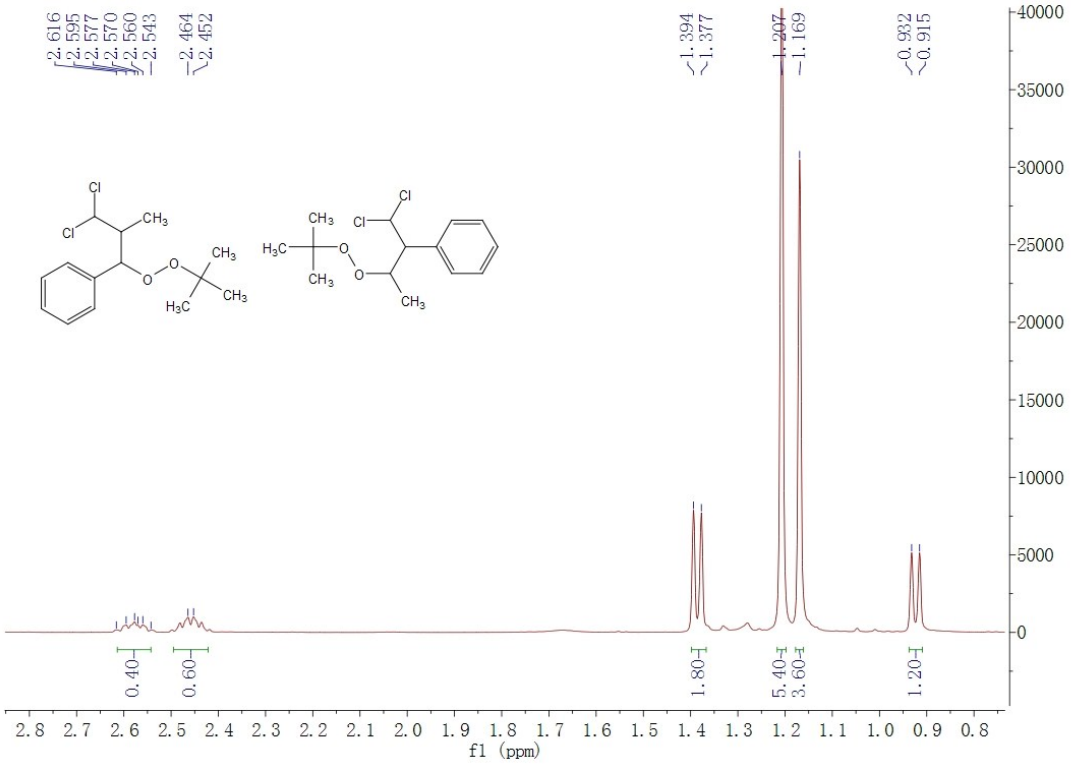

5.430
5.406
3.826
3.817
3.801
3.792
1.04
1.05
f1 (ppm)

