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Oxacycle Synthesis via Intramolecular Reaction of Carbanions and Peroxides

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Oxacycle Synthesis via Intramolecular Reaction of Carbanions and Peroxides

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Abstract

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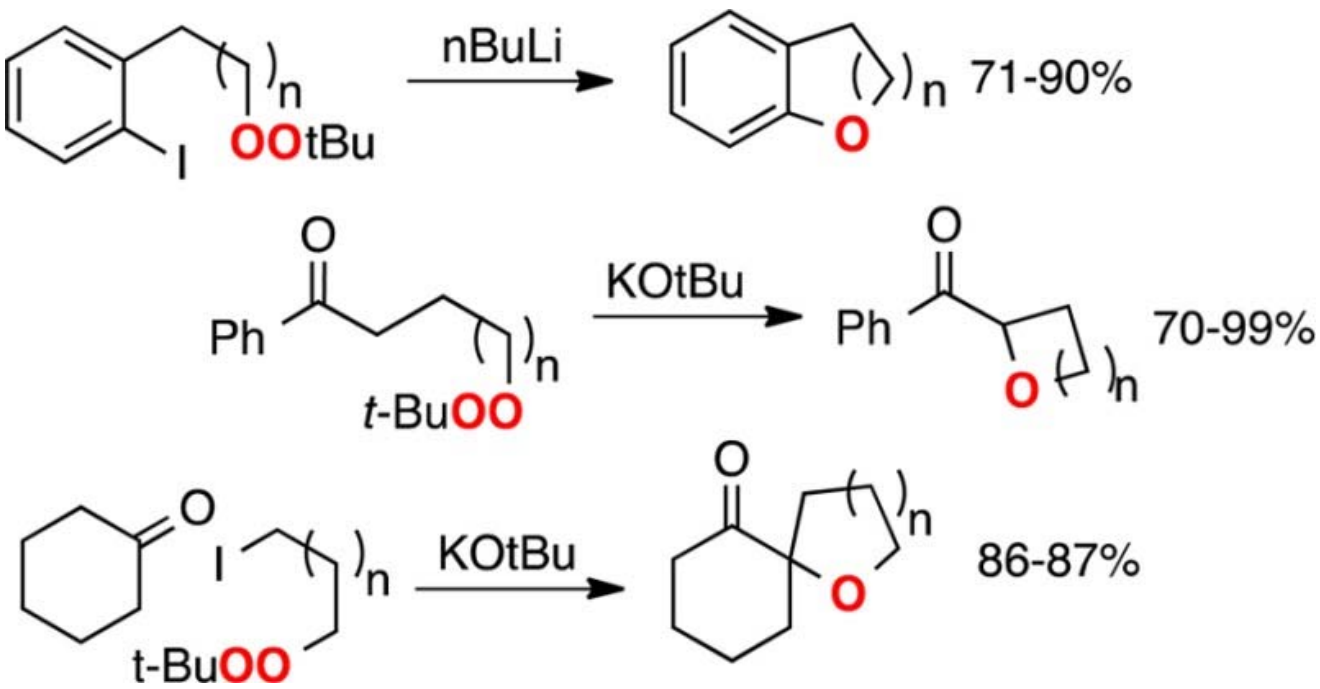


The intramolecular reaction of dialkyl peroxides with carbanions, generated via chemoselective metal-heteroatom exchange or deprotonation, provides a new approach to cyclic ethers. Applied in tandem with C–C bond formation, the strategy enables a one-step annelation to form oxaospirocycles.

Ethers, which comprise critical substructures in many bioactive molecules and natural products,[1] are typically synthesized through attack of nucleophilic oxygen on an electrophilic carbon.[1,2] The converse of this strategy, attack of a carbanion on electrophilic oxygen, has been investigated to only a limited extent for intermolecular reactions and is essentially unexplored for intramolecular reactions. We now demonstrate that chemoselective generation of carbanions in the presence of appropriately positioned O–O bonds of dialkyl peroxides allows the

efficient introduction of cyclic ethers (Figure 1), including frameworks (for example, **15a** or **19b**, vide infra) challenging to approach via existing methodology.

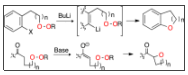
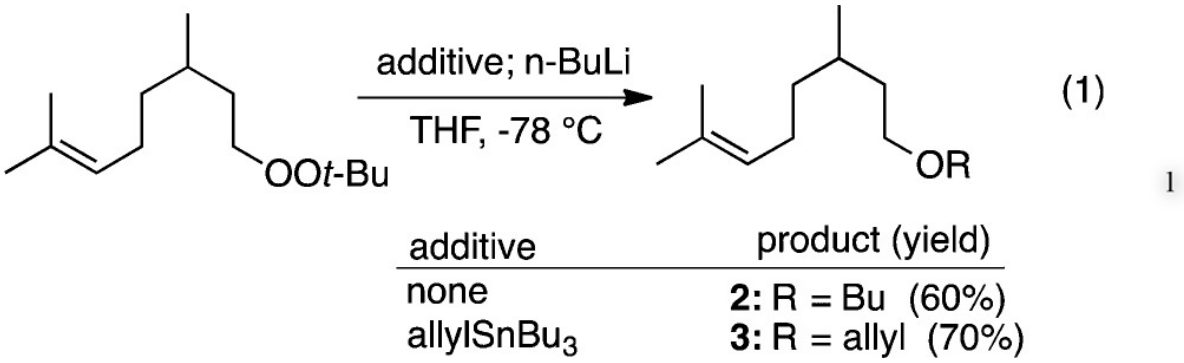


Figure 1

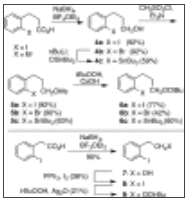
Overview of oxacycle synthesis via reactions of peroxides and carbanions.

Previous reports have described the intermolecular reaction of simple organometallics with dialkyl peroxides,[3] peresters,[4] and endoperoxides.[5] Bissilyl peroxides and lithiated hydroperoxides have been applied to oxygenation of lithiated arenes and alkenes.[6,7] However, the only precedent for the corresponding *intra*molecular reactions of carbanions with peroxides is the 3-*exo* cyclization of short-lived enolate intermediates formed during nucleophilic epoxidation reactions.[8]

At the outset of these studies, we faced two major uncertainties: first, would it be possible to generate reactive carbanions in the presence of a peroxide; and, second, would the carbanion/peroxide pair undergo intramolecular C–O bond formation. The question of chemoselective generation of an organolithium nucleophile was initially investigated using a dialkyl peroxide (**1**) derived from reaction of *t*-butyl hydroperoxide with dihydrogeraniol methanesulfonate.[9] Consistent with previous observations,[3a] reaction of **1** with *n*-BuLi proceeded readily to furnish butyl ether **2** (eq 1). Repeating this reaction in the presence of a slight excess of allyl tributylstannane resulted in predominant formation of the allyl ether (**3**), demonstrating that Li/heteroatom exchange proceeds much more rapidly than C–O bond formation.



Confident of our ability to selectively generate a carbanion in the presence of a peroxide, we prepared a family of substrates (**6a**–**c** and **9**) incorporating a dialkyl peroxide and a precursor aryllithium precursor (Scheme 1). The peroxide was either installed via displacement of a sulfonate (base) or iodide (Ag_2O).[10] The lower yield for phenethyl peroxide **9** reflects a tendency for Kornblum elimination in this skeleton.[11]

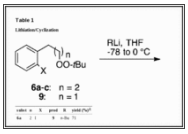


Scheme 1

Synthesis of Aryl Peroxide Substrates

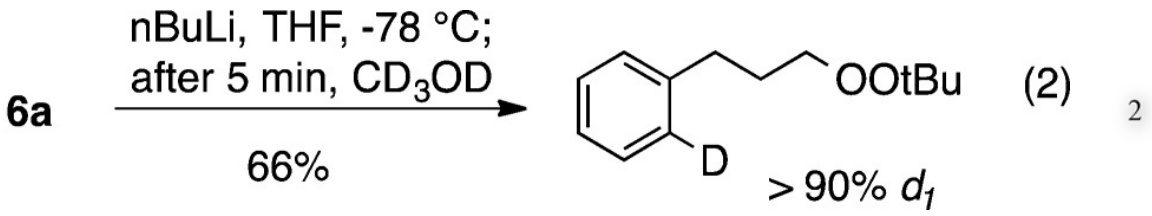
Table 1 illustrates the results of metal-heteroatom exchange for peroxides **6a**–**c** and **9**. Addition of either *n*-BuLi or PhLi to a–78 °C solution of **6a** (iodide) or **6b** (bromide), followed by warming of the reaction mixture to 0 °C, afforded good yields of dihydrobenzopyran **10**. The corresponding reactions of the tributylstannyl arene (**6c**) proceeded in much lower yield (PhLi) or essentially not at all (BuLi). Lithiation of *o*-iodophenethyl peroxide **9** furnished dihydrobenzofuran in excellent yield.

Table 1

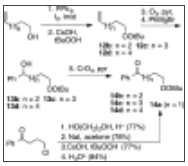


Lithiation/Cyclization

Repeating the lithiation of **6a** and quenching the reaction with MeOH-d_4 prior to warming resulted in formation of a monodeuterated peroxide (eq 2), demonstrating that lithiation occurs more rapidly and at lower temperature than intramolecular C–O bond formation.



We next investigated corresponding cyclizations of enolate anions, prepared as illustrated in Scheme 2.



Scheme 2

Synthesis of Peroxyketones

Conditions for cyclization were initially investigated for the 5-*exo* closure of peroxide **14b** (Table 2). The reaction, which generates *tert*-butoxide anion as a byproduct, proceeded rapidly in THF in the presence of KOtBu or KH. Only traces of products were observed using LDA.

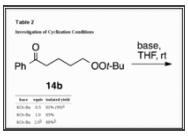


Table 2

Investigation of Cyclization Conditions

Application of the KO*t*-Bu conditions to the cyclization of **14a**–**c** furnished good yields of the oxetane, tetrahydrofuran, and tetrahydropyran (Table 3). Peroxide **14d** failed to undergo 7-*exo* closure to the oxepane, instead slowly undergoing decomposition.[11]

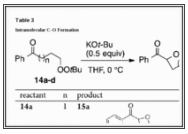
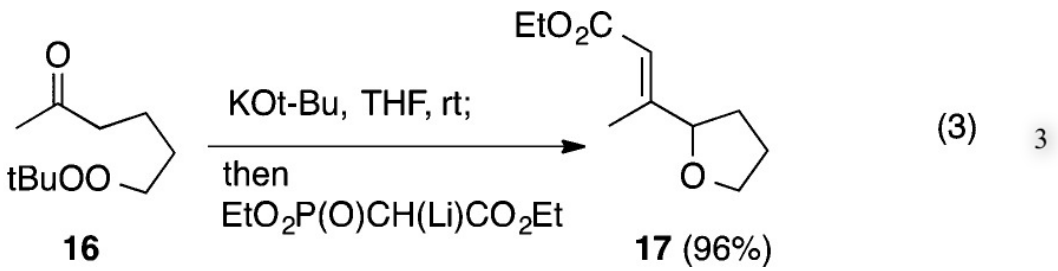


Table 3

Intramolecular C–O Formation

The transformation was not limited to aryl ketones, as evidenced by cyclization of peroxyhexanone **16** (eq 3); the volatile product was isolated after homologation with a Horner–Emmons reagent.



Finally, we investigated the reaction of enolates with a series of *t*-butyl iodoalkyl peroxides **18a**–**d**, available in one step from the corresponding 1,*n*-dihalides (Table 4). The results demonstrate the ability to achieve, in one step, a high-yielding annelation of spirocyclic ethers onto ketone frameworks, opening the door to a class of spirocycles previously approachable mainly through cationic ring expansions.[12] The isolation of the homologated peroxide (**20**) during attempted formation of a 7-membered ring provides strong evidence that the formation of the 5- and 6-membered spirocycle proceeds via initial formation of a C–C bond.

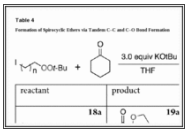


Table 4

Formation of Spirocyclic Ethers via Tandem C–C and C–O Bond Formation

In conclusion, we have demonstrated the chemoselective generation of carbanions in the presence of dialkyl peroxides and the application of the resulting intermediates to establish new C–O bonds. This alternative to more traditional etherifications provides a new approach to synthesis of spirocyclic ethers, aryl ethers, and various oxacycles including oxetanes.

Acknowledgments

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National Institutes of Health, United States

Supporting Information Available

Go to:

Experimental procedures, spectral listings, and selected ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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‡ These authors contributed equally.

Notes

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The authors declare no competing financial interest.

Supplementary Material

Go to:

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Supporting Information (Section SI-1)

Oxacycle Synthesis via Intramolecular Reaction of Carbanions and Peroxides

Rachel Willand-Charnley, [‡] Benjamin Puffer, [‡†] and Patrick H. Dussault*

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Contents

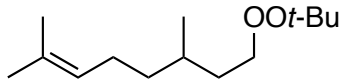
See SI-section 2 for ^{1}H NMR and ^{13}C NMR spectra

I. General Methods

Except where noted, all reactions were conducted under an atmosphere of N_2 in glassware that had been flame dried prior to use. All reagents and solvents were used as supplied commercially, except CH_2Cl_2 (distilled from CaH_2), THF (distilled from Na/benzophenone) and DMF (distilled from CaH_2 under reduced pressure). ^{1}H NMR and ^{13}C NMR spectra were acquired in $CDCl_3$; the spectrometer frequency is described within individual experimental descriptions. Chemical shifts are reported relative to residual chloroform (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). IR spectra were obtained on neat films (ZnSe, ATR mode) with selected absorbances reported in wavenumbers (cm^{-1}). GC/MS was performed using a 30 m DB-5MS column with a 1:200 injector split and 1 mL/min flow of He gas with analysis on an ion trap scanning in EI mode over 50−650 m/z range; the ion source was set at 200 °C. Flash column chromatography was performed on 230-400 uM silica gel. Thin-layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates containing a fluorescent indicator; developed TLC plates were visualized with a hand-held UV lamp or by heating after staining with 1% ceric sulfate/10% ammonium molybdate in 10% H_2SO_4 (general dip) or a peroxide-specific dip composed of a solution of 1.2g of *N, N*-dimethyl-p-phenylene diamine dihydrochloride in 1mL acetic acid, 20 mL H_2O, and 100 mL MeOH.[1] Abbreviations throughout: EA = ethyl acetate; Hex = hexane

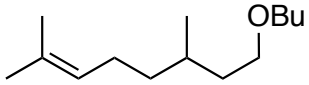
***tert*-Butyl 3,7-dimethyloct-6-en-1-yl peroxide** (**1**).

Synthesis of the methanesulfonate precursor: A 0.12M solution of citronellol (467 mg, 3.0 mmol) in methylene chloride at 0 °C was added Et_3N (1.25 mL, 9 mmol) followed by methanesulfonyl chloride (0.35 mL, 0.35 mmol) slowly. The reaction was allowed to warm slowly to room temperature and stirred for 16 h. The reaction was quenched with 25 mL of water and extracted with methylene chloride. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (25% EA/Hex) to yield 662 mg (94%) of 3,7-dimethyloct-6-en-1-yl methanesulfonate (42602-37-9) as a light yellow oil. R_f: 0.5 (25% EA/Hex). Spectral data matched those previously reported.[2]



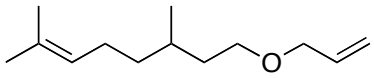
Introduction of the peroxide employed a variant of a known procedure.[3] To a suspension of CsOH monohydrate (6.76 g, 40 mmol) in DMF (80 mL) at 0 °C was slowly added *t*-butyl hydroperoxide (8.8 mL, 48 mmol, from a nominally 5.5 M solution in The mixture was allowed to stir for 30 min, then methanesulfonate 1 (6.3 g, 27 mmol) was added
dropwise in 5 mL of DMF. The reaction was allowed to slowly warm to room temperature. After 5 h, 50 mL of water was added and the resulting mixture was extracted with ether. The combined organic layers were washed with brine and dried with Na_2SO_4. The reside was concentrated under reduced pressure and purified by column chromatography (2.5% EA/Hex) to yield 3.9g (64%) of the peroxide as a colorless oil. R_f: 0.65 (10% EA/Hex). 1H NMR (400 MHz): δ 0.92 (d, 3H, J= 6.6), 1.18 (m, 1H), 1.26 (s, 9H), 1.30-1.47 (2H, unresolved overlapping signals), 1.50-1.68 (singlet overlapping unresolved signal, 5H), 1.70 (d, 3H, J= 0.9), 1.99 (m, 2H), 3.99 (m, 2H), 5.11 (app. triplet of quintets, 1H, J= 7.2, 1.4). ^{13}C NMR (100 MHz): δ 17.6 (CH3), 19.6 (CH3), 25.4 (CH3), 25.7 (CH2), 26.3 (tBu CH3's), 29.7 (CH), 34.6 (CH2), 37.1 (CH2), 73.4 (CH2), 80.0 (C), 124.7 (CH), 131.2 (C). IR: 2975, 2927, 2873, 1456, 1377, 1361, 1241, 1197, 884. HRMS calculated for C14H28O2Na $[M+Na]^+$: 251.1623; found 251.1624.

Butyl 3,7-dimethyloct-6-en-1-yl ether (2)



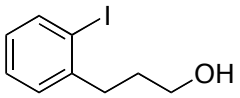
To a 0.2 M solution of peroxide 2 (234 mg, 1.0 mmol) in THF at -78 °C was added nBuLi (2.0 mmol, 0.80 mL of a nominally 2.5 solution in hex) drop wise. After stirring for 10 min, the reaction was allowed to warm to room temperature and after 4 h quenched with water (5 mL) and extracted with ether. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by column chromatography (2.5% EA/Hex) to yield 138 mg (63%) of the ether as a colorless oil. R_f: 0.5 (10% CH_2Cl_2/Hex). ^{1}H NMR (400 MHz): δ 0.89-0.97 (s and d overlapping, 6H), 1.18 (m, 1H), 1.30-1.47 (overlapping signals, 4H), 1.52-1.67 (singlet overlapping with 2 other signals, 7H), 1.70 (d, J= 1.0), 2.00 (m, 2H), 3.36-3.51 (overlapping signals, 4H), 5.12 (app. t of q, J= 7.2, 1.3). ^{13}C NMR (100 MHz): δ 13.9 (CH3), 17.6 (CH2), 19.4 (CH3), 19.6 (CH3), 25.5 (CH2), 25.7 (CH3), 29.6 (CH), 31.9 (CH2), 36.7 (CH2), 37.2 (CH2), 69.2 (CH2), 70.7 (CH2), 124.9 (CH), 131.1 (C). IR: 2959, 2926, 2856, 1256, 1376, 1131, 830, 737. HRMS calculated for $C_{14}H_{28}O$: 213.2218; found 213.2215.

Allyl 3,7-dimethyloct-6-en-1-yl ether (3)



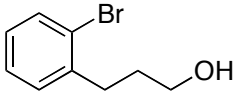
To a 0.2 M solution of peroxide **1** (229 mg, 1.0 mmol) in THF was added allyltributyltin (0.62 mL, 2.0 mmol). The solution was cooled to -78 °C, and *n*BuLi (2.5 mmol, 1.0 mL of a 2.5 M solution in hexane) was added drop wise. After 30 min the reaction was quenched with 10 mL of water and extracted with ether. The combined organic layers were dried with Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by column chromatography (2.5% EA/Hex) to yield 137 mg (70%) of the allyl ether as a colorless oil. Rf: 0.25 (5% EA/Hex). Spectral details matched those previously reported.[4]

3-(2-Iodophenyl)propanol (4a)



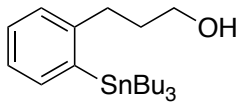
To a 0.42 M solution of commercially available 3-(2-iodophenyl)propionic acid (2.926 g, 10.6 mmol) in a 0 °C solution of THF was added $NaBH_4$ (825 mg, 21.8 mmol) in one portion. BF_3OEt_2 (2.74 mL, 21.8 mmol) was then added drop wise and the reaction stirred for 1 hour. The reaction was quenched with 12 mL MeOH followed by 12 mL of 1M aq. HCl. The mixture was then diluted with EA and the organic layer separated and dried with Na_2SO_4. The resulting solution was concentrated under reduced pressure and the residue purified by flash chromatography (30% EA/Hex) to yield 2.63g (95%) of the title compound as a light yellow oil. Rf : 0.33 (30% EA/Hex) Spectral details matched those previously reported.[5]

3-(2-Bromophenyl)propanol (4b)



To a 0.5 M solution of commercially available 3-(2-bromophenyl)propionic acid (771 mg, 3.37 mmol) in THF at 0 °C was added $NaBH_4$ (255 mg, 6.7 mmol) in one portion. $BF_3{\bullet}OEt_2$ (0.842 mL, 6.7 mmol) was then added dropwise and the reaction stirred for 1 hour. The reaction was quenched with methanol (4 mL) followed by 1M HCl (4 mL). The mixture was diluted with EA (15 mL) and the separated organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (30% EA/Hex) to yield 668 mg (92%) of the alcohol as a colorless oil: R_f : 0.33 (30% EA/Hex). Spectral details matched those previously reported.[6]

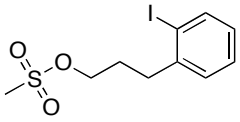
3-(2-(tributylstannyl)phenyl)propan-1-ol (4c)



To a 0.1 M solution of 3-(2-bromophenyl)propan-1-ol **4b** (0.50 mmol, 104 mg) in THF at -78 °C was added nBuLi (nominaly 1.6 M in Hex, 1.1 mmol, 0.69 mL) slowly drop wise. The mixture was stirred for 10 minutes at -78 °C, then tributyltin chloride (1.1 mmol, 0.30 mL) was added. The reaction was then allowed to warm slowly to room temperature. After 5 hours the reaction was quenched by sequential addition of small amounts of water and sat. aq. NH_4Cl. The resulting mixture was extracted with ether and the extracts dried with Na_2SO_4. The mixture was concentrated under reduced pressure and purified via column chromatography (10% EA/Hex) to yield 126 mg (59%) of the title compound as a colorless oil. R_f : 0.40 (20% EA/Hex); ^{1}H NMR (400 MHz): δ 0.91 (t, 9H, J= 7.3), 1.10 (m, 6H), 1.35 (m, 6H), 1.53 (m, 6H), 1.90 (m, 2H), 2.70 (m, 2H), 3.76 (dd, 2H,

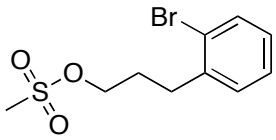
J=11.3, 6.2), 7.12-7.50 (m, 5H). 13C NMR (100 MHz): δ 10.4 (CH3), 13.7 (CH2), 27.4 (CH2), 29.2 (CH2), 35.2 (CH2), 35.4 (CH2), 62.7 (CH2), 125.4 (CH), 128.0 (CH), 128.4 (CH), 136.9 (C), 141.8 (CH), 148.6 (C). HRMS (ESI): calcd for $C_{21}H_{38}OSn$ $(M+Na)^+$: 449.1742; found: 449.1845. IR: 3332, 3051, 2953, 2921, 2870, 2851, 1463, 1433, 1417, 1375, 1339, 1291, 1151, 1056, 959, 864, 749, 662, 589.

3-(2-Iodophenyl)propyl methanesulfonate (5a)



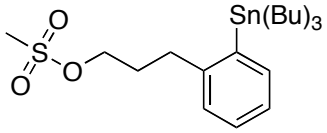
Alcohol **4a** (1.78 g, 5.23 mmol) was converted to the corresponding methanesulfonate (2.14 g, 92%, light yellow oil) by the same procedure employed for compound **5b** (below). R_f: 0.5 (30% EA/Hex). Spectral details matched those previously reported.[7]

3-(2-Bromophenyl)propyl methanesulfonate (5b)



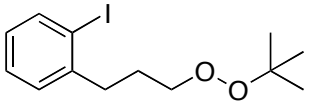
To a 0.2 M solution of alcohol **4b** (1.83 g, 8.51 mmol) in CH_2Cl_2 at 0 °C was added Et_3N (4.7 mL, 34 mmol) followed by methanesulfonyl chloride (0.99 mL, 12.8 mmol, drop wise). The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 20 mL of water and the separated aqueous layer was extracted with additional methylene chloride (2 X 30 mL). The combined organic layers were dried with Na_2SO_4. The crude mixture was concentrated under reduced pressure and purified by flash chromatography (20% EA/Hex) to yield 2.24 g (90%) of the methanesulfonate as a light yellow oil: Rf: 0.45 (20% EA/Hex). Spectral details matched those previously reported.[8]

3-(2-(Tributylstannyl)phenyl)propyl methansulfonate (5c)



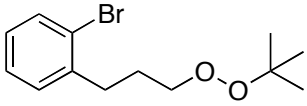
Alcohol **4c** (42.5 mg, 0.10 mmol) was converted to the corresponding methanesulfonate by the same procedure employed for compound **5b** to yield 31.7 mg (63%) of a colorless oil. R_f: 0.6 (30% EA/Hex). ^{1}H NMR δ 0.91 (t, 9H J= 7.3), 1.10 (m, 6H), 1.36 (quintet, 6H, J= 7.3), 1.53 (m, 6H), 2.07 (tdd, 2H, J= 7.3, 9.8, 6.4), 2.74 (m, 2H), 3.04 (s, 3H), 4.31 (t, 2H, J= 6.5), 7.15-7.35 (m, 4H), 7.35-7.50 (m, 1H). ^{13}C NMR (100 MHz): δ 10.4 (CH3), 13.7 (CH2), 27.4 (CH2), 29.1 (CH2), 31.5 (CH2), 34.9 (CH2), 37.4 (CH3), 69.2 (CH2), 125.7 (CH), 127.9 (CH), 128.5 (CH), 137.1 (CH), 141.9 (C), 147.2 (C). HRMS (ESI): calcd for $C_{22}H_{40}O_3SSn$ $(M+Na)^+$: 527.1618; found: 527.1619. IR: 2954, 2921, 2870, 2851, 1463, 1355, 1173, 1072, 1000, 959, 921, 873, 833, 806, 751, 730, 667, 591.

3-(2-Iodophenyl)propyl tert-butyl peroxide (6a)



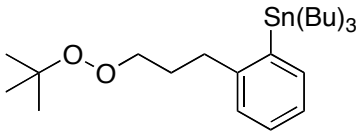
Methanesulfonate **5a** (2.14 g, 6.30 mmol) was converted to the t-butyl peroxide (1.61 g, 77%, light yellow oil) by the same procedure employed for compound **6b** (below). R_f: 0.45 (5% EA/Hex). ^{1}H NMR (400 MHz): δ 1.23 (s, 9H), 1.94 (tdd, 2H, J= 6.4, 9.0, 6.5), 2.82 (m, 2H), 4.03 (t, 2H, J= 6.4), 6.90 (td, 1H, J=7.4, 1.9), 7.27 (m, 2H), 7.83 (dd, 1H, J= 7.8, 1.1). ^{13}C NMR (100 MHz): δ 26.4 (CH3), 28.4 (CH2), 37.4 (CH2), 74.0 (CH2), 80.1 (C), 100.6 (C), 127.8 (CH), 128.3 (CH), 129.4 (CH), 139.5 (CH), 144.3 (C). HRMS (ESI): calcd for $C_{13}H_{19}IO_2$ $(M+Na)^+$: 357.0327; found: 357.0315. IR: 2975, 2867, 1562, 1465, 1434, 1361, 1240, 1195, 1079, 1048, 1008, 876, 746, 646.

