Supporting Informations

Copper (I) Promoted Cycloalkylation-Peroxidation of Unactivated Alkenes *via* sp^3 C–H Functionalisation

Arghya Banerjee, Sourav K. Santra, Aniket Mishra, Nilufa Khatun and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati

Email: patel@iitg.ernet.in

Contents:

1. Instrumentation and chemicals S1–S2
2. Optimisation of reaction conditions S2–S4
3. Figures and Schemes S4-S7
4. Experimental Procedure S8
5. Determination of regioisomeric mixture S8–S9
6. Crystallographic description S10–S11
7. Mechanistic investigations S11-S12
8. Spectral data S13–S22
9. Spectra (^{1}H and ^{13}C NMR) of compounds S23–S78

Instrumentation and Chemicals:

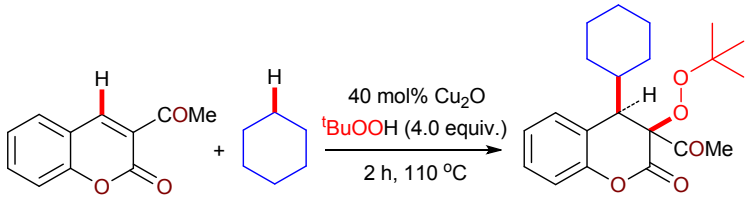
All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 and 600 MHz), $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 and 150

MHz). MS spectra were recorded using ESI mode. IR spectra were recorded in KBr or neat. Starting materials (3-substituted coumarins) (**1-22**) are prepared by reacting salicylaldehydes with active methylene compounds (diethyl malonate / ethylcyanoacetate / ethyl acetoacetate etc.) in presence of catalytic amount of piperidine using Knoevenagel condensation.[1]

1. M. Ghandi, A.-T. Ghomi, and M. Kubicki, *J. Org. Chem.*, 2013, **78**, 2611.

Optimisation of reaction conditions:

Table S1. Screening of Reaction Conditions



(**1**) (**a**) (**1a**) (±)

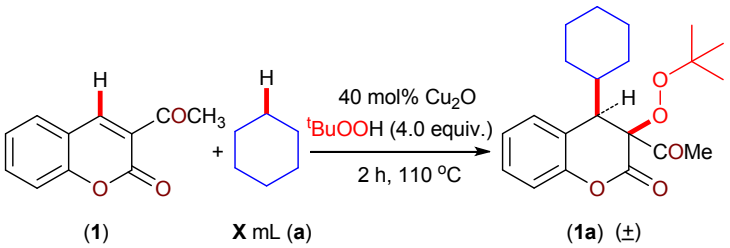
Entry	Cu cat. (mol %)	Solvent	Oxidant (equiv.)	Yield (%)[a,b]
1	CuBr (20.0)	C_6H_{12}	TBHP (4.0)	21
2	Cu_2O (20.0)	C_6H_{12}	TBHP (4.0)	47
3	CuCl (20.0)	C_6H_{12}	TBHP (4.0)	23
4	CuI (20.0)	C_6H_{12}	TBHP (4.0)	20
5	$CuBr_2$ (20.0)	C_6H_{12}	TBHP (4.0)	18
6	$CuCl_2$ (20.0)	C_6H_{12}	TBHP (4.0)	02
7	$Cu(OAc)_2$ (20.0)	C_6H_{12}	TBHP (4.0)	15
8	Cu_2O (30.0)	C_6H_{12}	TBHP (4.0)	54
9	**Cu_2O (40.0)**	**C_6H_{12}**	**TBHP (4.0)**	**60**
10	Cu_2O (40.0)	C_6H_{12}	DTBP (4.0)	07
11[c]	Cu_2O (40.0)	C_6H_{12}	TBHP (4.0)	45
12	——	C_6H_{12}	TBHP (4.0)	00

[a]Reaction conditions: **1** (0.5 mmol), cyclohexane (C_6H_{12}) (**a**) (2.5 mL) at 110 °C for 2 h. [b]Isolated yield. [c]TBHP in 70% water was used in lieu of TBHP in decane.

Detailed Optimisation of the reaction conditions

Detailed studies of the reaction parameters such as amount of cyclohexane and *tert*-butyl hydroperoxide and reaction temperature are given here.

Table S2. Screening of Amount of Cyclohexane

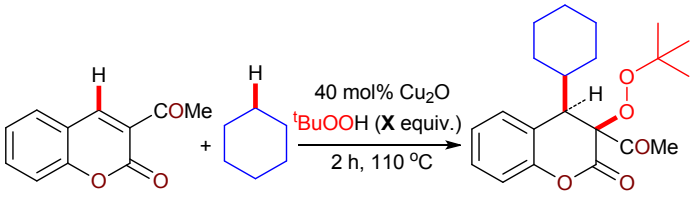


(**1**) **X** mL (**a**) (**1a**) (±)

Entry	Cyclohexane (mL)	Yield[a,b]
1	0.5 mL	18
2	1.0 mL	31
3	1.5 mL	42
4	2.0 mL	53
5	2.5 mL	60
6	3.0 mL	61
7	**a**:chlorobenzene	00[c]
8	**a**:DCE	06[c]
9	**a**:benzene	00[c]

[a]Reaction conditions: **1** (0.5 mmol), cyclohexane (**a**) (**X mL**) and TBHP (4 equiv.) at 110 °C for 2 h. [b]Isolated yield. [c]cyclohexane (2 mmol) was used in 2.5 mL of respective solvents.

Table S3. Screening of TBHP Amount

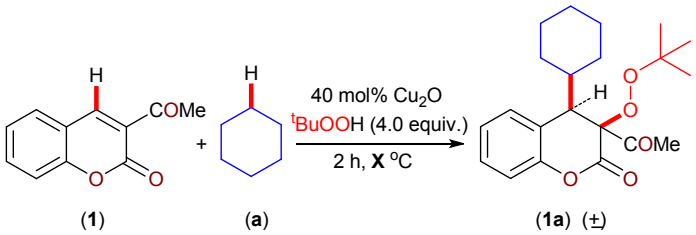


(**1**) (**a**) (**1a**) (±)

Entry	Oxidant (equiv.)	Yield[a,b]
1	TBHP (1.0)	08
2	TBHP (2.0)	22
3	TBHP (3.0)	43
4	TBHP (4.0)	60
5	TBHP (5.0)	62

Reaction conditions: **1** (0.5 mmol), cyclohexane (**a**) (2.5 mL) and TBHP (**X** equiv.) at 110 °C for 2 h. [b]Isolated yield.

Table S4. Screening of Reaction Temperature



Entry	Temperature	Yield[a,b]
1	60 °C	07
2	80 °C	16
3	100 °C	38
4	110 °C	60
5	120 °C	60

Reaction conditions: **1** (0.5 mmol), cyclohexane (**a**) (2.5 mL) and TBHP (4 equiv.) at **X** °C for 2 h. [b]Isolated yield.

Figures and Schemes:

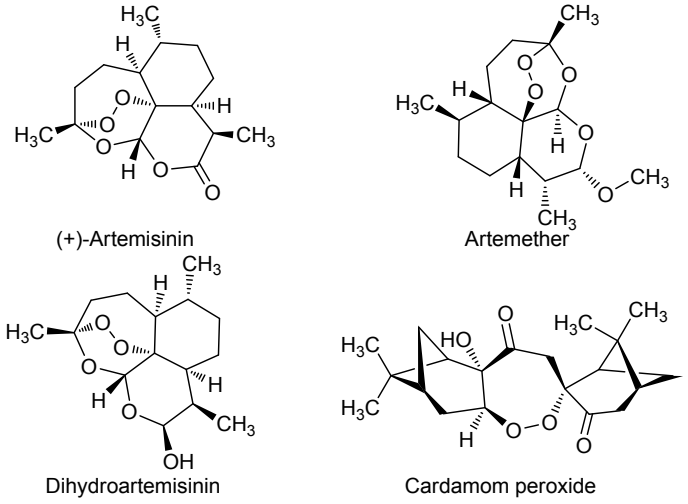


Fig. S1. Some potent anti-malarial drugs

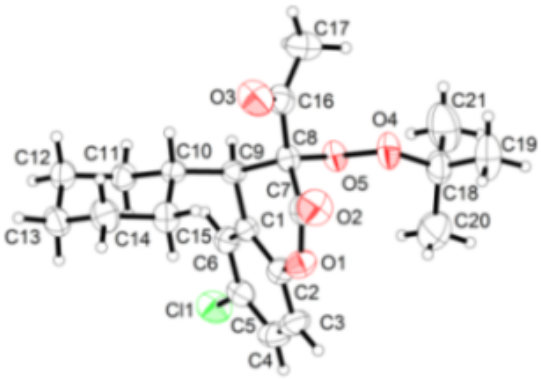


Fig. S2. ORTEP molecular diagram of **2a**.

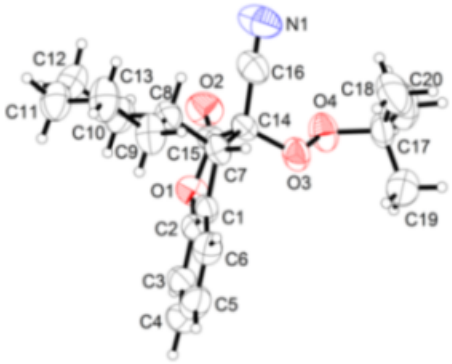


Fig. S3. ORTEP molecular diagram of **20a**.