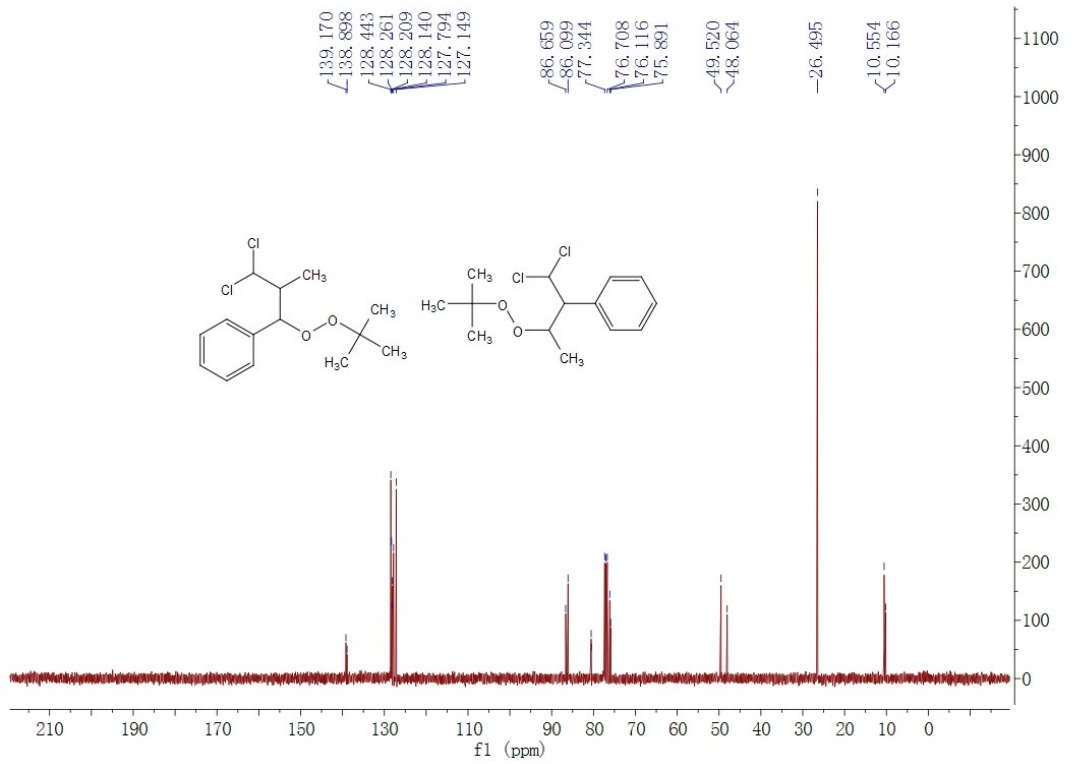


1-(3-(tert-butylperoxy)-1,1-dichlorobutan-2-yl)benzene (2s) and 1-(1-(tert-butylperoxy)-3,3-dichloro-2-methylpropyl)benzene (2t)