3-(2-Bromophenyl)propyl tert-butyl peroxide (**6b**, 897 mg, 42%) was prepared from methanesulfonate **5b** (2.29 g, 7.8 mmol) by a similar procedure as for peroxide **1**. R_f: 0.45 (5% EA/Hex) ^{1}H NMR (400 MHz): δ 1.29 (s, 9H), 1.97 (tdd, 2H, J = 7.0, 9.7, 6.4), 2.84 (m, 2H), 4.02 (t, 2H, J= 6.5), 7.07 (m, 1H), 7.26 (m, 2H), 7.55 (d, 1H, J= 7.9). ^{13}C NMR (100 MHz): δ 26.4 (CH3), 28.0 (CH2), 32.8 (CH2), 74.1 (CH2), 80.1 (C), 124.5 (C), 127.4 (CH), 127.6 (CH), 130.4 (CH), 132.8 (CH), 141.1 (C). HRMS (ESI): calcd for $C_{13}H_{19}BrO_2$ $(M+Na)^+$: 309.0466; found: 309.0457. IR: 2975, 2869, 2358,1470, 1438, 1384, 1361, 1240, 1195, 1019, 877, 746, 657.



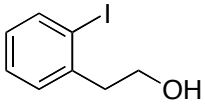
3-(2-(Tributylstannyl)phenyl)propyl tert-butyl peroxide (6c)

Methanesulfonate **5c** (418 mg, 0.83 mmol) was converted to the peroxide (246 mg, 60%) by the same procedure employed for peroxide **1**. R_f: 0.5 (5% EA/Hex). ^{1}H NMR (400 MHz): δ 0.91 (t, 9H, J= 7.3), 1.1 (m, 6H), 1.29 (s, 9H), 1.36 (quintet, 6H, J= 7.3), 1.54 (m, 6H), 1.93 (m, 2H), 2.70 (m, 2H), 4.05 (t, 2H, J= 6.5), 7.01-7.33 (m, 3H), 7.41 (m, 1H). ^{13}C NMR (100 MHz): δ 10.4 (CH3), 13.7 (CH2), 26.4 (CH3), 27.4 (CH2), 29.2 (CH2), 30.5 (CH2), 35.9 (CH2), 74.6 (CH2), 80.1 (C), 125.3 (CH), 127.9 (CH), 128.4 (CH), 136.8 (CH), 141.8 (C), 148.6 (C). HRMS (ESI): calcd for $C_{25}H_{45}O_2Sn$ $(M+Na)^+$: 521.2417; found: 521.2430. IR: 3051, 2955, 2922, 2870, 2852, 2360, 1463, 1434, 1375, 1361, 1241, 1196, 1071, 1020, 959, 875, 750, 667, 592.



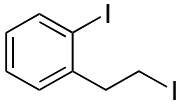
2-(2-Iodophenyl)ethanol (7)

2-(2-Iodophenyl)acetic acid (1.00 g, 3.8 mmol) was converted to the corresponding alcohol (915 mg, 97%, colorless oil) by the same procedure employed for compound **4a**. R_f: 0.25 (20% EA/Hex). Spectral details matched those previously reported.[7]



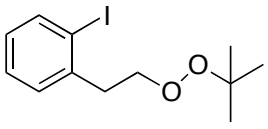
1-Iodo-2-(2-iodoethyl)benzene (8)

Alcohol **7** (898 mg, 3.62 mmol) was converted to the iodide (**8**, 906) mg, 70%, light yellow oil) using the general procedure described below except that CH_2Cl_2 was used as solvent. R_f: 0.95 (5% EA/Hex). ^{1}H NMR (400 MHz): δ 3.26-3.41(overlapping signals, 4H), 6.98 (m, 1H), 7.23-7.38 (overlapping signals, 2H), 7.85 (m, 1H). ^{13}C NMR (100 MHz): δ 3.3 (CH2), 44.9 (CH2), 99.9 (C), 128.5 (CH), 128.8 (CH), 129.8 (CH), 139.8 (CH), 143.3 (C). Spectra matched those previously reported.[7]

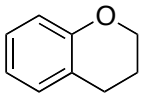


2-(2-Iodophenyl) ethyl tert-butyl peroxide (9)

Diiodide **8** (107 mg, 0.30 mmol) was converted to iodoaryl peroxide (21.5 mg, 22%, light yellow oil) using the same procedure as employed for peroxide **1**. The transformation could also be conducted using Ag_2O in THF. R_f: 0.80 (5% EA/Hex). ^{1}H NMR (400 MHz): δ 1.25 (s, 9H), 3.09 (t, 2H, J= 7.1), 4.15 (t, 2H, J= 7.1), 6.92 (m, 1H), 7.25-7.33 (overlapping signals, 2H), 7.83 (d, 1H, J= 7.7). ^{13}C NMR (100 MHz): δ 26.3 (CH3), 39.3 (CH2), 74.1 (CH2), 80.4 (C), 100.6 (C), 128.2 (CH), 128.3 (CH), 130.3 (CH), 139.5 (CH), 141.2 (CH). HRMS (ESI): calcd for $C_{12}H_{17}IO_2$ $(M+Na)^+$: 343.0171; found: 343.0168.



3,4-dihydro-2H-1-benzopyran (10)

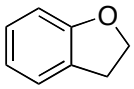


To a 0.2 M solution of 3-(2-iodophenyl)propyl tert-butyl peroxide **6a** (0.344 mg, 2.0 mmol) in THF at -78 °C was dropwise added PhLi (2.2 mmol, 1.4 mL of a nominally 1.6 M solution in Hex). The reaction was allowed to warm to rt and after 1.5 h, was quenched with sat. aq. NH_4Cl. The ether extract was filtered through a plug of silica, diluted with methanol to a standard volume and analyzed for yield by comparison with a standard curve derived using five standardized solutions of reference samples of dihydrobenzopran, prepared as described below. Following analysis, the solution was concentrated under reduced pressure. Spectra of the residue matched those of the dihydrobenzofuran prepared as described below. R_f: 0.3 (2.5 % EA/Hex).

Preparation of GC standard: Bromophenyl 3-bromopropyl ether was prepared using a variant of a reported procedure.[9] To a 0.5 M solution of 2-bromophenol (3.46 g, 20 mmol) in DMF was added K_2CO_3 (5.5 g, 40 mmol) followed by 1,3-dibromopropane (10 mL, 100 mmol). The reaction was stirred for 24 h and then quenched with sat. aq. NH_4Cl. The ether extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (5% EA/Hex) to yield 4.24 g (72%) of 2-bromophenyl 3-bromopropyl ether as a colorless oil. R_f: 0.45 (5% EA/Hex). The ^1H NMR spectra matched the literature report.[9]

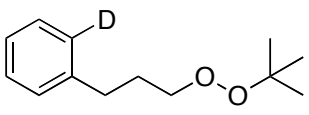
To a 0.2 M solution of 2-bromophenyl 3-bromopropyl ether (588 mg, 2.0 mmol) in THF at -78 °C was dropwise added nBuLi (2.2 mmol, 1.4 mL of a nominally 1.6 M solution in Hex). The reaction was allowed to warm to rt and after 1.5 h, was quenched with sat. aq. NH_4Cl. The ether extract was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (2.5% EA/Hex) to yield **10** (211 mg, 79%) as a colorless oil. R_f: 0.3 (2.5 % EA/Hex) Spectra matched those previously reported.[10] The product was used to construct a GC/MS response curve in the same manner as described below for 2,3-dihydrobenzofuran.

2,3-Dihydrobenzofuran (11)



To a -78 °C 0.2M solution of 2-(2-iodophenyl) ethyl *tert*-butylperoxide **9** (0.320 g, 1.0 mmol) in THF was added 1.1 equivalent of nBuLi (nominally 1.6 M in hexane) dropwise under nitrogen. After 5 min, the cooling bath was removed and the reaction was allowed to stir for an additional hour. The reaction was then quenched with a small amount of sat. ammonium chloride. The ether extract was diluted with methanol to a fixed volume and the GC/MS response compared against a standard curve constructed by analysis of commercial **11** (99% grade) to indicate a 90% yield. Alternatively, the ether extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography (2.5% EA/Hex) to afford 58% isolated yield of **11**. Rf: 0.3 (2.5 % EA/Hex. The spectra matched those of commercial samples of **11**.

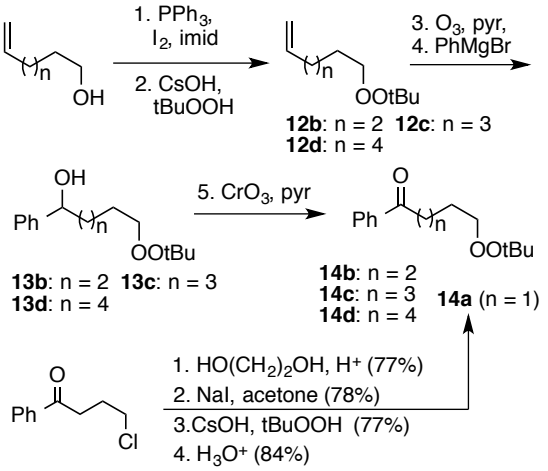
3-(2-Deuterophenyl)propyl tert-butyl peroxide



To a -78 °C solution of peroxide **6a** (66.5 mg, 0.2 mmol) in THF (0.2 M) was dropwise added a nominally 1.6 M solution of nBuLi in hexanes (0.14 mL, 0.22 mmol). The resulting mixture was stirred at -78 °C for five minutes and then quenched with excess CD_3OD (1 mL). The mixture was concentrated under reduced pressure and the residue purified by flash

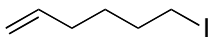
chromatography (5% EA/Hex) to yield 27.5 mg (66%) of a *t*-butyl phenylpropyl peroxide showing **>90**% deuterium incorporation at the ortho position based upon the reduction in the integral for the aromatic region in the ^{1}H NMR. R_f: 0.25 (5% EA/Hex). ^{1}H NMR (400 MHz): δ 1.29 (s, 9H), 1.97 (tdd, 2H, J= 6.5, 9.4, 6.4), 2.73 (AB dd, 2H), 4.00 (t, 2H, J= 6.5), 7.18-7.35 (m, 4H). ^{13}C NMR (100 MHz) : δ 26.4 (CH3), 29.6 (CH2), 32.4 (CH2), 74.2 (CH2), 80.1 (C), 125.8 (C), 128.2 (CH), 128.36 (CH), 128.42 (CH), 141.7 (C). HRMS (ESI): calcd for $C_{13}H_{19}DO_2$ $(M+Na)^+$: 232.1424; found: 232.1420.

General Synthetic Scheme for *n*-peroxyalkylphenones

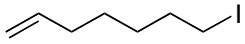


Syntheses of iodoalkenes employed a reported procedure.[11] A flame dried round bottom flask with magnetic stir bar was charged with 1 mmol of the alcohol and THF (substrate concentration 0.2M). The flask was placed in a 0 °C bath and protected from light (foil). The following reagents were added sequentially: imidazole (1.5 mmol), PPh_3 (1.0 mmol) and iodine (1.5 mmol). After the reaction was judged complete (2 h, TLC), it was quenched with sat. aq. $Na_2S_2O_3$. The organic layer was separated and the aqueous layer was washed with ether/EA (3x). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

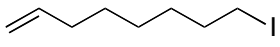
6-Iodohex-1-ene [18922-04-6] was prepared (3.30 g, 93%) from 5-hexen-1-ol by the general procedure described above. Spectral details matched those previously reported.[12]



7-Iodohept-1-ene [107175-49-5] was prepared (3.30 g, 95%) from 7-hepten-1-ol by the general procedure described above. Spectral details matched those previously reported.[13]



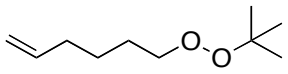
8-iodooct-1-ene [38380-55-1] was prepared (5.00 g, 94%) from 7-octen-1-ol by the procedure described above. Spectral details matched those previously reported. [14]



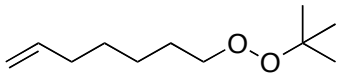
Syntheses of peroxides **12b-d** were performed according to an established procedure.[3]

A flame dried round bottom flask with magnetic stir bar was charged with 1.39 mmol of CsOH, which was dissolved in dry DMF (0.2M). The solution was cooled to 0 °C and the iodoalkene (1.0 mmol) was added, followed by dropwise addition of tert-butyl hydroperoxide (1.4 equiv, nominally 5.5M solution in hex). The reaction was allowed to proceed for 3 hours and then diluted with water. The organic layer was separated and the aqueous layer was washed with EA (3 x). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (EA/hex).

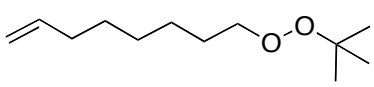
6-(*tert*-butylperoxy)hex-1-ene (12b) [107671-69-2] was prepared (5.90 g, 70%) from 6-iodohex-1-ene by the procedure described above. Spectral details matched those previously reported.[15]



7-(*tert*-butylperoxy)hept-1-ene (12c) [107671-70-5] was prepared (6.9 g, 79%) from 6-iodohept-1-ene by the procedure described above. Spectral details matched those previously reported.[15]

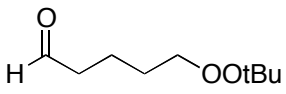


8-(tert-butylperoxy)oct-1-ene (12d) was prepared (5.40 g, 92%) from 8-iodooct-1-ene by the general procedure described above: ^{1}H NMR (300 MHz): δ 5.82 (ddd, 1H, J=6.7, 16.8), 4.97 (m, 2H), 3.95 (t, 2H, J= 6.7) 2.06 (q, 2H, J=6.2), 1.59 (m, 2H), 1.37 (m, 6H), 1.24 (s, 9H) 13C NMR (300 MHz): δ 139.05 (C, H), 114.2 (C, H_2), 80.0 (C), 75.0 (C, H_2), 33.6 (C, H_2), 28.9 (C, H_2), 28.7 (C, H_2), 26.3 (C, H_2), 21.9 (C, H_3). (HRMS) ESI: calcd for $C_{12}H_{24}O_3$ $(M+Na)^+$: 223.1776; found: 223.1672. IR: 2976.1, 2933.9, (m), 1684.0(s). R_f: 0.35 (15% EA/Hex.

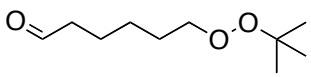


Peroxyalkanals **13b-d** were prepared according to an established procedure.[16]
A flame dried round bottom flask with a magnetic stir bar was charged with a 0.2 M solution of alkene (1 mmol) n CH_2Cl_2. The solution was cooled to – 78 °C whereupon pyridine (3 mmol) was added. A gas solution of 2% O_3/O_2 (approximately 1 mmol/minute) was introduced for 1 minute. The reaction was warmed to room temperature and diluted with sat. aq $NaHCO_3$. The organic layer was separated and the aqueous layer was washed with dichloromethane (3x). The combined organic layer were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

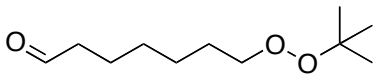
5-(*tert*-Butylperoxy)pentanal was prepared (5.90 g, 79%) from 6-(*tert*-butylperoxy)hex-1-ene by the procedure described above. ^{1}H NMR (400 MHz): δ 9.78 (t, 1H, J=1.5), 3.97 (t, 2H, J= 6.3), 2.49 (ddd, 2H, J= 1.9, 7.3, 14.5), 1.70 (m, 4H), 1.25 (s, 9H). ^{13}C NMR (500 MHz): δ 202.3 (CH), 80.1 (C), 74.4 (CH2), 43.6 (CH_2), 27.4 (CH_2), 26.3 (CH_3), 18.94 (CH_2). HRMS (ESI, NaOAc): calcd for $C_9H_{18}O_3$ $(M+Na)^+$: 199.1310; found: 199.1256. IR: 2939 (n), 1716 (s). R_f: 0.93 (20% EA/Hex).



6-(*tert*-Butylperoxy)hexanal was prepared (3.90 g, 85%) from 7-(*tert*-butylperoxy)hept-1-ene by the procedure described above. ^{1}H NMR (400 MHz): δ 9.78 (s, 1H) 3.95 (t, 2H, J= 7.1), 2.48 (t, 2H, J= 6.5), 2.16 (s, 3H), 1.64 (m, 5H), 1.25 (s, 9H). ^{13}C NMR (400 MHz): δ 208.7 (C), 80.3 (C), 74.6 (CH2), 43.4 (CH_2), 29.9 (CH_2), 27.3 (CH_2), 26.3 (CH_3), 20.5 (CH_2). HREIMS calcd for $C_{10}H_{20}O_3$ $(M+Na)^+$: 211.1412, found: 211.1310. IR: 2977.5 (n), 1715.6 (s). R_f: 0.20 (15 % EA/Hex).

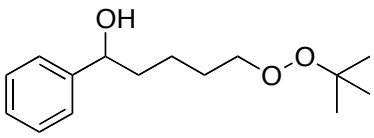


7-(tert-Butylperoxy)heptanal was prepared (5.0 g, 93%) from 8-(tert-butylperoxy)oct-1-ene by the general procedure described above: ^{1}H NMR (300 MHz): δ 9.75 (s, 1H), 3.92 (t, 2H, J=6.4), 2.42 (t, 2H, J= 8.0), 1.61 (m, 4H), 1.37 (m, 4H), 1.22 (s, 9H). 13C NMR (300 MHz): δ 202.7 (C, H), 80.1 (C), 74.8 (C, H_2), 43.7 (C, H_2), 28.6 (C, H_2), 27.6 (C, H_2), 26.3 (C, H_2), 25.9 (C, H_2), 21.9 (C, H_2). HRESI-MS calcd for $C_{11}H_{22}O_3$ $(M+Na)^+$: 225.1467; found: 225.1569. IR: 2976.1, 2933.9, (m), 1725.0(s). R_f: 0.49 (20% EA/Hex).

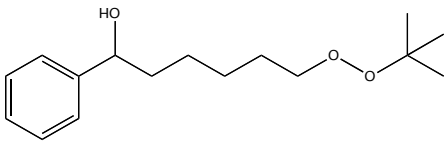


Syntheses of 1-phenyl-n-peroxyalkanols **13b-d** employed a reported procedure.[17]
A flame dried round bottom flask with magnetic stir bar was charged with 1 mmol of peroxyaldehyde, which was dissolved in THF (0.2M solution). The solution was cooled to -78 °C, whereupon 1.1 mmol of PhMgBr (nominally 1M in THF) was added dropwise. After an hour, the reaction was quenched by dropwise addition of water. The organic layer was separated and the aqueous layer was washed with ether (3x). The resulting solution was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

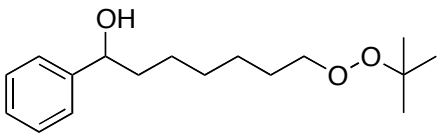
5-(*tert*-Butylperoxy)-1-phenylpentan-1-ol (13b) was prepared (3.60 g, 45%) from PhMgBr and 5-(tert-butylperoxy)pentanal by the procedure described above. ^{1}H NMR (400 MHz): δ 7.30 (M, 5H), 4.70 (dt, 1H, J=6.1, 7.5), 3.94 (t, 2H, J= 6.6) 1.80 (m, 3H), 1.65 (ddd, 2H, J= 6.6, 7.7, 15.6), 1.49 (m, 3H), 1.24 (s, 9H). ^{13}C NMR (400 MHz): δ 144.7 (C), 128.5 (CH), 127.6 (CH), 125.9 (CH), 80.1 (C), 74.8 (CH_2), 74.5 (CH_2), 38.9 (CH_2), 27.7 (CH_2), 26.3 (CH_3), 22.5 (CH_2). HRMS (ESI): calcd for $C_{15}H_{24}O_3$ $(M+Na)^+$: 275.1725; found: 275.1623. IR: 3401.2 (b), 2867.8 (m). R_f 0.43 (20% EA/Hex).



6-(tert-Butylperoxy)1-phenylhexan-1-ol (13c) was prepared (5.90 g, 85%) from 6-(*tert*-butylperoxy)hexanal by the procedure described above: ^{1}H NMR (300 MHz): δ 7.33 (m, 5H), 4.69 (m, 1H), 3.92 (t, 2H, J=6.3), 3.53 (t, 1H, J=6.5), 1.78 (m, 4H), 1.40 (m, 4H), 1.24 (s, 9H). ^{13}C NMR (500 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.9 (C, H_2), 74.6 (C, H), 38.9 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_2), 25.7 (C, H_2). (HRMS) ESI: calcd for $C_{16}H_{26}O_3$ $(M+Na)^+$; 289.1882, found: 289.1791. IR: 3401.3 (b), 2933.4 (m). R_f: 0.25 (15% EA/Hex).

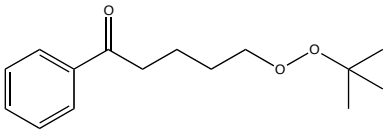


7-(tert-Butylperoxy)1-phenylhexan-1-ol (13d) was prepared (2.70 g, 89%) from 7-(tert-butylperoxy)heptanal by the procedure described above. ^{1}H NMR (300 MHz): δ 7.31 (m, 5H), 4.68 (m, 1H), 3.92 (t, 2H, J=6.3), 1.77 (m, 4H), 1.38 (m, 6H), 1.24 (s, 9H). 13C NMR (500 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.9 (C, H_2), 74.6 (C, H), 38.9 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_2), 25.7 (C, H_2). (HRMS) ESI: calcd for $C_{16}H_{26}O_3$ $(M+Na)^+$: 303.1584; found: 303.1580. IR: 3401.2 (b), 2976.9, (m). R_f: 0.25 (15% EA/Hex).

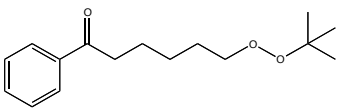


Syntheses of peroxyketones **14b-d** employed a reported procedure.[18] A flame dried round bottom flask with magnetic stir bar was charged with a solution of 6 mmol of pyridine in dichloromethane (0.2M) . To the stirring solution was added 3 mmol of CrO_3, resulting in a strongly colored (deep burgundy) solution. After the solution had stirred for 15 minutes, a CH_2Cl solution of 0.5 mmol of the alcohol (**13 a-d**) was added. A tarry, black deposit separated immediately. The solution was stirred for an additional 15 min and then decanted from the residue, which was washed with 200 ml of ether. The combined solutions were washed sequentially with 10 mL portions of 5% aq. NaOH (3x), 5% aq. HCl, 5% aq. $NaHCO_3$, and sat. aq. NaCl. The resulting solution was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography.

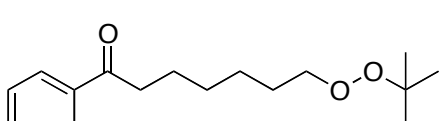
5-(tert-butylperoxy)-1-phenylpentan-1-one (14b) was prepared (2.90 g, 92%) from 5-(*tert*-butylperoxy)-1-phenylpentan-1-ol (**13b**) by the procedure described above. ^{1}H NMR (400 MHz): H_2). δ 8.00 (d, 2H, J=7.9), 7.58 (t, 1H, J= 7.4), 7.48 (t, 2H, J=7.9) 4.01 (t, 2H, J=6.6), 3.04 (t, 2H, J=7.1), 1.80 (p, 2H, J= 7.8), 1.74 (p, 2H, 7.8), 1.26 (s, 9H). ^{13}C NMR (400 MHz): δ 202.3 (C), 137.0 (C, H), 132.9 (C, H), 128.6 (C, H), 128.0 (C, H), 80.1 (C), 75.0 (C, H_2), 38.4 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.0 (C, H_3), 24.2 (C, H_2). (HRMS) ESI: calcd for $C_{15}H_{22}O_3$ ($M+Na^+$): 273.1569; found: 273.1457. IR: 2928.4 (m), 1686.5 (s). Rf: 0.23 (15% EA/Hex). R_f: 0.50 (20% EA/Hex).



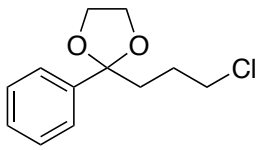
6-(tert-butylperoxy)1-phenylhexan-1-one (14c) was prepared (2.25 g, 90%) from 6-(tert-butylperoxy)1-phenylhexan-1-ol (**13c**) by the procedure described above. ^{1}H NMR (300 MHz): δ 7.96 (d, 2H, J=7.8), 7.58 (t, 1H, J= 7.3), 7.48 (t, 2H, J=7.5) 3.97 (t, 2H, J=6.8), 3.00 (t, 2H, J=7.5), 1.74 (m, 4H), 1.49 (m, 2H), 1.26 (s, 9H). ^{13}C NMR (500 MHz): δ 202.3 (C), 137.0 (C, H), 132.9 (C, H), 128.6 (C, H), 128.0 (C, H), 80.1 (C), 75.0 (C, H_2), 38.4 (C, H_2), 27.8 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_3), 26.0 (C, H_2), 24.2 (C, H_2). (HRMS) ESI: calcd for $C_{16}H_{24}O_3$ ($M+Na^+$): 287.1725; found 287.1633. IR: 2976.1, 2933.9, (m), 1684.0(s). R_f: 0.50 (20% EA/Hex).



7-(*tert*-butylperoxy)-1-phenylheptan-1-one (14d) was prepared (2.25 g, 91%) from 7-(tert-butylperoxy)1-phenylhexan-1-ol by the procedure described above. ^{1}H NMR (300 MHz): δ 7.33 (m, 5H), 4.69 (m, 1H), 3.92 (t, 2H, J=6.3), 3.53 (t, 1H, J=6.5), 1.78 (m, 4H), 1.40 (m, 4H), 1.24 (s, 9H). ^{13}C NMR (400 MHz): δ 144.8 (C), 128.4 (C, H), 127.5 (C, H), 125.8 (C, H), 80.1 (C), 74.6 (C, H_2), 39.0 (C, H_2), 29.3 (C, H_2), 27.7 (C, H_2), 26.3 (C, H_2), 26.1 (C, H_3), 26.0 (C, H_2). (HRMS) ESI: calcd for $C_{16}H_{26}O_3$ $(M+Na)^+$: 301.1791; found: 301.1882. IR: 2953.1, 2930.9, (m), 1684.0(s). R_f: 0.25 (15% EA/Hex).

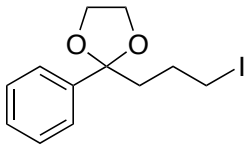


2-(3-Chloropropyl)-2-phenyl-1,3-dioxolane was prepared using a modification of a reported procedure.[19] A flame dried round bottom flask with magnetic stir bar and fitted with a Dean-Stark apparatus was charged with commercially available 4-chloro-1-phenylbutan-1-one (0.578 g, 3.0 mmol), ethylene glycol (0.558 g, 3.0 mmol), and p-toluenesulfonic acid monohydrate



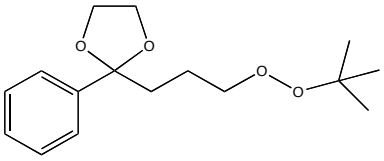
(0.044 g, 0.5 mmol) and toluene (30 mL). The solution was refluxed overnight with azeotropic removal of water and the organic layer was then washed with 5% $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo to give 77% (7.7 g) of 2-(3-chloropropyl)-2-phenyl-1,3-dioxolane [3308-98-3]. Spectral details matched those previously reported.[20]

2-(3-Iodopropyl)-2-phenyl-1,3-dioxolane



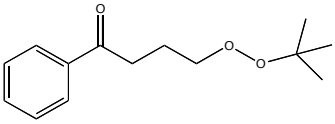
A flame dried round bottom flask with magnetic stir bar was charged with a solution of 2-(3-chloropropyl)-2-phenyl-1,3-dioxolane (5.0 g, 22 mmol), sodium iodide 15.0 g, mmol) and acetone (20 mL). The mixture was stirred and heated under reflux for 30 min, resulting in precipitation of solid sodium tosylate. The reaction was cooled and diluted with water. The lower layer was separated, and the (upper) aqueous layer was extracted with hexane. The combined organic layers were washed sequentially with water and brine and then dried ($MgSO_4$). The residue obtained upon concentration under reduced pressure was purified by column chromatography to give 5.5 g (78%) of the iodopropyl dioxolane [70969-99-2]. Spectral details matched those previously reported.[21]

2-(3-(*tert*-Butylperoxy)propyl)-2-phenyl-1,3-dioxolane was prepared from the iododoxolane (1.5g, 77%) by a similar procedure as described for peroxide **1**.