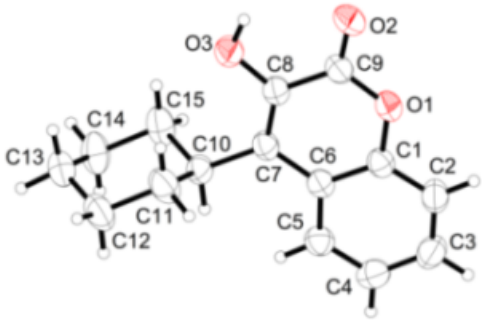
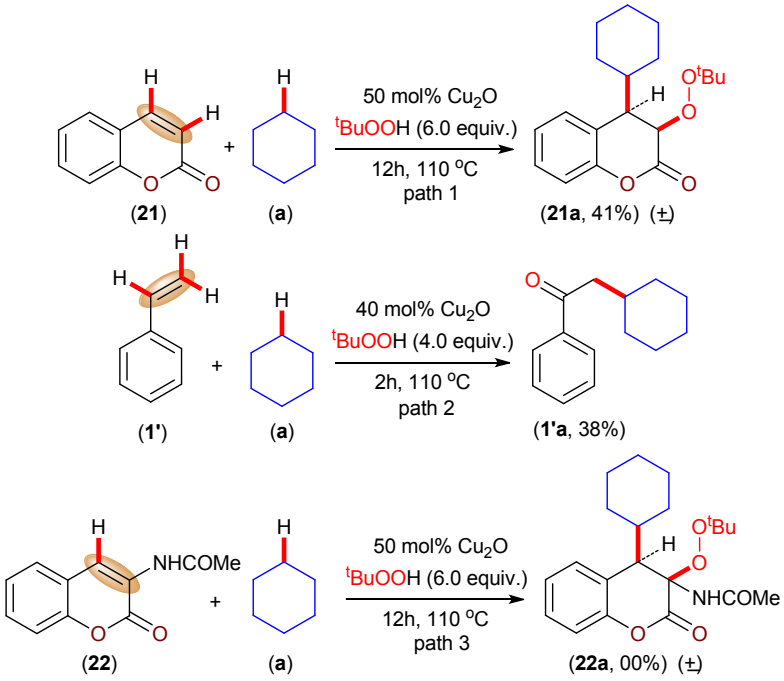
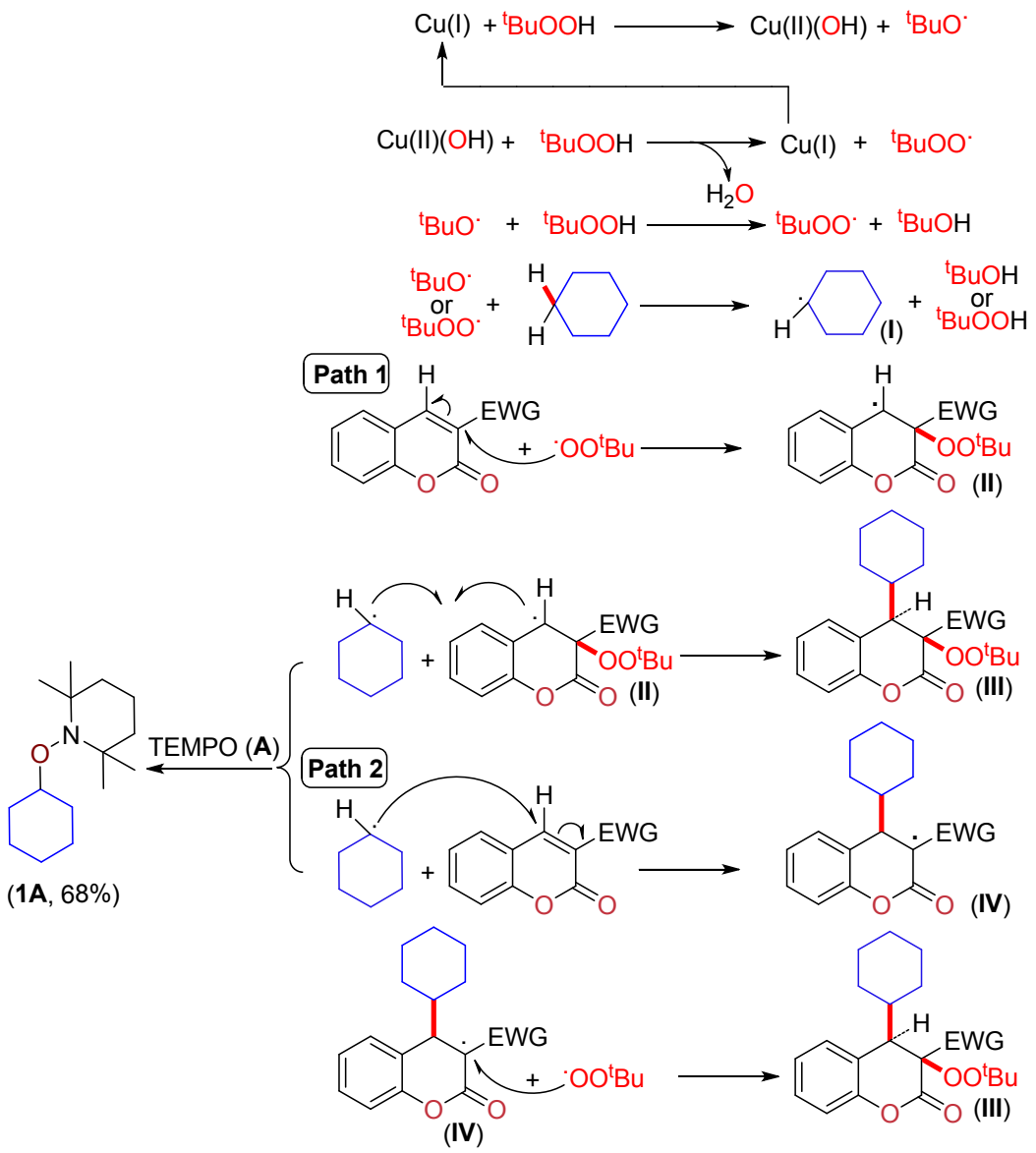


Fig. S4. ORTEP molecular diagram of **1a'**.

Scheme S1. Reactions of unsubstituted coumarin, styrene and 3-acetamidocoumarin



Scheme S2. Plausible mechanism for cycloalkylation-peroxidation

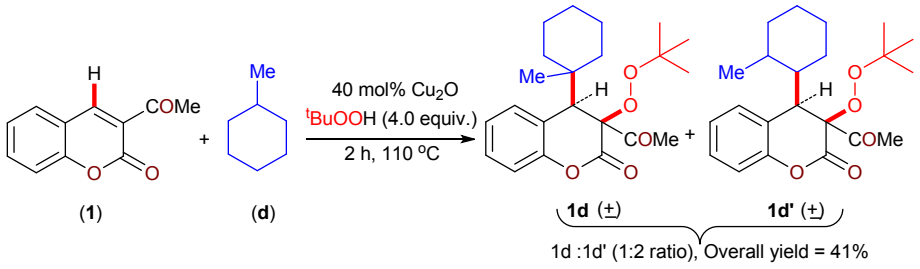


Experimental Procedure:

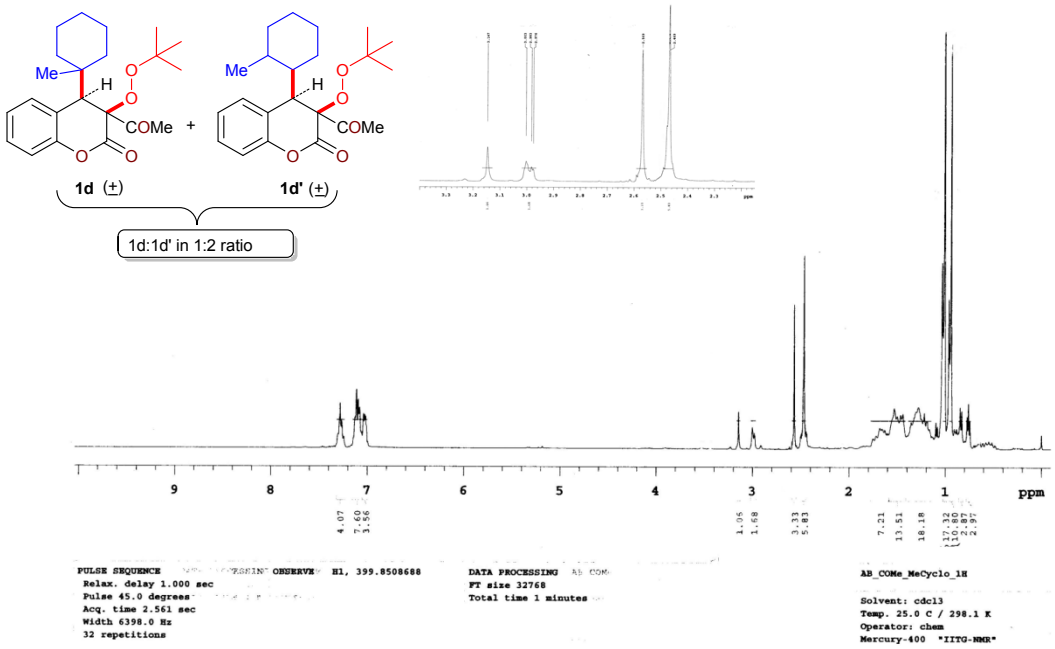
*Synthesis of 3-acetyl-3-(tert-butylperoxy)-4-cyclohexylchroman-2-one (**1a**) from 3-acetyl-2H-chromen-2-one (**1**), cyclohexane (**a**) and tert-butyl hydroperoxide*

To an oven-dried 25 mL round bottom flask fitted with a reflux condenser was added 3-acetylcoumarin (**1**) (0.094g, 0.5 mmol), decane solution of TBHP (5−6 M) (400 µL, 2.0 mmol), Cu_2O (0.030g, 0.2 mmol), and cyclohexane (2.5 mL). The reaction mixture was refluxed in an oil bath preheated to 110 °C. After completion of the reaction (2 h) solvent was evaporated under reduced pressure. The reaction mixture was cooled to room temperature, admixed with water (5 mL) and the product was extracted with ethyl acetate (2 x10 mL). The organic layer was dried over anhydrous sodium sulphate (Na_2SO_4), and solvent was evaporated under reduced pressure. The crude product so obtained was purified over a column of silica gel (hexane / ethyl acetate, 10:0.1) to give pure 3-acetyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (**1a**) (0.108g, yield 60%). The identity and purity of the product was confirmed by spectroscopic analysis.

