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Temperature-controlled solvent-free selective synhesis of *tert*-butyl peresters or acids from benzyl cyanides in the presence of TBHP/$Cu(OAc)_2$ system

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Outline

1. **Experimental section including general methods and procedure**
2. **Spectral data for synthesized compounds**
3. **References for synthesized compounds**
4. **Copy of ^{1}HNMR and ^{13}CNMR**

Experimental Section

General methods: All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under air atmosphere. Column chromatography was carried out with Merck silica gel 60 (63-200 mesh). Analytical TLC was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by ^{1}H NMR and ^{13}C NMR (400 MHz and 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz. IR spectra were recorded on a Perkin-Elmer FT/IR 1760 as KBr pellets. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected.

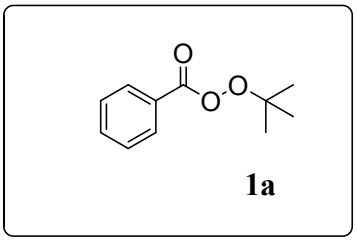
General procedure for the synthesis of tert-butyl persters 1a-p and acids 2a-p: A 10 mL Schlenk tube was charged with benzyl cyanide (1 mmol), $Cu(OAc)_2$ (18 mg, 10 mol-%), TBHP (70 wt.-% in H_2O, 4.0 mmol), and the mixture was stirred at room temperature for 5 h. Then the reaction mixture was diluted with ethyl acetate (5.0 mL), washed with saturated Na_2SO_3 (2 mL), to consumption of residual TBHP, and dried with Na_2SO_4. The solvent was removed under reduced pressure to give the products. Further purification was achieved by short column chromatography using *n*-hexane/EtOAc as the solvent system to afford the products **1a-p**. The same procedure was used for synthesis of acids except that the reaction was performed at 80 °C. The reaction was quenched with 10% $NaHCO_3$ solution (5 mL) and EtOAc (5 mL) on completion. The aquous layer was separated and neutralized with 1M Hcl solution. Then the aqueous mixture was extracted three times with EtOAc (3 × 5 mL). The collected organic layers were dryied over Na_2SO_4 and the solvent evaporated under reduced presuure.

Procedure for the detection of cyanide by indicator paper:[1] A solution of sodium bicarbonate (5.0 g) and picric acid (0.5 g) in water (100 mL) was used for preparation of picrate paper. After drying the paper, it was cut as strips and inserted into a 10 mL vial with a number of holes. Then the vial was inserted into the rubber stopper. 0.2 g of tartrate solid and 1.5 mL of the reaction solution were added to flask, which was stuffed

by rubber stopper fitted with vial, immediately. The flask was heated in the water bath under 80 ^{o}C for 20 minutes. The test paper appeared red proved the existence of CN^{-}.

1. Spectral data for synthesized compounds

1.1. *t*-Butyl benzoperoxoate (1a)[2]



1a

Yield: 80% (155mg).

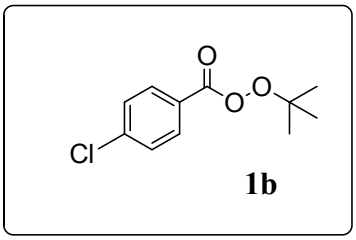
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.4, 133.4, 129.1, 128.6, 127.7, 84.0, 26.3.

Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27. Found: C, 68.12; H, 7.31.

IR (KBr, cm^{-1}): ν 1757.

1.2. *t*-Butyl 4-chlorobenzoperoxoate (1b)[2]



1b

Yield: 85% (194 mg).

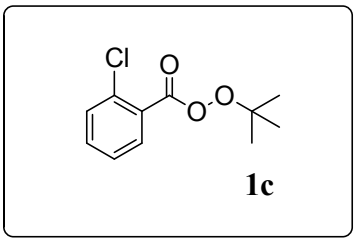
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.9, 140.3, 130.9, 129.4, 126.5, 84.6, 26.6.

Anal. Calcd for $C_{11}H_{13}ClO_3$ (228.67): C, 57.78; H, 5.73. Found: C, 57.85; H, 5.76.

IR (KBr, cm-1): ν 1752.

1.3. *t*-Butyl 2-chlorobenzoperoxoate (1c)[3]



1c

Yield: 82% (187 mg).

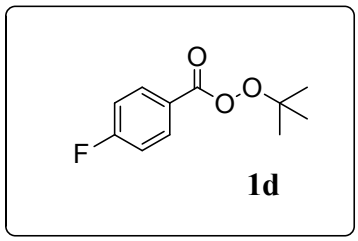
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.72-7.70 (m, 1H), 7.56 (d, *J* = 0.8 Hz, 1H), 7.55-7.54 (m, 1H), 7.47-7.42 (m, 1H), 1.42 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.1, 133.00, 132.6, 131.6, 131.00, 130.9, 127.8, 82.7, 26.2.

Anal. Calcd for $C_{11}H_{13}ClO_3$ (228.67): C, 57.78; H, 5.73. Found: C, 57.85; H, 5.76.

IR (KBr, cm^{-1}): ν 1768.

1.4. *t*-Butyl 4-fluorobenzoperoxoate (1d)[2]



1d

Yield: 82% (174 mg).

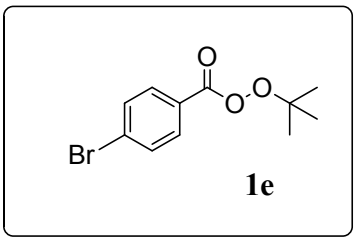
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.04-8.00 (m, 2H), 7.20-7.15 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.3, 165.3, 163.9, 132.2, 132.1, 124,3, 116.4, 116.2, 84.5, 26.7.

Anal. Calcd for $C_{11}H_{13}FO_3$ (212.22): C, 62.26; H, 6.12. Found: C, 62.18; H, 6.08.

IR (KBr, cm^{-1}): ν 1760.

1.5. *t*-Butyl 4-bromobenzoperoxoate (1e)[3]



1e

Yield: 80% (218 mg).

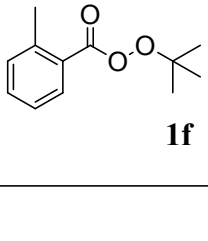
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.1, 132.7, 132.4, 131.03, 128.95, 84.64, 26.66.

Anal. Calcd for $C_{11}H_{13}BrO_3$ (273.12): C, 48.37; H, 4.80. Found: C, 48.40; H, 4.83.

IR (KBr, cm-1): ν 1766.

1.6. *t*-Butyl 2-chlorobenzoperoxoate (1f)[3]



1f

Yield: 70% (160 mg).

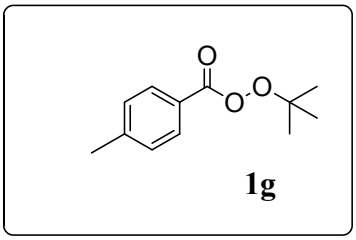
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.72-7.70 (m, 1H), 7.56 (d, *J* = 0.8 Hz, 1H), 7.55-7.54 (m, 1H), 7.47-7.42 (m, 1H), 1.42 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.1, 133.00, 132.6, 131.6, 131.00, 130.9, 127.8, 82.7, 26.2.

Anal. Calcd for $C_{11}H_{13}ClO_3$ (228.67): C, 57.78; H, 5.73. Found: C, 57.85; H, 5.76.

IR (KBr, cm^{-1}): ν 1768**.**

1.7. *t*-Butyl 4-chlorobenzoperoxoate (1g)[2]



1g

Yield: 75% (171 mg).

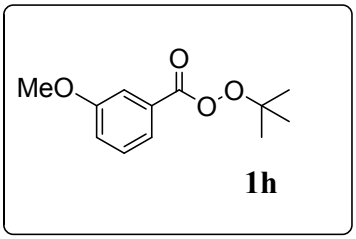
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.9, 140.3, 130.9, 129.4, 126.5, 84.6, 26.6.

Anal. Calcd for $C_{11}H_{13}ClO_3$ (228.67): C, 57.78; H, 5.73. Found: C, 57.85; H, 5.76.

IR (KBr, cm-1): ν 1752.

1.8. *t*-Butyl 3-methoxybenzoperoxoate (1h)



1h

Yield: 68% (152 mg).

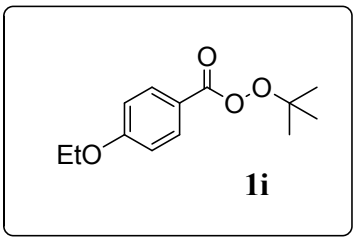
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.05 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 3.78 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.3, 159.7, 129.7, 128.9, 121.3, 119.6, 113.9, 84.03, 55.47, 26.25.

Anal. Calcd for $C_{12}H_{16}O_4$ (224.25): C, 64.27; H, 7.19. Found: C, 64.42; H, 7.23.

IR (KBr, cm^{-1}): ν 1769.

1.9. *t*-Butyl 4-ethoxybenzoperoxoate (1i)



1i

Yield: 68% (162 mg).

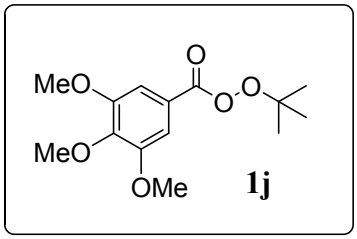
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82 (d, *J* = 9.2 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.31, 163.06, 131.19, 119.60, 114.35, 83.77, 63.77, 26.27, 14.65.

Anal. Calcd for $C_{13}H_{18}O_4$ (238.28): C, 65.53; H, 7.61. Found: C, 65.59; H, 7.68.

IR (KBr, cm^{-1}): ν 1754.

1.10. *t*-Butyl 3,4,5-tri methoxybenzoperoxoate (1j)



1j

Yield: 50% (142 mg).

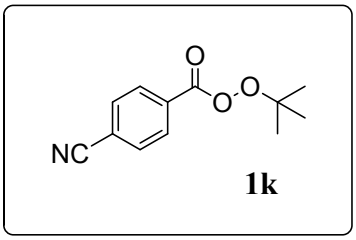
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 2H), 3.84 (s, 9H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.21, 153.14, 142.60, 122.50, 106.74, 106.45, 84.12, 60.96, 56.30, 26.28

Anal. Calcd for $C_{14}H_{20}O_6$ (284.31): C, 59.14; H, 7.09. Found: C, 58.98; H, 7.00.

IR (KBr, cm^{-1}): ν 1765.

1.11. *t*-butyl 4-cyanobenzoperoxoate (1k)



1k

Yield: 65% (142 mg).

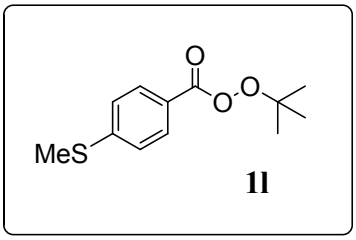
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.47-6.48 (m, 1H), 7.26-7.49 (m, 3H), 7.64-7.74 (m, 3H), 7.93-7.95 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 107.6, 115.2, 126.2, 126.5, 129.2, 140.2, 141.0.

Anal. Calcd for $C_{12}H_{13}NO_3$ (219.24): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.70; H, 5.99; N, 6.42.

IR (KBr, cm^{-1}): ν 1767.

1.12. *t*-Butyl 4-(methylthio)benzoperoxoate (1l)[2]



1l

Yield: 60% (144 mg).

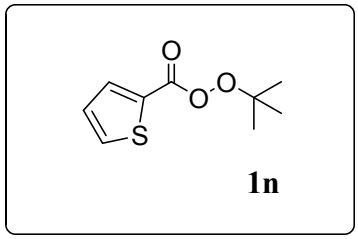
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 2.44 (s, 3H);, 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.2, 146.3, 129.4, 125.1, 123.8, 83.9, 26.3, 14.8.

Anal. Calcd for $C_{12}H_{16}O_3S$ (240.32): C, 59.97; H, 7.66; N, 6.71, S, 13.34. Found: C, 60.02; H, 6.73, S, 13.39.

IR (KBr, cm^{-1}): ν 1748.

1.13. tert-Butyl thiophene-2-carboxylate (1n)[3]



1n

Yield: 78% (156 mg).

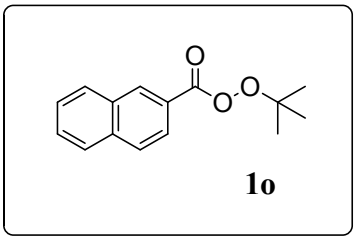
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.73 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.54 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.07-7.05 (m, 1H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 160.4, 133.8, 132.8, 129.3, 127.8, 84.3, 26.2.