^{1}H NMR (400 MHz): δ 7.74 (m, 2H), 7.33 (m, 3H), 4.03 (ddd, 2H, J=9.9, 14.5, 17.6), 3.93 (t, 2H, J=6.8), 3.79 (ddd, 2H, J= 10.8, 14.5,18.2), 1.98(m, 2H), 1.69 (m, 2H). ^{13}C NMR (400 MHz): δ 142.5 (C), (C, H), 128.1 (C, H), 125.8 (C, H), 125.7 (C, H), 110.2 (C), 80.1 (C), 74.9 (C, H_2), 64.6 (C, H_2), 37.1 (C, H_2), 26.3 (C), 22.3 (C, H_2). HRMS (ESI): calcd for $C_{16}H_{24}O_3$ $(M+Na)^+$: 303.1573; found: 303.1675. IR: 2976 (m).

4-(*tert*-Butylperoxy)-1-phenylbutan-1-one (**14a**)



A flame dried round bottom flask with magnetic stir bar was charged with 1.00 mmol (0.280 g) of 2-(3-(*tert*-butylperoxy)propyl)-2-phenyl-1,3-dioxolane in THF (0.2 M). 5% aq. HCl (1.5 mL) was then added and the reaction was allowed to proceed overnight. The organic layer was separated and the aqueous layer was washed with EA (3x). The resulting solution was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give 0.200 g (84%) of the ketone. ^{1}H NMR (400 MHz): δ 8.00 (dt, 2H, J= 2.0, 8.6), 7.45 (tt, 1H, J= 1.3, 2.8), 7.48 (tt, 2H, J=2.0, 3.3), 3.93 (t, 2H, J=6.0), 3.12 (t, 2H, J= 7.1), 2.08 (p, 2H, J = 6-7), 1.26 (s, 9H). ^{13}C NMR (400 MHz): δ 199.7 (C), 136.9 (CH), 132.9 (CH), 128.6 (CH), 128.0 (CH), 80.2 (C), 74.0 (CH_2), 35.13 (CH_2), 26.4 (CH_3), 26.1 (CH_2), 22.65 (CH_2). HRMS (ESI): calcd for $C_{14}H_{20}O_3$ $(M+Na)^+$: 259.1412; found: 259.1310. IR: 2976 (m), 2931 (m), 1686 (s). R_f: 0.23 (15% EA/Hex).

Standard Procedure for cyclizations of peroxyketones.

A round bottom flask with a magnetic stir bar was flame-dried, then topped with a septum and placed under vacuum until the flask cooled. The flask was filled with nitrogen and charged with

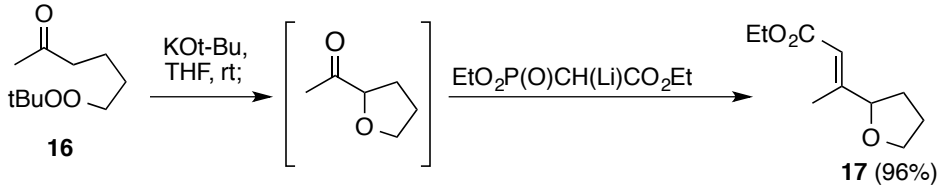
1-1.5 mmol of potassium tert-butoxide. The flask was again evacuated and then flushed with nitrogen. THF was added to dissolve the base (final concentration, 0.2 M) whereupon a 0.2M THF solution of the peroxyketone (**14a-d**, 1.00 mmol) was added dropwise to the stirring solution, resulting in a clear reddish-brown solution. Upon disappearance of starting material (TLC), the reaction was quenched by dropwise addition of excess water. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give the cyclic ethers **15a-c**.

Oxetan-2-yl(phenyl)methanone (15a) was prepared (2.25 g, 70%) from 4-(*tert*-butylperoxy)-1-phenylbutan-1-one **14a** by the procedure described above. ^{1}H NMR (400 MHz): δ 7.93 (d, 2H, J=8.7), 7.55 (t, 1H, J= 7.3), 7.49 (t, 2H, J=7.8) 5.94 (dd, 1H, J=7.1, 8.6), 4.84 (q, 1H, J= 7.5), 4.67 (dt, 1H, J=6.4, 15.2), 3.03 (m, 2H). ^{13}C NMR (500 MHz): δ 199. 8 (C), 133.7 (C, H_2), 128.8 (C, H), 128.5 (C, H2), 82.3 (CH), 69.5 (CH_2), 25.8 (CH_2). HRMS (HREI): calcd for $C_{10}H_{10}O_2$ $(M+Na)^+$: 185.0681; found: 185.0580. IR: 2976 (m), 1683 (s). R_f: 0.23 (15% EA/Hex).

Phenyl(tetrahydrofuran-2-yl)methanone (15b, [141957-79-1]) was prepared (0.168 g, 99% yield) from 5-(*tert*-butylperoxy)-1-phenylpentanone-1-one **14b** using the procedure described above. R_f: 0.25 (15% EA/Hex). Spectral details matched those previously reported.[22]

Phenyl(tetrahydro-2*H*-pyran-2-yl)methanone (15c) **[**73504-72-0] was prepared (0.138 g, 80% yield) from peroxyhexanone **14c** using the procedure described above. R_f: 0.27 (15% EA/Hex). Spectral details matched those previously reported.[23]

Cyclization of 6-t-butylperoxy-hexan-2-one:



16 **17** (96%)

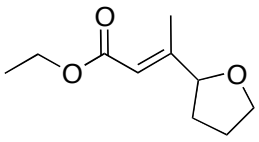
6-iodohex-1-yne was prepared (10.0 g, 92%) from commercially available 5-hexynyl iodide by a route similar to that described for **8**. Spectral details matched those previously reported. [24]

6-(*tert*-butylperoxy)hex-1-yne [184941-42-2] was prepared (2.61 g, 78%) from 6-iodohex-1-yne by a procedure similar to that described for **1**. Spectral details matched those previously reported. [25]

6-(*tert*-butylperoxy)hexan-2-one (16) was prepared from peroxyalkyne by an adapation of a reported procedure.[26] A flame dried round bottom flask with magnetic stir bar was charged with the peroxyalkyne (6.0 mmol (0.340 mg) of

the peroxyalkyne, 1 mL H_2O, and 10mL MeOH. AuCl (0.027g) was added. Following disappearance of starting material (TLC), the majority of solvent was removed under reduced pressure and the remaining suspension was diluted with ether and washed with a 1:1 mixture of brine/aq. NH_4Cl. The separated aqueous layer was washed with ether (3x) and the combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to afford the peroxyketone (1.03 g, 93%). ^{1}H NMR (300 MHz): δ 3.96 (t, 2H, J=6.3), 2.27 (t, 2H, J= 6.3), 1.7 (s, 3H, J), **1.65** (m, 4H), 1.24 (s, 9H). ^{13}C NMR (400 MHz): δ 208.7 (C), 80.0 (C), 74.6 (C, H_2), 43.4 (C, H_2), 29.8 (C, H_2), 27.3 (C, H_2), 26.0 (C, H_2), 20.2 (C, H_2). (HRMS) ESI: calcd for $C_{16}H_{24}O_3$ $(M+Na)^+$: 287.1725; found 287.1633. IR: 2976, 2933, (m), 1684 (s). R_f: 0.50 (20% EA/Hex).

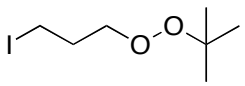
(*E*)-Ethyl 3-(tetrahydrofuran-2-yl)but-2-enoate (17)



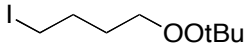
A round bottom flask with a magnetic stir bar was flame-dried and then cooled under vacuum. The flask was flushed with N_2 and then charged with (0.045 g, mmol) of potassium tert-butoxide. The flask was again evacuated and then backfilled with nitrogen. Sufficient THF was added to bring the base to 0.2M and the mixture was stirred until the base dissolved. A solution of 0.5 mmol of compound 6-(*tert*-butylperoxy)hexan-2-one in THF (3 mL) was then added dropwise to the stirring solution. Following disappearance of starting material, reaction was monitored via TLC, upon disappearance of starting material 1.00 mmol of triethyl phosphonoacetate (.244g, 1mmol) was added to the reaction. After two hours, brine was added. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic layers were dried over Na_2SO_4 and the residue obtained upon concentration purified by chromatography to afford 0.080 g (96%) of the enoate (two steps). R_f: 0.18 (20% EA/Hex) ^{1}H NMR (400 MHz): δ 3.71 (ddd, 1H, J=4.4, 3.0, 11.7), 3.34 (ddd, 1H, J= 3.3, 11.2, 2.8), 2.71 (ddd, 1H, J= 5.5, 12.2, 5.7) 2.22 (ddd, 1H, J=1.2, 4.1, 12.0), 2.01 (m, 4H), 1.61 (m, 7H), 1.24 (ddd, 1H, J= 4.6, 1.6, 16.4). ^{13}C NMR (500 MHz): δ 215.3 (C), 80.3 (C), 64.7 (CH2), 41.6 (CH_2), 39.1 (CH_2), 30.8 (CH_2), 29.1 (CH_2), 25.67 (CH_2), 20.4 (CH_2) and 19.7 (CH_2). HRMS (HREI): calcd for $C_{10}H_{16}O_3$ (M+ Na): 207.1099; found: 207.0997. IR: 2939 (n), 1716 (s).

Synthesis of 1,*n*- iodoperoxides employed a modification of a reported procdure.[3] A flame dried round bottom flask with a magnetic stir bar was charged with 0.2M solution of $CsOH•H_2O$ (1.2 mmol) in DMF, followed by the 1,*n*-diiodide (1.00 mmol) and then *tert*-butyl peroxide (1.2mmol), added dropwise. Upon disappearance of starting material (TLC, ~ 3 h), the reaction was quenched with an equal volume of water. The separated aqueous layer was washed with hexane and dried over $MgSO_4$. The residue obtained after concentration was purified by filtration through silica gel (hexane).

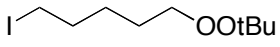
1-(*tert*-butylperoxy)-3-iodopropane (18a) [101860-37-1] was prepared (0.540 g, 70% yield) from t-butyl hydroperoxide and 1,3-diodopropane using the procedure described above. Spectral details matched those previously reported. [27]



1-(*tert*-butylperoxy)-4-iodobutane (18b) was prepared (0.240 g, 72% yield) from 1,4-diiodobutane using the procedure described above. ^{1}H NMR (400 MHz): δ

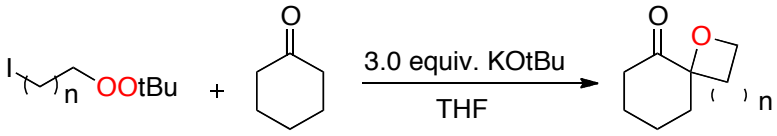


3.98 (t, 2H, J=6.34), 3.23 (t, 3H, J= 6.87), 1.95 (p, 2H, J= 7.05), 1.72 (m, 2H), 126 (s, 9H). ^{13}C NMR (300 MHz): δ 80.2 (C), 73.6 (CH_2), 30.3 (CH2), 28.9 (CH_2), 26.3 (CH_3), 6.5 (CH_2). HRMS (HREI): calcd for $C_8H_{17}O_2I$: 272.0300; found: 272.0273. IR: 2939 (m). R_f: 0.19 (10% EA/Hex).

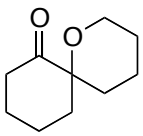


1-(*tert*-butylperoxy)-5-iodopentane (18c) was prepared (0.789 g, 64% yield) from 1,5-diiodopentane by the procedure described above. ^{1}H NMR (400 MHz): δ 3.95 (t, 2H, J=6.14), 3.21 (t, 3H, J= 6.55), 1.87 (p, 2H, J= 7.25), 1.72 (m, 2H), 1.66 (m, 2H), 1.64 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (300 MHz): δ 80.0 (C), 74.8 (CH_2), 33.3 (CH2), 27.7 (CH_2), 26.3 (CH_3), 22.9 (CH_2), 6.5 (CH_2). HRMS (HREI): calcd for $C_9H_{19}O_2$ (M^+): 286.0400; found: 286. IR: 286.0430 (m). Rf: 0.20 (15% EA/Hex).

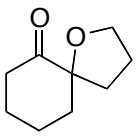
General Procedure for annelation of spirocyclic ethers onto cyclohexanone. Illustrated for **1-oxaspiro[5.5]undecan-7-one (19b)**



Potassium tert-butoxide (3.00 mmol, 0.336 g) was weighed into a flame dried round bottom flask with a magnetic stir bar. A septum was placed into the round bottom flask, and the atmosphere was removed and replaced with N_2 (3 x). The base was dissolved into THF (15 mL). A solution of cyclohexanone (3.00 mL, 0.294 g) in THF (15 mL, 0.2M) was added dropwise and the reaction stirred for 15 minutes, whereupon a solution of 1-(*tert*-butylperoxy)-4-iodobutane (**18b**, 1 mmol, 0.272 g) in THF (5 mL, 0.2 M) was added dropwise, resulting in development of slight pacity and yellow-orange coloration. After disappearance of starting material (TLC), the reaction was quenched via drop wise addition of water. The organic phase was separated and the aqueous phase was washed 3x with ether/EA. The combined organic phases were dried with Na_2SO_4 and the solvent was removed *in vacuo*. The residue was purified on silica (5% EA/hex) to furnish 0.430 g (87%) of the oxaspiroundecanone **19b**. ^{1}H NMR (400 MHz): δ 3.71 (ddd, 1H, J=4.4, 3.0, 11.7), 3.34 (ddd, 1H, J= 3.3, 11.2, 2.8), 2.71 (ddd, 1H, J= 5.5, 12.2, 5.7) 2.22 (ddd, 1H, J=1.2, 4.1, 12.0), 2.01 (m, 4H), 1.61 (m, 7H), 1.24 (ddd, 1H, J= 4.6, 1.6, 16.4). ^{13}C NMR (500 MHz): δ 215.3 (C), 80.3 (C), 64.7 (CH2), 41.6 (CH_2), 39.1 (CH_2), 30.8 (CH_2), 29.1 (CH_2), 25.67 (CH_2), 20.4 (CH_2) and 19.7 (CH_2). HRMS (HREI): calcd for $C_{10}H_{16}O_2$ (M^+): 168.112; found: 168.115. IR: 2939 (n), 1716 (s). R_f: 0.23 (15% EA/Hex).



1-oxaspiro[4.5]decan-6-one [19a, 129529-81-3] was prepared (0.134 g, 86% yield) from the reaction of cyclohexanone with *t*-butyl 3-iodopropyl peroxide **18a** using the procedure described above. Spectral details matched those previously reported.[28]



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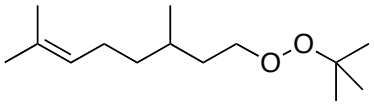
Oxacycle Synthesis via Intramolecular Reaction of Carbanions and Peroxides

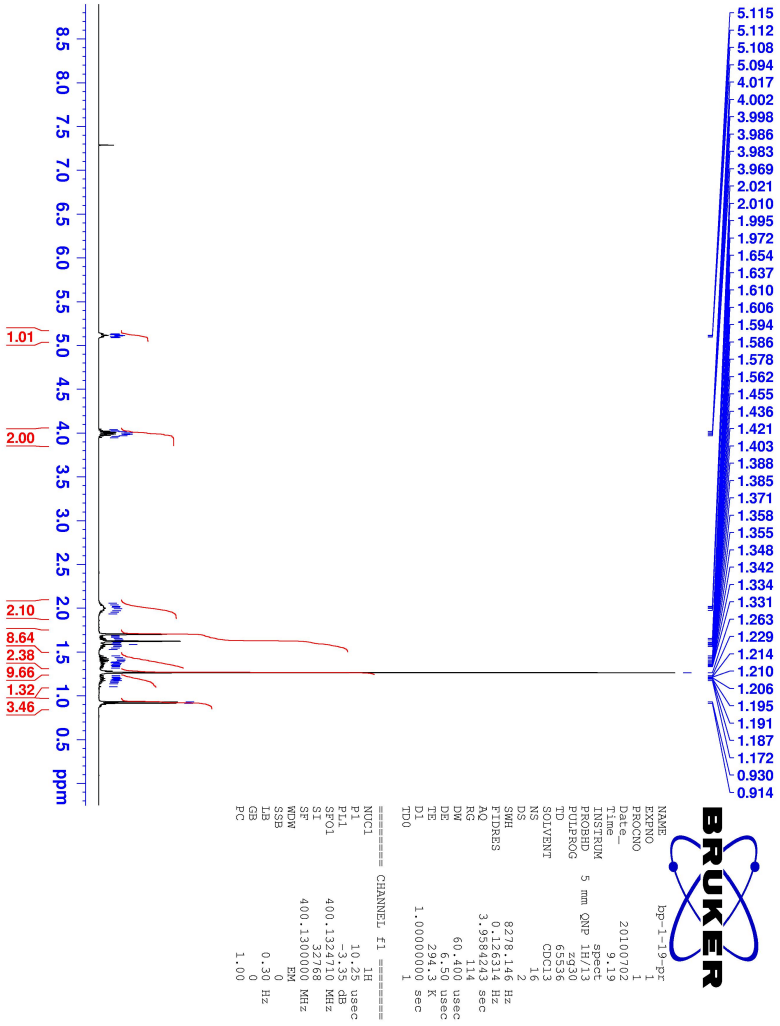
Rachel Willand-Charnley, Benjamin Puffer, and Patrick H. Dussault

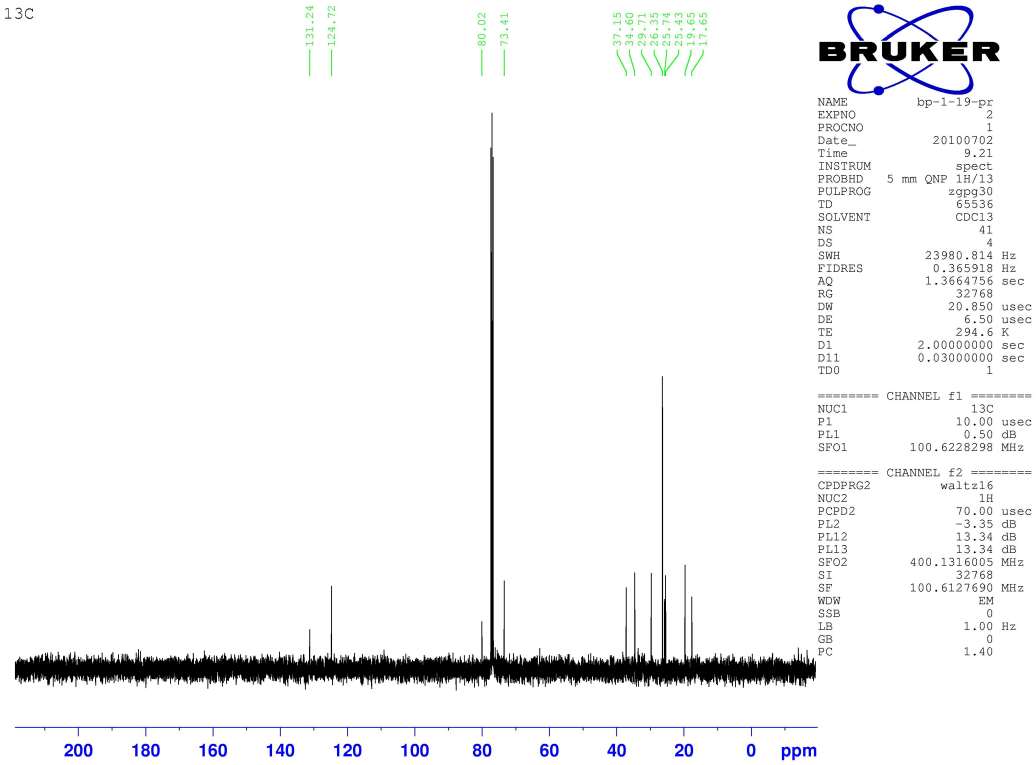
SUPPORTING INFORMATION Section 2 (Spectral Data)

^{1}H NMR and ^{13}C NMR spectra of selected products:

tert Butyl 3,7-dimethyloct-6-en-1-yl peroxide (1)





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TD                       65536
SOLVENT                  CDCl3
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DS                           4
SWH                 23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                       32768
DW                     20.850 usec
DE                      6.50 usec
TE                     294.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.00 usec
PL1                       0.50 dB
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    70.00 usec
PL2                      -3.35 dB
PL12                     13.34 dB
PL13                     13.34 dB
SFO2              400.1316005 MHz
SI                       32768
SF                100.6127690 MHz
WDW                         EM
SSB                          0
LB                       1.00 Hz
GB                           0
PC                        1.40
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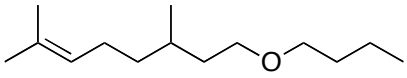
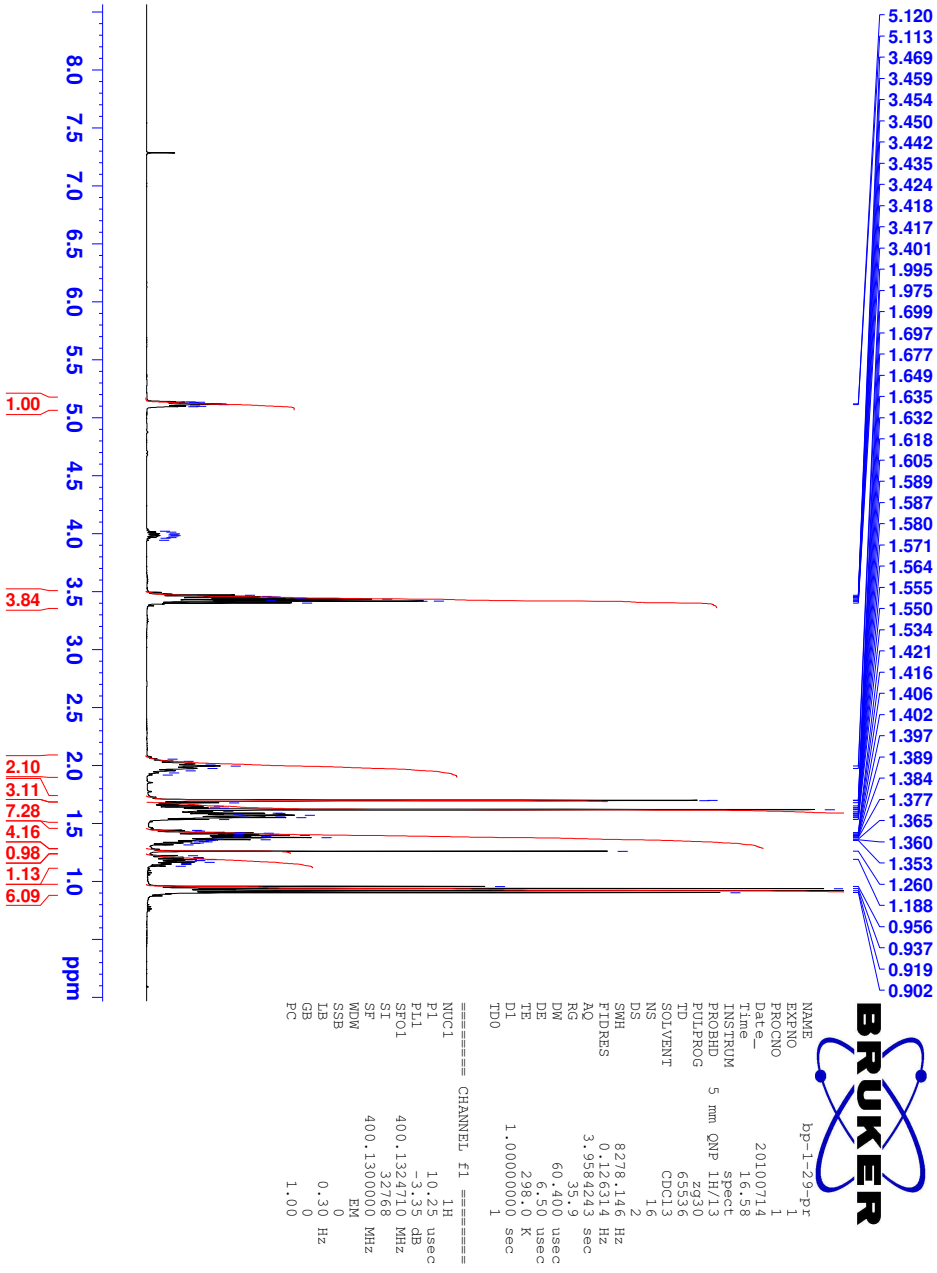
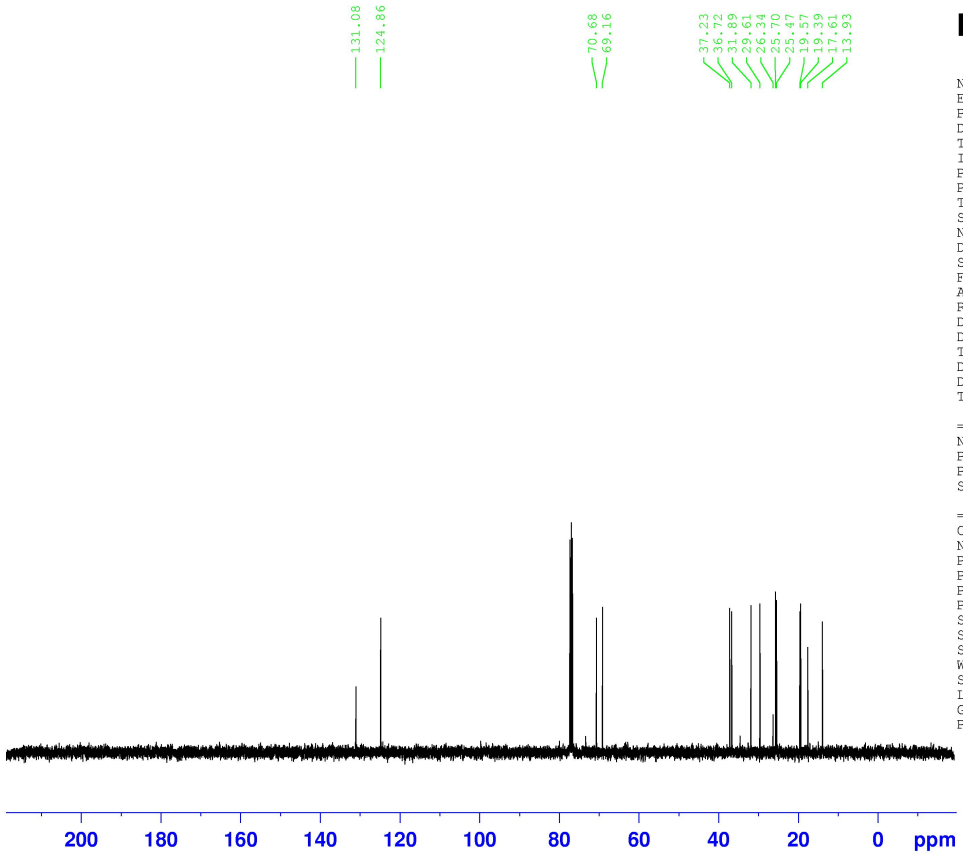
Butyl 3,7- dimethyloct-6-en-1-yl-ether (2)