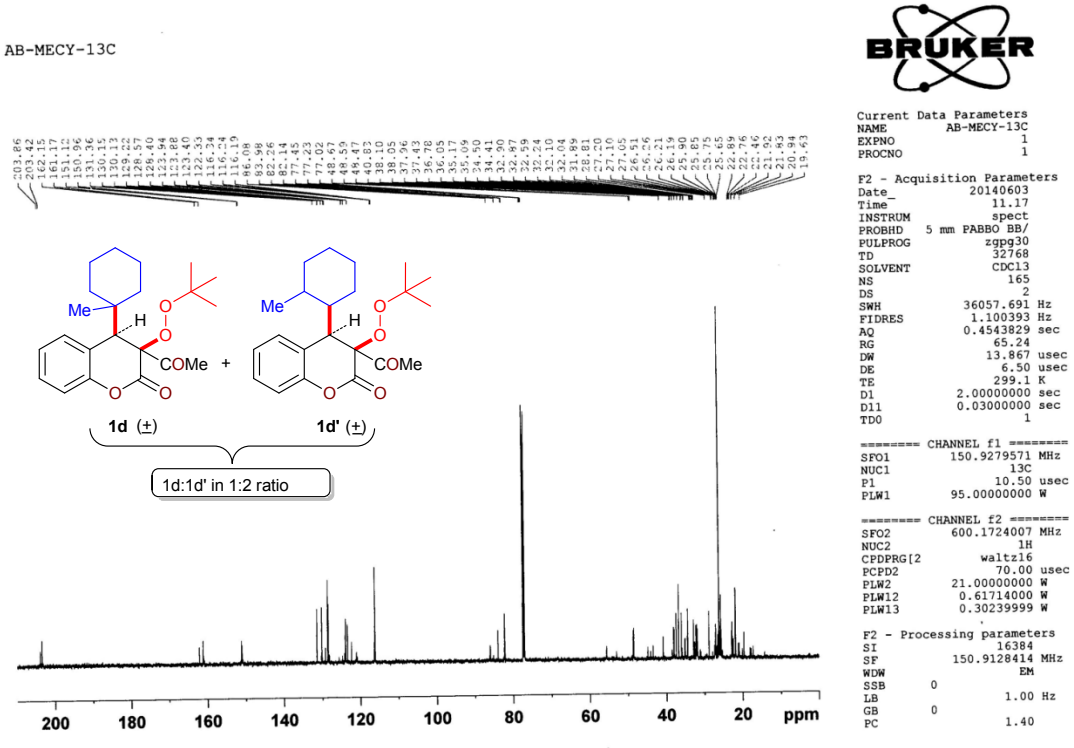
Determination of Regioisomeric Mixture: *(A) Cu-catalyzed cycloalkylation-peroxidation of methyl cyclohexane (**d**) with 3-acetylcoumarin (**1**).*



^{1}H NMR (400 MHz, $CDCl_3$) of regioisomeric peroxides derived from methyl cyclohexane (**d**):



^{13}C NMR (150 MHz, $CDCl_3$) of regioisomeric peroxides derived from methylcyclohexane (**d**):



Crystallographic Description

Crystal data were collected with Bruker Smart Apex-II CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. Cell parameters were retrieved using SMART [a] software and refined with SAINT[a] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarisation effects. Absorption corrections were applied with the program SADABS[b]. The structure was solved by direct methods implemented in SHELX-97[c] program and refined by full-matrix least-squares methods on F2. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. colourless crystals were isolated in rectangular shape from acetonitrile at room temperature.

a. SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
b. SAINT V 4.035 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1995.
c. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen (Germany), 1997.

CCDC number for compound 2a: CCDC 1011616. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Crystallographic description of 2a: Crystal dimension (mm): 0.34 x 0.22 x 0.20. $C_{21}H_{27}ClO_5$, Mr = 394.88. monoclinic, space group p 21/n; a = 17.6306(4)Å, b = 6.5284(2)Å, c = 18.1875(4) Å; α = 90°, β = 96.701(1)°, γ = 90°, V = 2079.07(9) Å^3 ; Z = 4; ρ_{cal}= 1.262g/cm^3; μ (mm^{-1}) = 0.211; *F (000)* = 840.0; Reflection collected / unique = 3665 / 3560; Refinement method = Full-matrix least-squares on F^2; Final R indices [I>2σ_I] R1 = 0.0395, wR2 = 0.0988, R indices (all data) R1 = 0.0484, wR2 = 0.1038; goodness of fit = 1.078.

CCDC number for compound 20a: CCDC 1011614. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

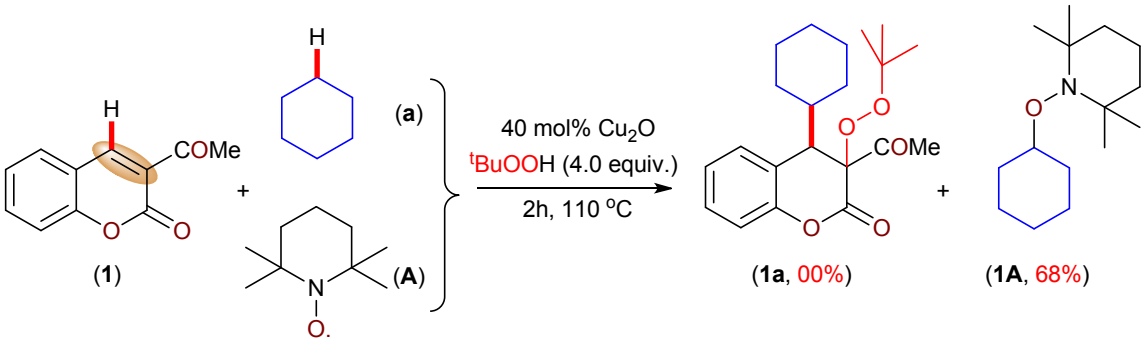
Crystallographic description of 20a: Crystal dimension (mm): 0.34 x 0.22 x 0.20. $C_{20}H_{25}NO_4$, Mr = 343.41. monoclinic, space group p 21/n; a = 9.6382(7) Å, b = 12.5190(9) Å, c = 16.1542(12) Å; α = 90°, β = 101.439(2) °, γ = 90°, V = 1910.5(2) Å^3 ; Z = 4; ρ_{cal}= 1.194g/cm^3; μ (mm^{-1}) = 0.083; *F (000)* = 736.0; Reflection collected / unique = 1879 / 1469; Refinement method = Full-matrix least-squares on F^2; Final R indices [I>2σ_I] R1 = 0.0374, wR2 = 0.0980, R indices (all data) R1 = 0.0483, wR2 = 0.1100; goodness of fit = 1.150.

CCDC number for compound 1a': CCDC 1011615. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Crystallographic description of 1a': Crystal dimension (mm): 0.32 x 0.20 x 0.18. $C_{15}H_{16}O_3$, Mr = 244.28. monoclinic, space group p 21/n; a = 5.518(2)) Å, b = 26.082(10) Å, c = 8.581(5) Å; α = 90°, β = 94.23(4) °, γ = 90°, V = 1231.6(10) Å^3 ; Z = 4; ρ_{cal}= 1.379 g/cm^3; μ (mm^{-1}) = 0.091; *F (000)* = 520.0; Reflection collected / unique = 2175 / 2174; Refinement method = Full-matrix least-squares on F^2; Final R indices [I>2σ_I] R1 = 0.0522, wR2 = 0.1400, R indices (all data) R1 = 0.0677, wR2 = 0.1497; goodness of fit = 1.144.

Mechanistic investigation:

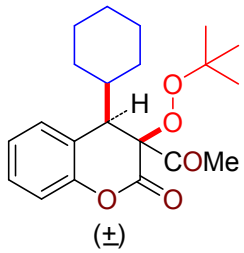
Trapping of radical intermediates with radical scavenger TEMPO: An oven-dried 25 mL round bottom flask was charged with 3-acetylcoumarin (**1**) (0.094 g, 0.5 mmol), Cu_2O (0.030 g, 40 mol %), decane solution of TBHP (5−6 M) (400 μL, 4 mmol), TEMPO (**A**) (0.078 g, 0.5 mmol) in cyclohexane (**a**) (2.5 mL). The flask was fitted to a reflux condenser and the reaction mixture was stirred in a preheated oil bath at 110 °C for 2 h. After completion of the reaction the cyclohexyl-TEMPO adduct 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (**1A**) was isolated in 68% yield but no traces of the desired product (**1a**) was obtained. This experiment supports the formation of cyclohexyl radical in the medium from cyclohexane (**a**) induced radically by Cu_2O/TBHP and also the radical nature of the mechanism.