Anal. Calcd for $C_9H_{12}O_3S$ (200.25): C, 53.98; H, 6.04; S,16.01. Found: C, 54.03; H, 6.06; S, 16.05.

IR (KBr, cm^{-1}): ν 1750.

1.14. t-Butyl naphthalene-2-carboperoxoate (1o)[3]



1o

Yield: 78% (190 mg).

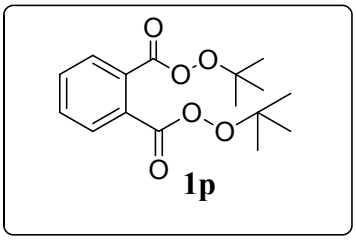
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.99-7.96 (m, 2H), 7.92-7.88 (m, 2H), 7.64-7.55 (m, 2H), 1.49 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.6, 135.6, 132.4, 130.8, 129.3, 128.6, 128.5, 127.8, 126.9, 124.9, 124.5, 84.1, 26.3.

Anal. Calcd for $C_{15}H_{16}O_3$ (244.29): C, 73.75; H, 6.60; N, 5.71. Found: C, 74.00; H, 5.81.

IR (KBr, cm^{-1}): ν 1745.

1.15. 1,2-di-*t*-Butyl benzoperoxoate (1p)



1p

Yield: 60% (186 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.04-8.00 (m, 2H), 7.20-7.15 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 167.3, 165.3, 163.9, 132.2, 132.1, 124.3, 116.4, 116.2, 84.5, 26.7.

Anal. Calcd for $C_{16}H_{22}O_6$ (310.14): C, 61.92; H, 7.15. Found: C, 61.98; H, 7.15.

IR (KBr, cm^{-1}): ν 1762.

1.16. Benzoic acid (CAS No. 65-85-0) (2a)[6]

The general procedure afforded 103 mg (85%) of the title compound. The melting point (124-126 °C) and IR (KBr, cm^{-1}): 3001, 1686, 1450,720, 650.

1.17. 4-Chlorobenzoic acid (CAS No. 74-11-3) (2b)[6]

The general procedure afforded 130 mg (83%) of the title compound. The melting point (239-241 °C) and IR (KBr, cm^{-1}): 2981, 1678, 1460,1115, 847.

1.18. 2-Chlorobenzoic acid (CAS No. 118-91-2) (2c)[5]

The general procedure afforded 125 mg (80%) of the title compound. The melting point (137-139 °C) and IR (KBr, cm^{-1}): 3010, 1691, 1460,1110, 749.

1.19. 4-Fluorobenzoic acid (CAS No. 456-22-4) (2d) [4]

The general procedure afforded 109 mg (78%) of the title compound. The melting point (184-186 °C) and IR (KBr, cm^{-1}): 3009, 1689, 1462,1212, 841.

1.20. 4-Bromobenzoic acid (CAS No. 586-76-5) (2e)[6]

The general procedure afforded 161 mg (80%) of the title compound. The melting point (250-252 °C) and IR (KBr, cm^{-1}): 3007, 1689, 1458,1052, 850.

1.21. 2-Methylbenzoic acid (CAS No. 118-90-1) (2f)[5]

The general procedure afforded 95 mg (70%) of the title compound. The melting point (102-104 °C) and IR (KBr, cm^{-1}): 3091, 2982, 1680, 1451,750.

1.22. 4-Methylbenzoic acid (CAS No. 99-94-5) (2g)[6]

The general procedure afforded 115 mg (85%) of the title compound. The melting point (180-182 °C) and IR (KBr, cm^{-1}): 3095, 2984, 1683, 1455, 820

1.23. 3-Methoxybenzoic acid (CAS No. 586-38-9) (2h)[5]

The general procedure afforded 111 mg (73%) of the title compound. The melting point (106-107 °C) and IR (KBr, cm^{-1}): 3027, 3010, 1702,1466, 1260, 1045, 760, 690.

1.24. 4-Ethoxybenzoic acid (CAS No. 619-86-3) (2i)

The general procedure afforded 144 mg (68%) of the title compound. The melting point (200-202 °C). and IR (KBr, cm^{-1}): 3020, 2989, 2950, 1681, 1456, 1465, 1258, 1054, 847.

1.25. 3,4,5-Trimethoxybenzoic acid (CAS No. 118-41-2) (2j)[7]

The general procedure afforded 144 mg (68%) of the title compound. The melting point (171-173 °C) and IR (KBr, cm^{-1}): 3027, 3015, 1705, 1669,1466, 1265, 1046.

1.26. 4-Cynaobenzoic acid (CAS No. 619-65-8) (2k)

The general procedure afforded 92 mg (65%) of the title compound. The melting point (219-221 °C) and IR (KBr, cm^{-1}): 3018, 2225, 1705, 1449,1490, 851.

1.26. 4-(Methylthio)benzoic acid (CAS No. 13205-48-6) (2l)

The general procedure afforded 101 mg (60%) of the title compound. The melting point (195-197 °C)). and IR (KBr, cm^{-1}): 3015, 2990, 1680, 1456, 851.

1.29. 2-Thiophenecarboxylic acid (CAS No. 527-72-0) (2n)[4]

The general procedure afforded 117 mg (70%) of the title compound. The melting point (123-125 °C) and IR (KBr, cm^{-1}): 2998, 1682, 1450.

1.28. 2-Naphthoic acid (CAS No. 93-09-4) (2o)

The general procedure afforded 146 mg (85%) of the title compound. The melting point (190-192 °C) and IR (KBr, cm^{-1}): 3112, 2998, 1678, 1452.

1.30. Benzen-1,2-dicarboxylic acid (CAS No. 88-99-3) (2p)

The general procedure afforded 99 mg (60%) of the title compound. The melting point (210-212 °C) and IR (KBr, cm^{-1}): 3115, 1696, 1448, 750.

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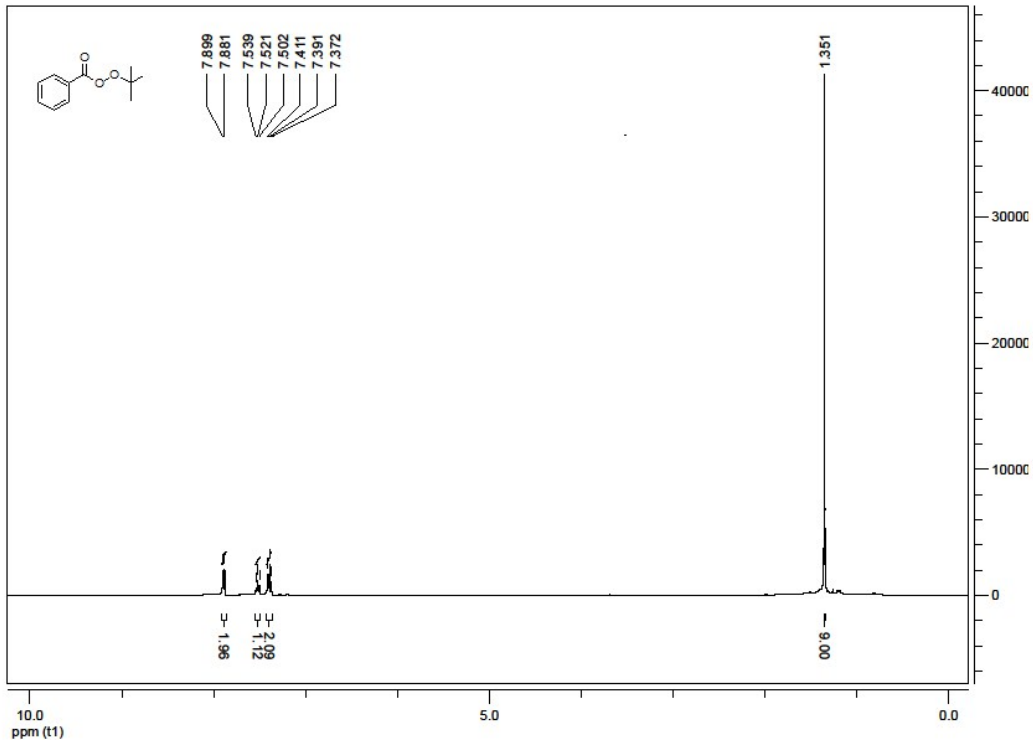
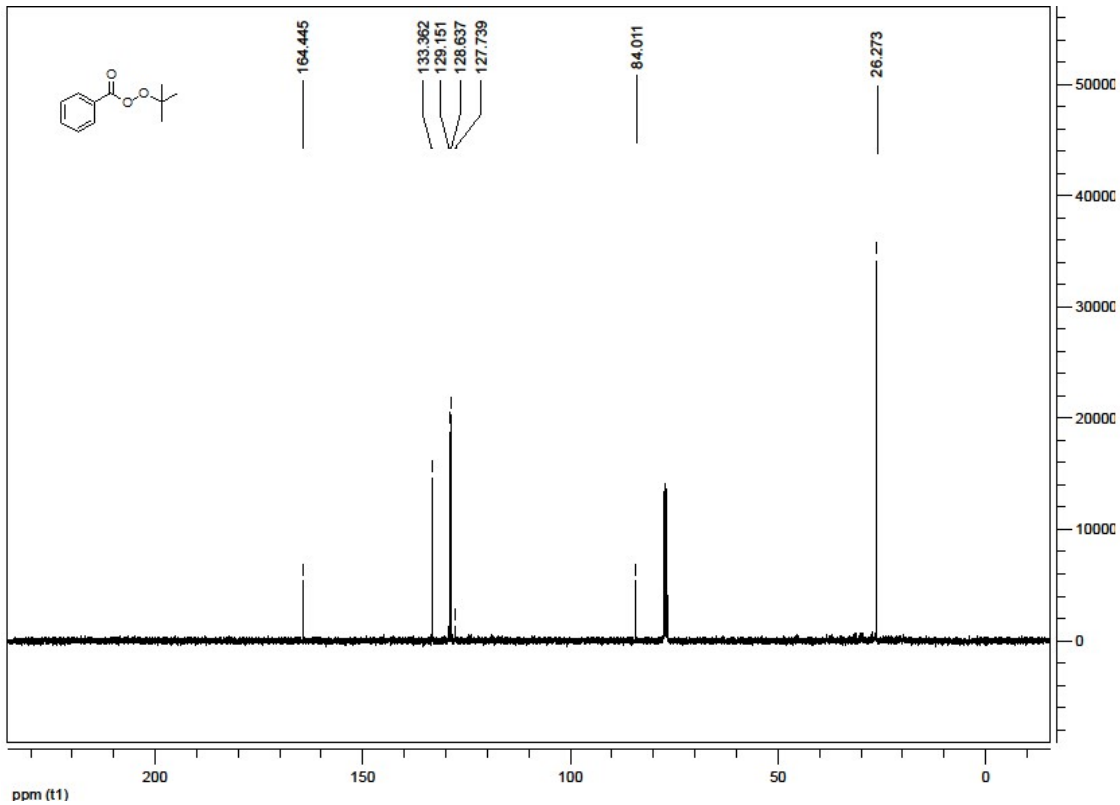
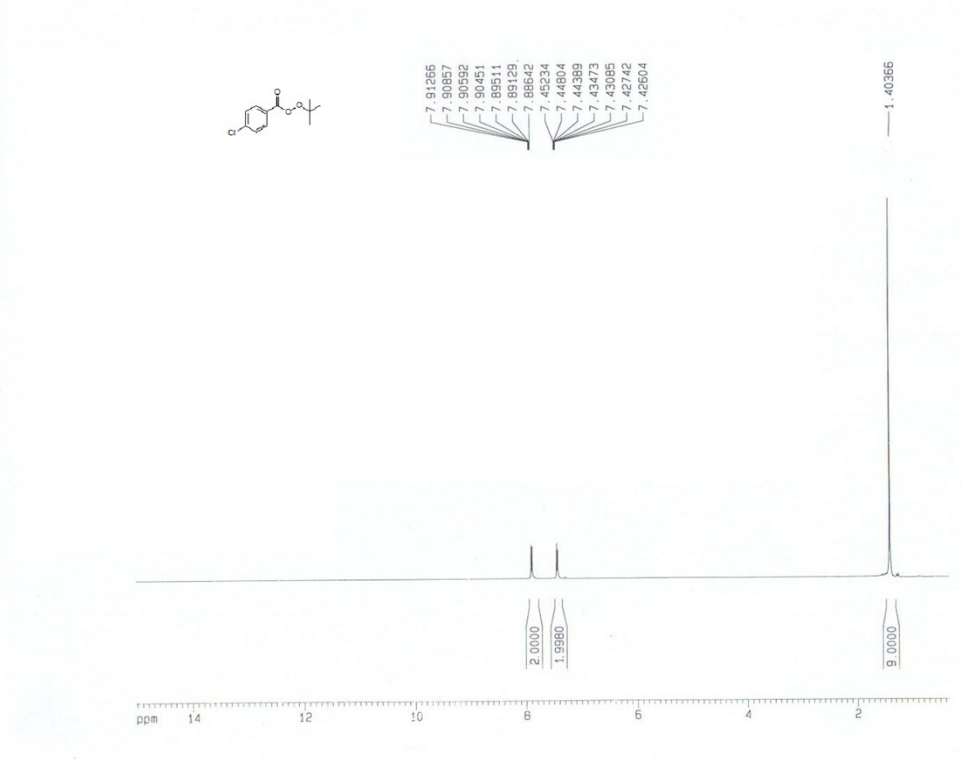
7. R. K. Sodhi, S. Paul, J. H. Clark, *Green Chem*. **2012**, 14, 1649-1656.