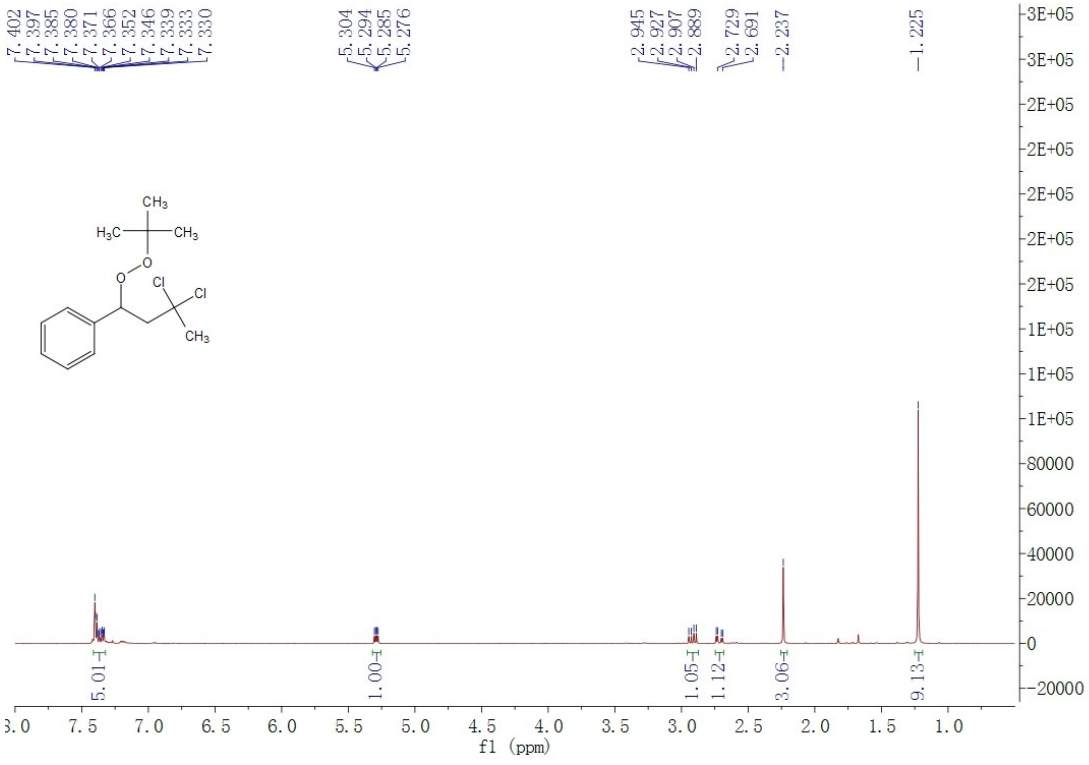


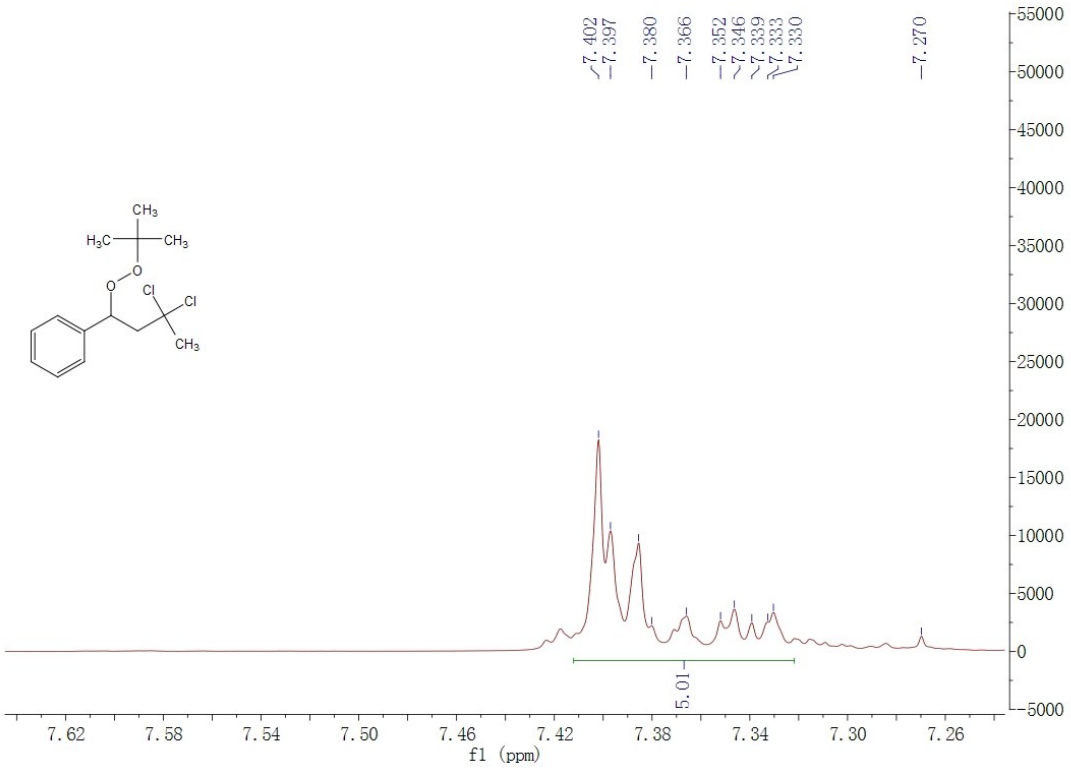

7.391
7.374
7.365
7.355
7.334
7.324
7.306
7.270
6.443
6.439
5.500
5.489
4.940
4.921
4.744
4.719
5.00
0.40
0.60
0.60
0.40
f1 (ppm)