Scheme S3: Trapping of cyclohexyl intermediate with TEMPO

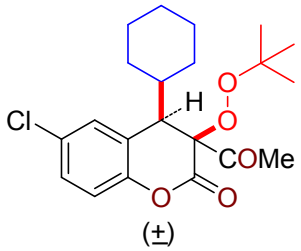
Spectral Data:

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (1a):



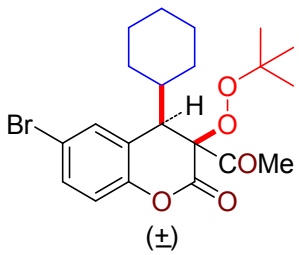
Solid; m.p. 179-181 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.27 (m, 1H), 7.14–7.07 (m, 2H), 7.03 (d, 1H, J = 8.0 Hz), 2.97 (d, 1H, J = 3.2 Hz), 2.47 (s, 3H), 1.76–1.51 (m, 6H), 1.30–1.12 (m, 3H), 1.01 (s, 9H), 0.91–0.81 (m, 1H), 0.64–0.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 203.5, 161.2, 151.2, 130.2, 128.6, 123.9, 121.1, 116.3, 86.1, 82.3, 48.9, 38.4, 32.4, 27.1, 26.9, 26.7, 26.2, 25.9, 25.8; IR (KBr, cm^{-1}): 2985, 2976, 2935, 2956, 1779, 1717, 1615, 1587, 1491, 1462, 1451, 1422, 1389, 1380, 1365, 1355, 1303, 1261, 1241, 1197, 1179, 1118, 1068, 1015, 918, 876, 779, 774; HRMS (ESI) calcd for $C_{21}H_{28}O_5$ (M + Na$^+$) 383.1829, found 383.1830.

3-Acetyl-3-(*tert*-butylperoxy)-6-chloro-4-cyclohexylchroman-2-one (2a):



Solid; m.p. 167-170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.25 (m, 1H), 7.08 (d, 1H, J = 2.4 Hz), 6.98 (d, 1H, J = 9.2 Hz), 2.95 (d, 1H, J = 2.4 Hz), 2.47 (s, 3H), 1.74–1.71 (m, 2H), 1.61–1.54 (m, 4H), 1.29–1.12 (m, 3H), 1.03 (s, 9H), 0.94–0.84 (m, 1H), 0.62–0.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.0, 160.6, 149.7, 129.8, 128.9, 128.7, 122.8, 117.5, 85.5, 82.5, 48.7, 38.2, 32.2, 27.0, 26.9, 26.5, 26.2, 25.8, 25.7; IR (KBr, cm^{-1}): 2983, 2945, 2924, 2857, 1794, 1723, 1482, 1452, 1415, 1364, 1357, 1273, 1258, 1227, 1215, 1196, 1179, 1147, 1118, 1094, 1083, 1066, 1042, 1029, 930, 911, 898, 891, 882, 873, 848, 835, 812, 790, 759, 745, 745, 713; HRMS (ESI) calcd for $C_{21}H_{27}ClO_5$ (M + Na$^+$) 417.1439, found 417.1438.

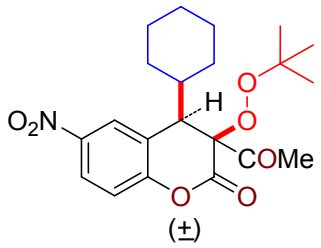
3-Acetyl-6-bromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (3a):



Solid; m.p. 152-154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, 1H, J = 8.4 Hz), 7.19 (d, 1H, J = 2.4 Hz), 6.89 (d, 1H, J = 9.2 Hz), 2.91 (d, 1H, J = 2.8 Hz), 2.44 (s, 3H), 1.71–1.68 (m, 2H), 1.59–1.51 (m, 4H), 1.23–1.09 (m, 3H), 1.00 (s, 9H), 0.92–0.86 (m, 1H), 0.56–0.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 202.9, 160.6, 150.4, 132.7, 131.7, 131.2, 118.9, 118.0, 85.6, 82.6, 48.8, 38.4, 32.3, 27.1, 26.9, 26.6, 26.3, 25.9, 25.8; IR (KBr, cm^{-1}): 2940,

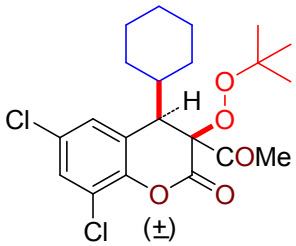
2926, 2852, 1791, 1702, 1697, 1684, 1653, 1633, 1559, 1478, 1450, 1412, 1389, 1364, 1260, 1245, 1225, 1175, 1153, 1093, 1022, 912, 891, 873, 858, 812, 773; HRMS (ESI) calcd for $C_{21}H_{27}BrO_5$ (M + Na^+) 461.0934, found 461.0928.

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-6-nitrochroman-2-one (4a):



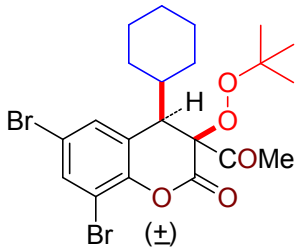
Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, 1H, J = 9.0 Hz), 8.02 (d, 1H, J = 2.8 Hz), 7.17 (d, 1H, J = 8.8 Hz), 3.09 (d, 1H, J = 2.8 Hz), 2.49 (s, 3H), 1.74–1.53 (m, 6H), 1.29–1.08 (m, 3H), 1.01 (s, 9H), 0.90–0.79 (m, 1H), 0.56–0.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.4, 159.6, 155.6, 143.8, 125.7, 124.7, 122.6, 117.2, 85.2, 82.8, 48.8, 38.2, 32.1, 27.1, 26.9, 26.4, 26.2, 25.8, 25.6; IR (KBr, cm^{-1}): 3090, 2984, 2925, 2853, 1792, 1726, 1627, 1589, 1559, 1527, 1483, 1450, 1433, 1392, 1367, 1341, 1322, 1308, 1260, 1232, 1219, 1184, 1154, 1119, 1087, 1066, 1043, 1029, 1010, 967, 932, 915, 902, 868, 841, 812, 777, 757, 752, 742; HRMS (ESI) calcd for $C_{21}H_{27}NO_7$ (M + Na^+) 428.1680, found 428.1678.

3-Acetyl-3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexylchroman-2-one (5a):



Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, 1H, J = 2.4 Hz), 6.94 (d, 1H, J = 2.0 Hz), 2.92 (d, 1H, J = 3.2 Hz), 2.41 (s, 3H), 1.67–1.64 (m, 2H), 1.55–1.48 (m, 4H), 1.22–1.04 (m, 3H), 0.98 (s, 9H), 0.88–0.78 (m, 1H), 0.56–0.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.6, 159.4, 145.8, 129.1, 128.8, 128.2, 124.3, 122.1, 85.2, 82.6, 49.0, 38.0, 32.2, 27.0, 26.9, 26.4, 26.0, 25.8, 25.6; IR (KBr, cm^{-1}): 3084, 2979, 2928, 2853, 1795, 1721, 1458, 1420, 1363, 1262, 1249, 1212, 1182, 1154, 1123, 1100, 1070, 1044, 1014, 973, 937, 917, 900, 881, 869, 855, 825, 786, 754, 747; HRMS (ESI) calcd for $C_{21}H_{26}Cl_2O_5$ (M + Na^+) 451.1049, found 451.1054.

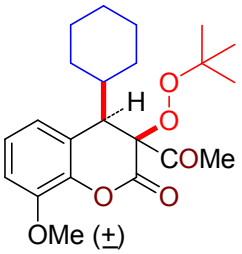
3-Acetyl-6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (6a):



Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, 1H, J = 2.4 Hz), 7.13 (d, 1H, J = 2.0 Hz), 2.91 (d, 1H, J = 3.2 Hz), 2.44 (s, 3H), 1.70–1.49 (m, 6H), 1.23–1.09 (m, 3H), 1.01 (s, 9H), 0.92–0.85 (m, 1H), 0.56–0.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.6, 159.5, 147.4, 134.8, 131.8, 124.8, 116.4, 111.1, 85.3, 82.8, 49.2, 38.2, 32.3, 27.1, 27.0, 26.9, 26.5, 26.2, 25.8, 25.7; IR (KBr, cm^{-1}): 2959, 2928, 2854, 1801, 1723, 1683, 1646, 1566, 1558, 1449,

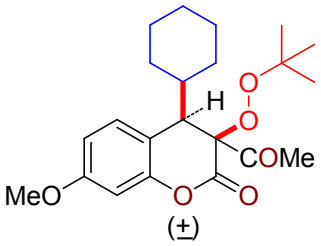
1413, 1365, 1261, 1244, 1189, 1148, 1095, 1023, 931, 865, 802; HRMS (ESI) calcd for $C_{21}H_{26}Br_2O_5$ (M + Na^+) 539.0039, found 539.0038.