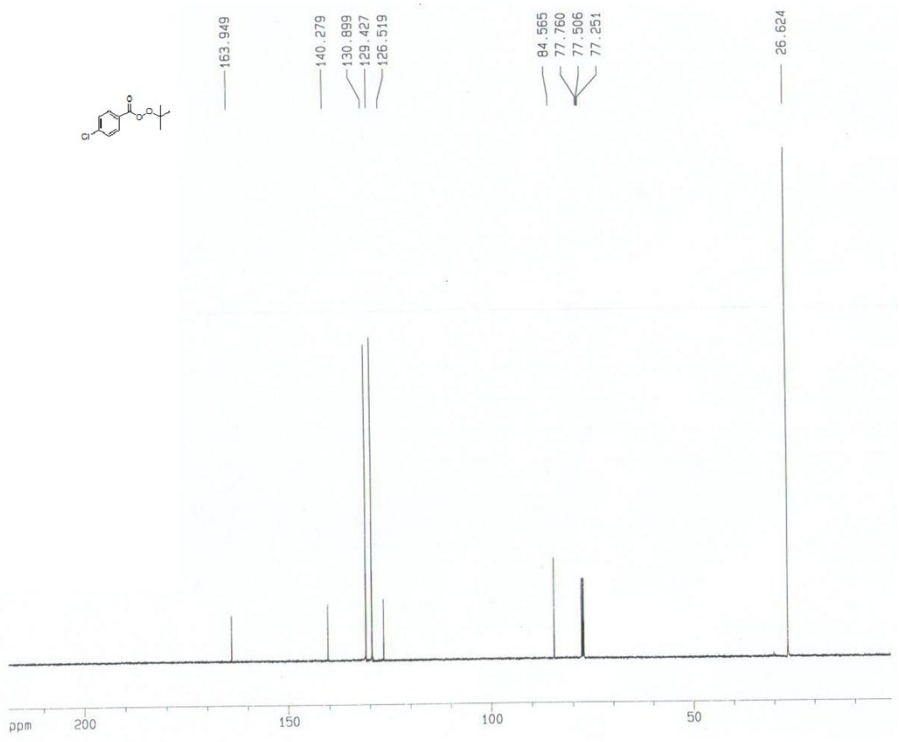
3.1. 1- *t*-Butyl benzoperoxoate (1a).



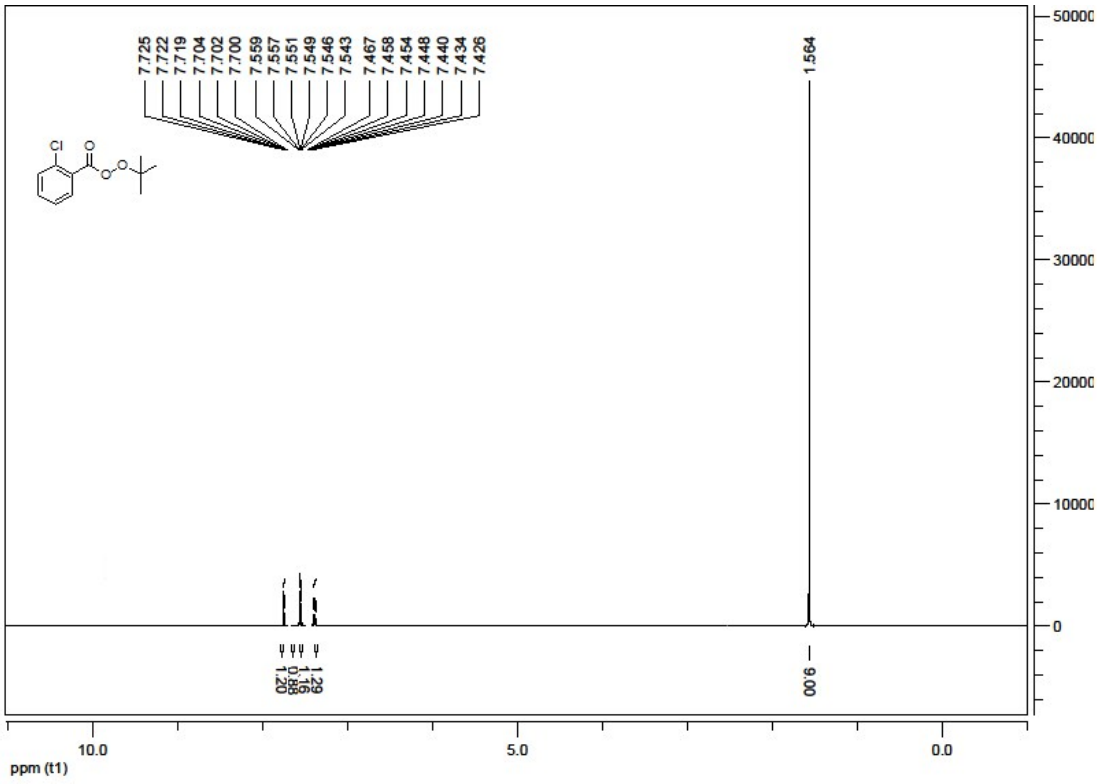


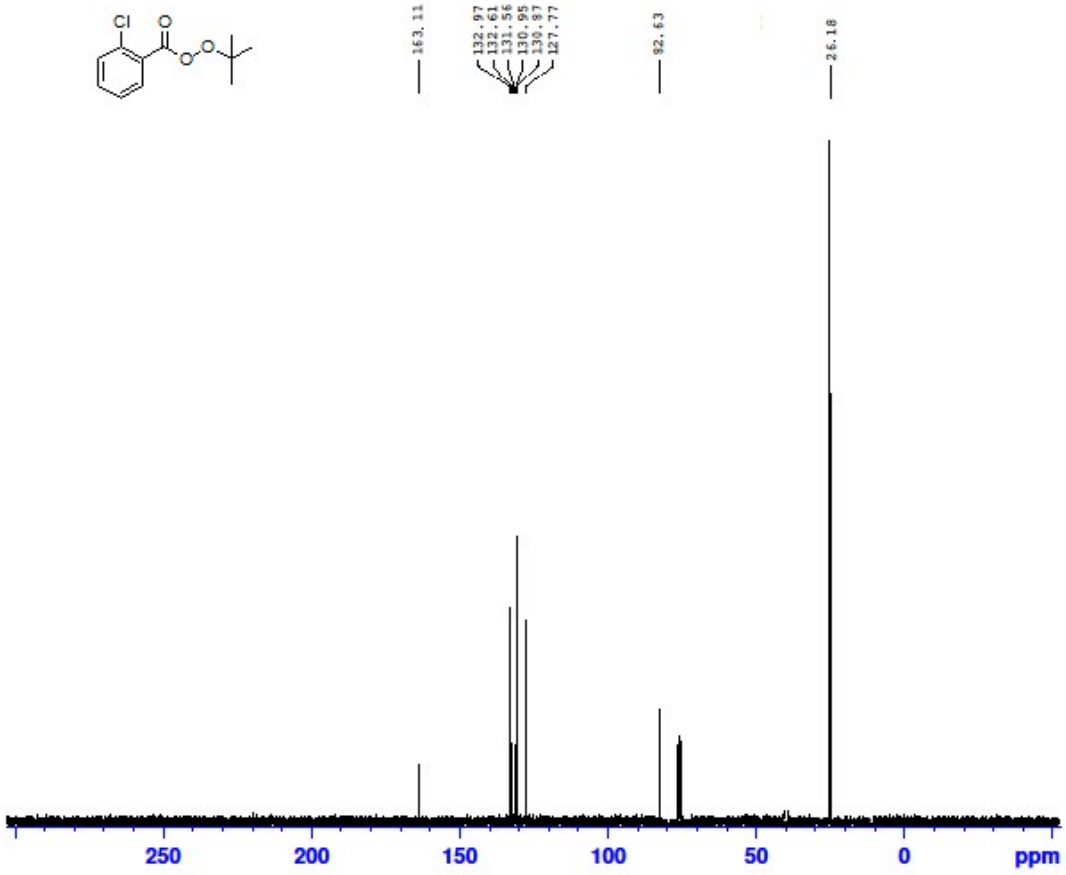
3.1.2. *t*-Butyl 4-chlorobenzoperoxoate (1b)