13C



BRUKER

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FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	812.7
DW	20.850 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
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NUC1	13C
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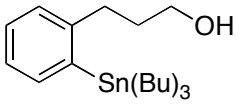
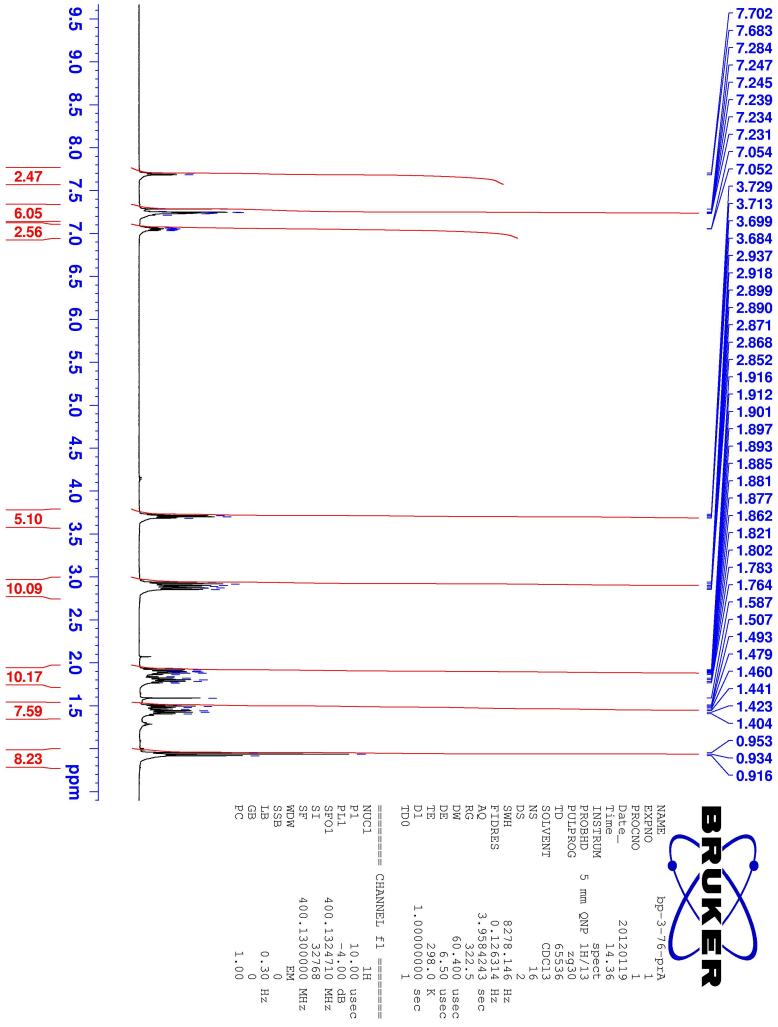
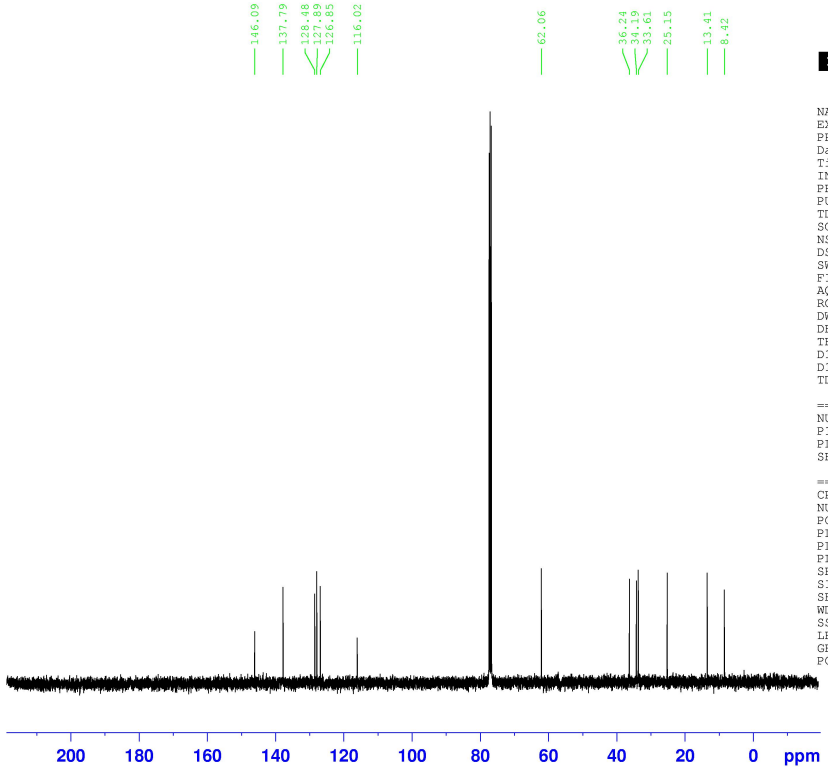
PL1	0.50 dB
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	-3.35 dB
PL12	13.34 dB
PL13	13.34 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

3-(2-(tributylstannyl)phenyl)propan-1-ol (4c)







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RG	5160.6
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NUC1	13C
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======== CHANNEL f2 ========	
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NUC2	1H
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PL12	12.90 dB
PL13	12.90 dB
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
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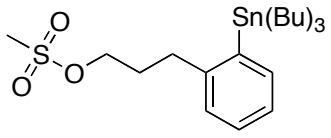
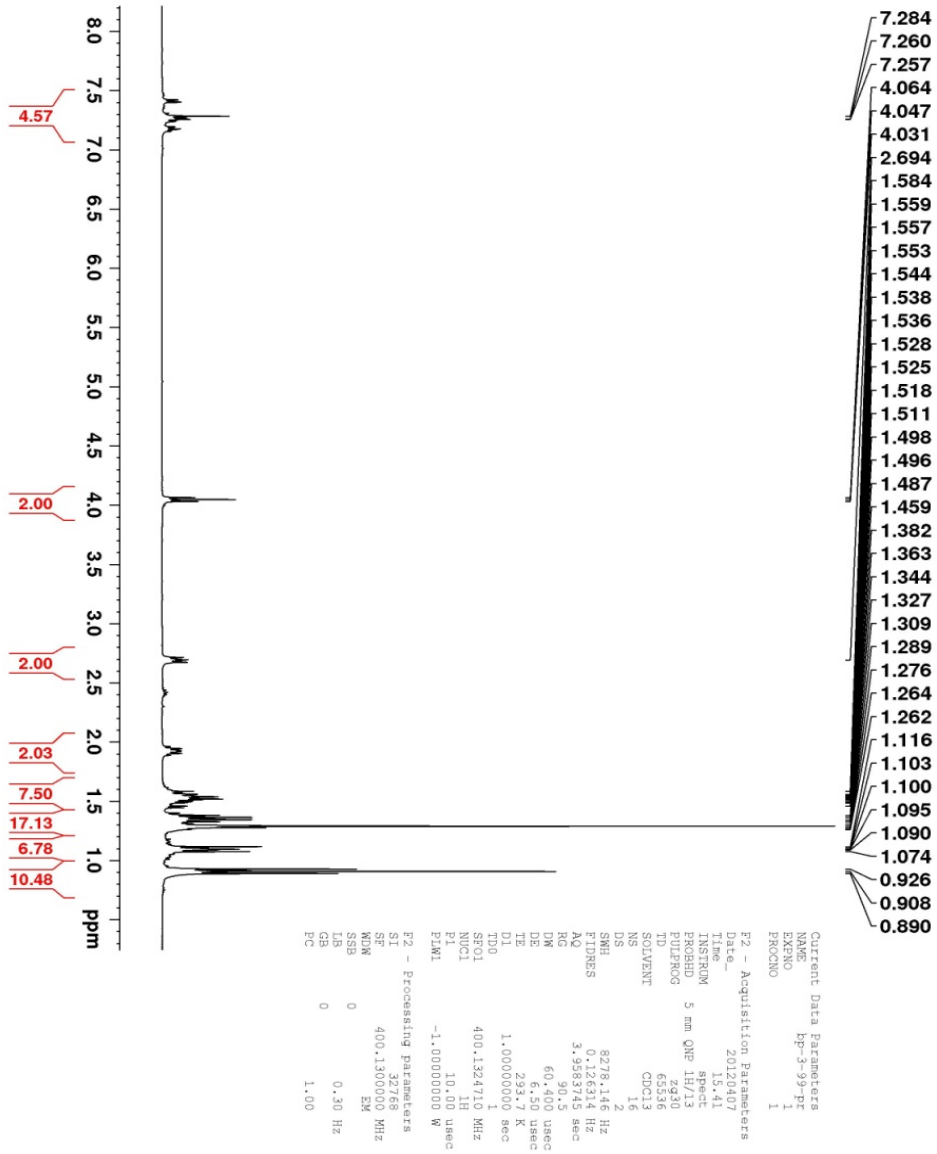
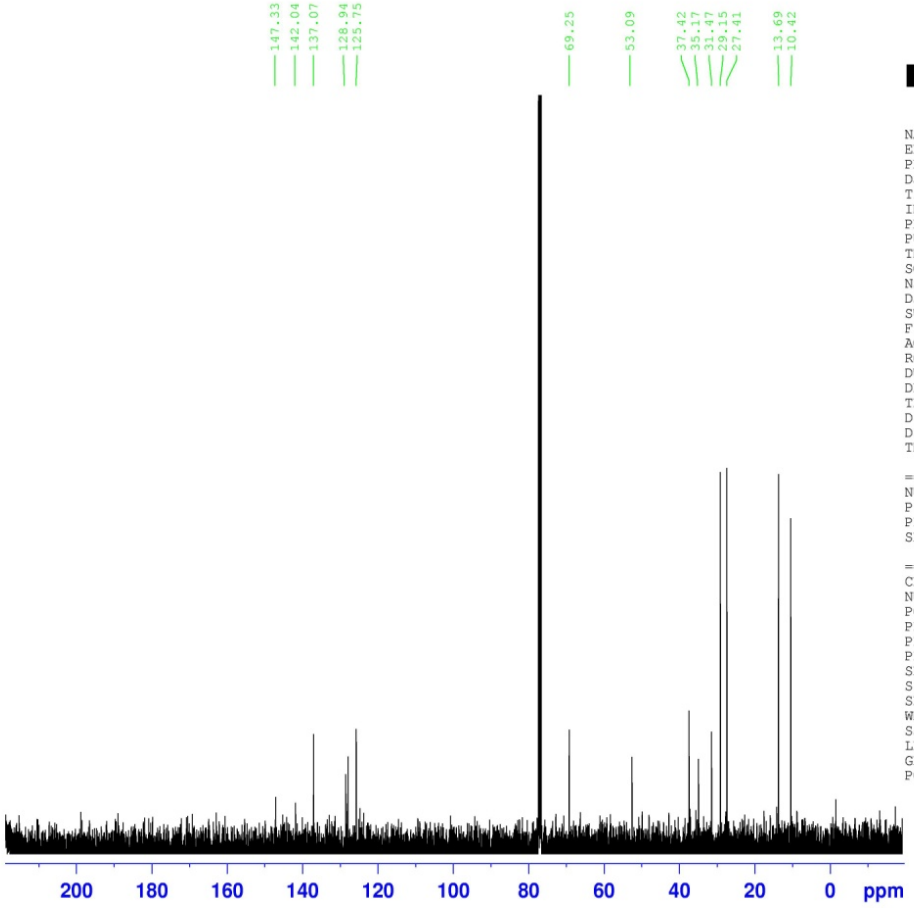
GB	0
PC	1.00

3-(2-(tributylstannyl)phenyl)propyl methansulfonate (5c)







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FIDRES             0.365918 Hz
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DE                    6.50 usec
TE                   293.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
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P1                     10.00 usec
PL1                     0.50 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
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NUC2                     1H
PCPD2                  70.00 usec
PL2                    -4.00 dB
PL12                   12.90 dB
PL13                   12.90 dB
SFO2           400.1316005 MHz
SI                     32768
SF             100.6127690 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
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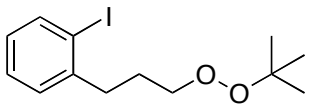

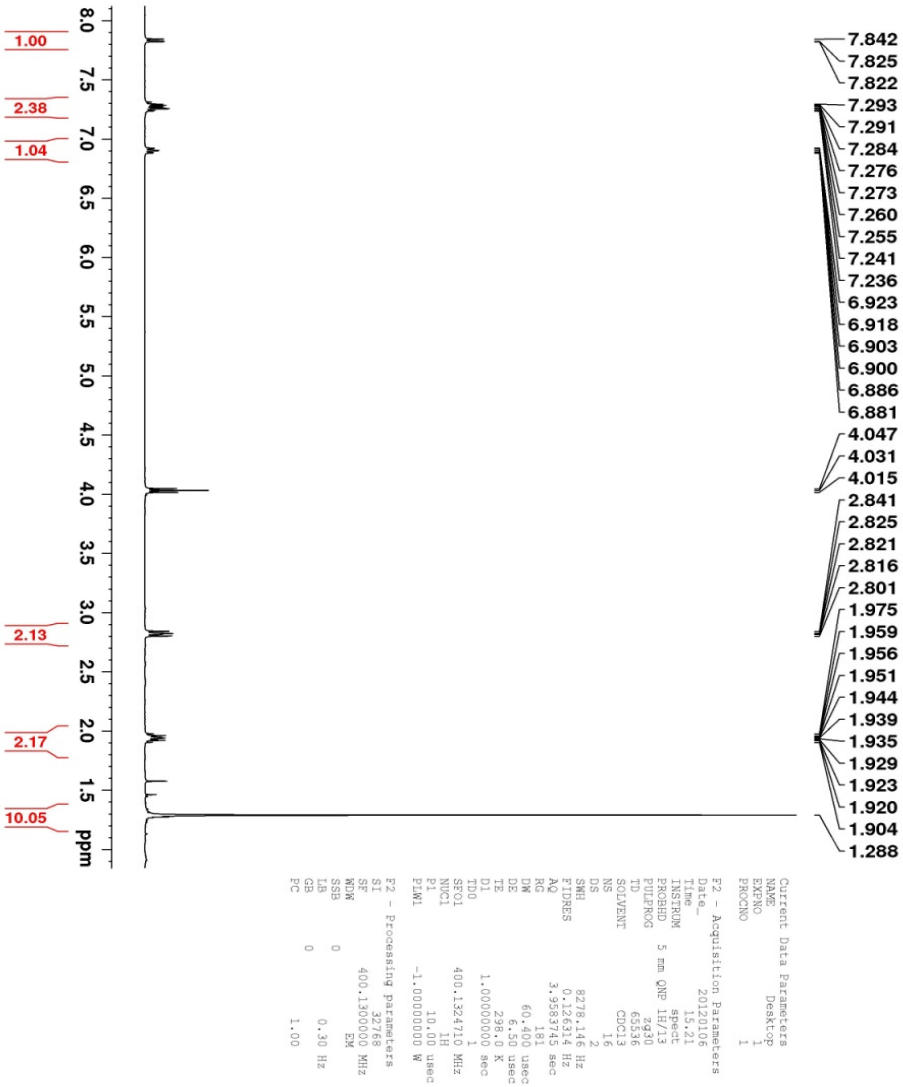

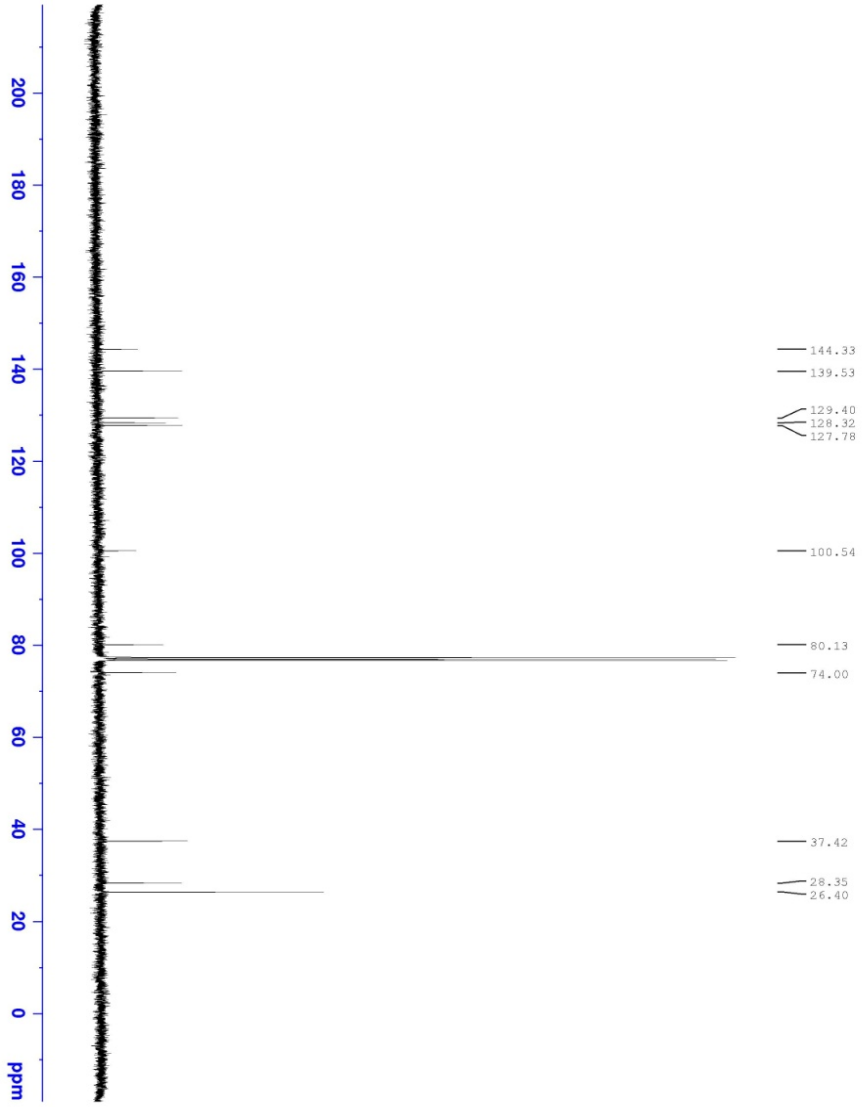
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129.40
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80.13
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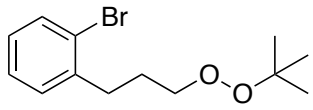
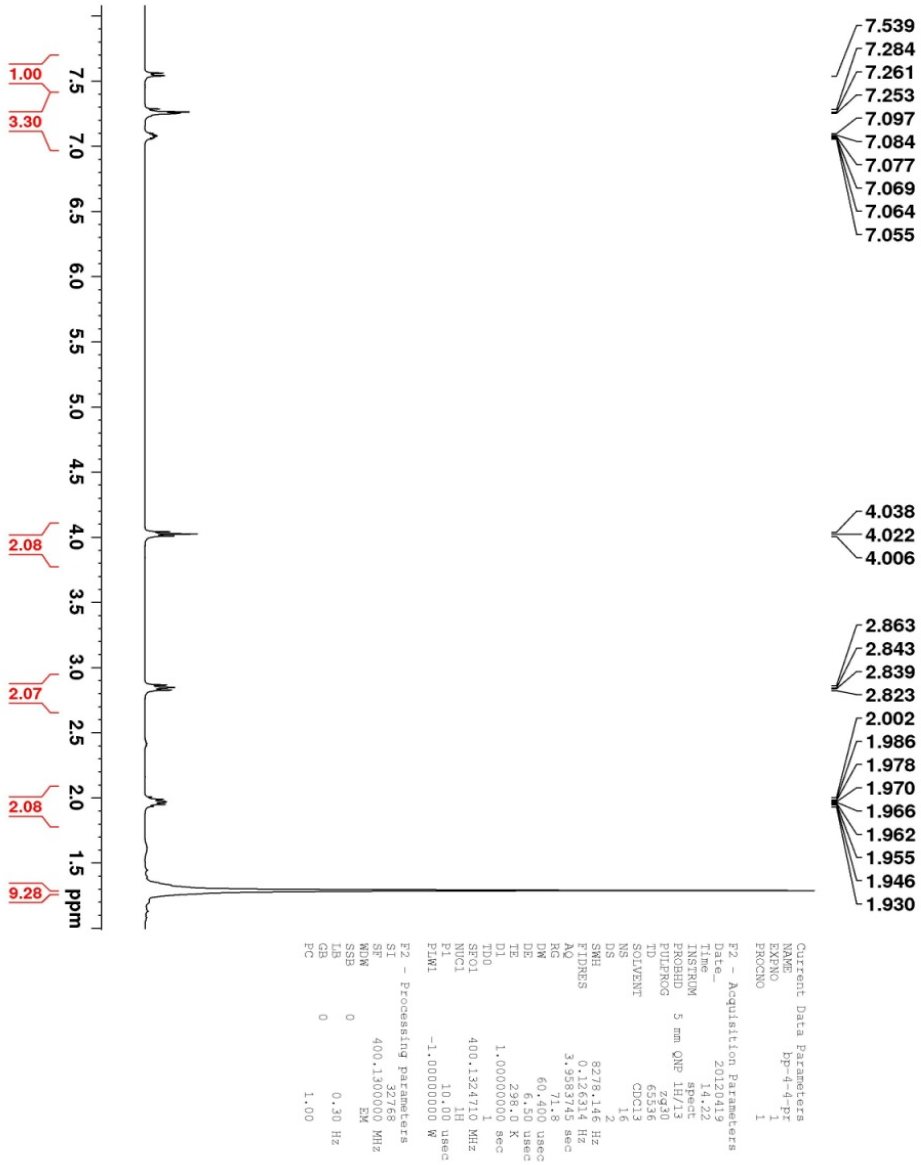
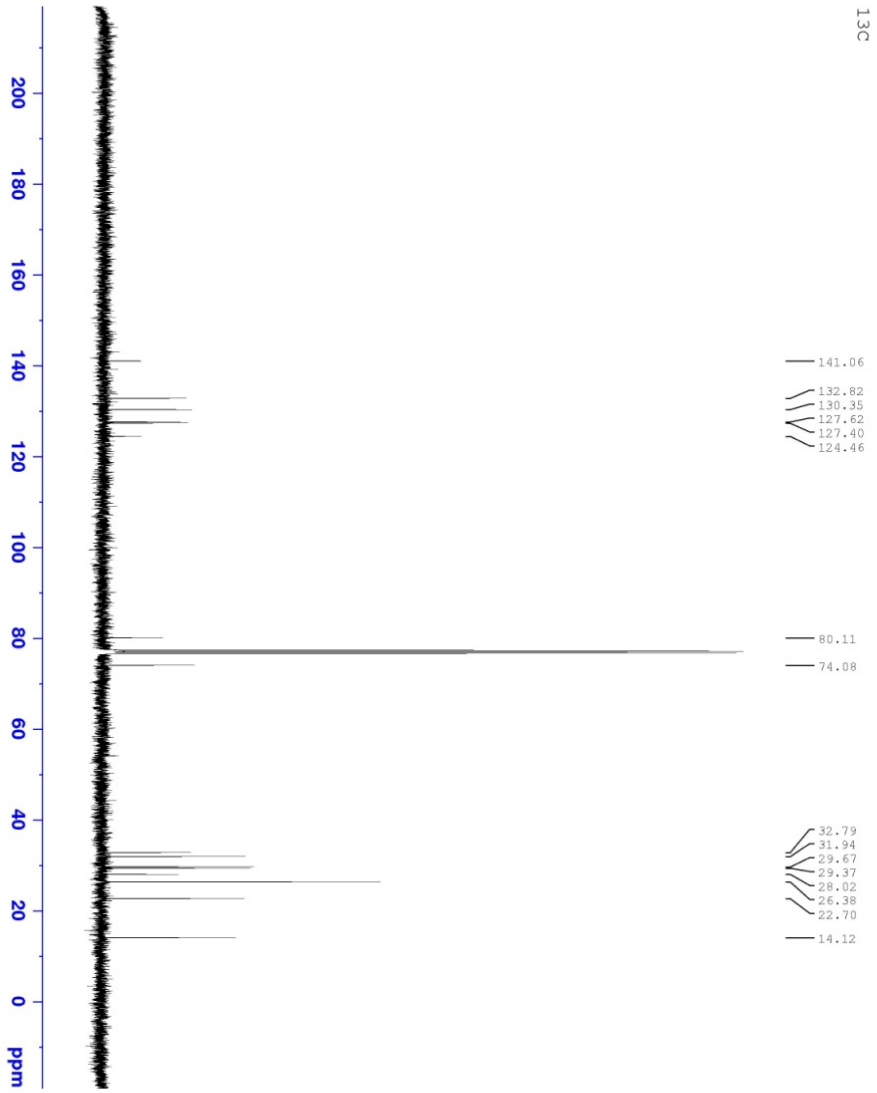
37.42
28.35
26.40

3-(2-Bromophenyl)propyl tert-butyl peroxide (6b)