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxychroman-2-one (7a):



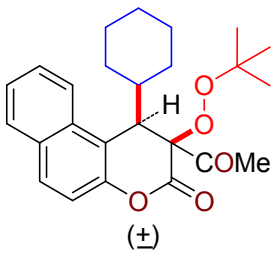
Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.02 (d, 1H, J = 7.8 Hz), 6.87 (d, 1H, J = 7.8 Hz), 6.64 (d, 1H, J = 7.2 Hz), 3.86 (s, 3H), 2.94 (d, 1H, J = 3.0 Hz), 2.46 (s, 3H), 1.73–1.48 (m, 6H), 1.26–1.10 (m, 3H), 0.99 (s, 9H), 0.87–0.83 (m, 1H), 0.64–0.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 203.5, 160.6, 147.1, 140.4, 123.7, 122.2, 121.8, 111.4, 85.8, 82.2, 56.2, 48.9, 38.2, 32.5, 27.2, 27.0, 26.7, 26.1, 25.9, 25.8; IR (KBr, cm^{-1}): 2980, 2931, 2855, 1781, 1721, 1618, 1588, 1558, 1506, 1485, 1458, 1366, 1322, 1305, 1276, 1248. 1185, 1161, 1108, 1062, 1016, 971, 913, 869, 800, 785, 761, 734; HRMS (ESI) calcd for $C_{22}H_{30}O_6$ (M + Na^+) 413.1934, found 413.1940.

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-7-methoxychroman-2-one (8a):



Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.96 (d, 1H, J = 8.4 Hz), 6.66 (dd, 1H, J_1 = 9.0 Hz, J_2 = 3.0 Hz), 6.58 (d, 1H, J = 2.4 Hz), 3.80 (s, 3H), 2.91 (d, 1H, J = 3.0 Hz), 2.45 (s, 3H), 1.73–1.66 (m, 2H), 1.58–1.49 (m, 4H), 1.27–1.12 (m, 3H), 1.03 (s, 9H), 0.88–0.85 (m, 1H), 0.59–0.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 203.5, 161.2, 159.9, 151.9, 130.7, 112.9, 109.9, 101.9, 86.2, 82.3, 55.7, 48.3, 38.6, 32.3, 27.0, 26.8, 26.7, 26.3, 25.9, 25.8; IR (KBr, cm^{-1}): 2990, 2969, 2927, 2850, 1775, 1722, 1624, 1585, 1559, 1507, 1453, 1432, 1364, 1321, 1285, 1277, 1238, 1210, 1189, 1156, 1124, 1090, 1045, 1030, 922, 902, 886, 870, 859, 838, 806, 792, 763, 747, 712; HRMS (ESI) calcd for $C_{22}H_{30}O_6$ (M + Na^+) 413.1934, found 413.1944.

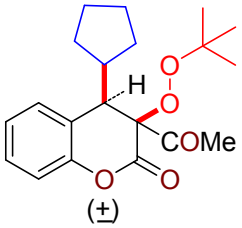
2-Acetyl-2-(*tert*-butylperoxy)-1-cyclohexyl-1H-benzo[*f*]chromen-3(2H)-one (9a):



Solid; m.p. 153-155 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, 1H, J = 8.8 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.77 (d, 1H, J = 8.8 Hz), 7.55 (d, 1H, J = 7.2 Hz), 7.45 (t, 1H, J = 7.0 Hz), 7.20 (t, 1H, J = 9.2 Hz), 3.75 (d, 1H, J = 3.6 Hz), 2.54 (s, 3H), 1.84–1.42 (m, 6H), 1.18–1.05 (m, 3H), 0.88 (s, 9H), 0.85–0.79 (m, 1H), 0.75–0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.7, 161.3, 148.8, 132.3, 131.2, 129.4, 129.1, 127.1, 125.1, 123.9, 116.7, 116.2, 85.5, 82.3, 44.3, 39.1, 33.3, 28.6, 27.5, 26.8, 26.4, 26.2, 25.6; IR (KBr, cm^{-1}):

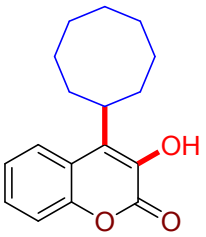
2942, 2927, 2851, 1786, 1747, 1721, 1628, 1603, 1559, 1516, 1507, 1463, 1438, 1395, 1367, 1264, 1220, 1186, 1161, 1117, 1080, 1063, 1045, 1028, 975, 91, 864, 817, 789, 752; HRMS (ESI) calcd for $C_{25}H_{30}O_5$ (M + Na^+) 433.1985, found 433.1990.

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclopentylchroman-2-one (1b):



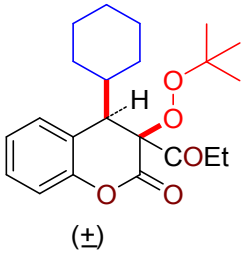
Solid; m.p. 160-162 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.25 (m, 1H), 7.12–7.06 (m, 2H), 7.01 (d, 1H, J = 8.0 Hz), 3.25 (d, 1H, J = 4.0 Hz), 2.46 (s, 3H), 1.93–1.84 (m, 1H), 1.69–1.65 (m, 2H), 1.43–1.35 (m, 4H), 1.29–1.21 (m, 1H), 0.99 (s, 9H), 0.79–0.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.3, 161.2, 151.3, 130.4, 128.7, 123.9, 121.7, 116.3, 86.5, 82.3, 45.6, 39.7, 31.1, 27.2, 26.5, 26.2, 24.4, 23.5; IR (KBr, cm^{-1}): 2987, 2957, 2872, 1781, 1717, 1615, 1588, 1489, 1460, 1423, 1377, 1366, 1356, 1226, 1197, 1169, 1132, 1117, 1093, 1056, 1017, 988, 918, 904, 774, 754, 720; HRMS (ESI) calcd for $C_{20}H_{26}O_5$ (M + Na^+) 369.1672, found 369.1674.

4-Cyclooctyl-3-hydroxy-2H-chromen-2-one (1c'):



Solid; m.p. 149-152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, 1H, J = 8.4 Hz), 7.46–7.43 (m, 1H), 7.41–7.23 (m, 2H), 6.42 (s, 1H), 2.22–2.14 (m, 1H), 1.88–1.54 (m, 14H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.7, 152.9, 149.4, 136.5, 130.5, 128.3, 127.4, 124.3, 117.4, 38.2, 31.9, 27.1, 26.9, 26.6; IR (KBr, cm^{-1}): 3427, 3353, 3282, 2921, 2850, 1705, 1630, 1600, 1558, 1489, 1455, 1372, 1339, 1299, 1275, 1250, 1176, 1156, 1120, 1002, 943, 775, 753, 740; HRMS (ESI) calcd for $C_{17}H_{20}O_3$ (M - H^+) 271.1332, found 271.1323.

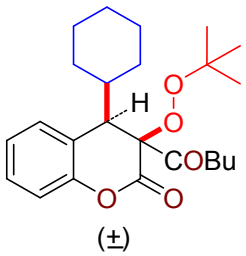
3-(*tert*-Butylperoxy)-4-cyclohexyl-3-propionylchroman-2-one (10a):



Solid; m.p. 159-161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (t, 1H, J = 8.0 Hz), 7.13–7.07 (m, 2H), 7.03 (d, 1H, J = 8.4 Hz), 3.05–2.97 (m, 1H), 2.95 (d, 1H, J = 2.4 Hz), 2.84–2.74 (m, 1H), 1.79–1.67 (m, 2H), 1.59–1.48 (m, 4H), 1.34–1.21 (m, 2H), 1.17 (t, 3H, J = 7.0 Hz), 1.00 (s, 9H), 0.96–0.81 (m, 2H), 0.63–0.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.9, 161.3, 151.2, 130.1, 128.5, 123.9, 121.2, 116.2, 86.2, 82.2, 49.2, 38.4, 32.3, 31.9, 26.9, 26.6, 26.2, 25.9, 25.8, 7.6; IR (KBr, cm^{-1}): 2973, 2931, 2857, 1784, 1718, 1615, 1588, 1490, 1458, 1401, 1389, 1376, 1368, 1363, 1351, 1323, 1260, 1225, 1179, 1155, 1119, 1082, 1066, 1020, 965,

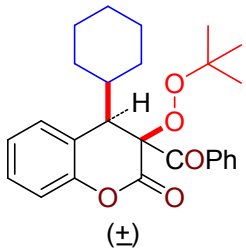
940, 907, 898, 875, 842, 788, 757, 749, 703; HRMS (ESI) calcd for $C_{22}H_{30}O_5$ (M + Na^+) 397.1985, found 397.1981.

3-(*tert*-Butylperoxy)-4-cyclohexyl-3-pentanoylchroman-2-one (11a):



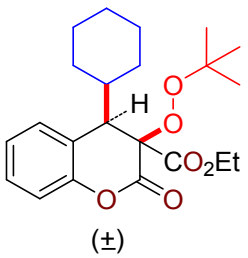
Solid; m.p. 130-134 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (t, 1H, J = 7.4 Hz), 7.13–7.06 (m, 2H), 7.02 (d, 1H, J = 8.4 Hz), 2.96 (s, 1H), 2.92–2.88 (m, 1H), 2.78–2.70 (m, 1H), 1.78–1.67 (m, 4H), 1.58–1.53 (m, 4H), 1.24–1.12 (m, 4H), 1.00 (s, 9H), 0.99–0.93 (m, 3H), 0.89–0.80 (m, 2H), 0.62–0.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.3, 161.3, 151.2, 130.1, 128.5, 123.8, 121.2, 116.2, 86.0, 82.2, 49.1, 40.4, 38.3, 32.3, 26.8, 26.7, 26.2, 25.9, 25.8, 16.7, 13.9; IR (KBr, cm^{-1}): 2976, 2926, 2854, 1783, 1723, 1614, 1585, 1488, 1457, 1365, 1259, 1222, 1185, 1157, 1147, 1114, 1084, 1021, 966, 948, 911, 898, 877, 791, 764, 705; HRMS (ESI) calcd for $C_{24}H_{34}O_5$ (M + Na^+) 425.2298, found 425.2302.