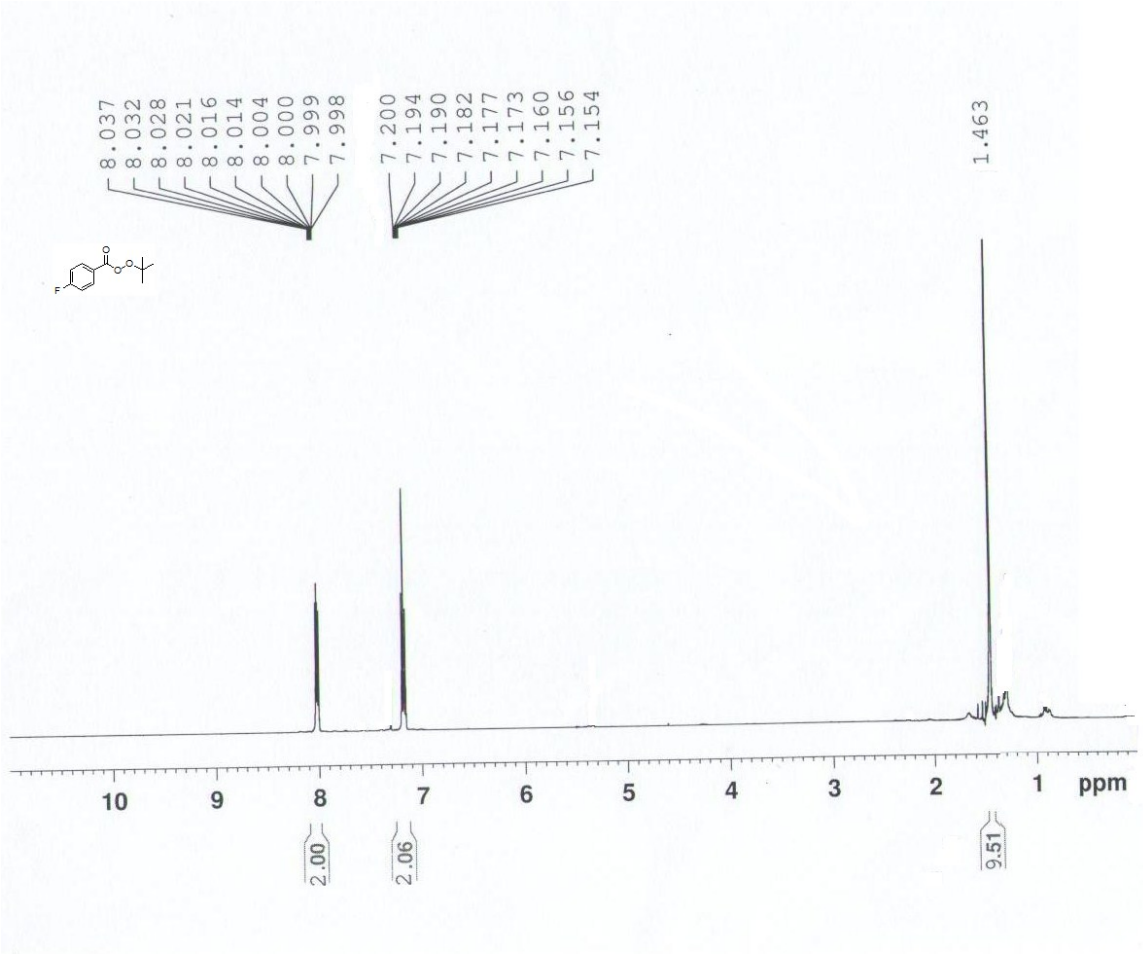


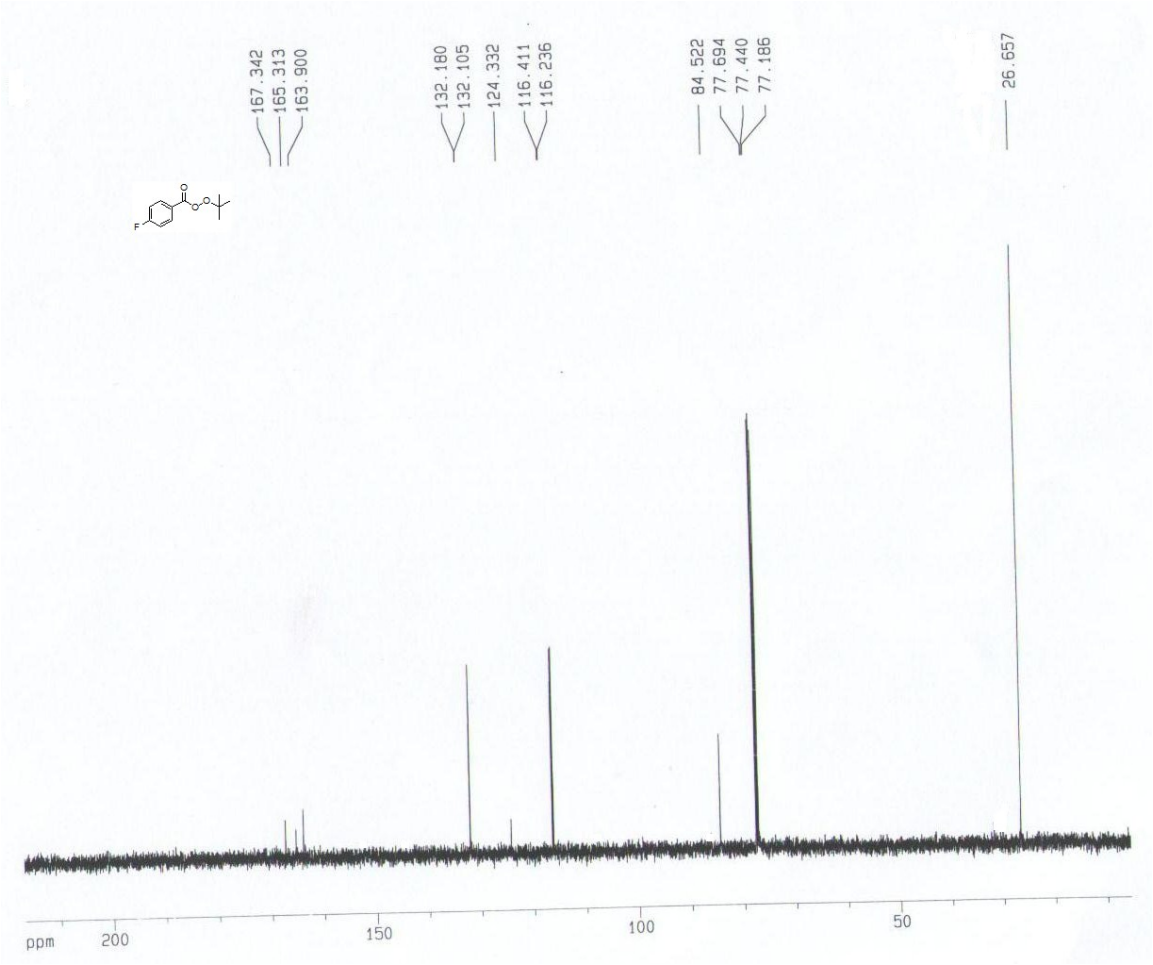
3.1.3. *t*-Butyl 2-chlorobenzoperoxoate (1c)



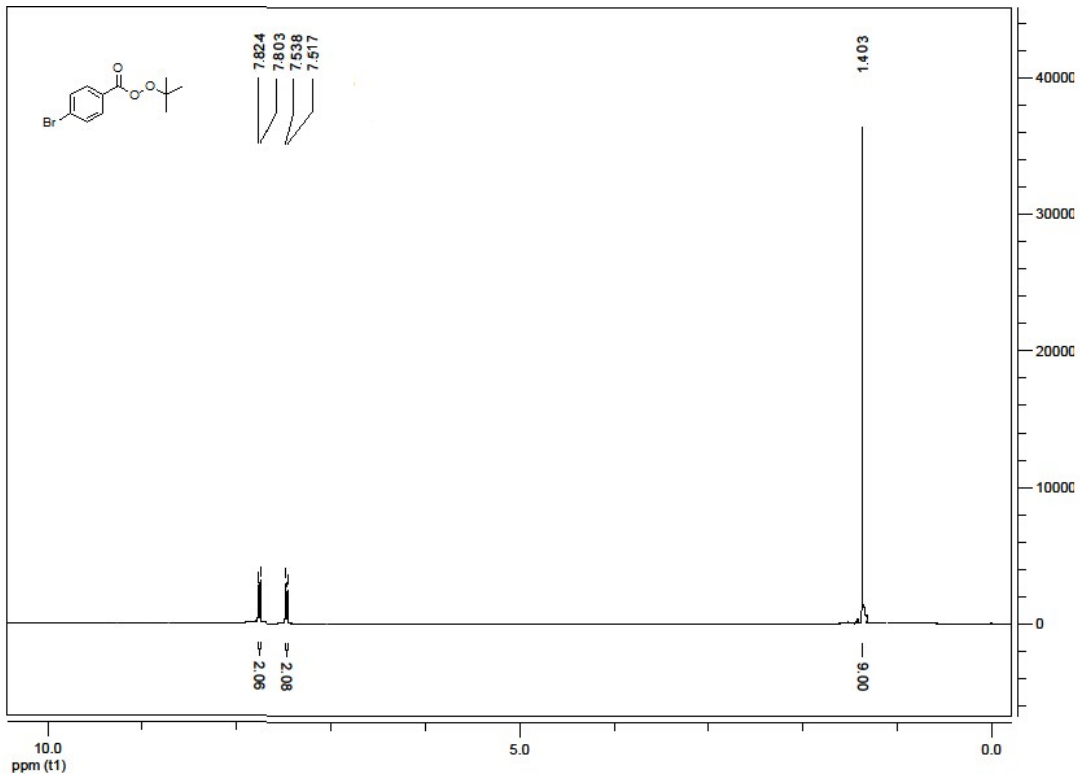

Cl
O
O
O
163.11
132.97
132.61
131.56
130.95
130.97
127.77
92.63
26.18
250
200
150
100
50
0
ppm

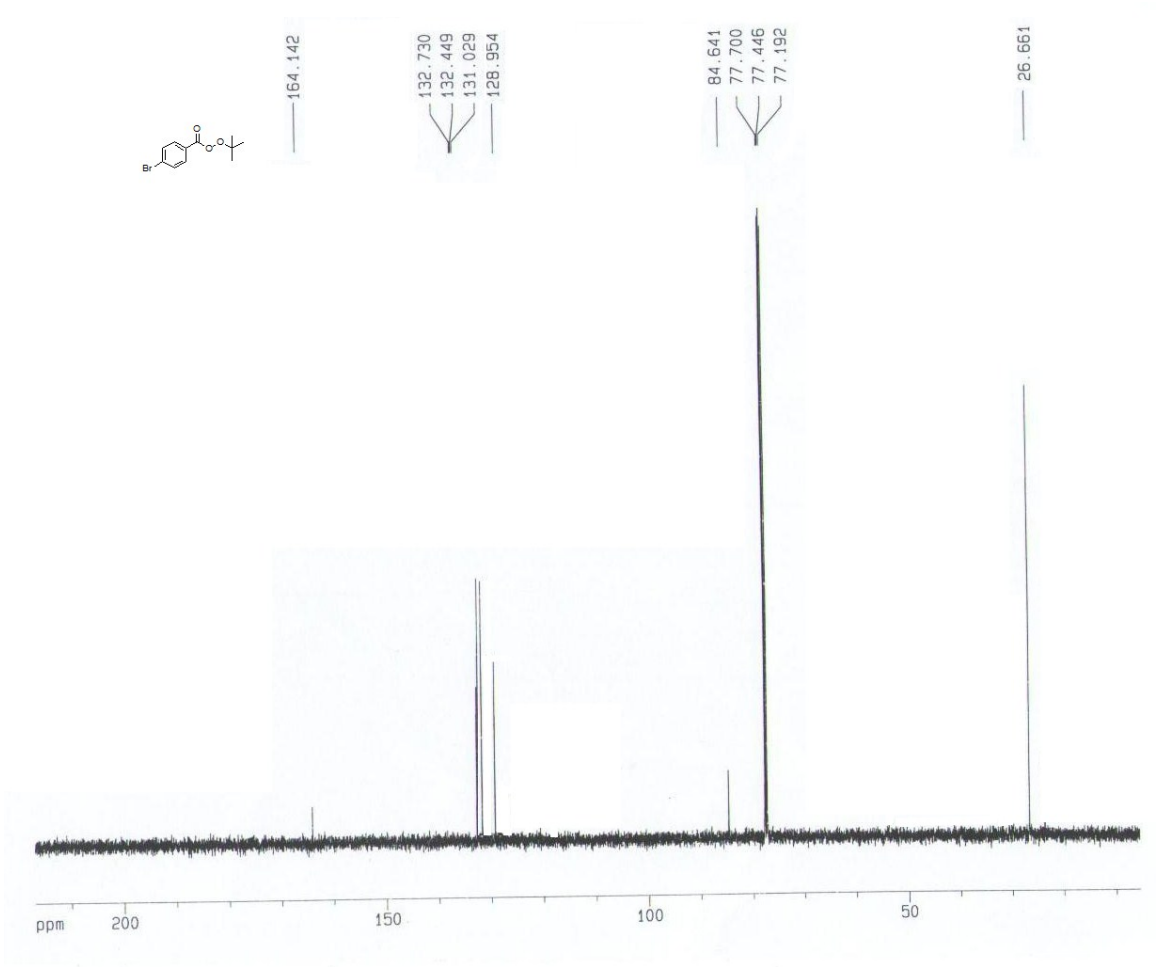
3.1.4. *t*-Butyl 4-fluorobenzoperoxoate (1d)