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180
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100
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60
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20
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74.08
32.79
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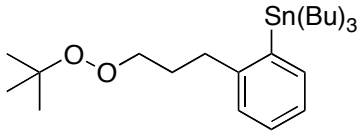
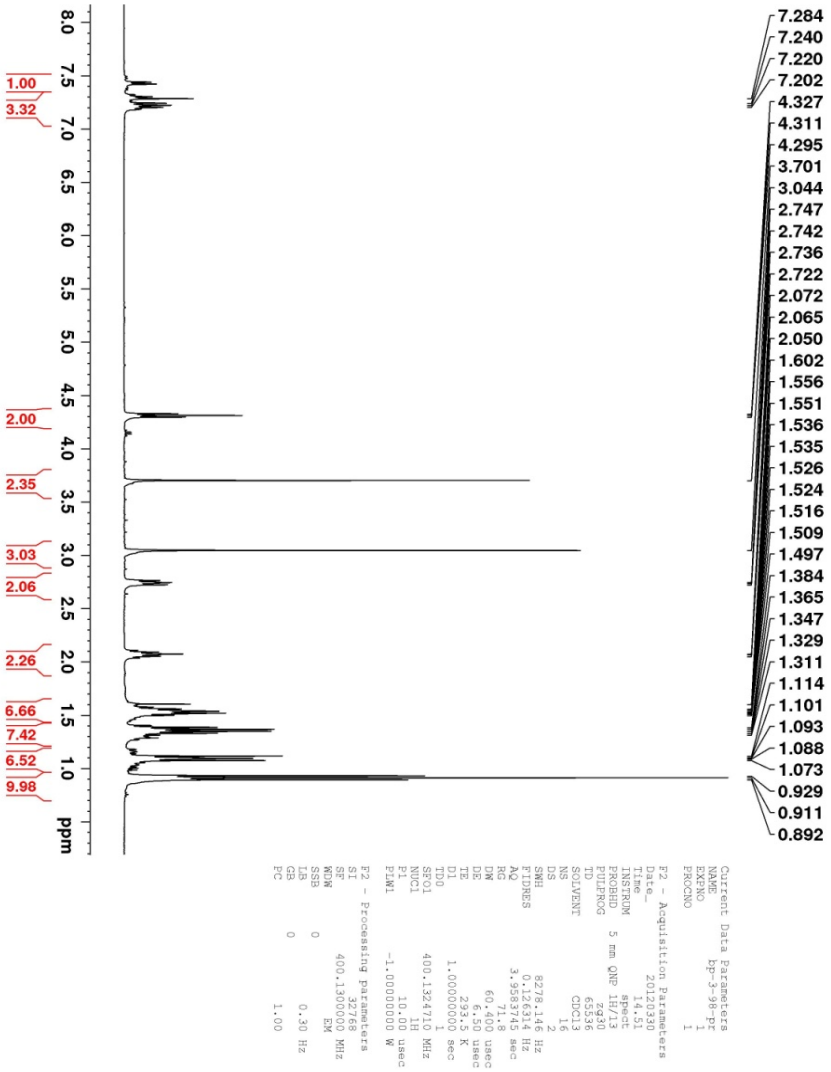
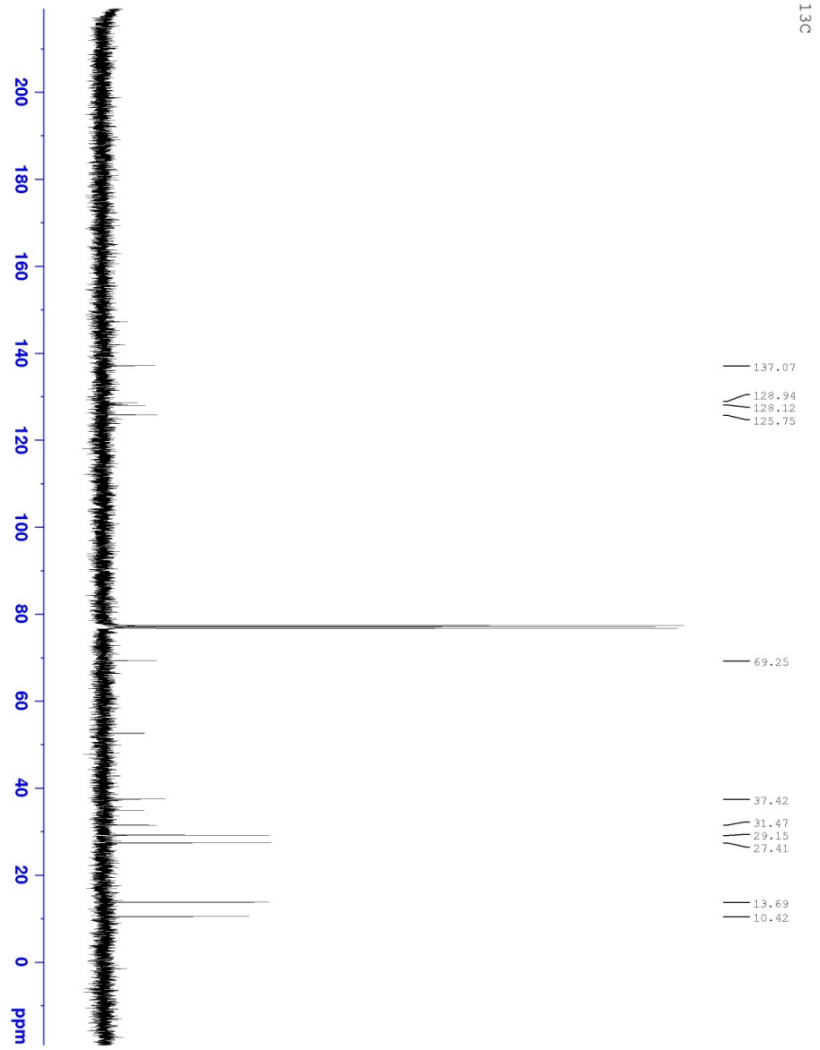
14.12

3-(2-(tributylstannyl)phenyl)propyl tert-butyl peroxide (6c)






13C
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128.94
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125.75
69.25
37.42
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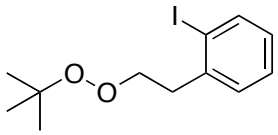
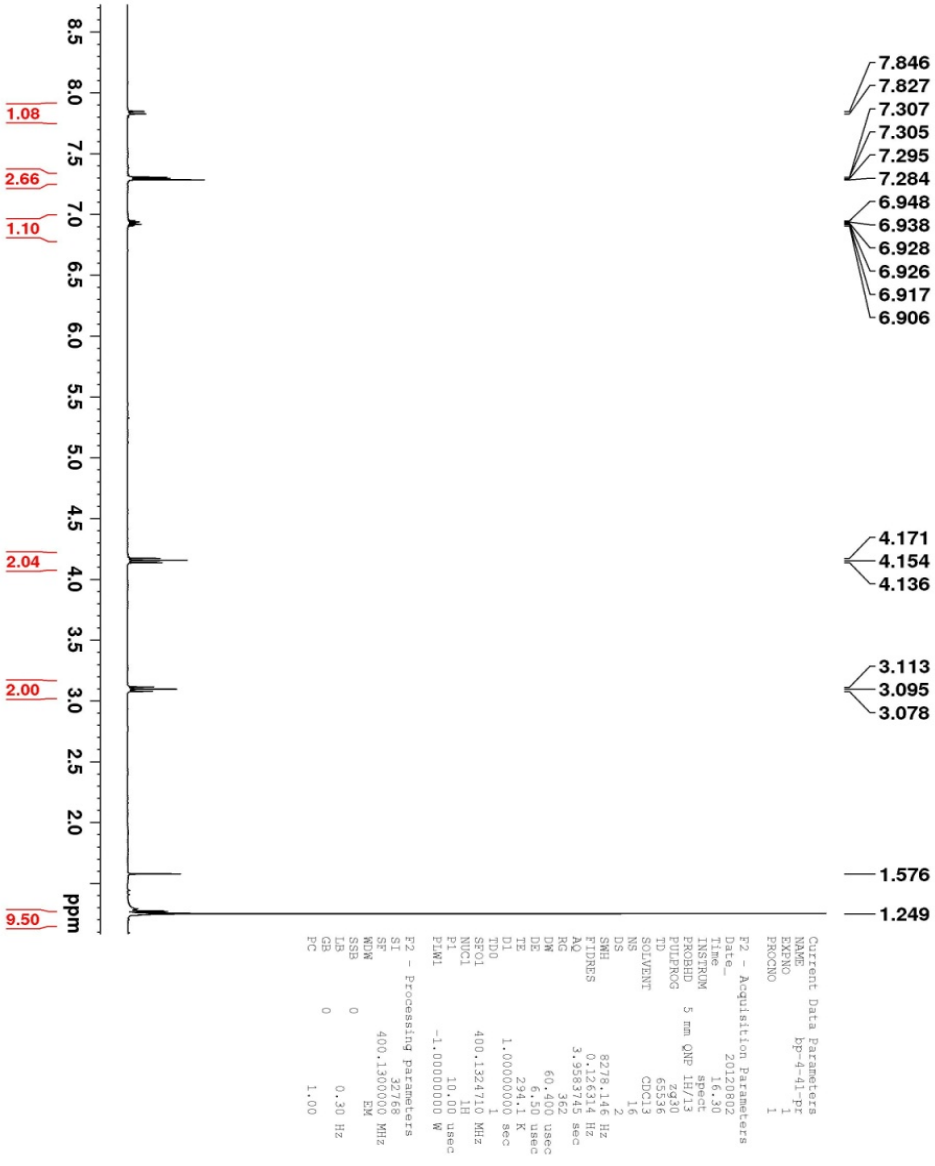
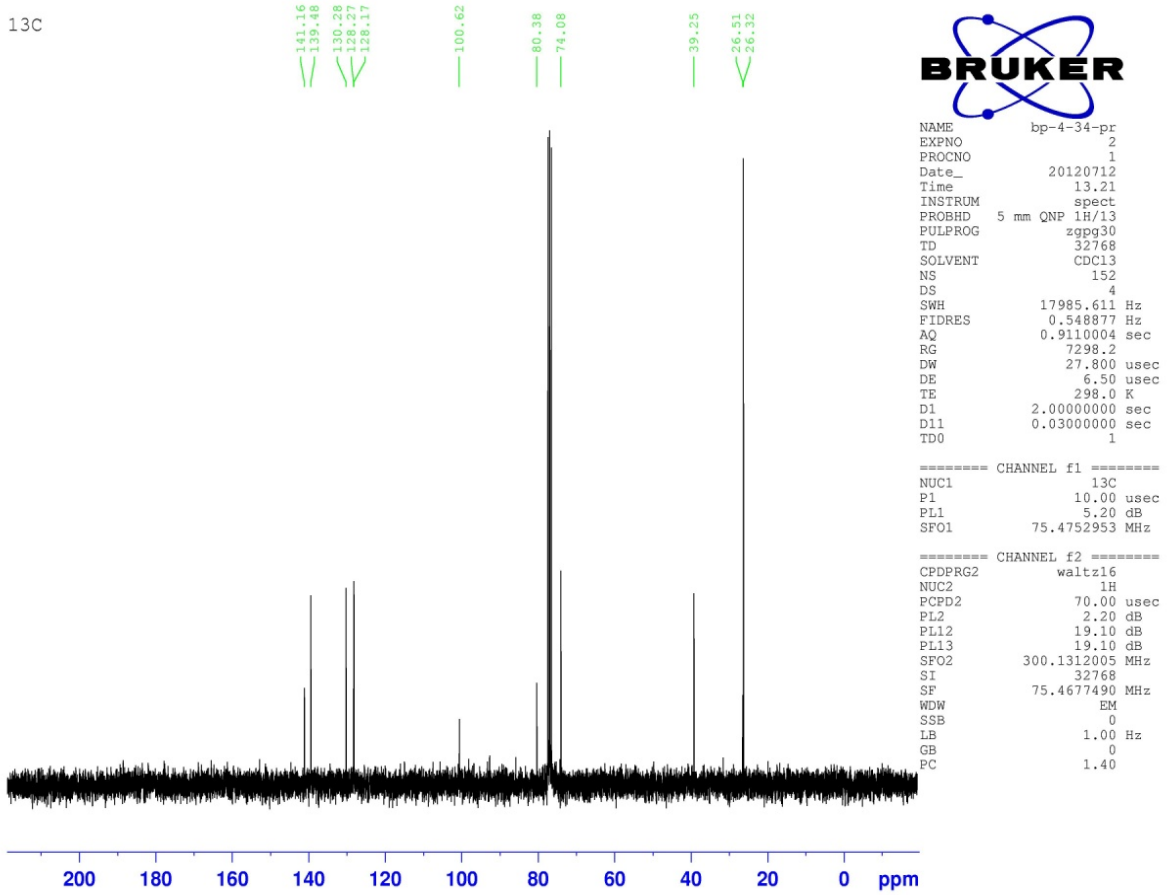
29.15
27.41
13.69
10.42
200
180
160
140
120
100
80
60
40
20
0
ppm

2-(2-Iodophenyl) ethyl tert-butyl peroxide (9)



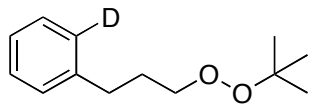


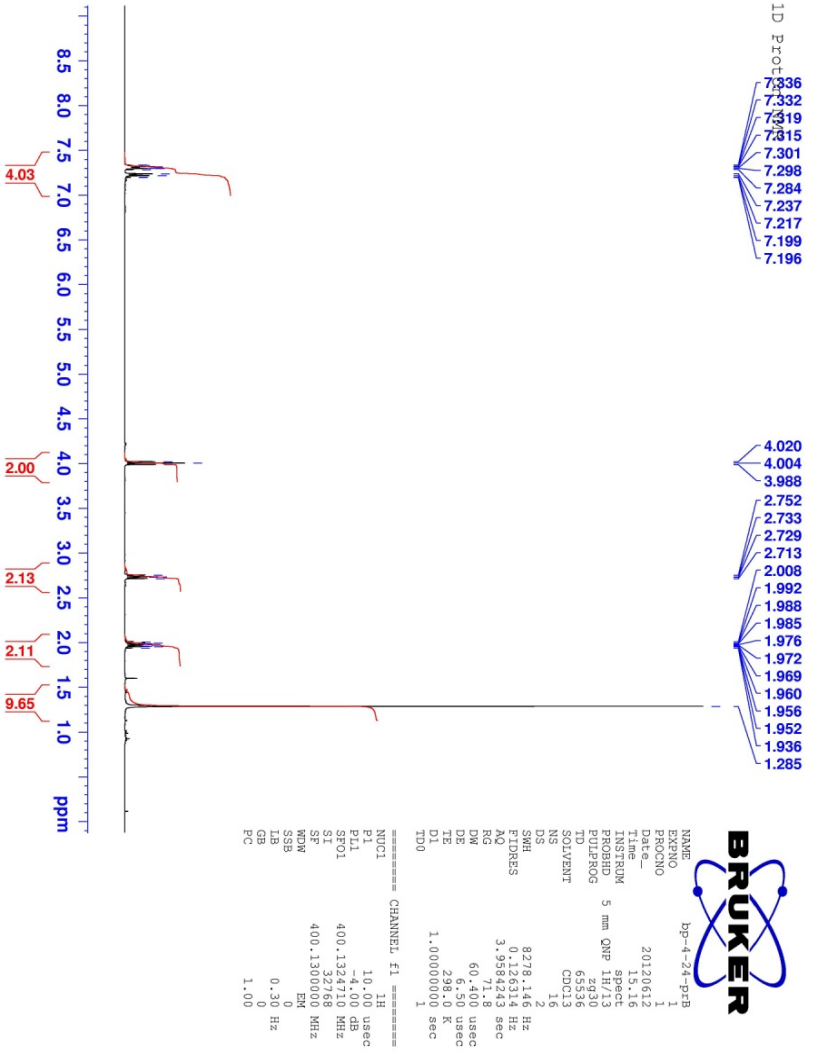


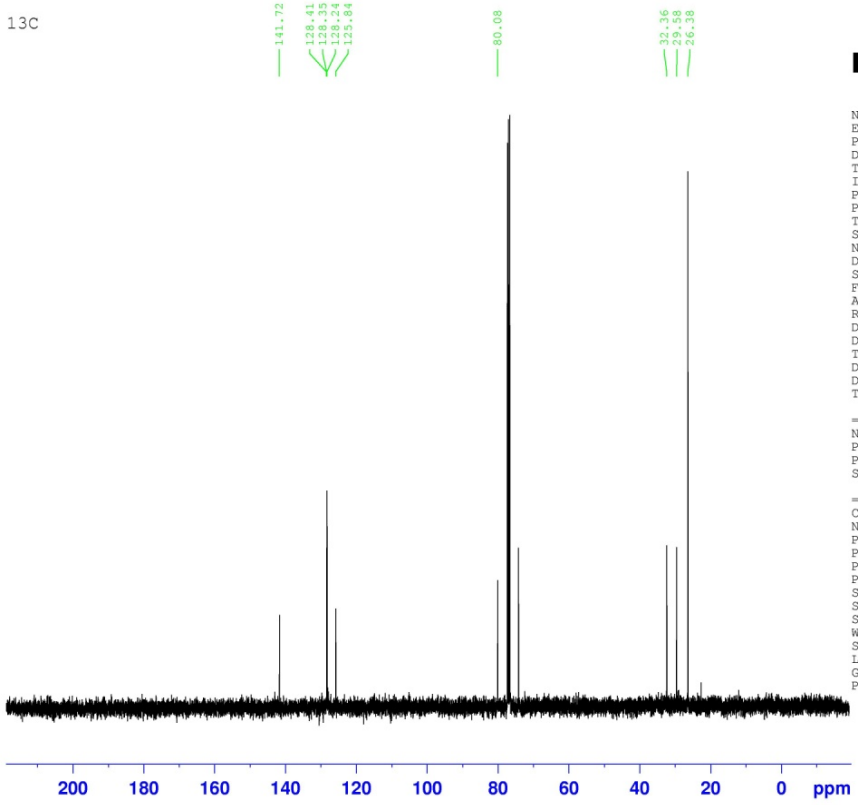
BRUKER

NAME	bp-4-34-pr
EXPNO	2
PROCNO	1
Date_	20120712
Time	13.21
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	152
DS	4
SWH	17985.611 Hz
FIDRES	0.548877 Hz
AQ	0.9110004 sec
RG	7298.2
DW	27.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	5.20 dB
SFO1	75.4752953 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	2.20 dB
PL12	19.10 dB
PL13	19.10 dB
SFO2	300.1312005 MHz
SI	32768
SF	75.4677490 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

3-(2-Deuterophenyl)propyl tert-butyl peroxide

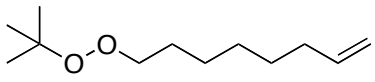


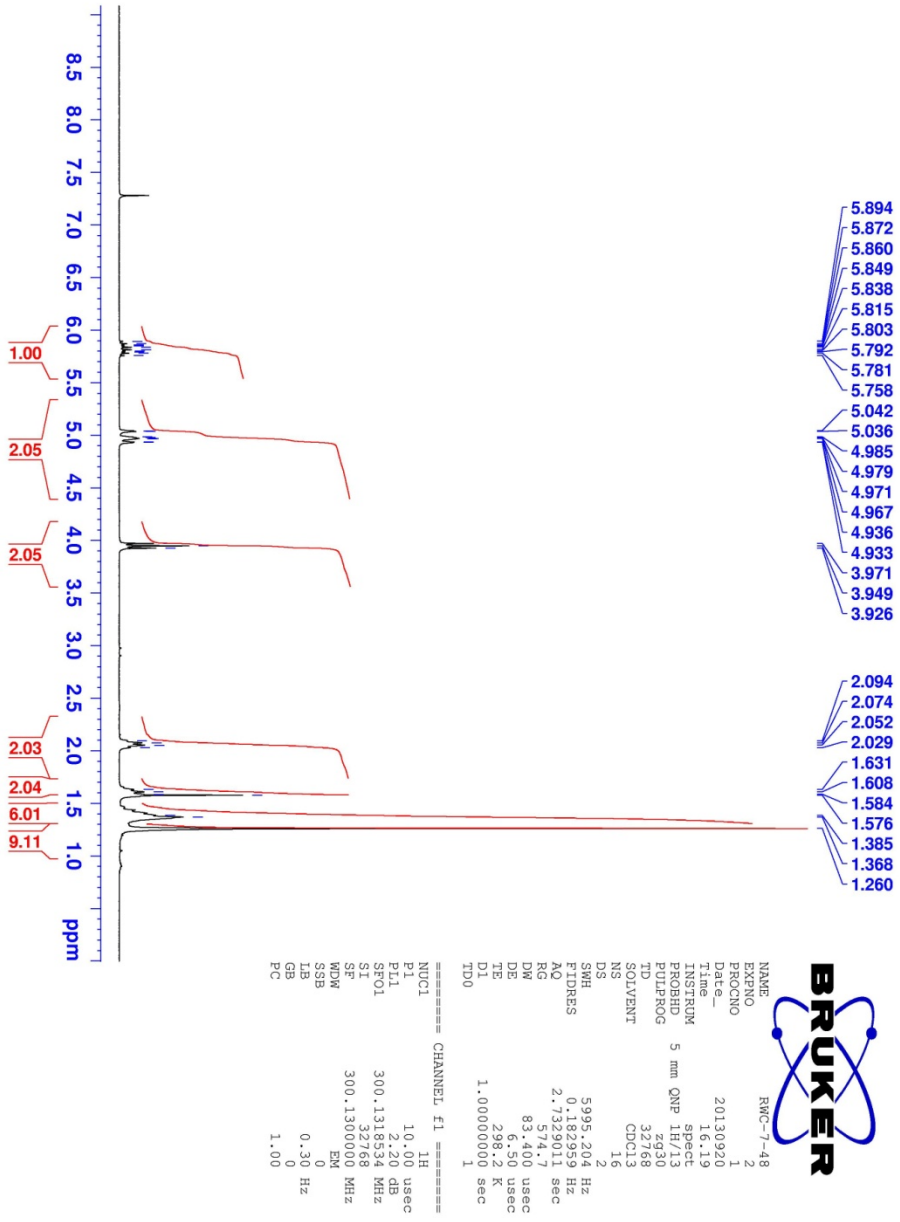


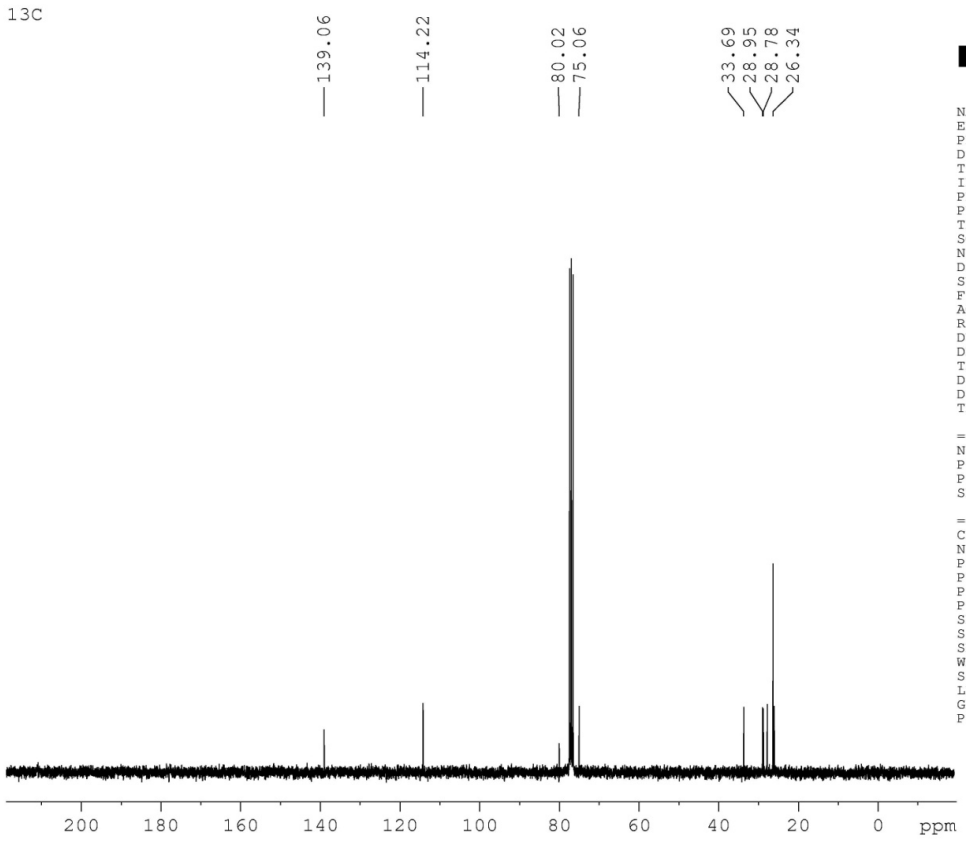



```
NAME                bp-4-24-prB
EXPNO                         2
PROCNO                        1
Date_                  20120612
Time                      15.19
INSTRUM                   spect
PROBHD    5 mm QNP 1H/13
PULPROG                zgpg30
TD                         65536
SOLVENT                  CDCl3
NS                         107
DS                           4
SWH                  23980.814 Hz
FIDRES                0.365918 Hz
AQ                    1.3664756 sec
RG                       7298.2
DW                       20.850 usec
DE                        6.50 usec
TE                       298.1 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        13C
P1                       10.00 usec
PL1                       0.50 dB
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    70.00 usec
PL2                      -4.00 dB
PL12                     12.90 dB
PL13                     12.90 dB
SFO2                400.1316005 MHz
SI                         32768
SF                  100.6127690 MHz
WDW                          EM
SSB                           0
LB                        1.00 Hz
GB                            0
PC                        1.40
```

8-(tert-butylperoxy)oct-1-ene (12d)