3-Benzoyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (12a):



Solid; m.p. 158-160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, 2H, J = 7.2 Hz), 7.57 (t, 1H, J = 7.0 Hz), 7.45 (t, 2H, J = 7.4 Hz), 7.31–7.28 (m, 1H), 7.14–7.13 (m, 2H), 7.06 (d, 1H, J = 8.4 Hz), 3.35 (s, 1H), 1.90–1.87 (m, 1H), 1.71–1.58 (m, 4H), 1.53–1.49 (m, 2H), 1.32–1.18 (m, 3H), 0.89 (s, 9H), 0.73–0.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.3, 160.5, 151.2, 136.4, 132.9, 130.2, 129.6, 128.7, 128.3, 123.9, 120.9, 116.2, 87.8, 82.3, 50.6, 38.6, 32.4, 26.7, 26.6, 26.2, 25.9, 25.8; IR (KBr, cm^{-1}): 2977, 2927, 2853, 1778, 1737, 1689, 1615, 1600, 1489, 1457, 1446, 1365, 1276, 1247, 1223, 1198, 1171, 1131, 1116, 1066, 1019, 952, 924, 880, 812, 770, 754; HRMS (ESI) calcd for $C_{26}H_{30}O_5$ (M + Na^+) 445.1985, found 445.1992.

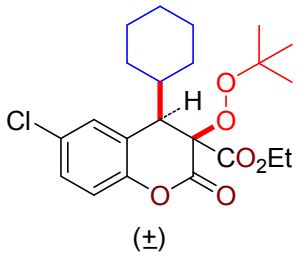
Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (13a):



Gummy; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.29–7.28 (m, 1H), 7.09 (t, 1H, J = 7.2 Hz), 7.06–7.02 (m, 2H), 4.49–4.46 (m, 1H), 4.37–4.34 (m, 1H), 3.08 (d, 1H, J = 3.0 Hz), 1.79–1.69 (m, 1H), 1.68–1.63 (m, 2H), 1.62–1.58 (m, 2H), 1.55–1.53 (m, 1H), 1.39 (t, 3H, J = 7.2 Hz), 1.25–1.21 (m, 2H), 1.20–1.14 (m, 1H), 1.01 (s, 9H), 0.89–0.87 (m, 1H), 0.65–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.7, 160.7, 151.1, 130.1, 128.6, 123.9, 120.9, 116.2, 83.4, 81.9, 62.1, 50.0, 39.3, 32.1, 27.0, 26.8, 26.3, 26.1,

25.8, 14.4; IR (KBr, cm^{-1}): 2982, 2932, 2857, 1797, 1743, 1587, 1490, 1457, 1389, 1365, 1346, 1319, 1305, 1280, 1248, 1224, 1194, 1178, 1161, 1115, 1066, 1046, 1038, 991, 878, 863, 840, 808, 768, 758, 742, 706; HRMS (ESI) calcd for $C_{22}H_{30}O_6$ (M + Na^+) 413.1934, found 413.1936.

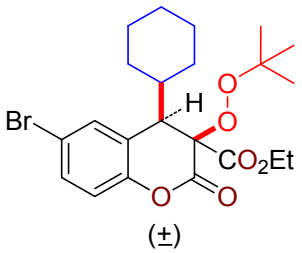
Ethyl 3-(*tert*-butylperoxy)-6-chloro-4-cyclohexyl-2-oxochroman-3-carboxylate (14a):



(±)

Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25 (d, 1H, J = 8.8 Hz), 7.05 (d, 1H, J = 2.4 Hz), 6.99 (d, 1H, J = 8.8 Hz), 4.52–4.44 (m, 1H), 4.40–4.32 (m, 1H), 3.06 (d, 1H, J = 3.2 Hz), 1.77–1.55 (m, 6H), 1.39 (t, 3H, J = 7.0 Hz), 1.32–1.27 (m, 1H), 1.24–1.11 (m, 2H), 1.03 (m, 9H), 0.97–0.87 (m, 1H), 0.68–0.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 160.1, 149.7, 129.7, 128.9, 128.6, 122.8, 117.5, 82.9, 82.0, 62.2, 49.9, 39.1, 31.9, 27.0, 26.7, 26.2, 25.9, 25.7, 14.4; IR (KBr, cm^{-1}): 2983, 2928, 2855, 1795, 1741, 1653, 1628, 1559, 1539, 1507, 1483, 1451, 1416, 1366, 1339, 1281, 1250, 1228, 1195, 1160, 1126, 1092, 1032, 975, 923, 861, 812, 754, 733; HRMS (ESI) calcd for $C_{22}H_{29}ClO_6$ (M + Na^+) 447.1545, found 447.1558.

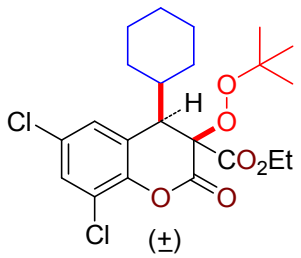
Ethyl 6-bromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (15a):



(±)

Gummy; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.40 (d, 1H, J = 8.4 Hz), 7.19 (d, 1H, J = 1.8 Hz), 6.93 (d, 1H, J = 8.4 Hz), 4.48–4.45 (m, 1H), 4.38–4.35 (m, 1H), 3.05 (d, 1H, J = 3.0 Hz), 1.76–1.55 (m, 6H), 1.39 (t, 3H, J = 7.5 Hz), 1.30–1.13 (m, 3H), 1.02 (s, 9H), 0.94–0.91 (m, 1H), 0.64–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.3, 159.9, 150.2, 132.6, 131.6, 123.2, 117.9, 116.4, 82.9, 82.0, 62.2, 49.8, 39.2, 31.9, 27.1, 26.6, 26.2, 25.9, 25.7, 14.3; IR (KBr, cm^{-1}): 2981, 2930, 2855, 1796, 1747, 1479, 1451, 1414, 1388, 1365, 1336, 1274, 1248, 1193, 1176, 1158, 1126, 1093, 1067, 1044, 1032, 876, 848, 818, 757; HRMS (ESI) calcd for $C_{22}H_{29}BrO_6$ (M + Na^+) 491.1040, found 491.1039.

Ethyl 3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexyl-2-oxochroman-3-carboxylate (16a):

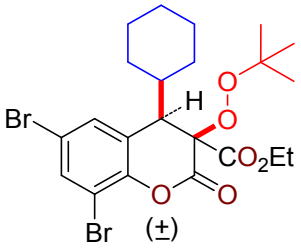


(±)

Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34 (d, 1H, J = 2.4 Hz), 6.93 (d, 1H, J = 2.4 Hz), 4.49–4.41 (m, 1H), 4.38–4.29 (m, 1H), 3.04 (d, 1H, J = 3.2 Hz), 1.73–1.53 (m, 6H), 1.36 (t, 3H, J = 7.2 Hz), 1.26–1.09 (m, 3H), 0.99 (s, 9H), 0.95–0.83 (m, 1H), 0.65–0.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.9, 158.9,

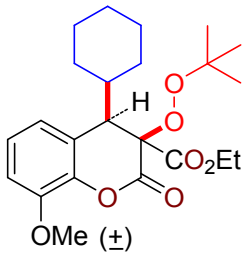
145.8, 129.2, 128.8, 128.2, 124.3, 122.2, 82.6, 82.3, 62.4, 50.3, 38.9, 32.1, 27.2, 26.6, 26.1, 25.9, 25.7, 14.3; IR (KBr, cm^{-1}): 2982, 2931, 2855, 1805, 1748, 1578, 1457, 1366, 1260, 1245, 1245, 1214, 1192, 1181, 1154, 1127, 1099, 1069, 1045, 1031, 996, 901, 860, 828, 755; HRMS (ESI) calcd for $C_{22}H_{28}Cl_2O_6$ (M + Na^+) 481.1155, found 481.1160.

Ethyl 6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (17a):



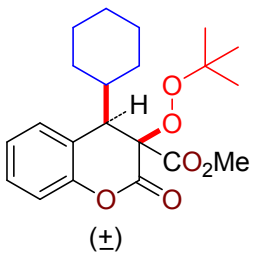
Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, 1H, J = 2.4 Hz), 7.11 (d, 1H, J = 2.4 Hz), 4.49–4.41 (m, 1H), 4.36–4.28 (m, 1H), 3.03 (d, 1H, J = 3.2 Hz), 1.73–1.53 (m, 6H), 1.36 (t, 3H, J = 7.0 Hz), 1.26–1.10 (m, 3H), 0.99 (s, 9H), 0.95–0.80 (m, 1H), 0.64–0.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.9, 158.9, 147.4, 134.7, 131.7, 124.7, 116.4, 110.9, 82.7, 82.3, 62.4, 50.3, 39.1, 32.1, 27.2, 26.7, 26.2, 25.9, 25.7, 14.3; IR (KBr, cm^{-1}): 2981, 2929, 2854, 1803, 1747, 1606, 1568, 1559, 1506, 1448, 1388, 1365, 1337, 1283, 1259, 1241, 1189, 1174, 1151, 1127, 1095, 1068, 1044, 1031, 995, 930, 900, 860, 798, 770, 752; HRMS (ESI) calcd for $C_{22}H_{28}Br_2O_6$ (M + Na^+) 569.0145, found 569.0146.

Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxy-2-oxochroman-3-carboxylate (18a):



Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.04 (t, 1H, J = 8.0 Hz), 6.89 (d, 1H, J = 8.0 Hz), 6.64 (d, 1H, J = 7.2 Hz), 4.52–4.44 (m, 1H), 4.39–4.31 (m, 1H), 3.89 (s, 3H), 3.08 (d, 1H, J = 2.8 Hz), 1.81–1.53 (m, 6H), 1.39 (t, 3H, J = 7.2 Hz), 1.27–1.15 (m, 3H), 1.01 (s, 9H), 0.94–0.86 (m, 1H), 0.74–0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 160.1, 147.1, 140.4, 123.7, 122.0, 121.8, 111.4, 83.2, 81.8, 62.1, 56.3, 50.1, 39.1, 32.2, 27.1, 26.8, 26.1, 26.0, 25.8, 14.4; IR (KBr, cm^{-1}): 2981, 2928, 2856, 1789, 1733, 1589, 1485, 1462, 1445, 1379, 1367, 1347, 1322, 1304, 1272, 1235, 1210, 1185, 1163, 1129, 1107, 1042, 1028, 985, 943, 900, 878, 856, 824, 805, 784, 753, 738, 713; HRMS (ESI) calcd for $C_{23}H_{32}O_7$ (M + Na^+) 443.2040,found 443.2050.

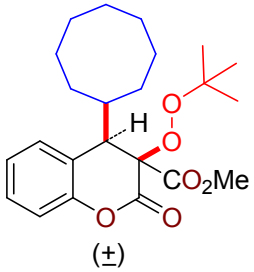
Methyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (19a):



Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28 (t, 1H, J = 7.2 Hz), 7.12–7.03 (m, 3H), 3.94 (s, 3H), 3.09 (s, 1H), 1.84–1.53 (m, 6H), 1.32–1.13 (m, 3H), 1.01 (s, 9H), 0.94–0.85 (m, 1H), 0.68–0.59 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 160.7, 151.1, 130.1, 128.6, 123.9, 120.9, 116.2, 83.6, 82.0, 52.9, 50.1, 39.5, 32.1, 27.1,

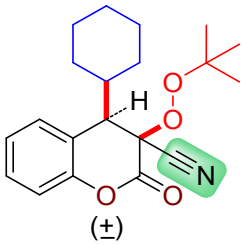
26.7, 26.3, 26.2, 25.8; IR (KBr, cm^{-1}): 2986, 2933, 2857, 1784, 1730, 1587, 1490, 1459, 1434, 1389, 1365, 1350, 1304, 1292, 1256, 1222, 1198, 1179, 1169, 1127, 1118, 1068, 1044, 1032, 1022, 924, 876, 834, 805, 777, 760, 742; HRMS (ESI)) calcd for $C_{21}H_{28}O_6$ ($M + Na^+$) 399.1778, found 399.1783.

Methyl 3-(*tert*-butylperoxy)-4-cyclooctyl-2-oxochroman-3-carboxylate (19c):



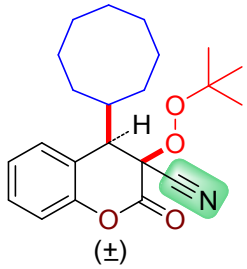
Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36–7.30 (m, 2H), 7.10 (t, 1H, J = 7.4 Hz), 7.04 (d, 1H, J = 8.0 Hz), 3.49 (s, 3H), 2.65 (m, 1H), 2.02–1.92 (m, 2H), 1.76–1.59 (m, 13H), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 166.4, 151.9, 130.9, 130.5, 124.0, 121.3, 116.4, 80.9, 79.3, 61.9, 52.7, 38.8, 30.2, 29.1, 27.8, 27.3, 26.8, 26.2, 25.8, 24.4; IR (KBr, cm^{-1}): 2987, 2923, 2855, 1781, 1736, 1558, 1539, 1506, 1489, 1458, 1434, 1363, 1339, 1260, 1228, 1193, 1151, 1126, 1005, 879, 759; HRMS (ESI) calcd for $C_{23}H_{32}O_6$ ($M + Na^+$) 427.2091, found 427.2090.

3-(*tert*-Butylperoxy)-4-cyclohexyl-2-oxochroman-3-carbonitrile (20a):



Solid; m.p. 152-154 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34 (t, 1H, J = 8.0 Hz), 7.18 (t, 1H, J = 7.4 Hz), 7.13–7.07 (m, 2H), 3.24 (d, 1H, J = 3.2 Hz), 2.17–2.11 (m, 1H), 1.83–1.75 (m, 2H), 1.68–1.55 (m, 3H), 1.40–1.19 (m, 3H), 1.09 (s, 9H), 0.96–0.86 (m, 1H), 0.73–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 150.5, 130.2, 129.3, 124.8, 119.1, 116.6, 114.5, 83.3, 80.8, 50.1, 39.6, 32.1, 27.2, 26.4, 26.1, 25.8, 25.6; IR (KBr, cm^{-1}): 2982, 2928, 2858, 2210, 1765, 1619, 1558, 1489, 1457, 1367, 1364, 1260, 1239, 1223, 1148, 1136, 1064, 1048, 1030, 1008, 910, 899, 856, 796, 767, 751, 705; HRMS (ESI) calcd for $C_{20}H_{25}NO_4$ ($M + Na^+$) 366.1676, found 366.1677.

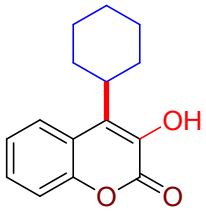
3-(*tert*-Butylperoxy)-4-cyclooctyl-2-oxochroman-3-carbonitrile (20c):



Gummy; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35–7.31 (m, 1H), 7.19–7.14 (m, 2H), 7.07 (d, 1H, J = 8.0 Hz), 3.30 (d, 1H, J = 2.8 Hz), 2.44–2.39 (m, 1H), 1.84–1.71 (m, 2H), 1.65–1.60 (m, 2H), 1.57–1.36 (m, 10H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.4, 150.5, 129.9, 129.3, 124.9, 119.7, 116.7, 114.6, 83.3, 81.1, 51.4, 39.2, 33.3, 28.2, 26.7, 26.3, 26.2, 26.1, 25.2; IR (KBr, cm^{-1}): 2981, 2927, 2854, 2215, 1776, 1586, 1558, 1506, 1488, 1458, 1390, 1221, 1180, 1149, 1117, 1055, 1034, 1016, 903, 867, 764,

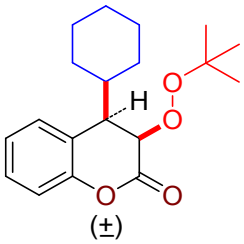
752; HRMS (ESI) calcd for $C_{22}H_{29}NO_4$ (M + Na^+) 394.1989, found 394.1998.

4-Cyclohexyl-3-hydroxy-2H-chromen-2-one (1a'):



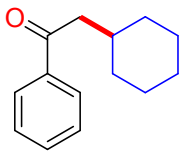
Solid; m.p. 196-200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (t, 1H, J = 8.0 Hz), 7.42–7.30 (m, 3H), 6.40 (s, 1H), 3.03 (bs, 1H), 2.20–2.05 (m, 2H), 1.91–1.72 (m, 4H), 1.46–1.34 (m, 3H), 0.87–0.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 161.0, 149.1, 139.8, 137.3, 130.7, 128.4, 125.0, 121.1, 117.4, 37.8, 29.1, 27.1, 26.2; IR (KBr, cm^{-1}): 3424, 3349, 3274, 2916, 2852, 1707, 1631, 1602, 1558, 1489, 1455, 1400, 1364, 1305, 1282, 1253, 1233, 1185, 1159, 1123, 754; HRMS (ESI) calcd for $C_{15}H_{16}O_3$ (M - H^+) 243.1019, found 243.1014.

3-(*tert*-Butylperoxy)-4-cyclohexylchroman-2-one (21a):



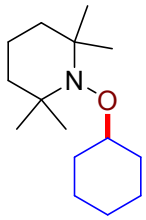
Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.34 (m, 2H), 7.14 (t, 1H, J = 7.6 Hz), 7.03 (d, 1H, J = 8.0 Hz), 4.95 (d, 1H, J = 1.2 Hz), 3.07 (d, 1H, J = 8.8 Hz), 1.84–1.54 (m, 7H), 1.37–1.26 (m, 1H), 1.19–1.09 (m, 2H), 1.06 (s, 9H), 0.89–0.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3, 152.3, 131.0, 130.9, 124.3, 119.2, 116.7, 80.8, 78.8, 50.3, 36.8, 31.3, 31.1, 26.3, 26.0, 25.9, 25.8; IR (KBr, cm^{-1}): 2977, 2990, 2854, 1771, 1717, 1613, 1590, 1486, 1459, 1386, 1363, 1352, 1291, 1243, 1221, 1186, 1155, 1127, 1109, 1085, 1052, 1025, 983, 966, 951, 903, 890, 877, 782, 760; HRMS (ESI) calcd for $C_{19}H_{26}O_4$ (M + Na^+) 341.1723, found 341.1730.