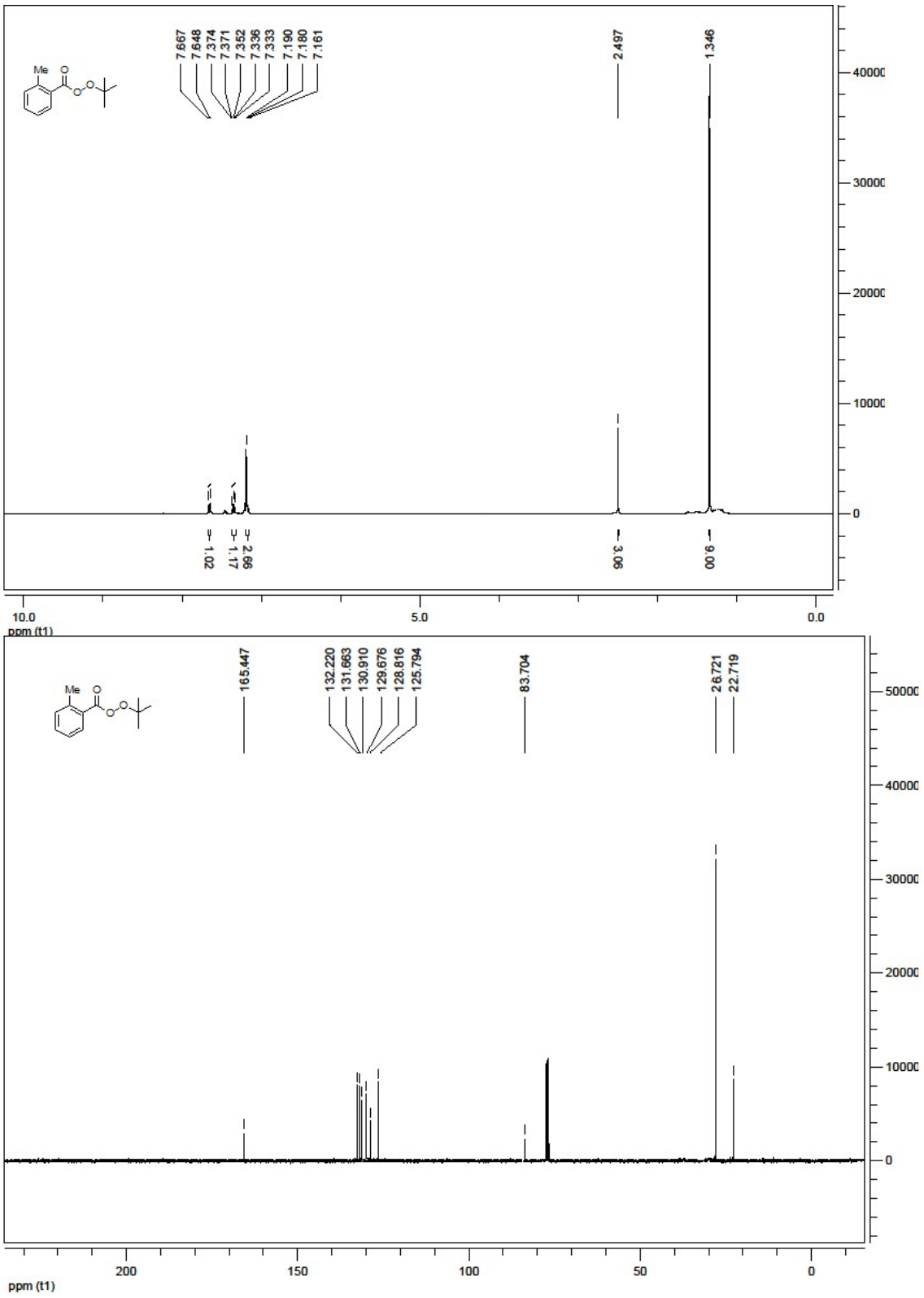

167.342
165.313
163.900
132.180
132.105
124.332
116.411
116.236
84.522
77.694
77.440
77.186
26.657
F
ppm
200
150
100
50

3.1.5. *t*-butyl 4-Bromobenzoperoxoate (1e)

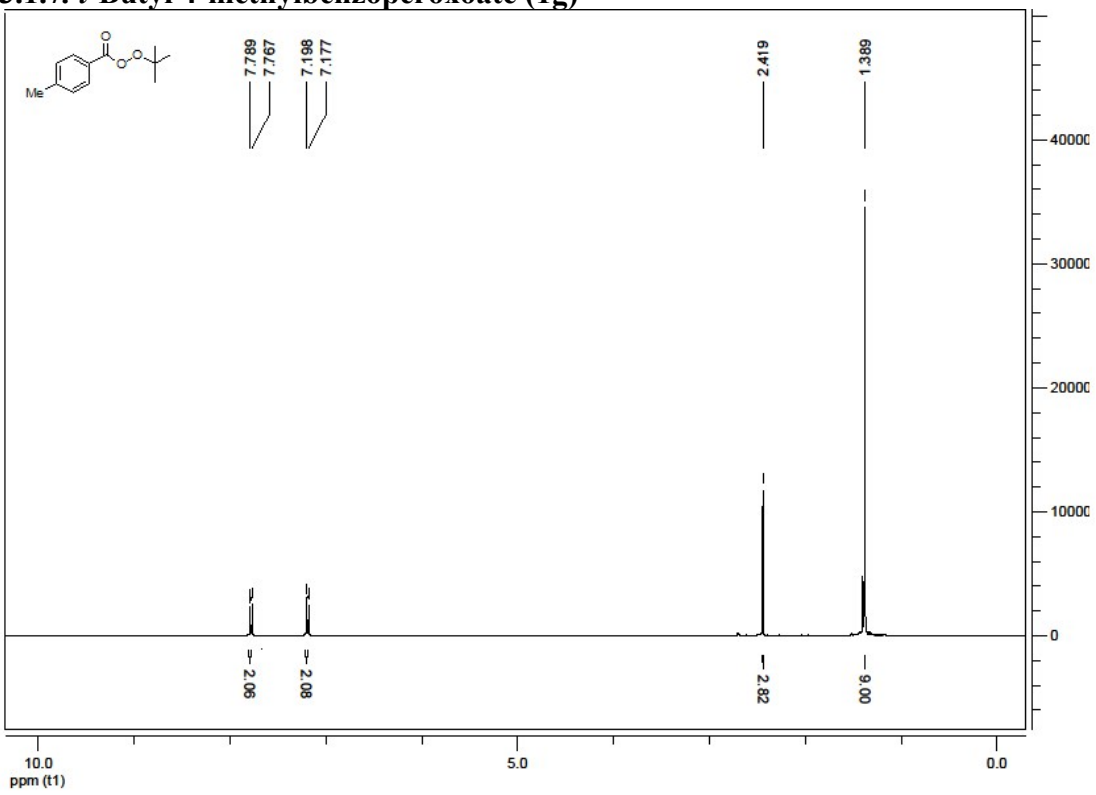


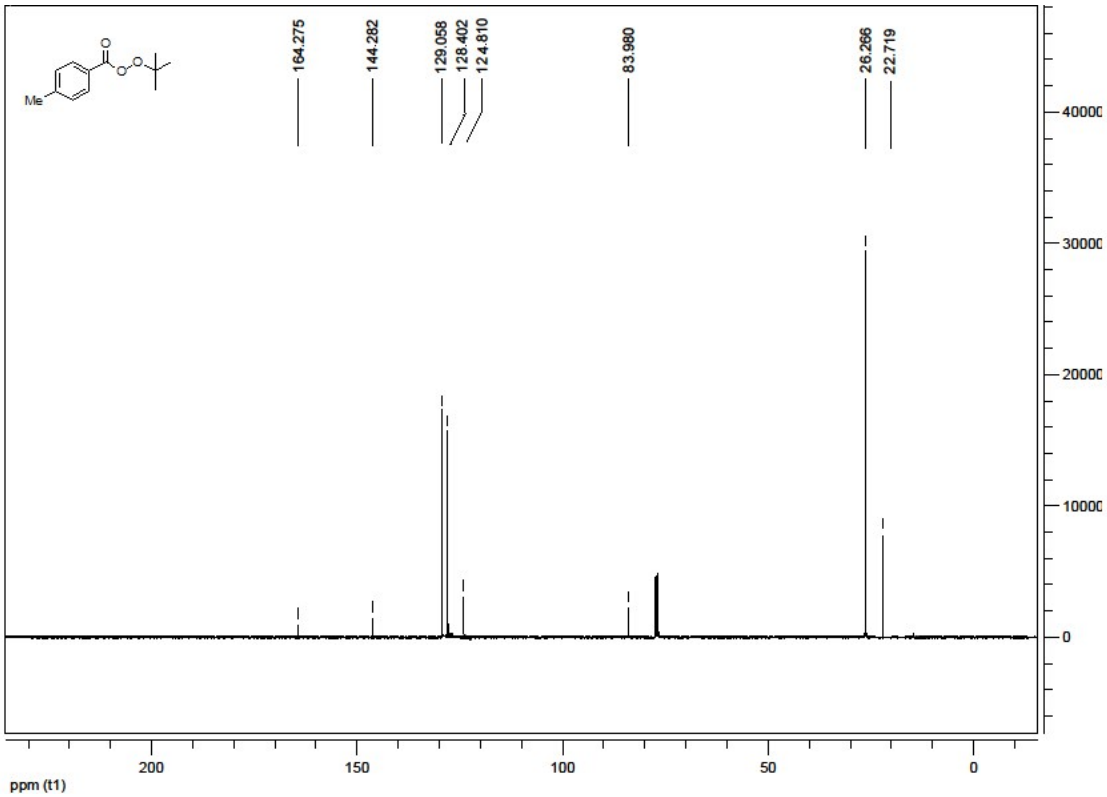

164.142
132.730
132.449
131.029
128.954
84.641
77.700
77.446
77.192
26.661
Br
ppm
200
150
100
50

3.1.6. *t*-Butyl 2-methylbenzoperoxoate (1f).