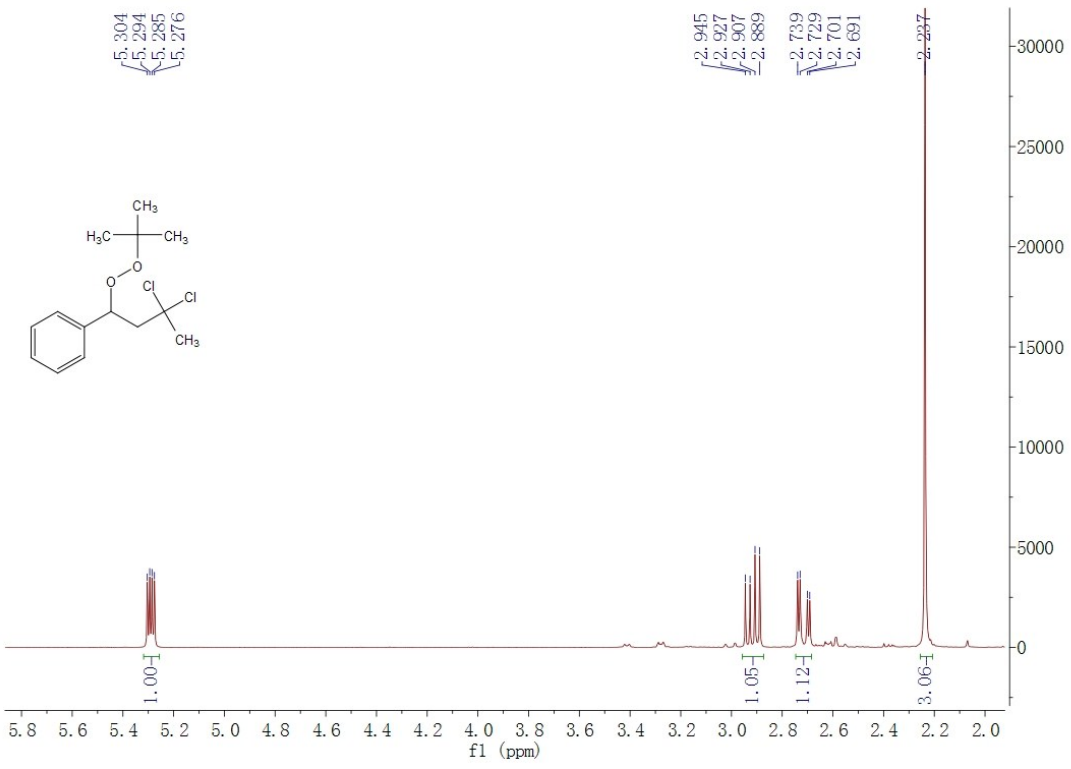

2.616
2.595
2.577
2.570
2.560
2.543
2.464
2.452
1.394
1.377
1.207
1.169
0.932
0.915
0.40
0.60
1.80
5.40
3.60
1.20
f1 (ppm)

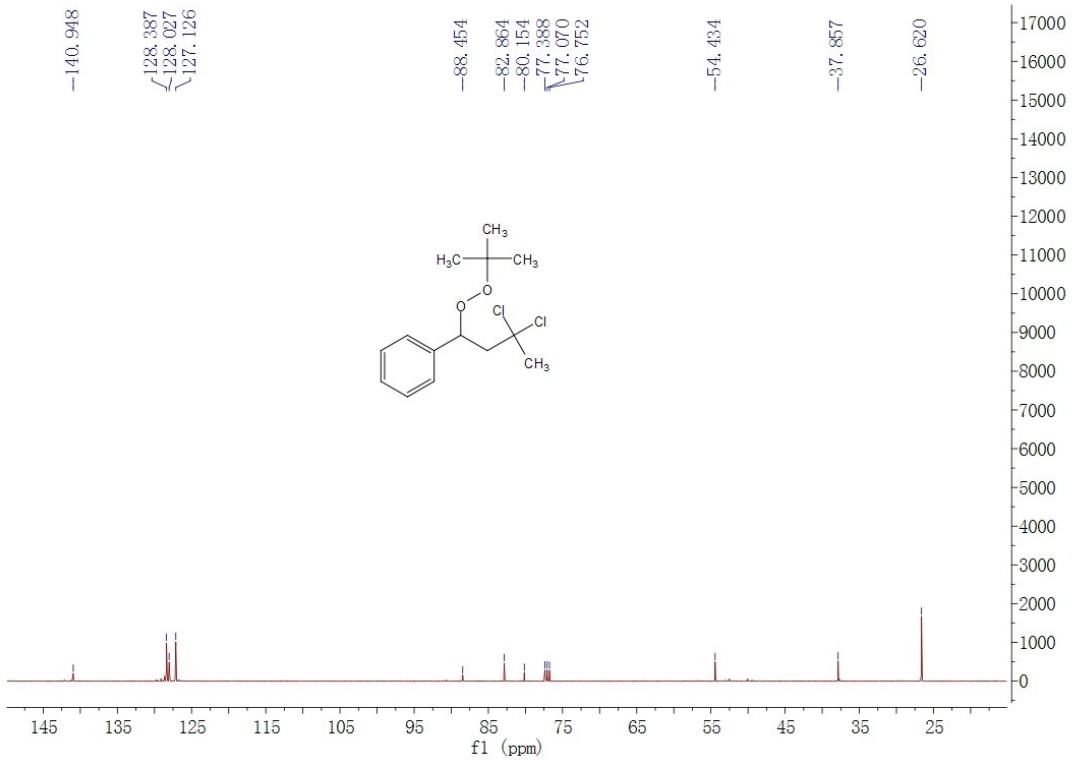


1-(1-(tert-butylperoxy)-3,3-dichlorobutyl)benzene (2u)