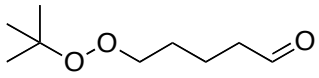


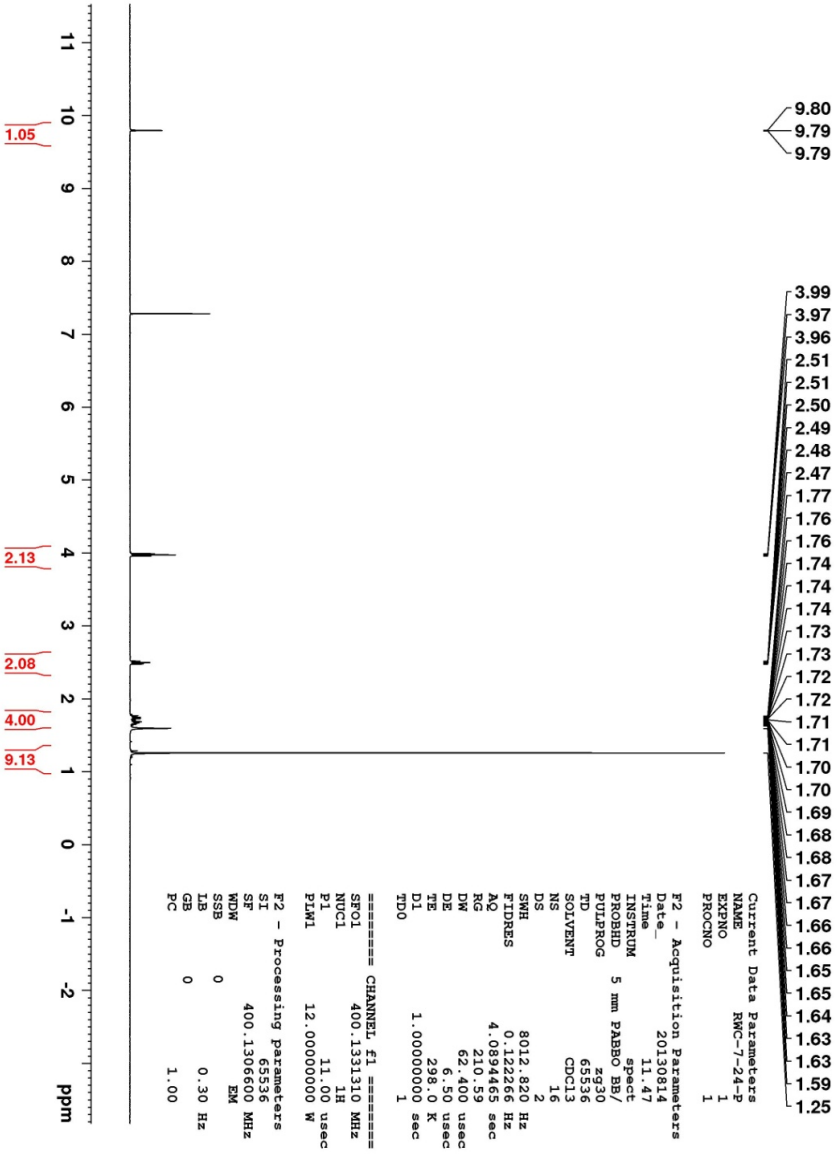


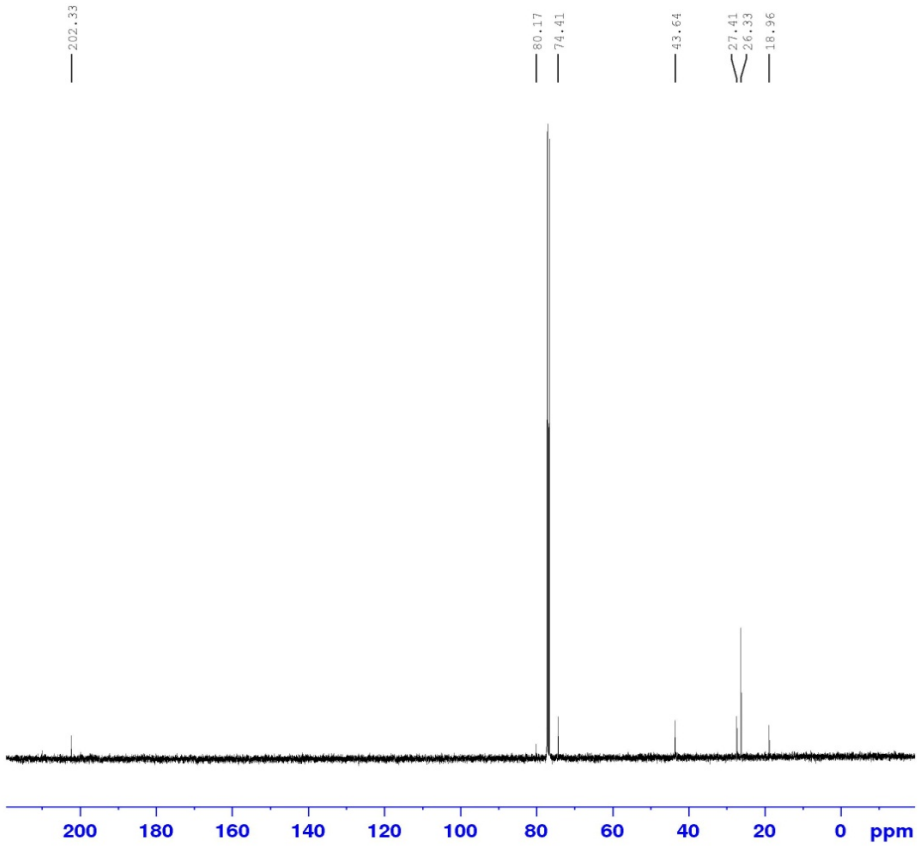



```
NAME          RWC-7-48-P-C
EXPNO                    2
PROCNO                   1
Date_             20130920
Time                 16.29
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                    32768
SOLVENT             CDCl3
NS                      652
DS                        4
SWH              17985.611 Hz
FIDRES            0.548877 Hz
AQ                0.9110004 sec
RG                  14596.5
DW                   27.800 usec
DE                    6.50 usec
TE                   298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.00 usec
PL1                   5.20 dB
SFO1           75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                70.00 usec
PL2                   2.20 dB
PL12                 19.10 dB
PL13                 19.10 dB
SFO2          300.1312005 MHz
SI                    32768
SF             75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

5-(*tert*-butylperoxy)pentanal

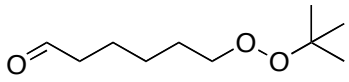


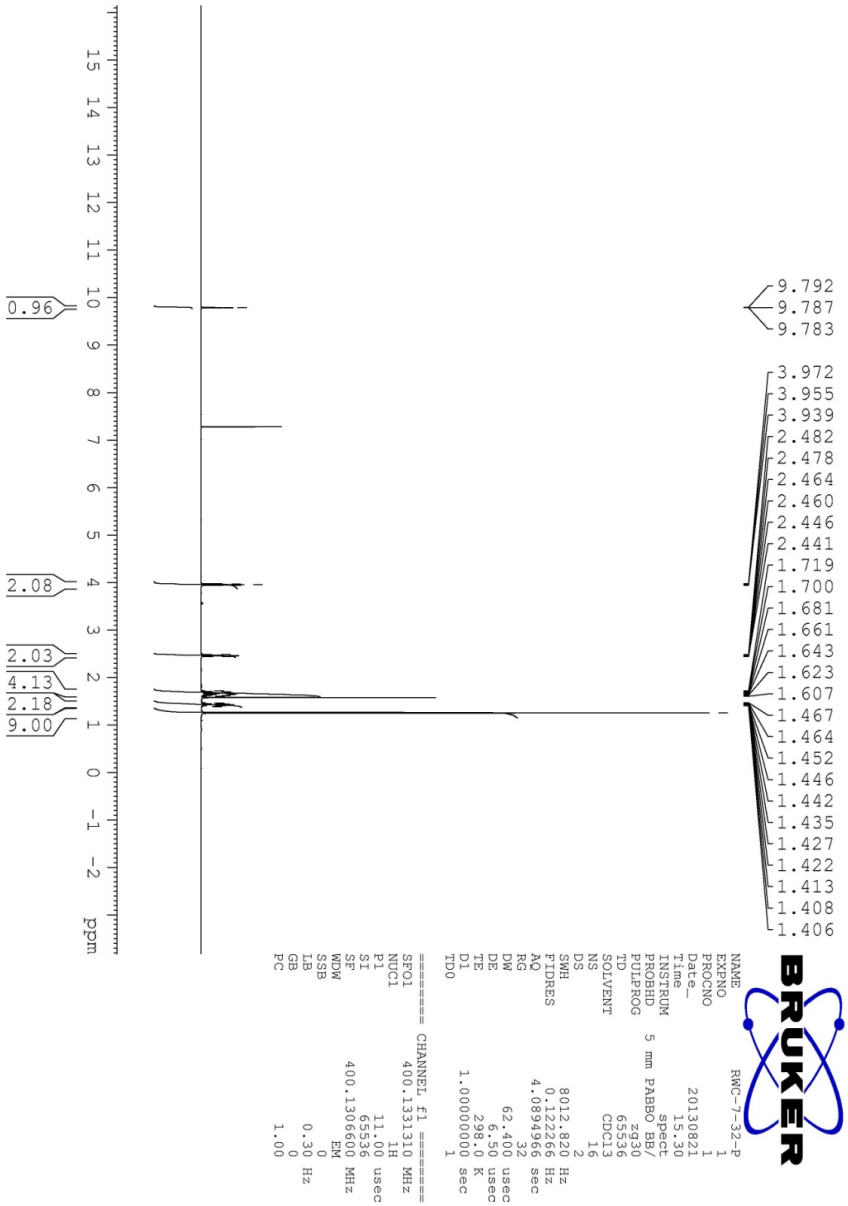


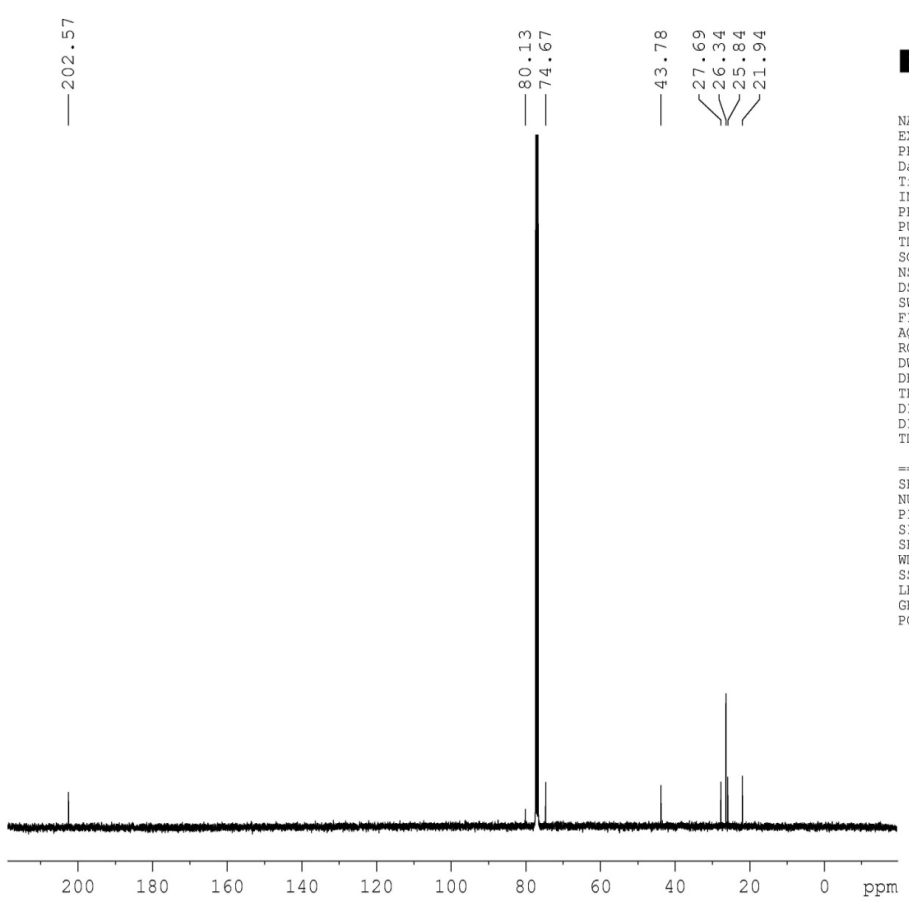



```
Current Data Parameters
NAME        RWC-7-24-P-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130814
Time              12.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 452
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                6.50 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       100.6229953 MHz
NUC1               13C
P1                9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2       400.1322605 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF         100.6129340 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

6-(*tert*-butylperoxy)hexanal



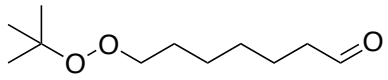


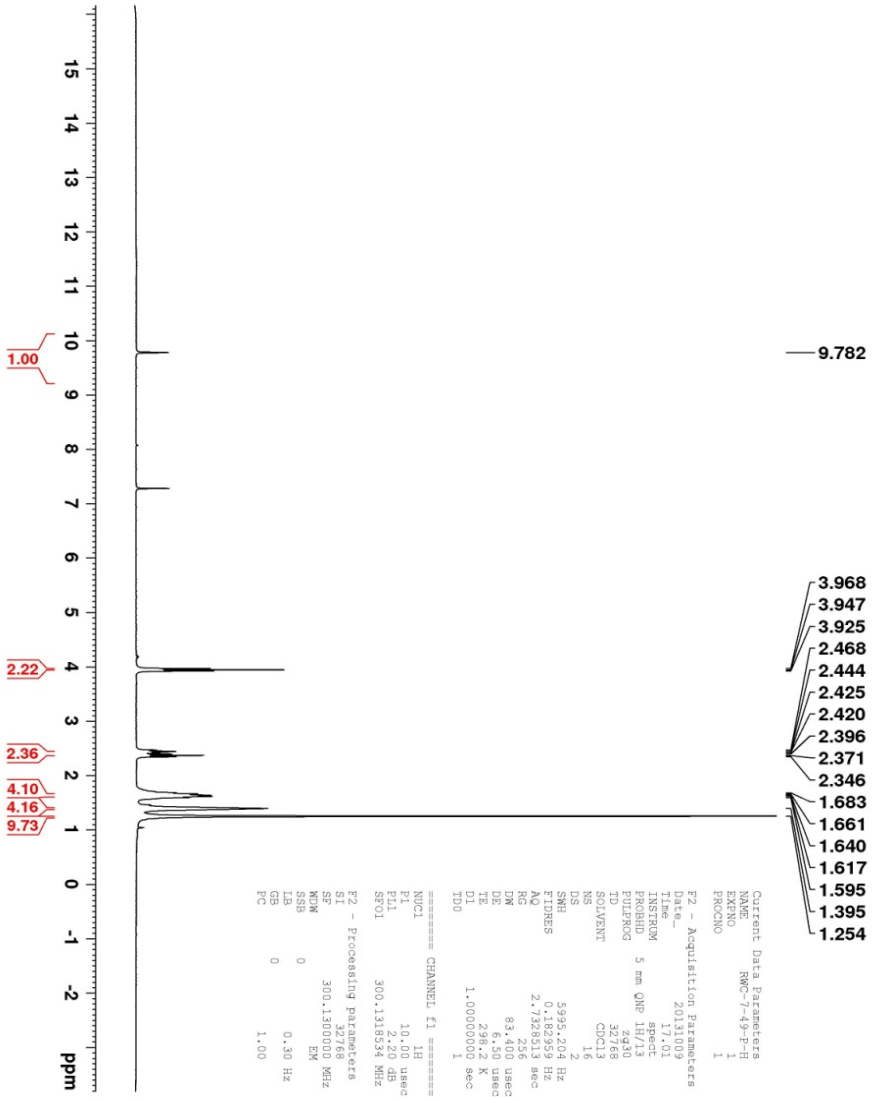


BRUKER

NAME	RWC-7-32-C13
EXPNO	2
PROCNO	1
Date_	20130822
Time	10.40
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	895
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	210.59
DW	20.800 usec
DE	6.50 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6229953 MHz
NUC1	13C
P1	9.00 usec
SI	32768
SF	100.6129340 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

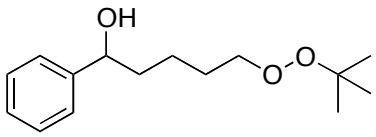
7-(tert-butylperoxy)heptanal

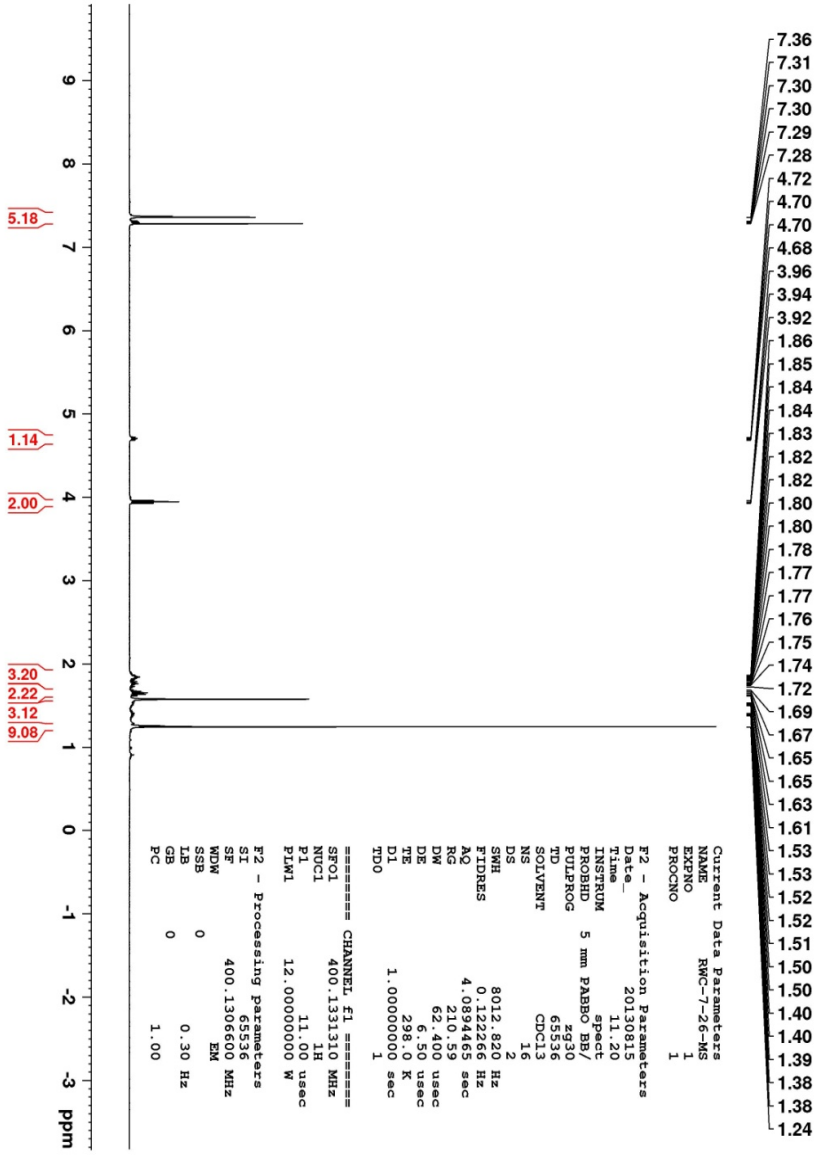


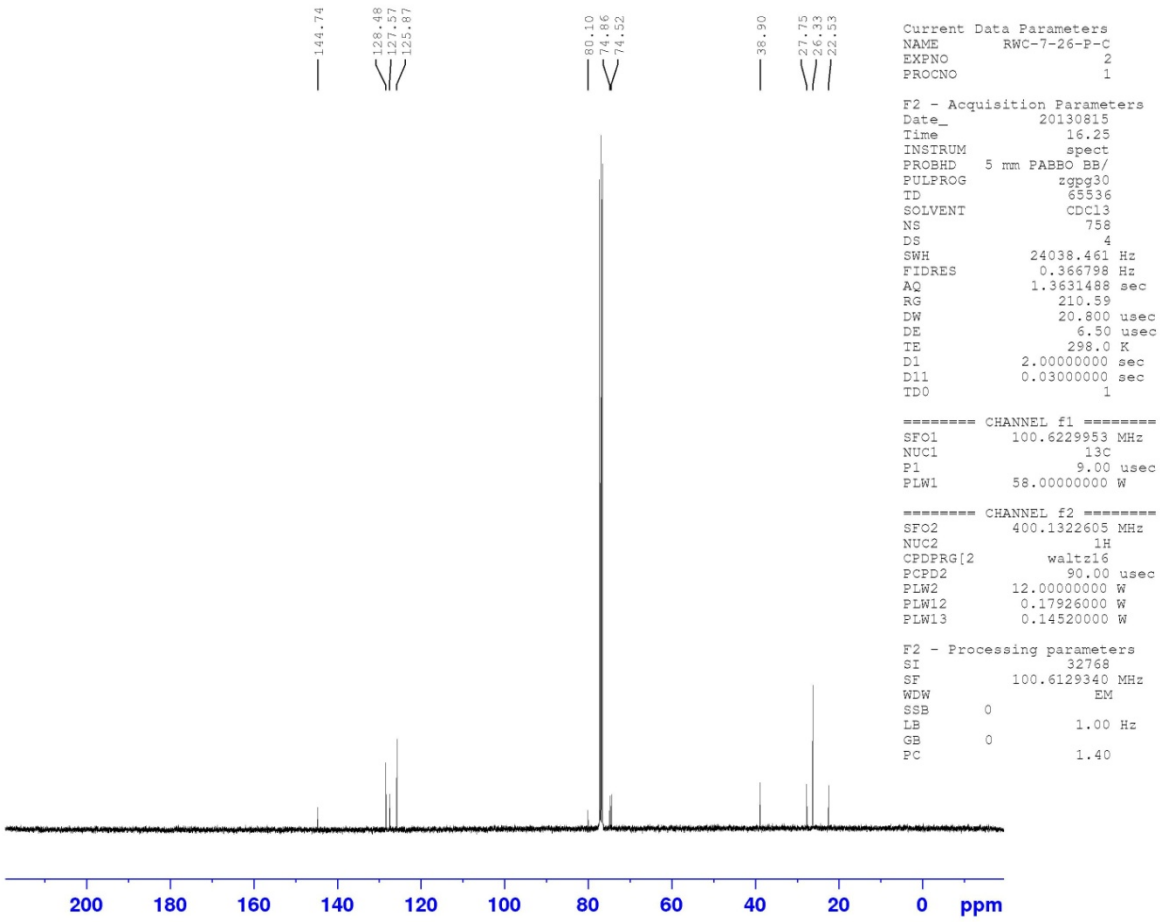


179.44
80.09
74.90
33.85
28.89
27.69
26.33
25.89
24.55
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME RWC-7-49-P-C
EXPNO 1
PROCNO 1
Date_ 20140210
Time 8.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 23
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6229953 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6129340 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

5-(*tert*-butylperoxy)-1-phenylpentan-1-ol (13b)