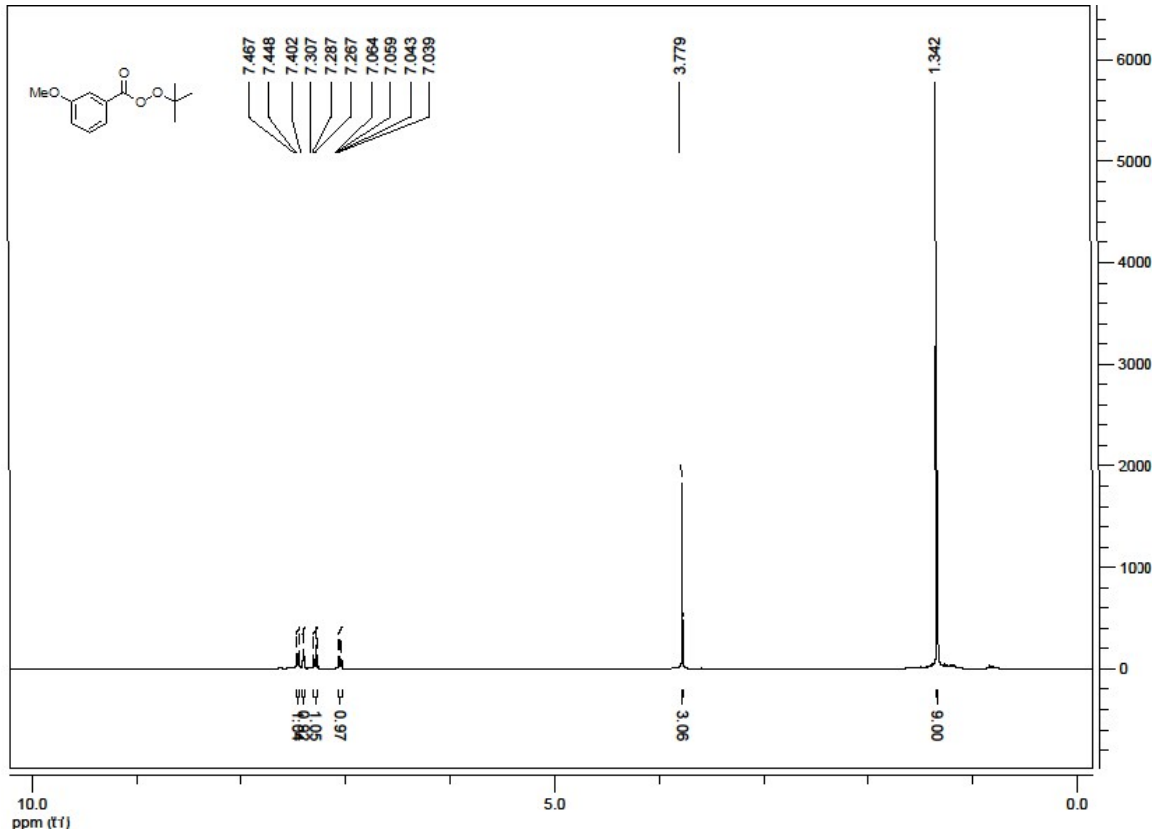


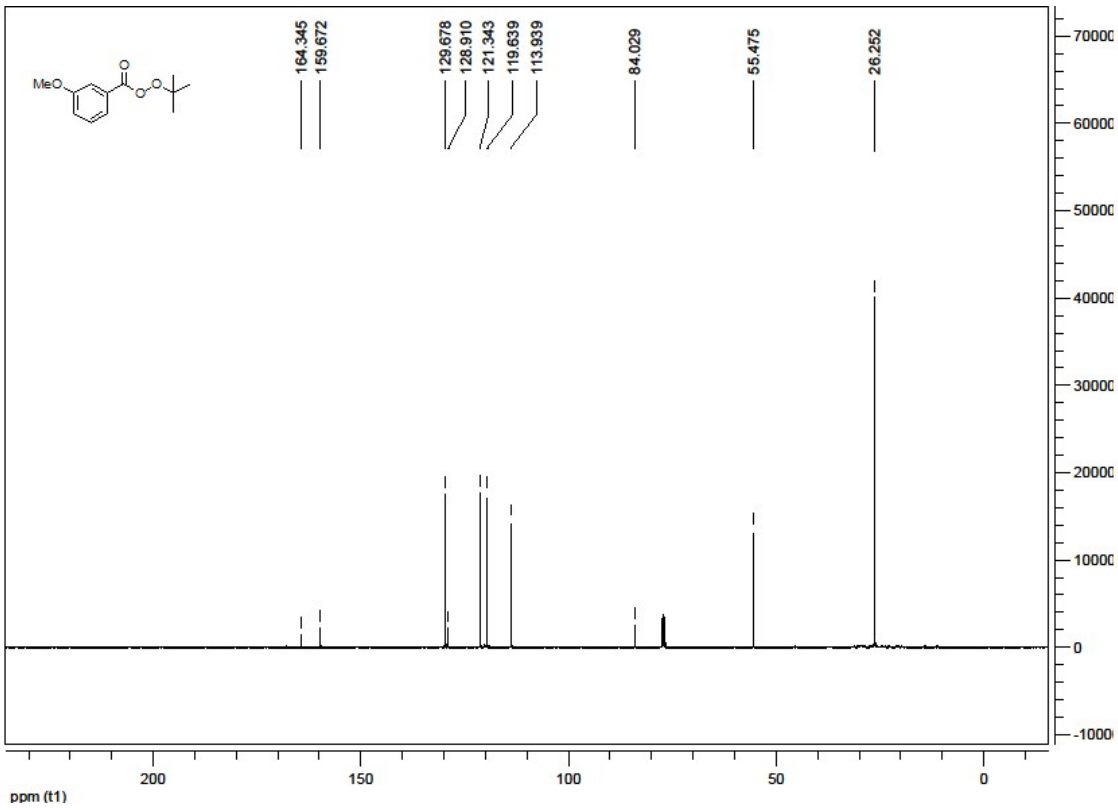
3.1.7. *t*-Butyl 4-methylbenzoperoxoate (1g)



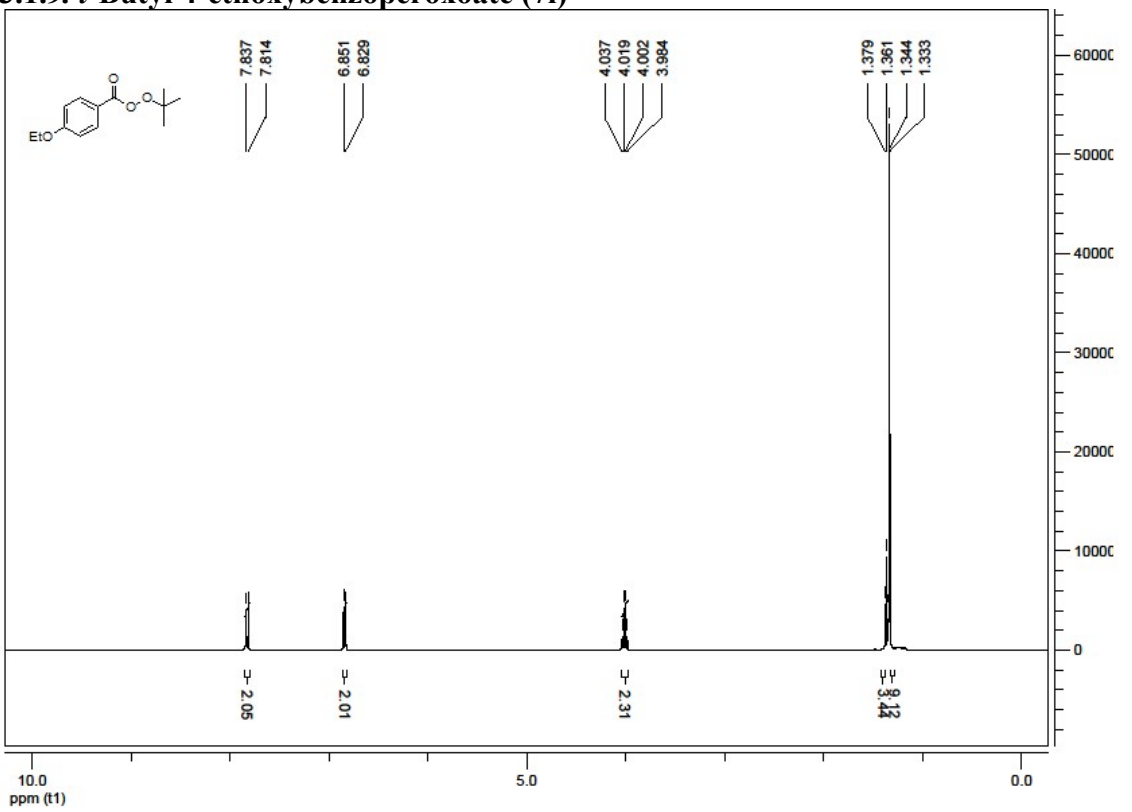


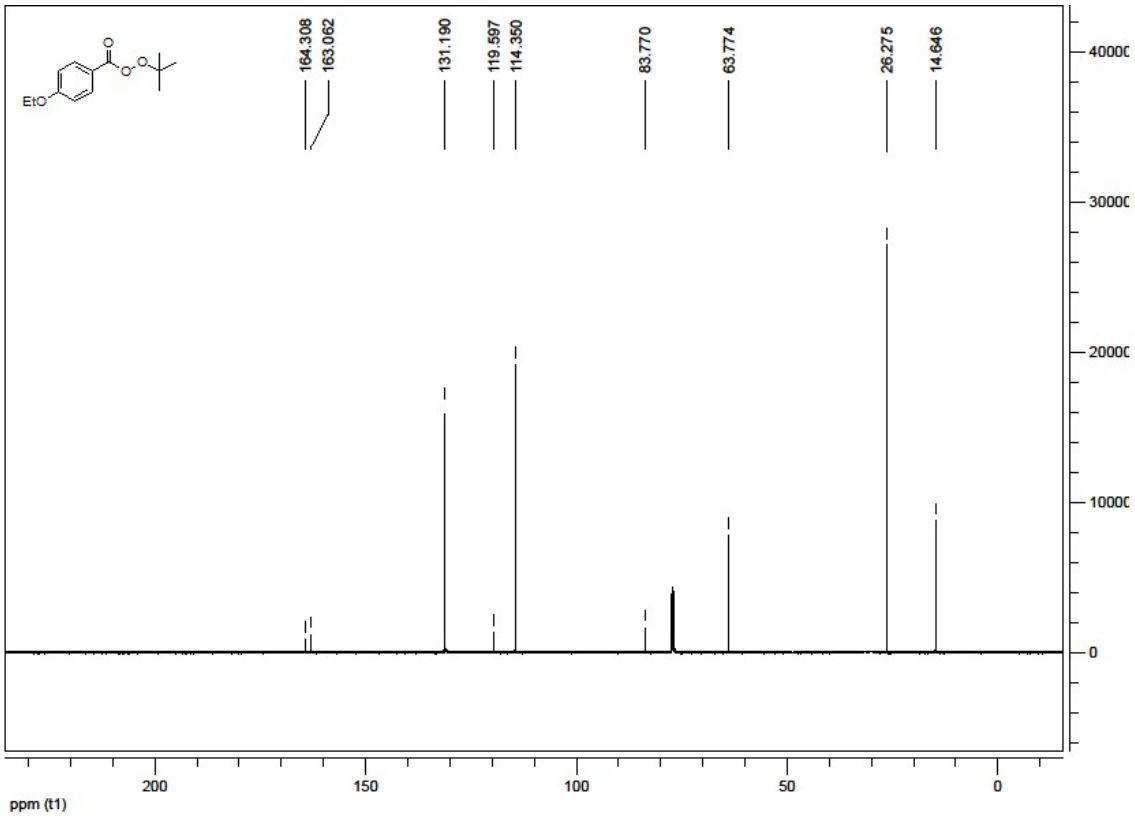
3.1.8. *t*-Butyl 3-methoxybenzoperoxoate (1h).



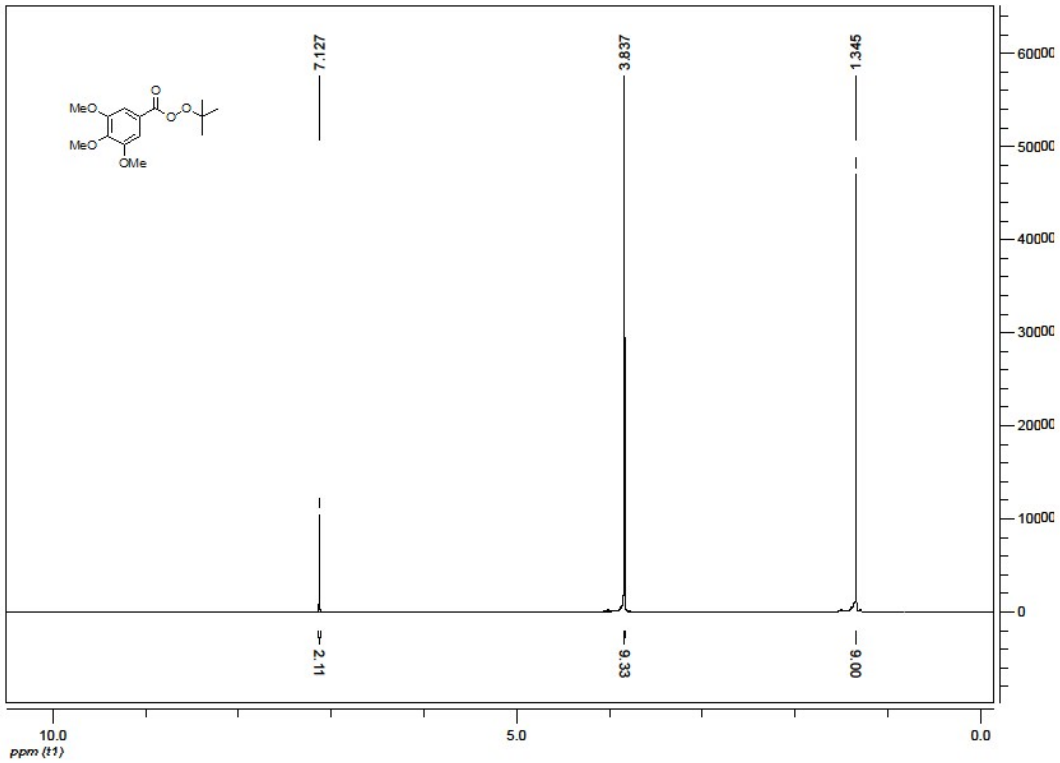

MeO
O
O
O
164.345
159.672
129.678
128.910
121.343
119.639
113.939
84.029
55.475
26.252
70000
60000
50000
40000
30000
20000
10000
0
-1000
200
150
100
50
0
ppm (t1)

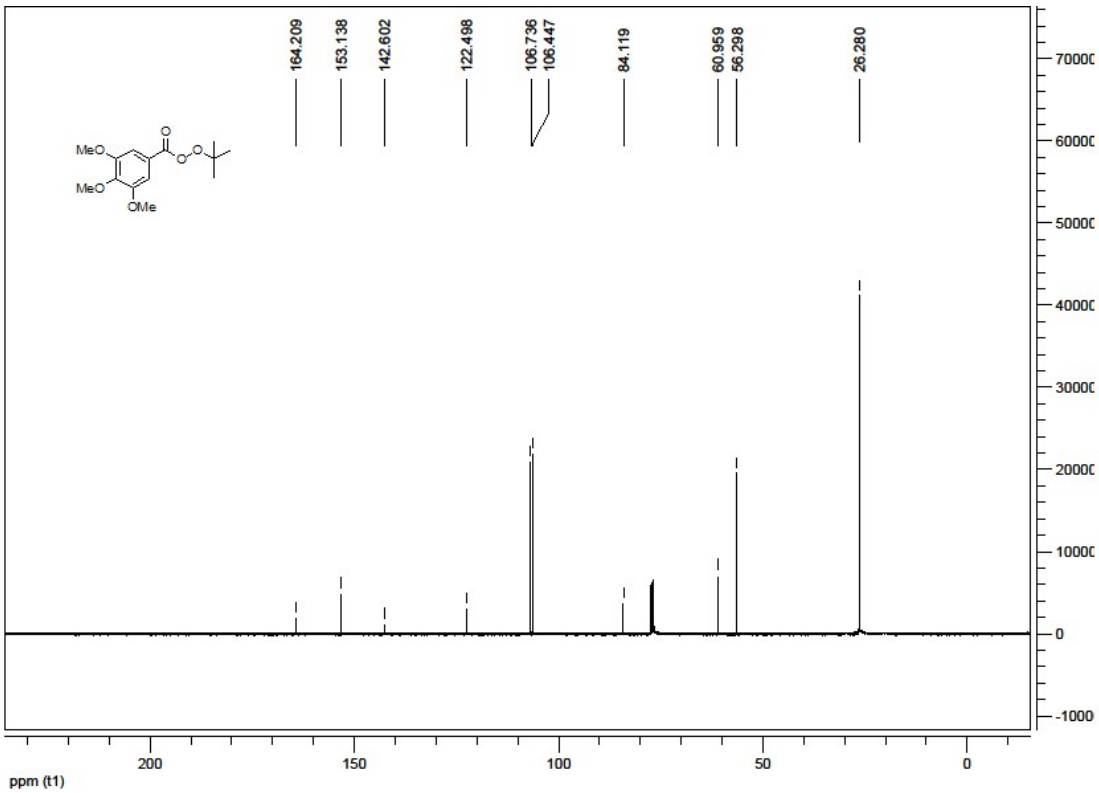
3.1.9. *t*-Butyl 4-ethoxybenzoperoxoate (7i)