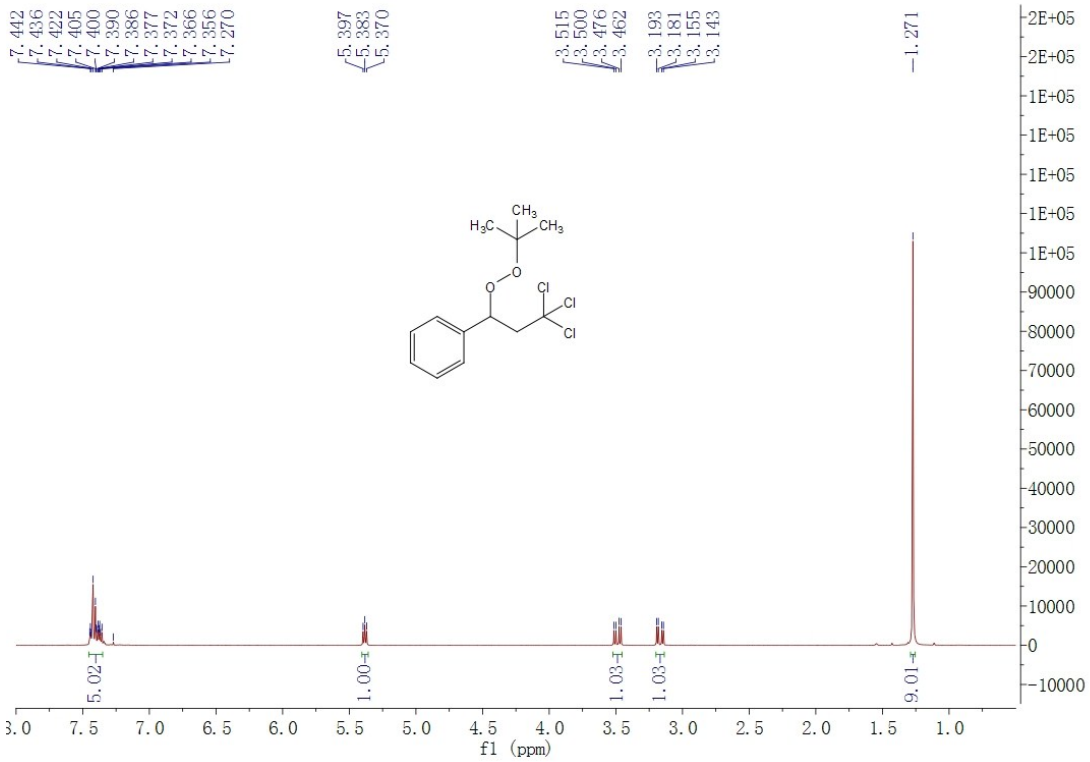


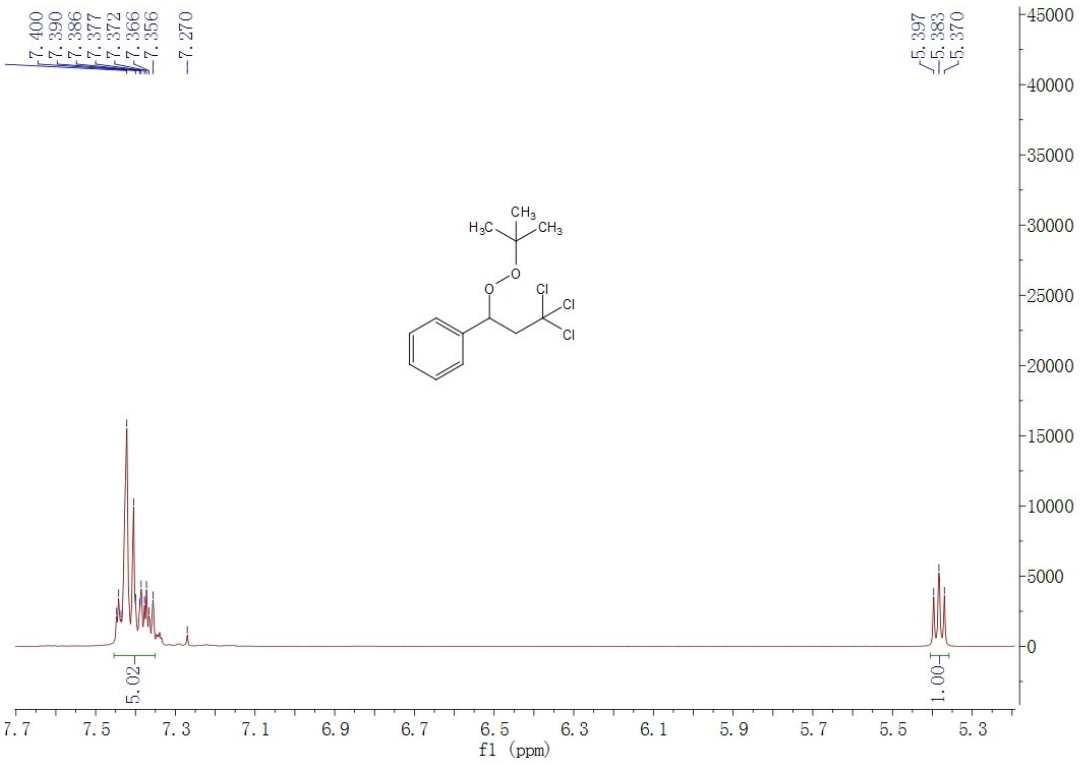

7.402
7.397
7.380
7.366
7.352
7.346
7.339
7.333
7.330
7.270
5.01
f1 (ppm)