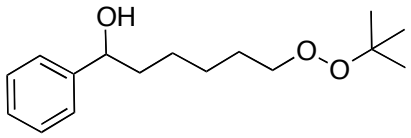


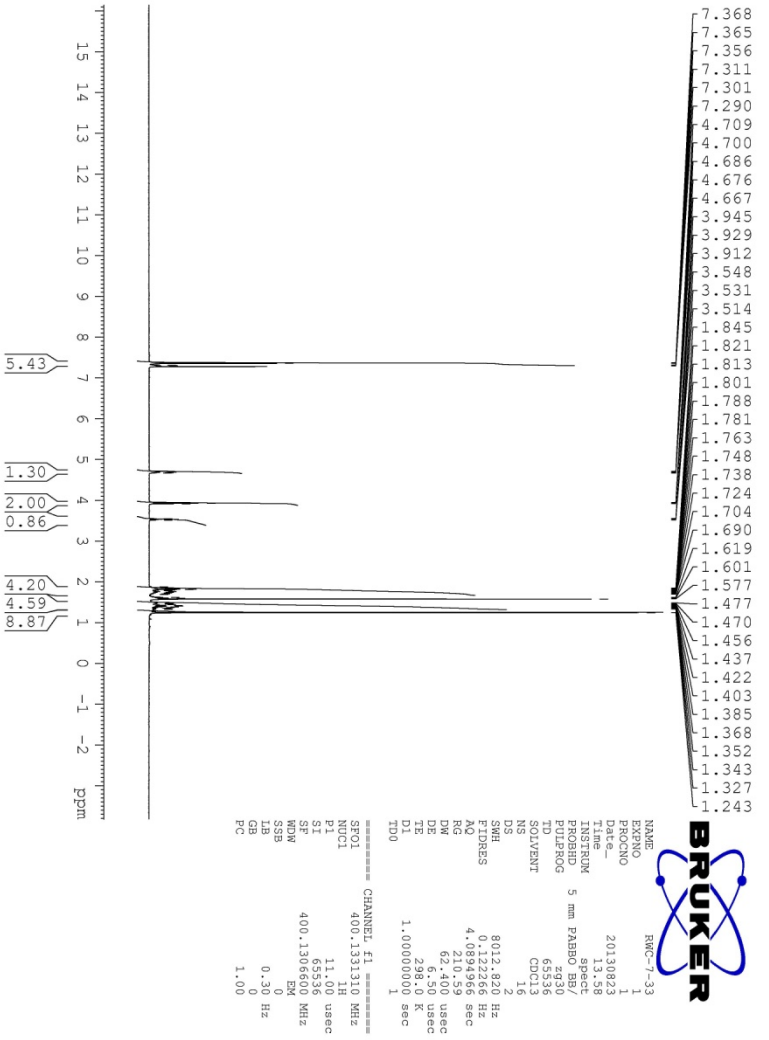


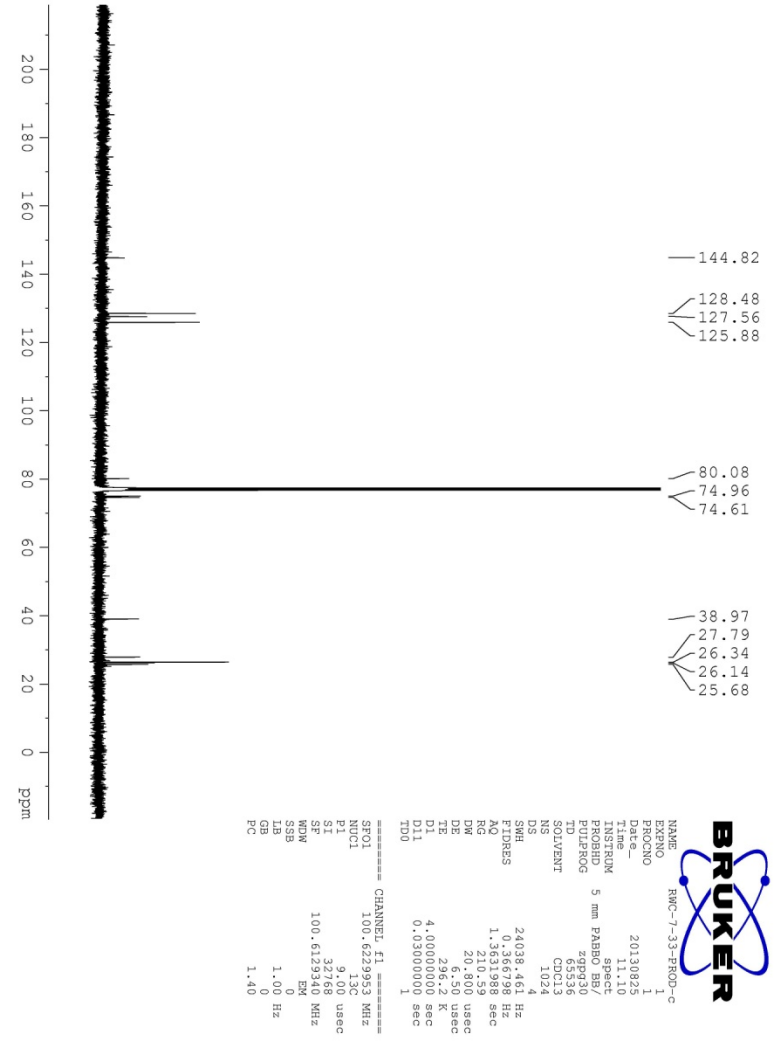



```
Current Data Parameters
NAME        RWC-7-26-P-C
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130815
Time              16.25
INSTRUM           spect
PROBHD    5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 758
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 sec
RG              210.59
DW              20.800 usec
DE               6.50 usec
TE              298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1               13C
P1                9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF          100.6129340 MHz
WDW                EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

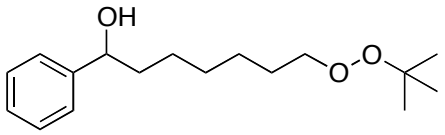
6-(tert-butylperoxy)1-phenylhexan-1-ol (13c)

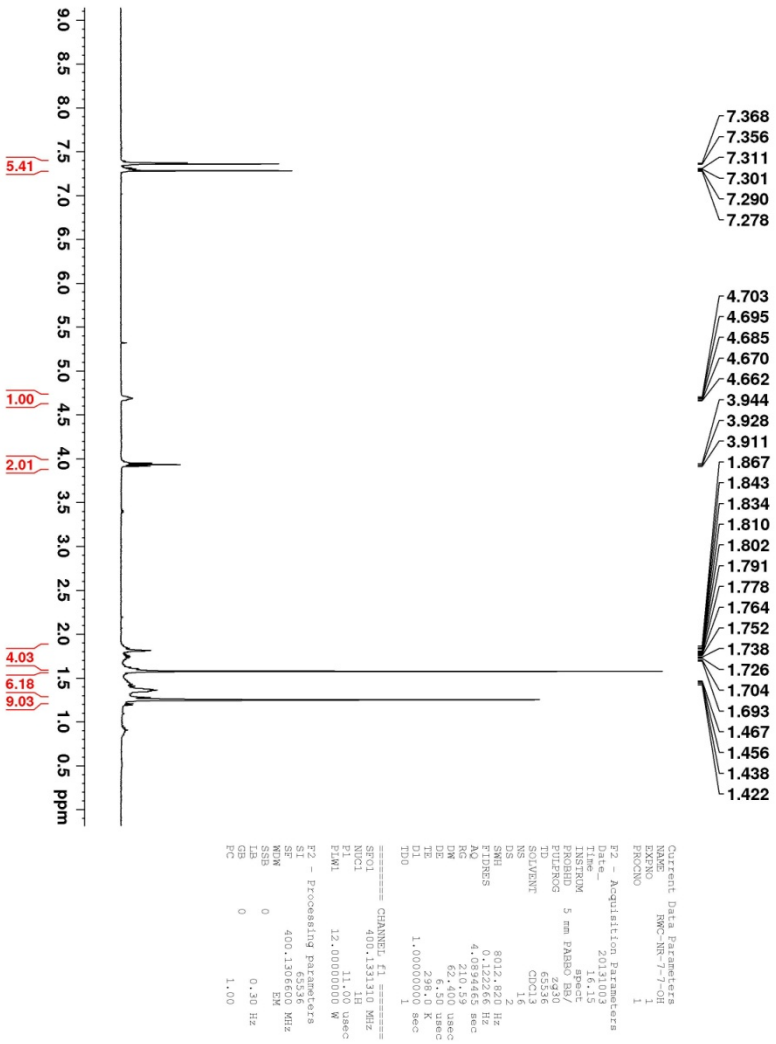


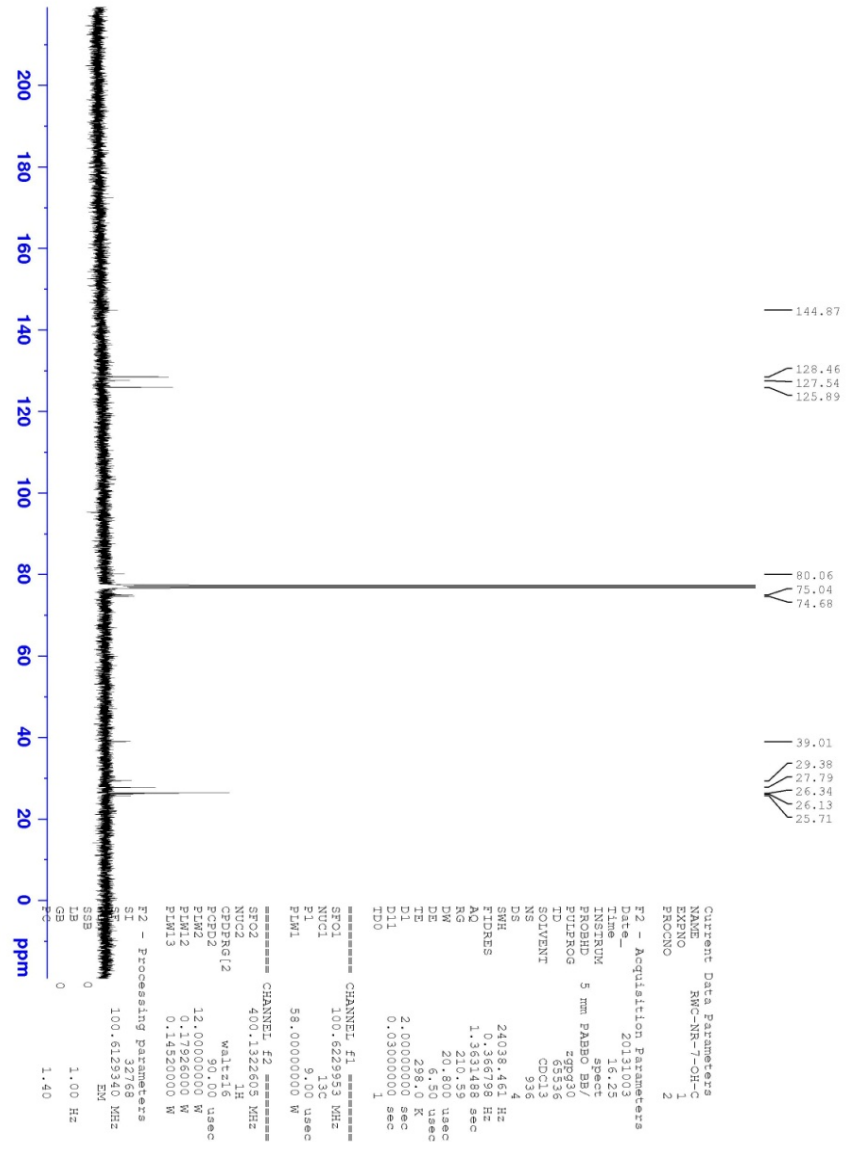



144.82
128.48
127.56
125.88
80.08
74.96
74.61
38.97
27.79
26.34
26.14
25.68
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME RWC-7-33-PROD-c
EXPNO 1
PROCNO 1
Date_ 20130825
Time 11.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6229953 MHz
NUC1 13C
P1 9.00 usec
SF 32768
SFO1 100.6129353 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

7-(tert-butylperoxy)1-phenylheptan-1-ol (13d)

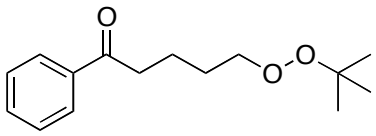


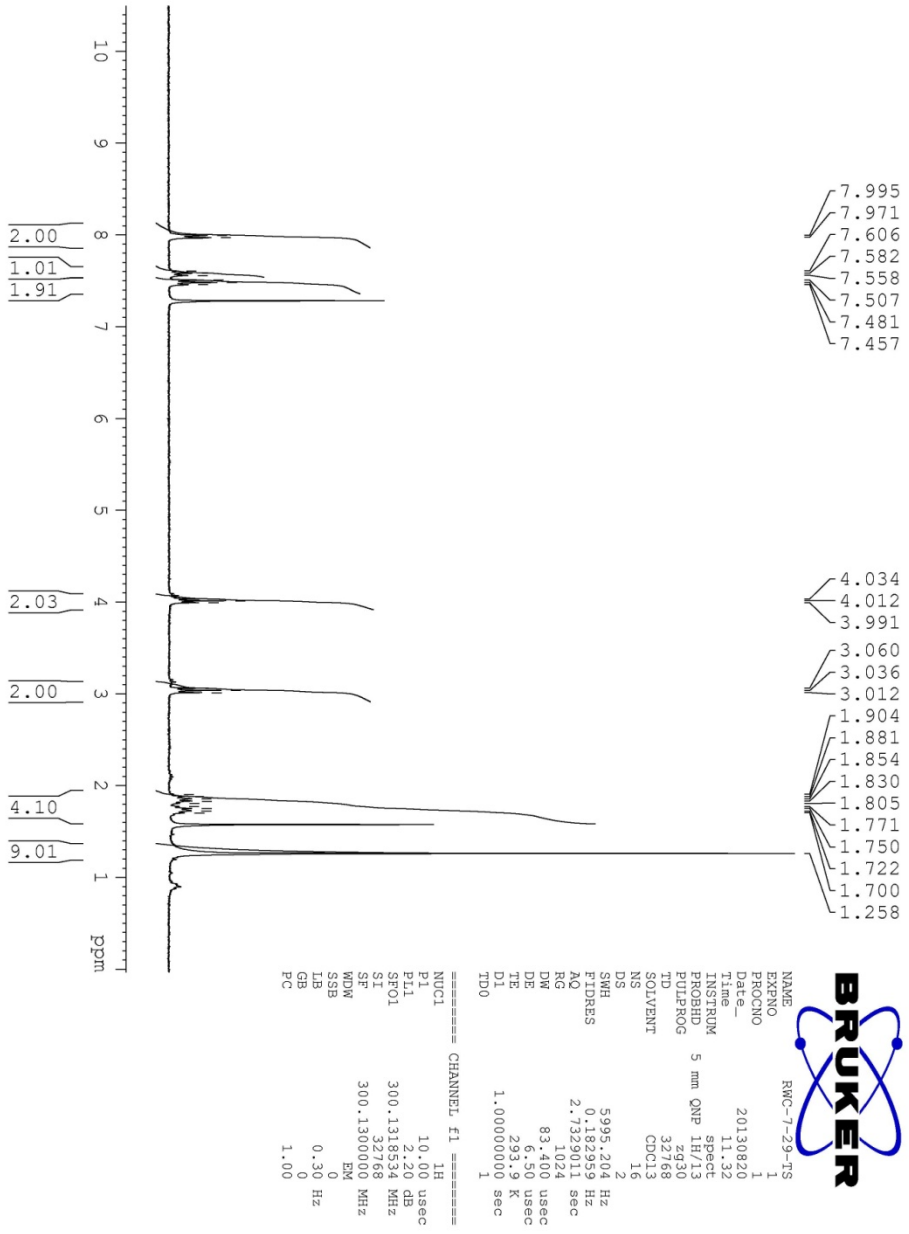





```
Current Data Parameters
NAME       RWC-NR-7-OH-C
EXPNO                  1
PROCNO                 2

F2 - Acquisition Parameters
Date_           20131003
Time            16.25
INSTRUM           spect
PROBHD     5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  936
DS                    4
SWH           24038.461 Hz
FIDRES            0.36678 Hz
AQ            1.3631488 sec
RG                  210.59
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6229953 MHz
NUC1                    13C
P1                   9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2          400.1322605 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2         12.00000000 W
PLW12         0.17926000 W
PLW13         0.14520000 W

F2 - Processing parameters
SI                  32768
SF          100.6129340 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

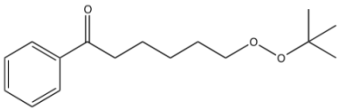
5-(tert-butylperoxy)-1-phenylpentan-1-one (14b)

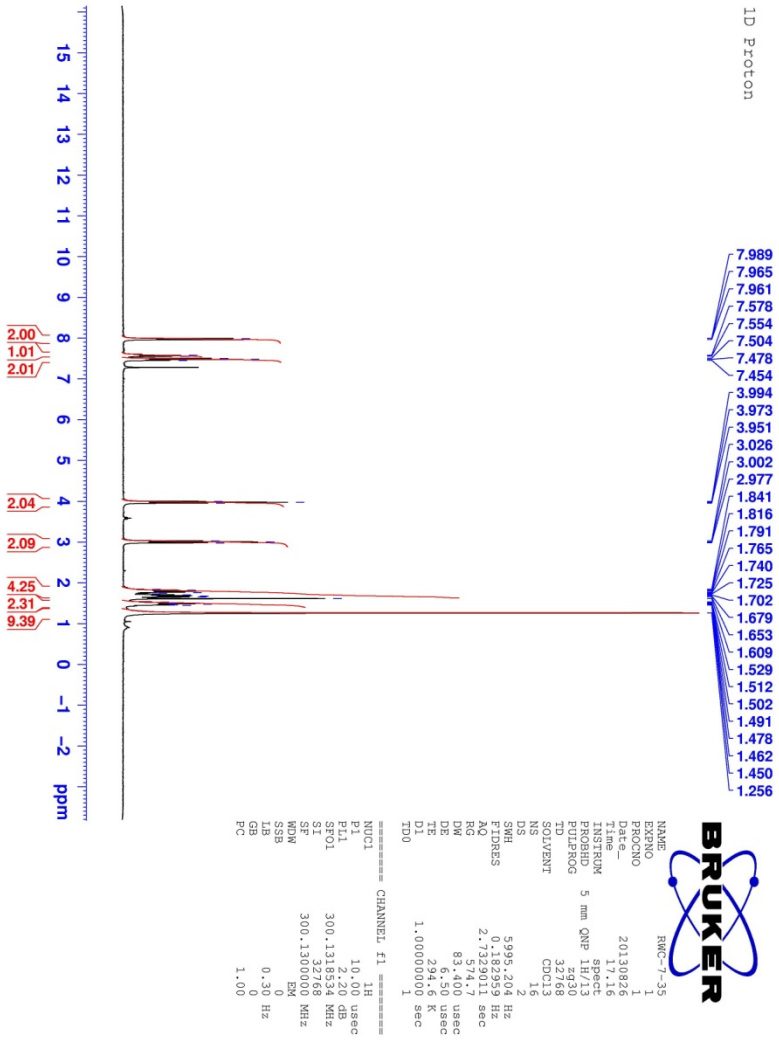




132.96
128.58
128.04
80.13
74.70
38.28
27.57
26.35
21.07
NAME RWC-7-29-P-C2
EXPNO 2
PROCNO 1
Date_ 20130820
Time 13.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 927
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 210.59
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6229953 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.6129340 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

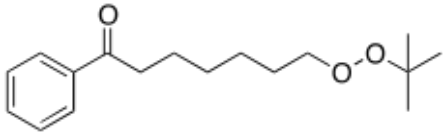
6-(tert-butylperoxy)1-phenylhexan-1-one (14c)

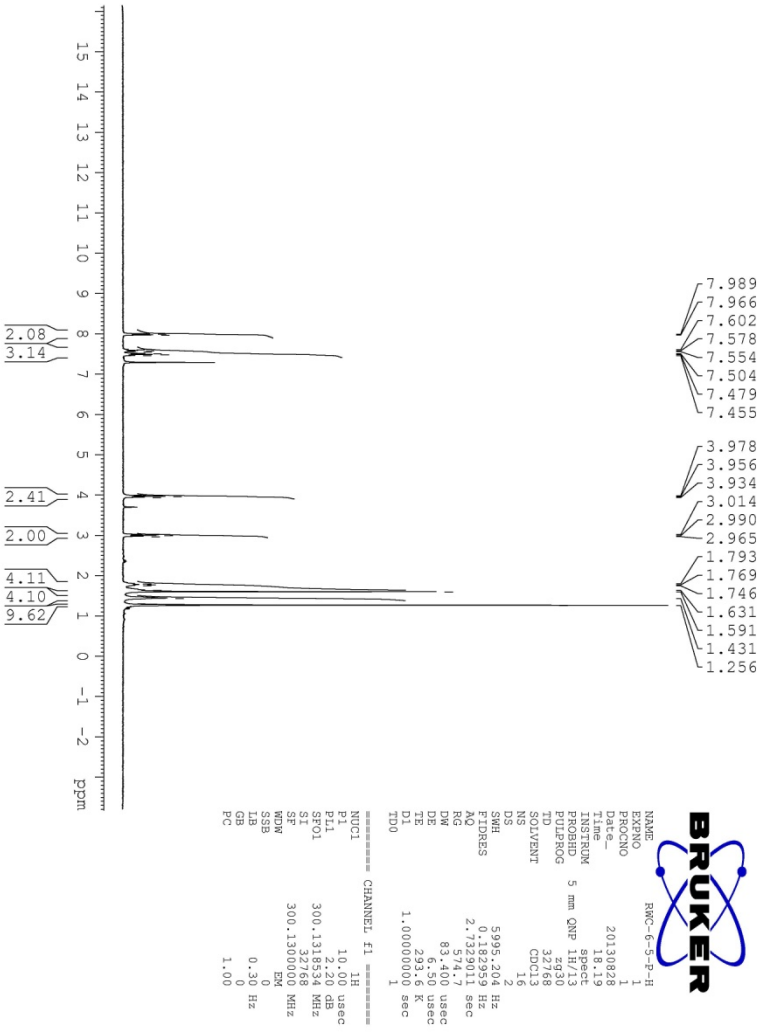


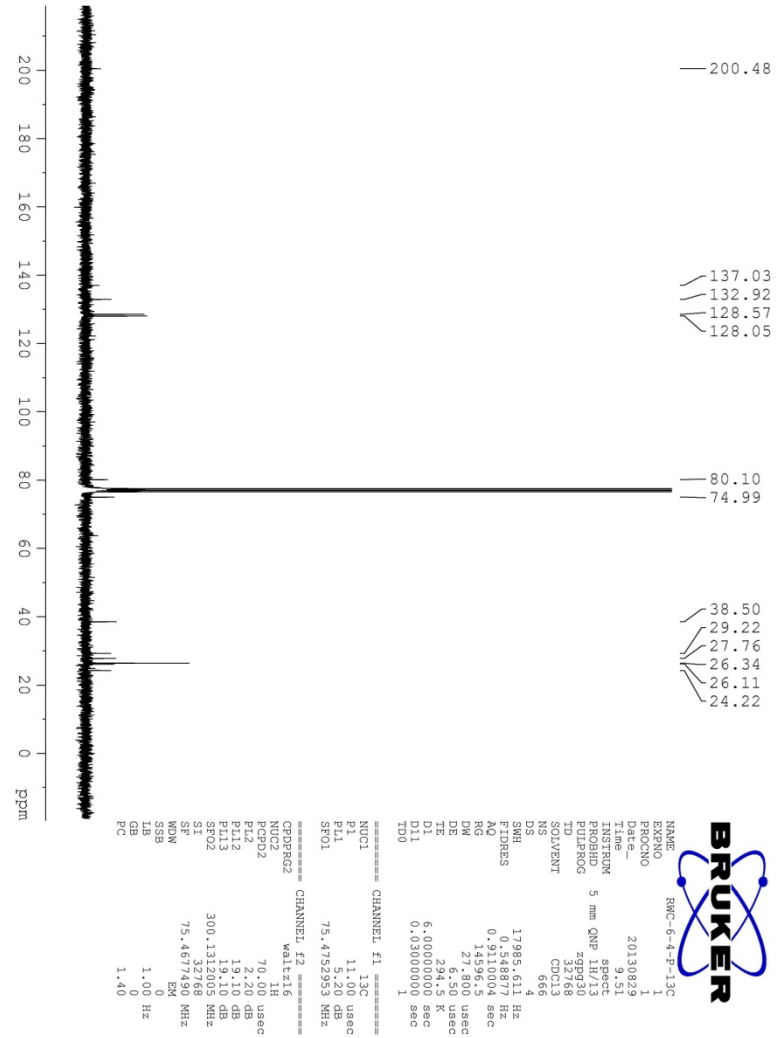


200.30
137.02
132.93
128.57
128.04
80.11
74.84
38.44
27.80
26.34
26.01
24.16
200
180
160
140
120
100
80
60
40
20
0
ppm
NAME RWC-7-35-P-C
EXPNO 1
PROCNO 1
Date_ 20130826
Time 17:25
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 737
DS 4
SWH 17985.611 Hz
FIDRES 0.548807 Hz
AQ 0.910007 sec
RG 14596.5
DW 27.800 usec
DE 6.50 usec
TE 295.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 15.20 dBm
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 2.20 dB
PL12 19.10 dB
PL13 19.10 dB
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

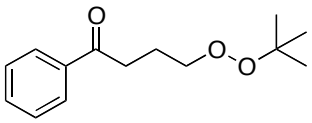
7-(*tert*-)-1-phenylheptan-1-one (14d)

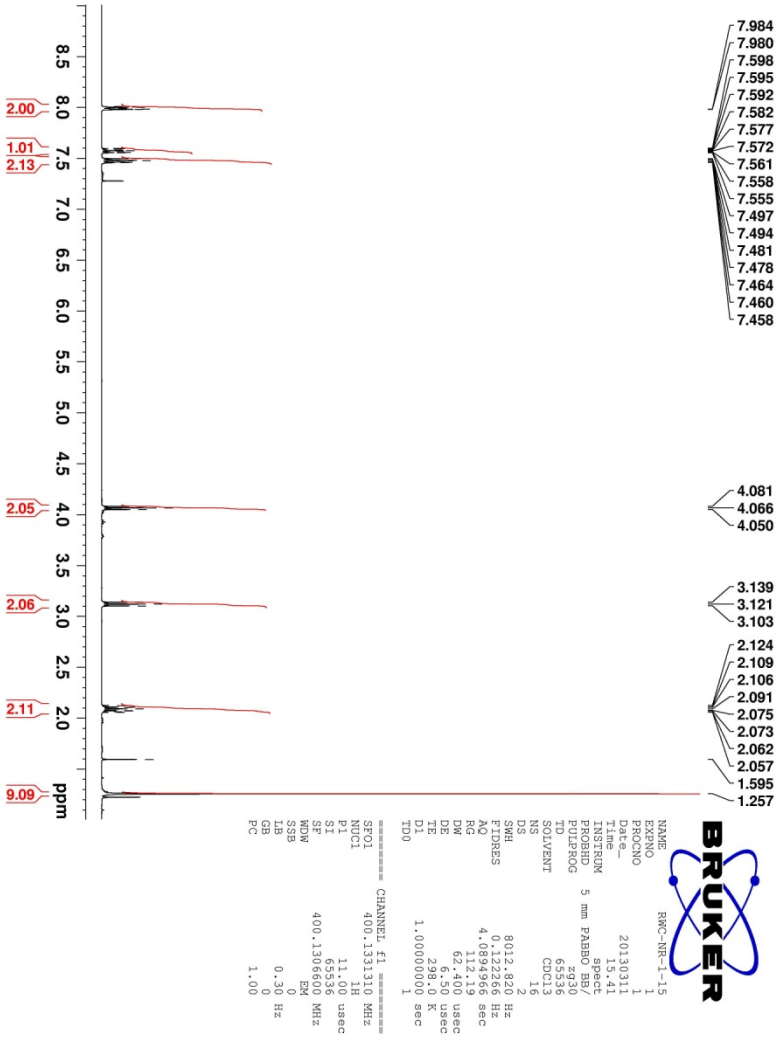


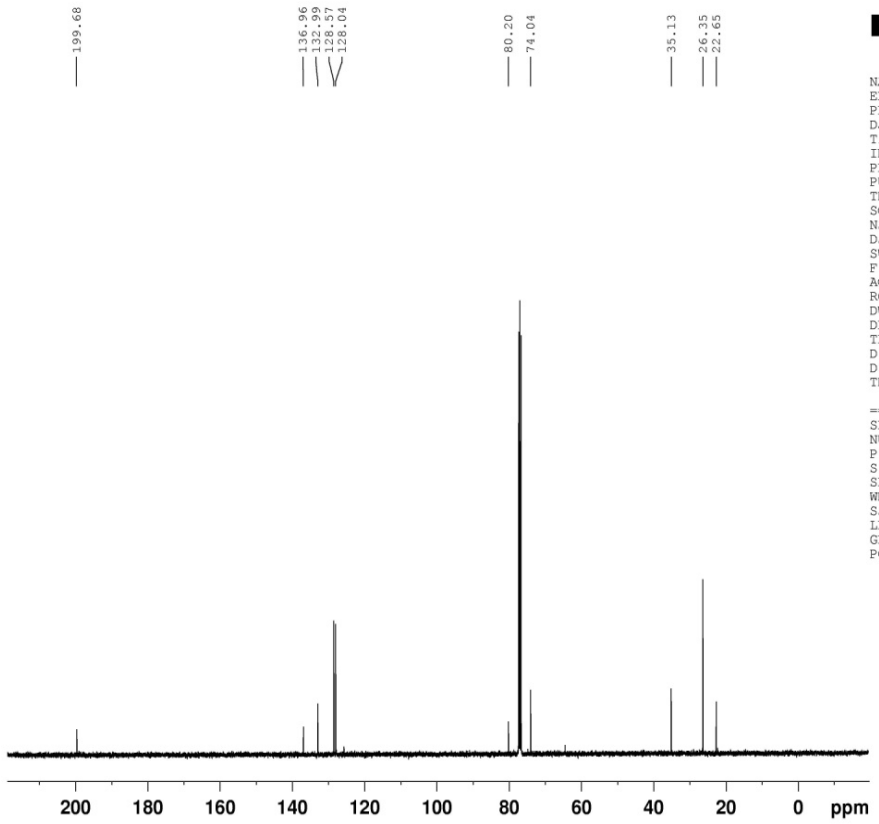



200.48
137.03
132.92
128.57
128.05
80.10
74.99
38.50
29.22
27.76
26.34
26.11
24.22
200
180
160
140
120
100
80
60
40
20
0
ppm

4-(*tert*-butylperoxy)-1-phenylbutan-1-one (14a)



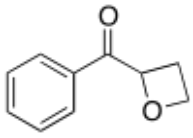


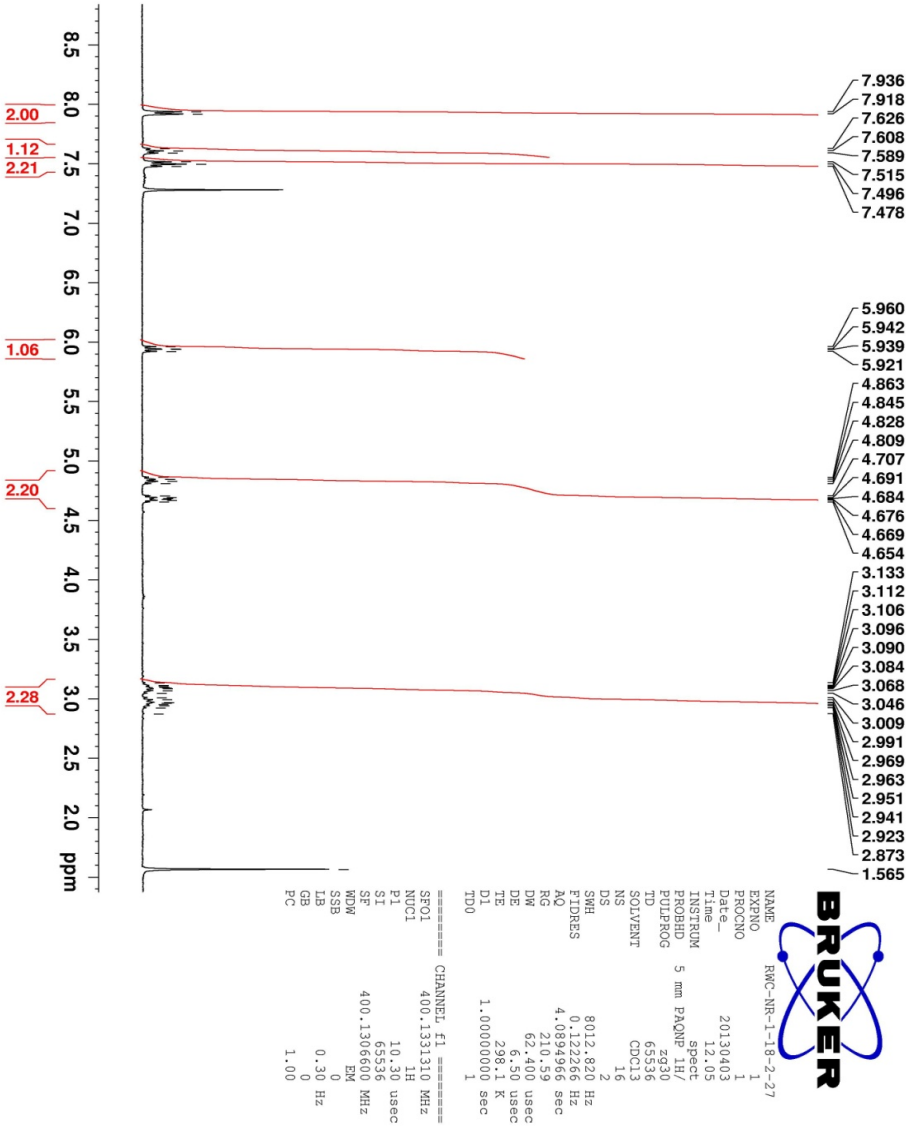


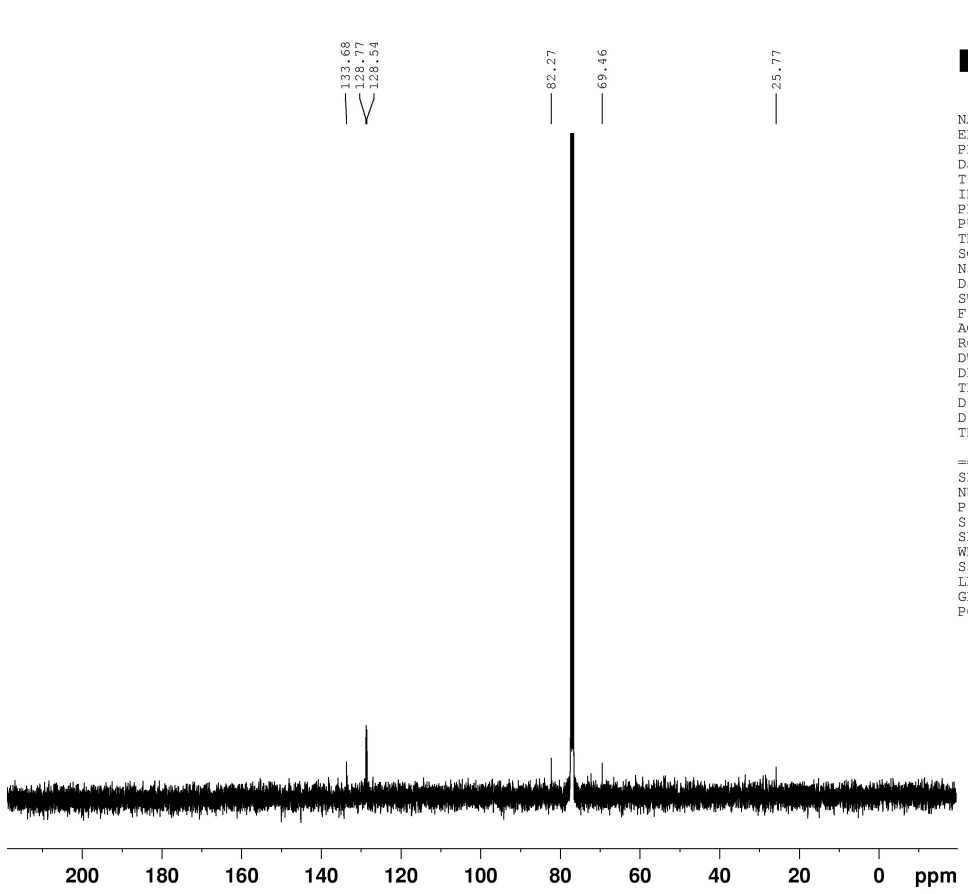
BRUKER

NAME	RWC-NR-1-15-C
EXPNO	2
PROCNO	1
Date_	20130311
Time	16.19
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	597
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	210.59
DW	20.800 usec
DE	6.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6229953 MHz
NUC1	13C
P1	9.00 usec
SI	32768
SF	100.6129340 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Oxetan-2-yl(phenyl)methanone (15a)