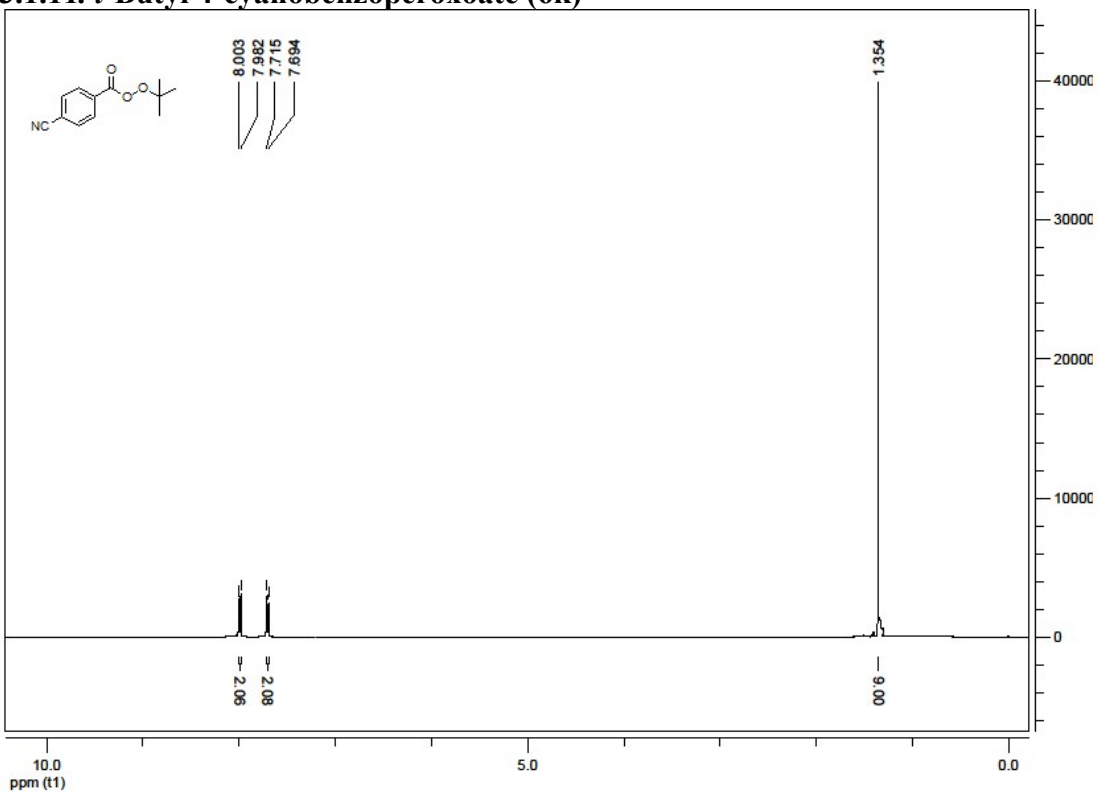


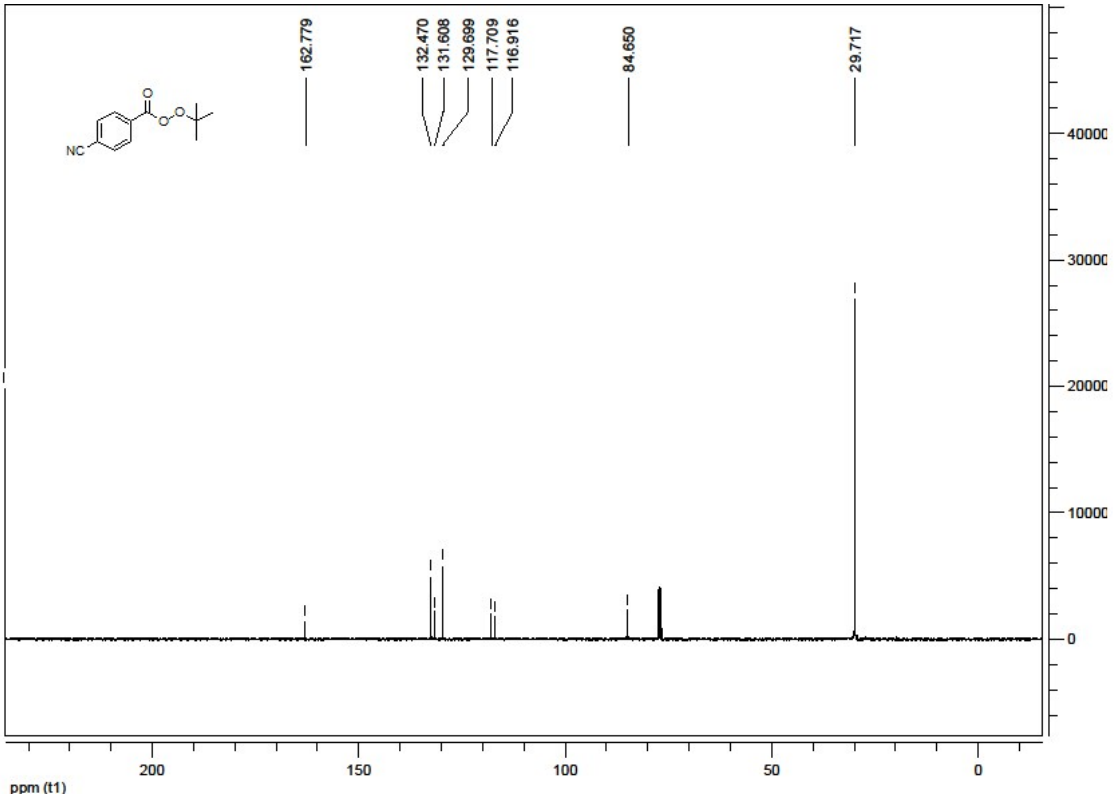
3.1.10. *t*-Butyl 3,4,5-tri methoxybenzoperoxoate (1j).



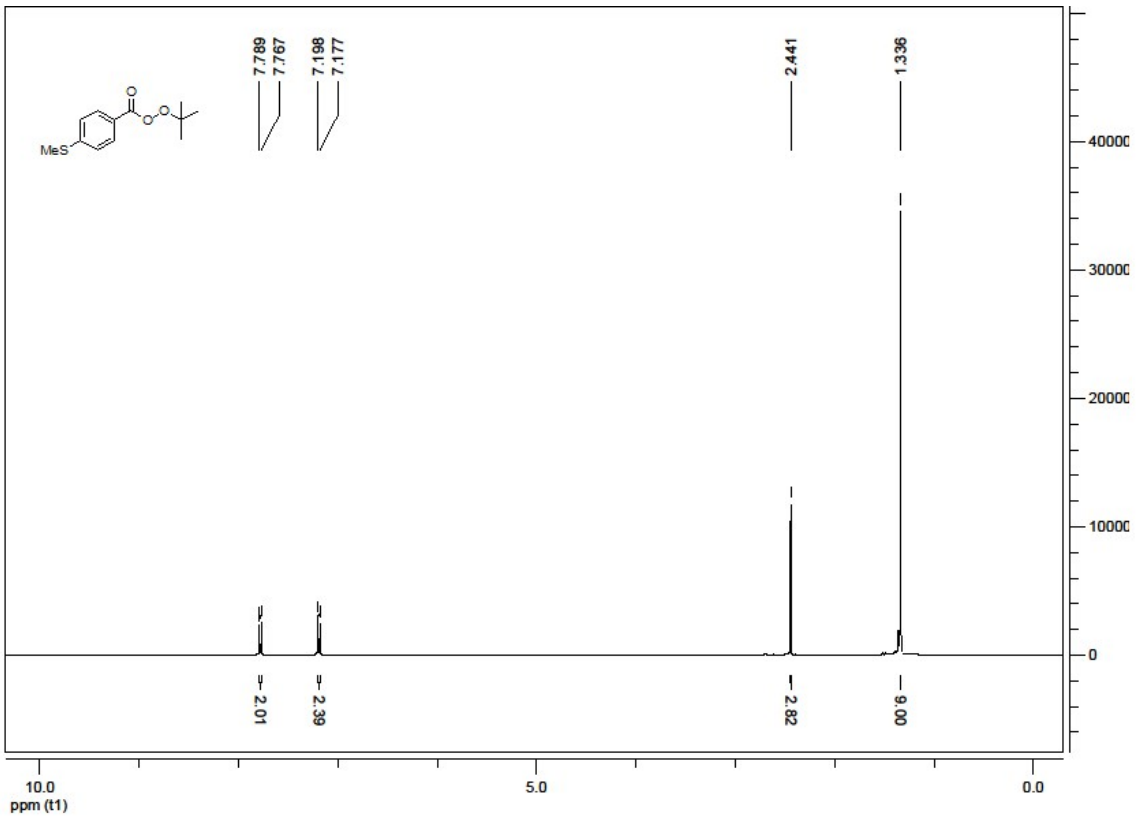


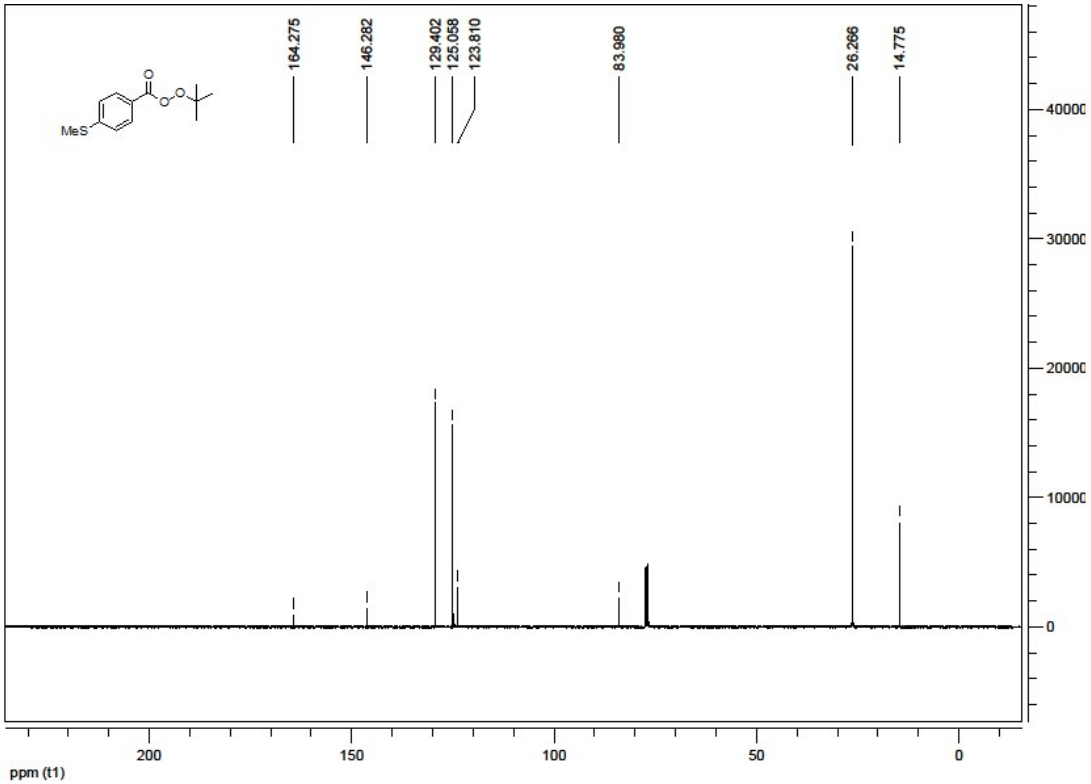
3.1.11. *t*-Butyl 4-cyanobenzoperoxoate (6k)