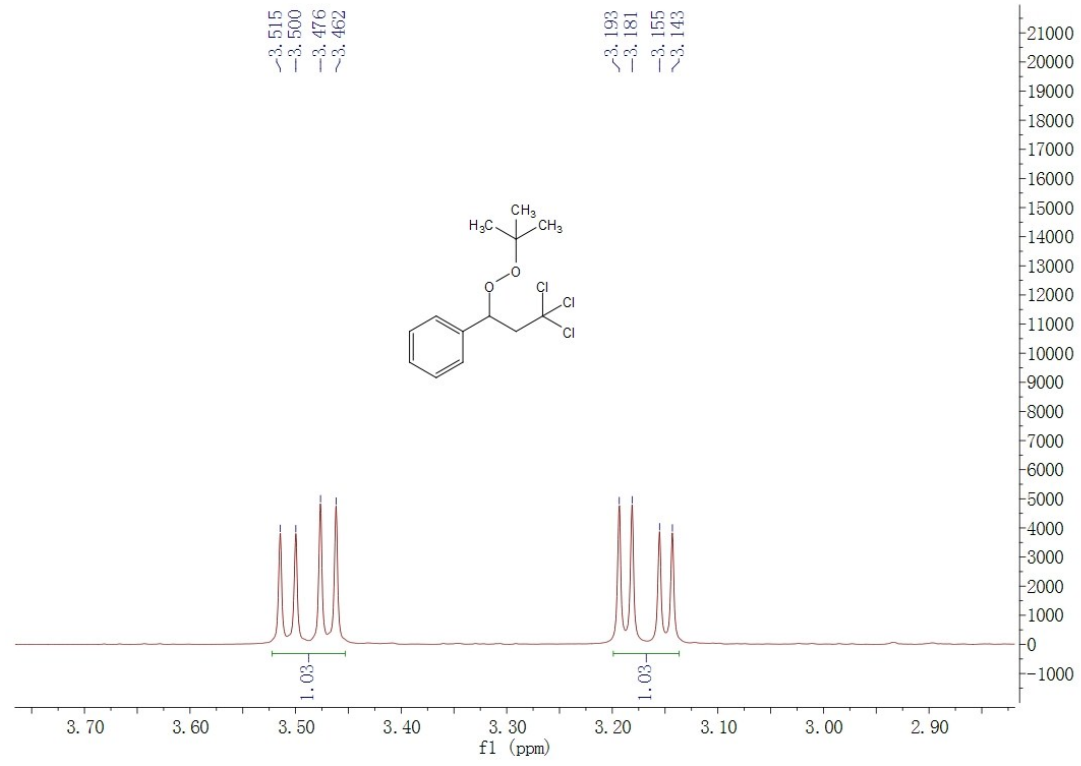

5.304
5.294
5.285
5.276
2.945
2.927
2.907
2.889
2.739
2.729
2.701
2.691
2.237
1.00
1.05
1.12
3.06
f1 (ppm)

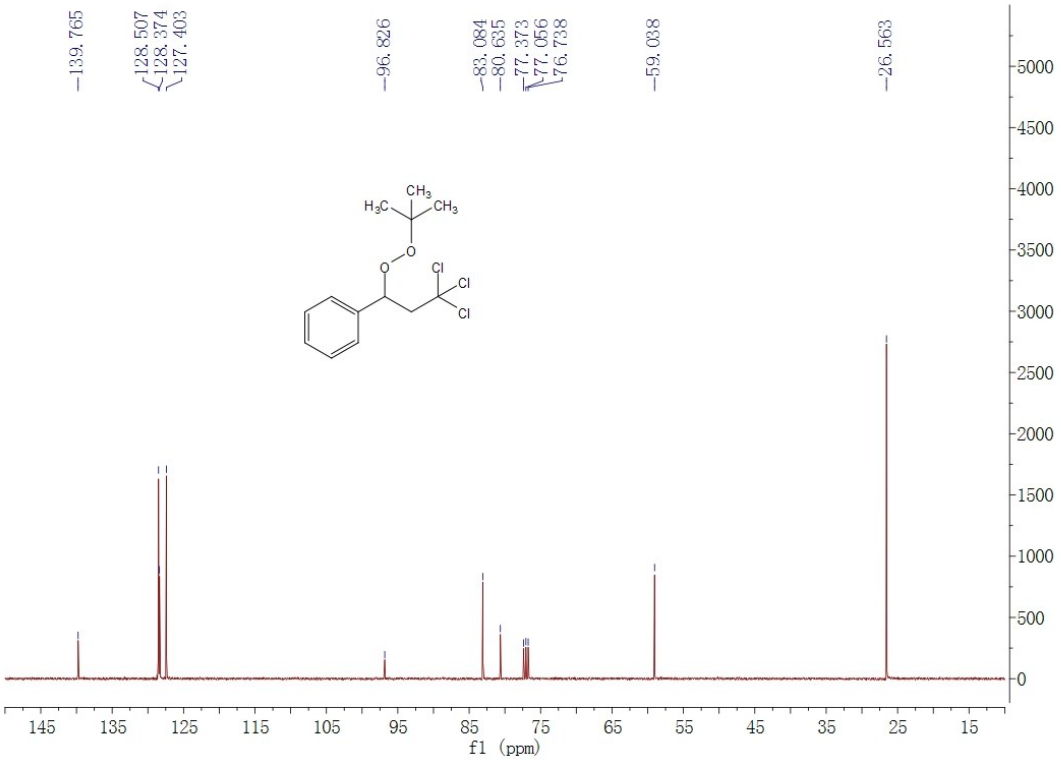


1-(1-(tert-butylperoxy)-3,3,3-trichloropropyl)benzene (2v)




7.400
7.390
7.386
7.377
7.372
7.366
7.356
7.270
5.397
5.383
5.370
CH3
H3C
CH3
O
O
Cl
Cl
Cl
5.02
1.00
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
f1 (ppm)


3.515
3.500
3.476
3.462
3.193
3.181
3.155
3.143
CH3
H3C
CH3
O
O
Cl
Cl
Cl
1.03
1.03
3.70
3.60
3.50
3.40
3.30
3.20
3.10
3.00
2.90
f1 (ppm)


139.765
128.507
128.374
127.403
96.826
83.084
80.635
77.373
77.056
76.738
59.038
26.563
CH3
H3C
CH3
O
O
Cl
Cl
Cl
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
145
135
125
115
105
95
85
75
65
55
45
35
25
15
f1 (ppm)