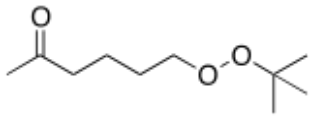


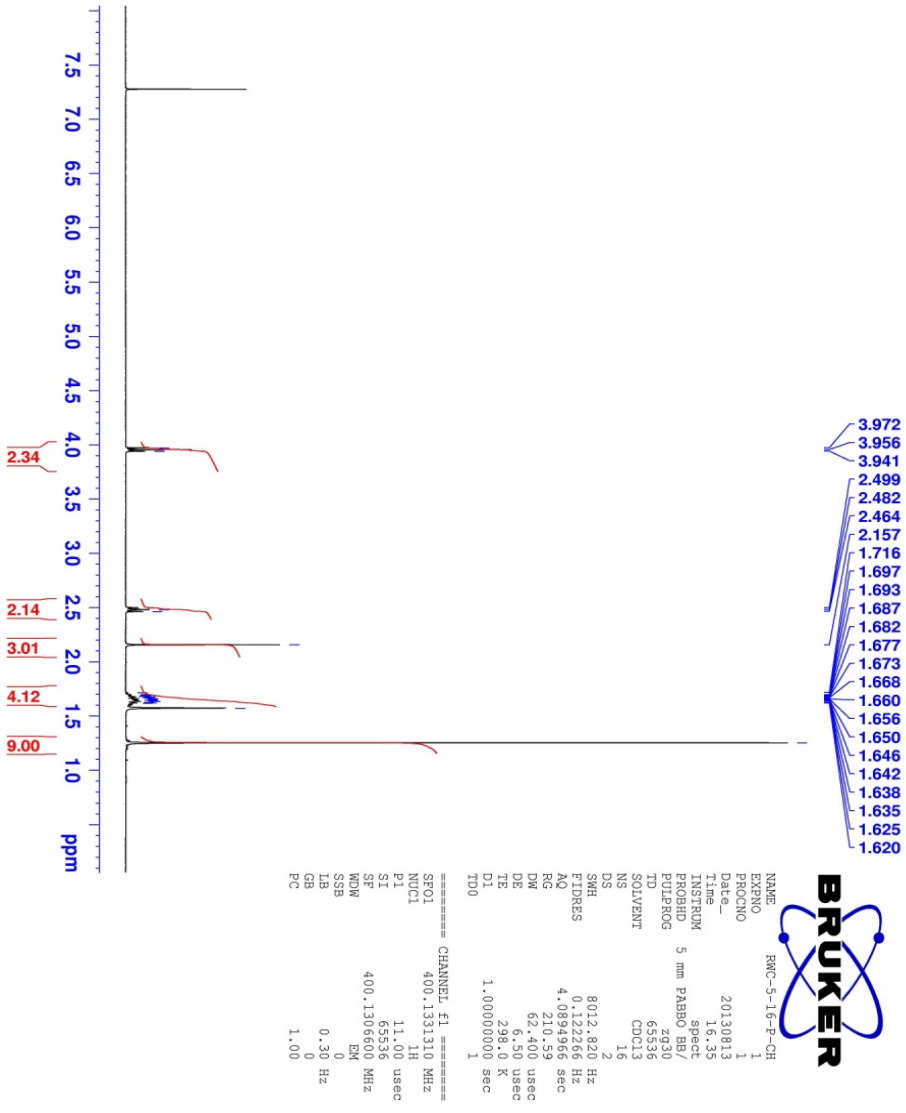


BRUKER

NAME	RWC-NR-1-18-P-C
EXPNO	2
PROCNO	1
Date_	20130403
Time	12.55
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	887
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	210.59
DW	20.800 usec
DE	6.50 usec
TE	298.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6229953 MHz
NUC1	13C
P1	8.00 usec
SI	32768
SF	100.6129340 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

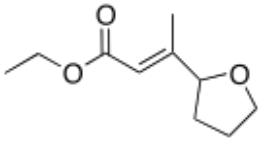
6-(*tert*-butylperoxy)hexan-2-one (16)

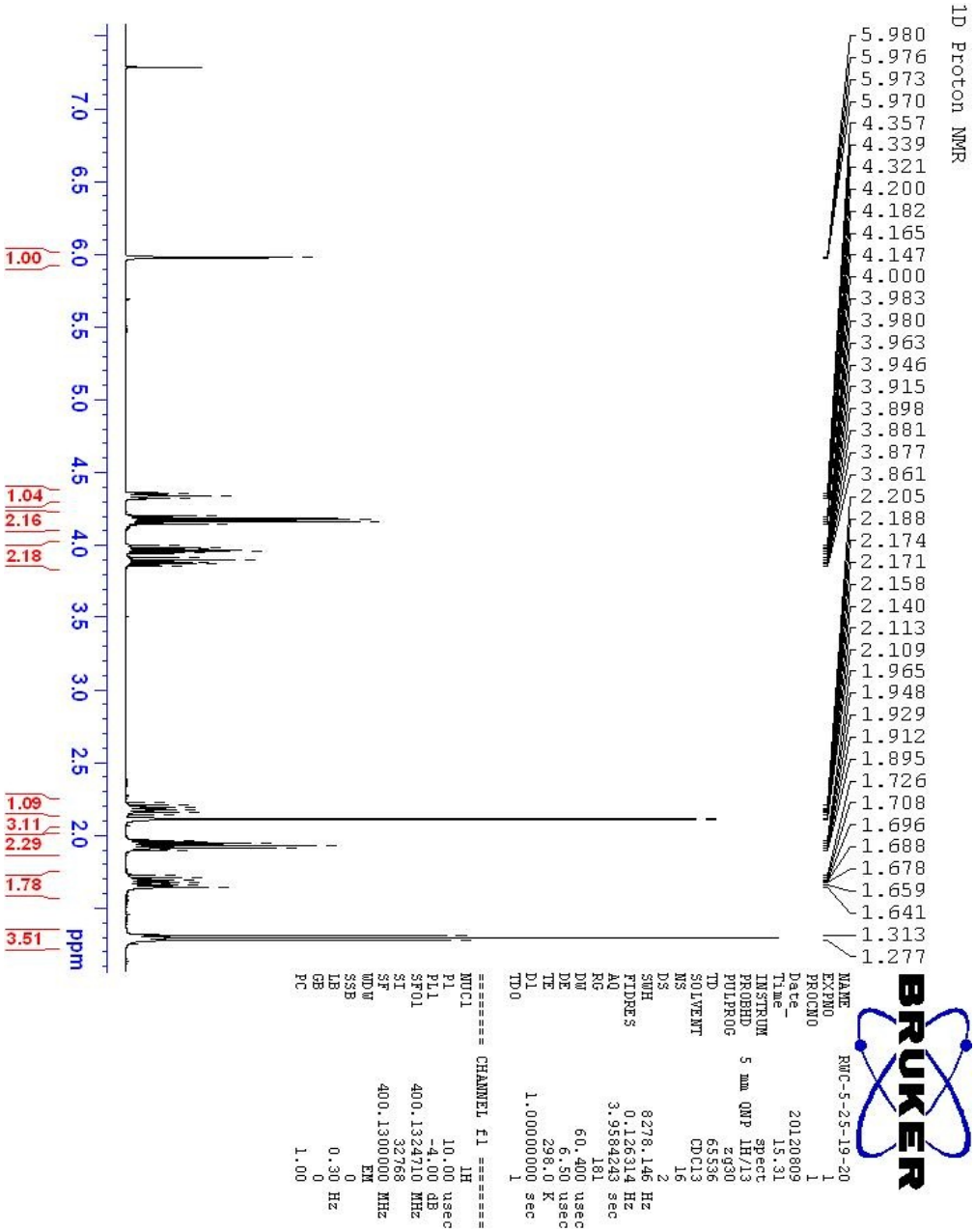


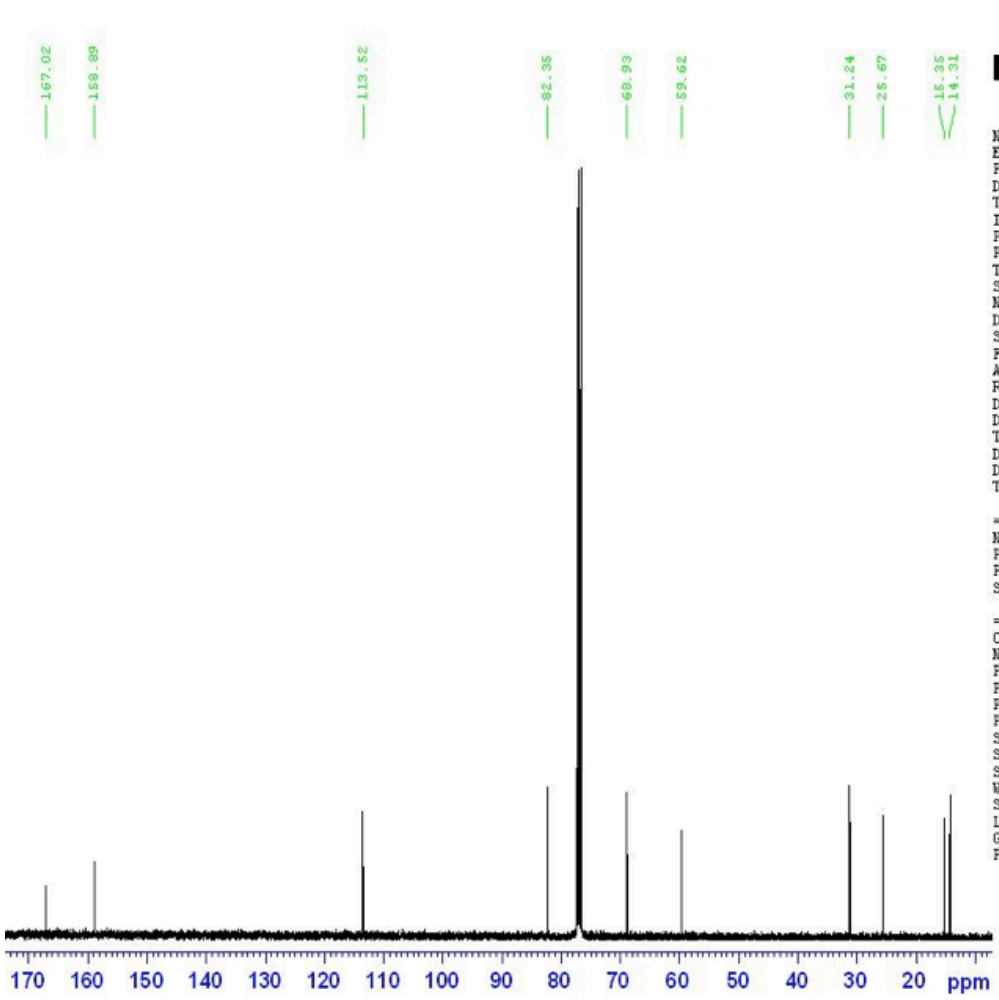


```
Current Data Parameters
NAME                  RWC-5-16-P-C
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_               20130813
Time                   16.55
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        867
DS                          4
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631488 sec
RG                     210.59
DW                     20.800 usec
DE                     6.50 usec
TE                     298.0 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1            100.6229953 MHz
NUC1                       13C
P1                        9.00 usec
PLW1           58.00000000 W

======== CHANNEL f2 ========
SFO2            400.1322605 MHz
NUC2                       1H
CPDPRG[2                   waltz16
PCPD2                     90.00 usec
PLW2           12.00000000 W
PLW12           0.17926000 W
PLW13           0.14520000 W

F2 - Processing parameters
SI                      32768
SF              100.6129340 MHz
WDW                        EM
SSB                     0
LB                      1.00 Hz
GB                      0
PC                      1.40
```

(*E*)-ethyl 3-(tetrahydrofuran-2-yl)but-2-enoate (17)



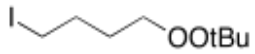


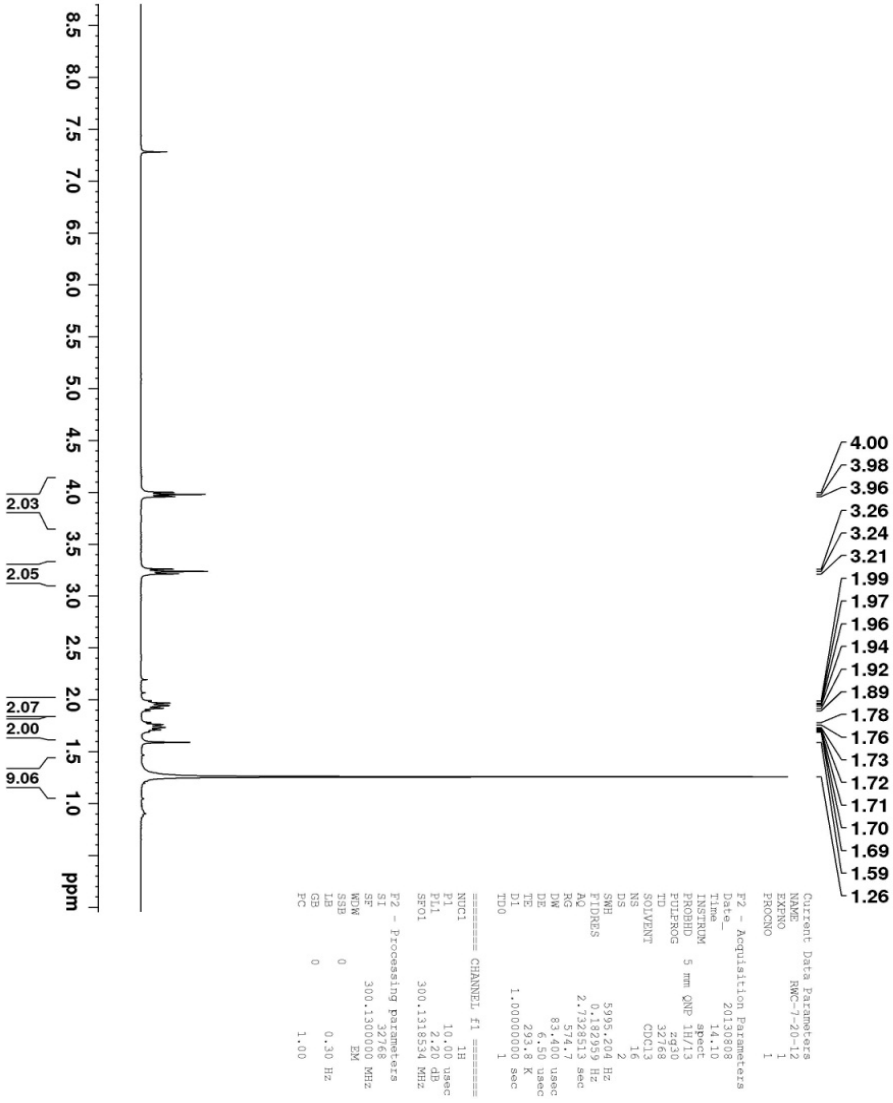


BRUKER

NAME	RWC-5-25-P-C	
EXPNO	1	
PROCNO	1	
Date_	20120809	
Time	17.02	
INSTRUM	spect	
PROBHD	5 mm QNP 1H/13	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	742	
DS	4	
SWH	23980.814	Hz
FIDRES	0.365918	Hz
AQ	1.3664756	sec
RG	3649.1	
DW	20.850	usec
DE	6.50	usec
TE	298.0	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	10.00	usec
PL1	0.50	dB
SF01	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	70.00	usec
PL2	-4.00	dB
PL12	12.90	dB
PL13	12.90	dB
SF02	400.1316005	MHz
SI	32768	
SF	100.6127690	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

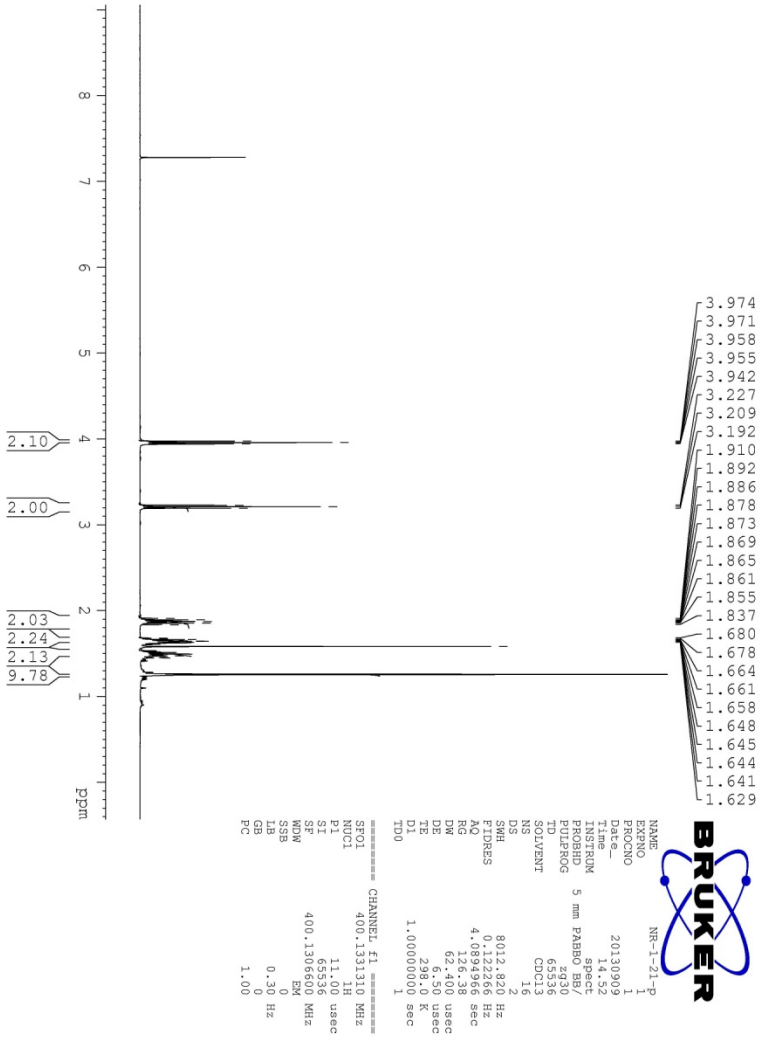
1-(tert-butylperoxy)-4-iodobutane (18b)





```
Current Data Parameters
NAME                  RWC-7-20-12-C
EXPNO                            1
PROCNO                           1

F2 - Acquisition Parameters
Date_               20130808
Time                14.16
INSTRUM             spect
PROBHD     5 mm QNP 1H/13
PULPROG             zgpg30
TD                  32768
SOLVENT             CDCl3
NS                  436
DS                    4
SWH           17985.611 Hz
FIDRES         0.548877 Hz
AQ             0.9109504 sec
RG                18390.4
DW                27.800 usec
DE                 6.50 usec
TE                294.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                11.00 usec
PL1               5.20 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                1H
PCPD2             70.00 usec
PL2               2.20 dB
PL12             16.10 dB
PL13             16.10 dB
SFO2        300.1322005 MHz

F2 - Processing parameters
SI                  32768
SF          75.4677490 MHz
WDW                    EM
SSB                 0
LB                  1.00 Hz
GB                  0
PC                  1.40
```

1-(*tert*-butylperoxy)-5-iodopentane (18c)



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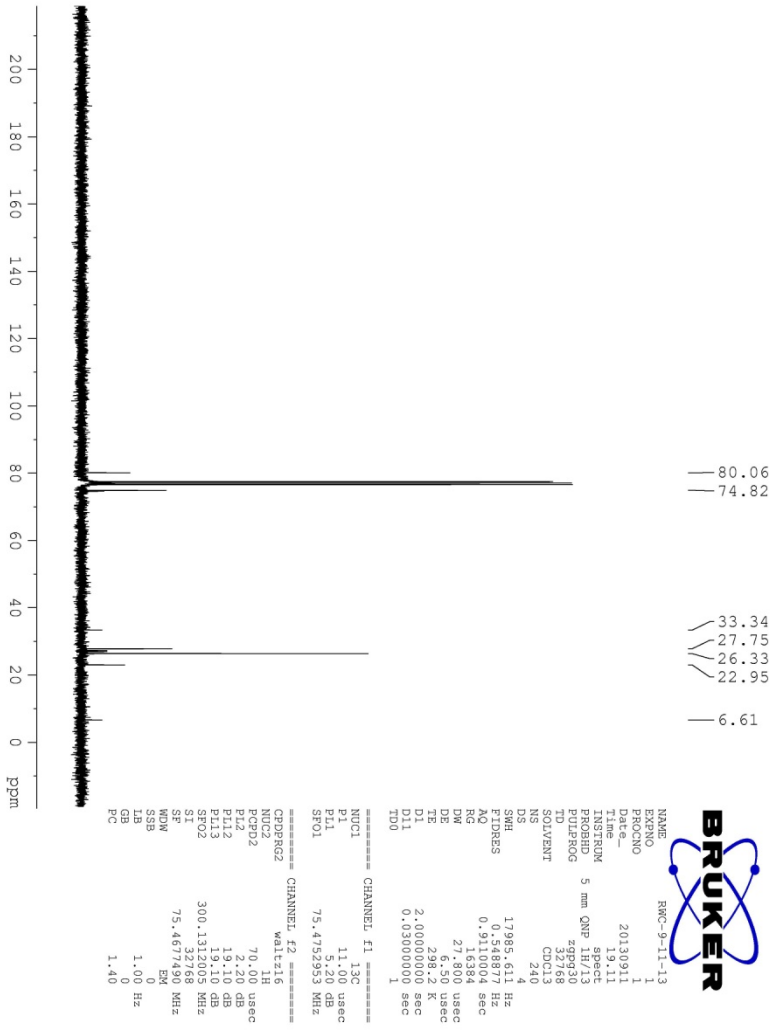
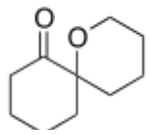
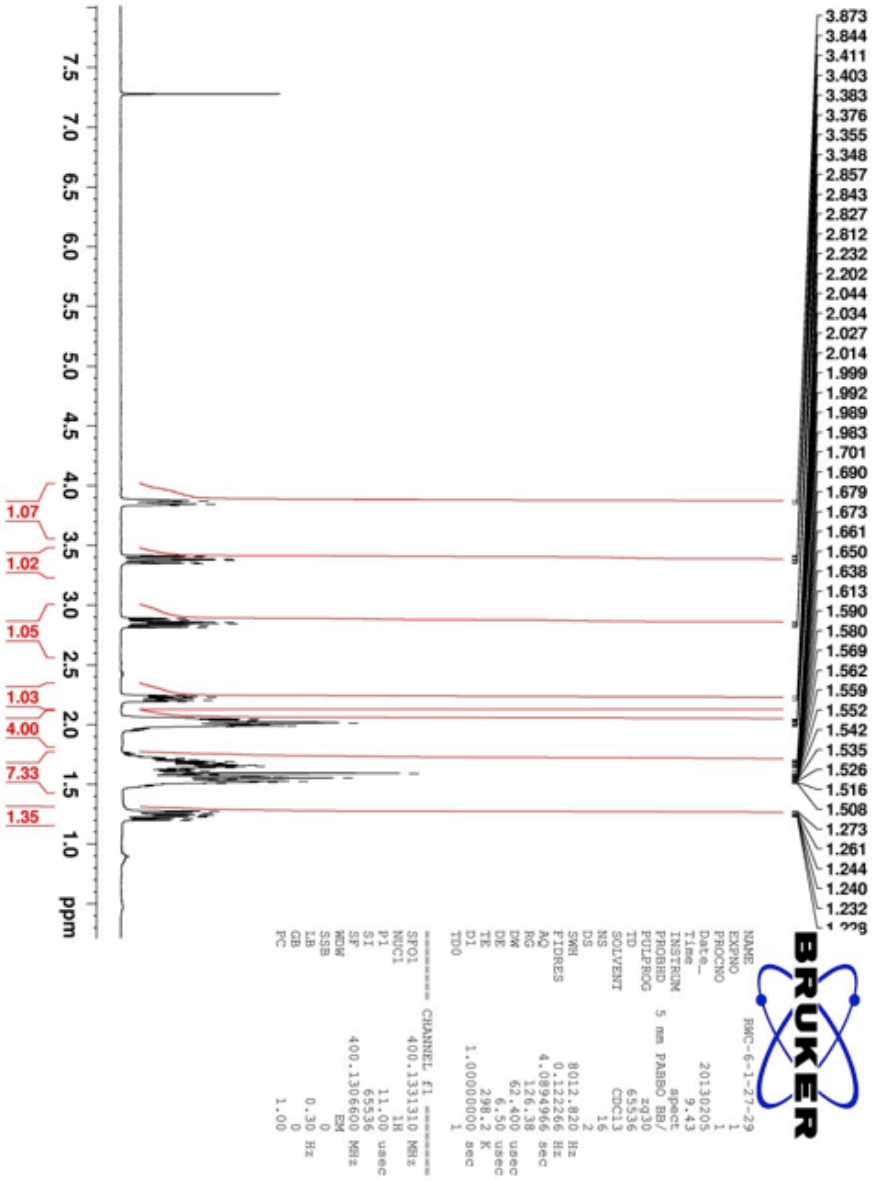

80.06
74.82
33.34
27.75
26.33
22.95
6.61
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME RWC-9-11-13
EXPNO 1
PROCNO 1
Date_ 20130911
Time_ 19.11
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 240
DS 4
SWH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 16384
DW 27.800 usec
DE 6.50 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.00 usec
PL1 5.20 dB
SFO1 75.475253 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 12.20 dB
PL12 19.10 dB
PL13 19.10 dB
SFO2 300.131205 MHz
SI 32768
SF 75.467749 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

oxaspiro[5.5]undecan-7-one (19b)





215.27
80.26
64.66
41.55
39.11
30.84
29.11
25.67
20.39
19.67
200
180
160
140
120
100
80
60
40
20
0
ppm