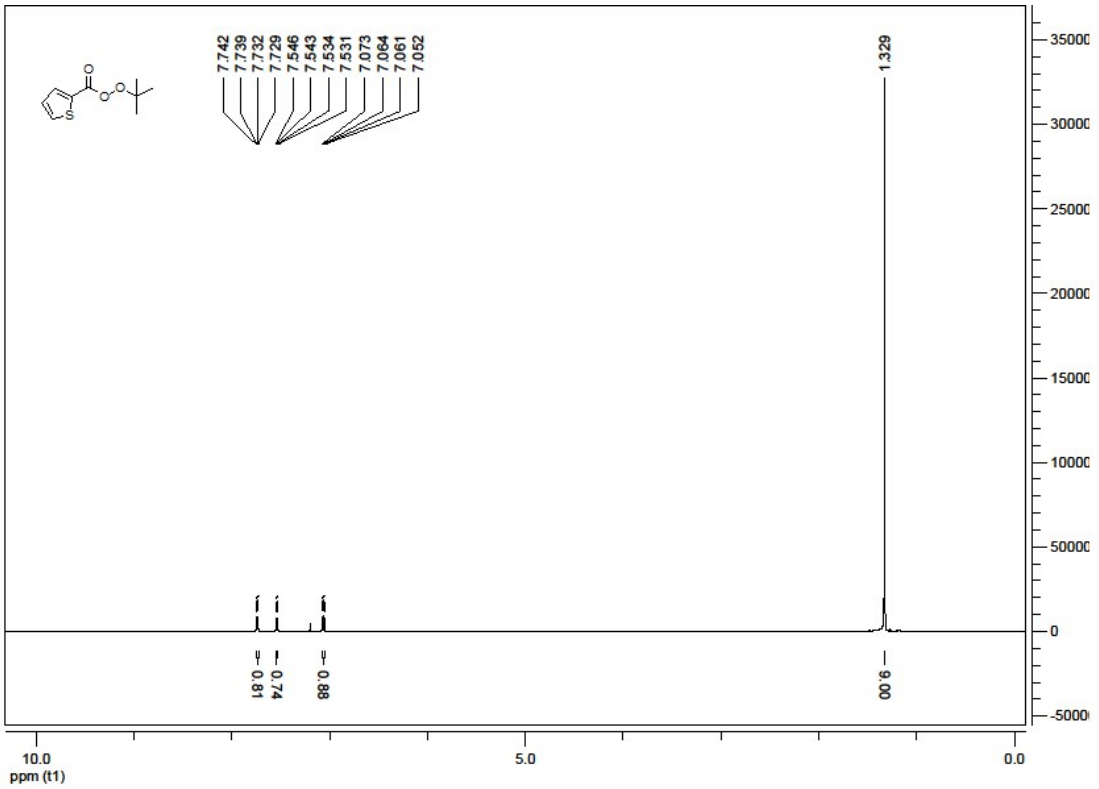


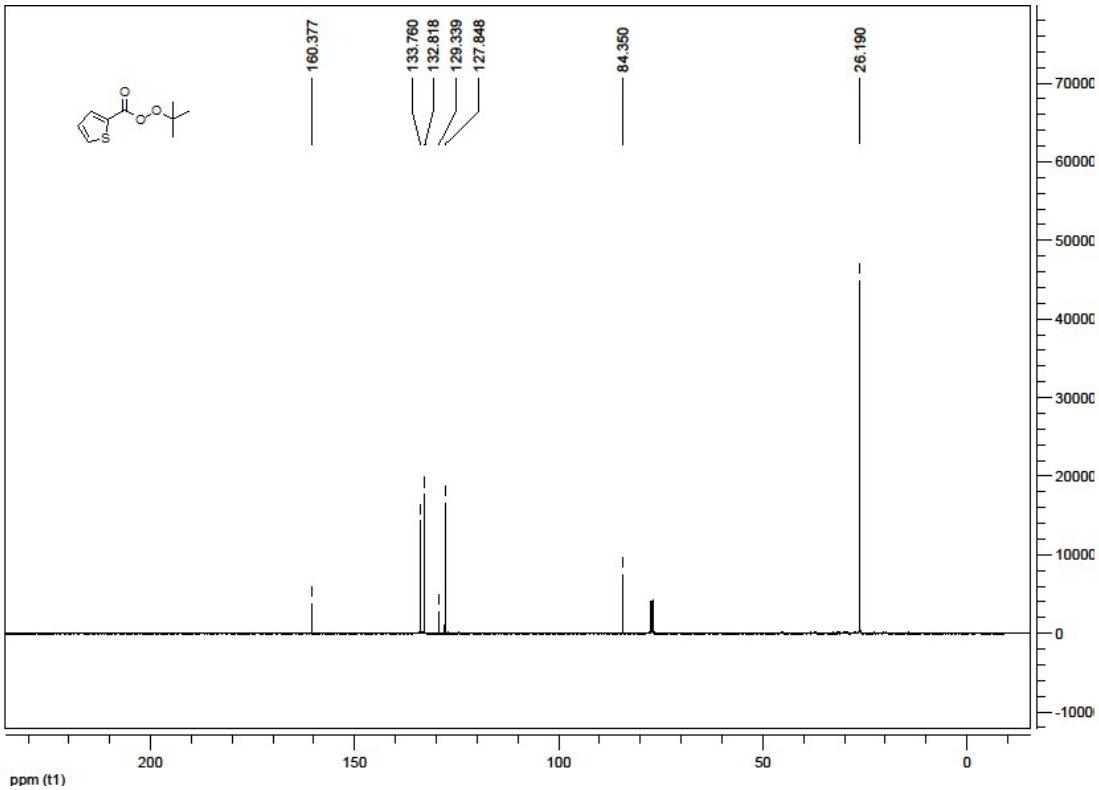
3.1.12. *t*-Butyl 4-(methylthio)benzoperoxoate (1l)



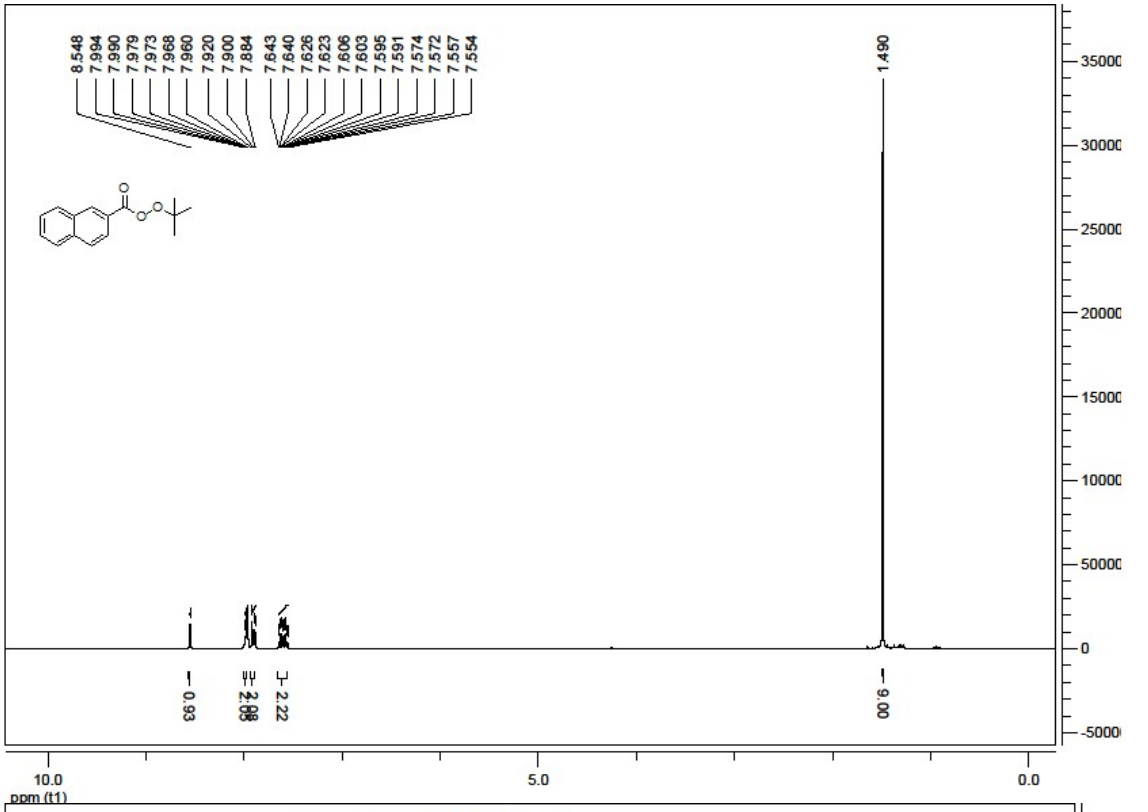


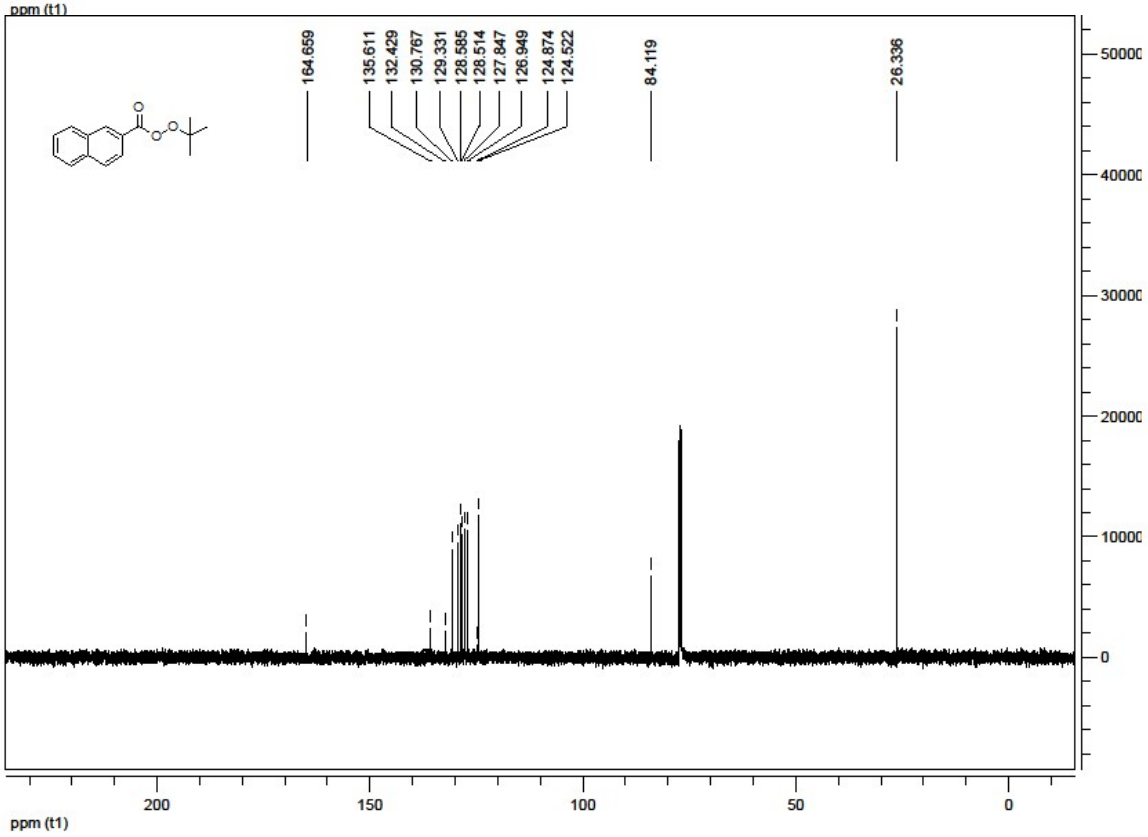
3.1.13. tert-Butyl thiophene-2-carboxylate (1n)





3.1.14. t-Butyl naphthalene-2-carboperoxoate (6o).





3.1.15. 1,2-di-*t*-Butyl benzoperoxoate (1p)