2-Cyclohexyl-1-phenylethanone (1'a):



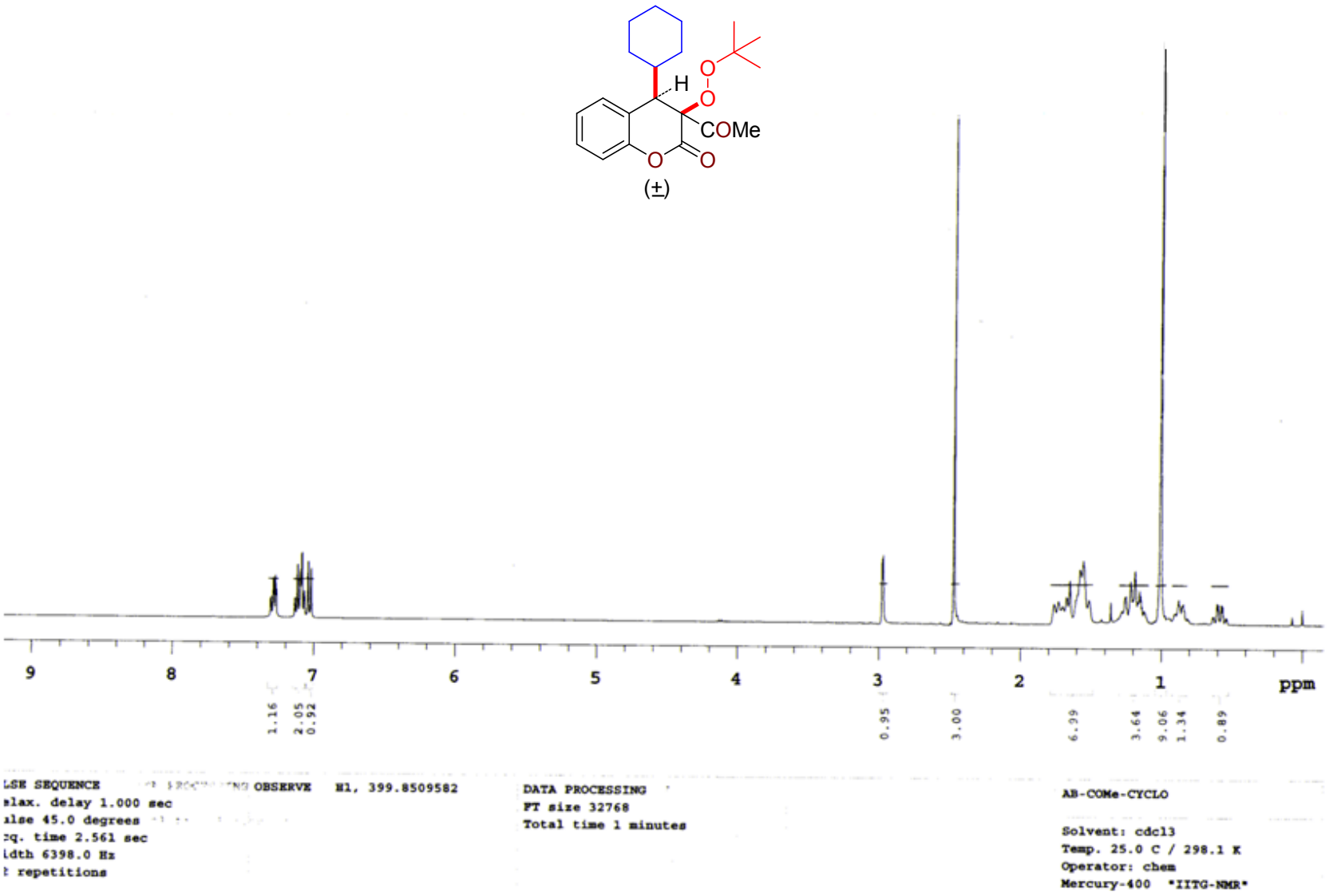
Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, 2H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.8 Hz), 7.45 (t, 2H, J = 8.0 Hz), 2.82 (d, 2H, J = 6.4 Hz), 2.0–1.95 (m, 1H), 1.77–1.71 (m, 3H), 1.67–1.59 (m, 2H), 1.33–1.24 (m, 2H), 1.20–1.14 (m, 1H), 1.05–0.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.5, 137.7, 133.0, 128.7, 128.3, 46.4, 34.8, 33.6, 26.5, 26.4; IR (KBr, cm^{-1}): 2922, 2851, 1716, 1684, 1597, 1581, 1493, 1448, 1355, 1314, 1270, 1222, 1193, 1177, 1111, 1070, 1026, 1001, 956, 750, 712; HRMS (ESI) calcd for $C_{14}H_{18}O$ (M + H^+) 203.1438, found 203.1440.

1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (1A):



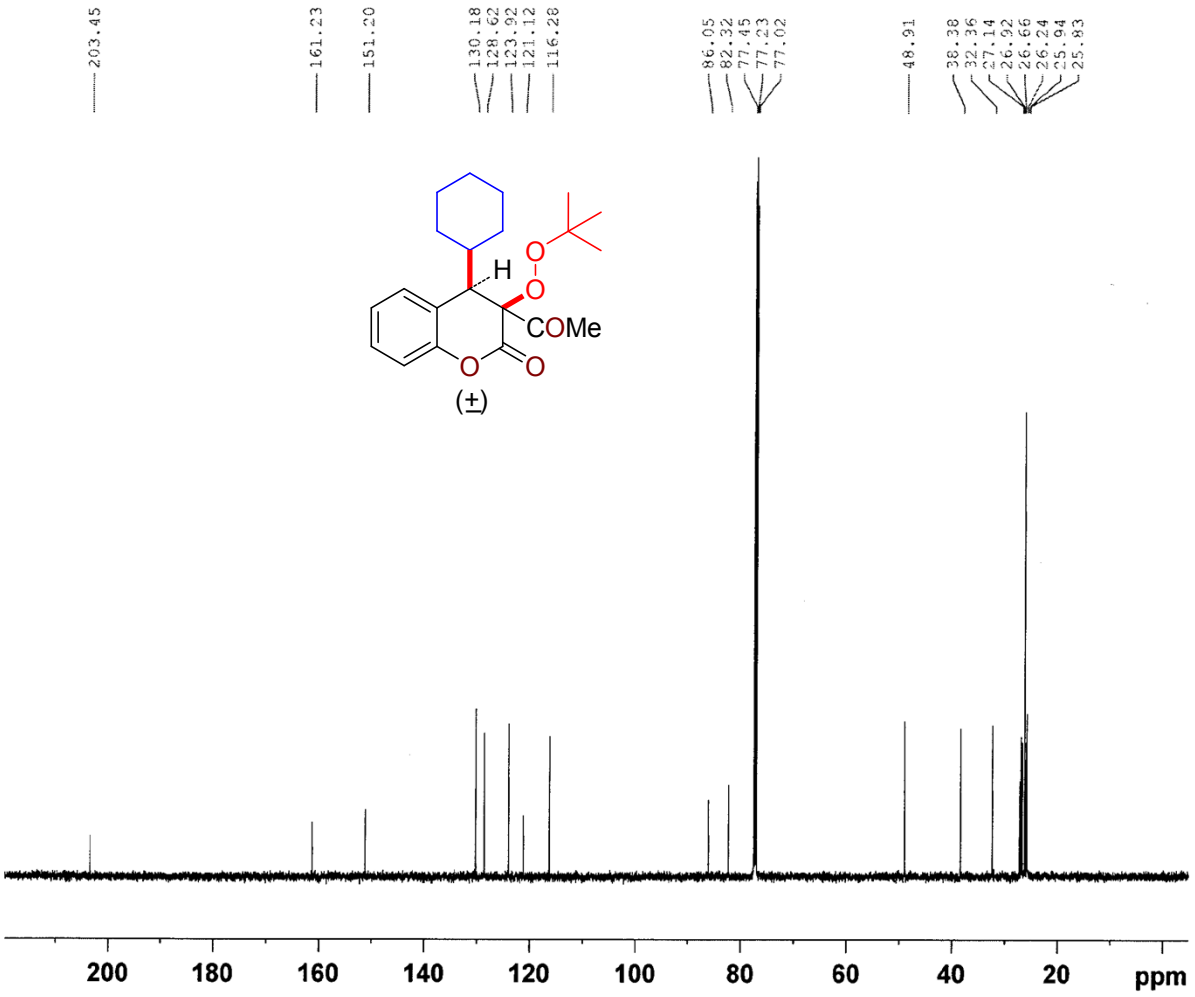
Gummy; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.58 (bs, 1H), 2.04 (bs, 2H), 1.74 (bs, 2H), 1.54–1.46 (m, 6H), 1.31–1.19 (m, 6H), 1.14 (s, 6H), 1.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 81.9, 59.8, 40.5, 34.7, 33.1, 26.2, 25.3, 17.6; IR (KBr, cm^{-1}): 2967, 2932, 2855, 1467, 1452, 1374, 1348, 1257, 1242, 1208, 1181, 1151, 1132, 1092, 1058, 1044, 1021, 993, 966, 913, 710; HRMS (ESI) calcd for $C_{15}H_{29}NO$ ($M + H^+$) 240.2329, found 240.2332.

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (1a): ^{1}H NMR ($CDCl_3$, 400 MHz)



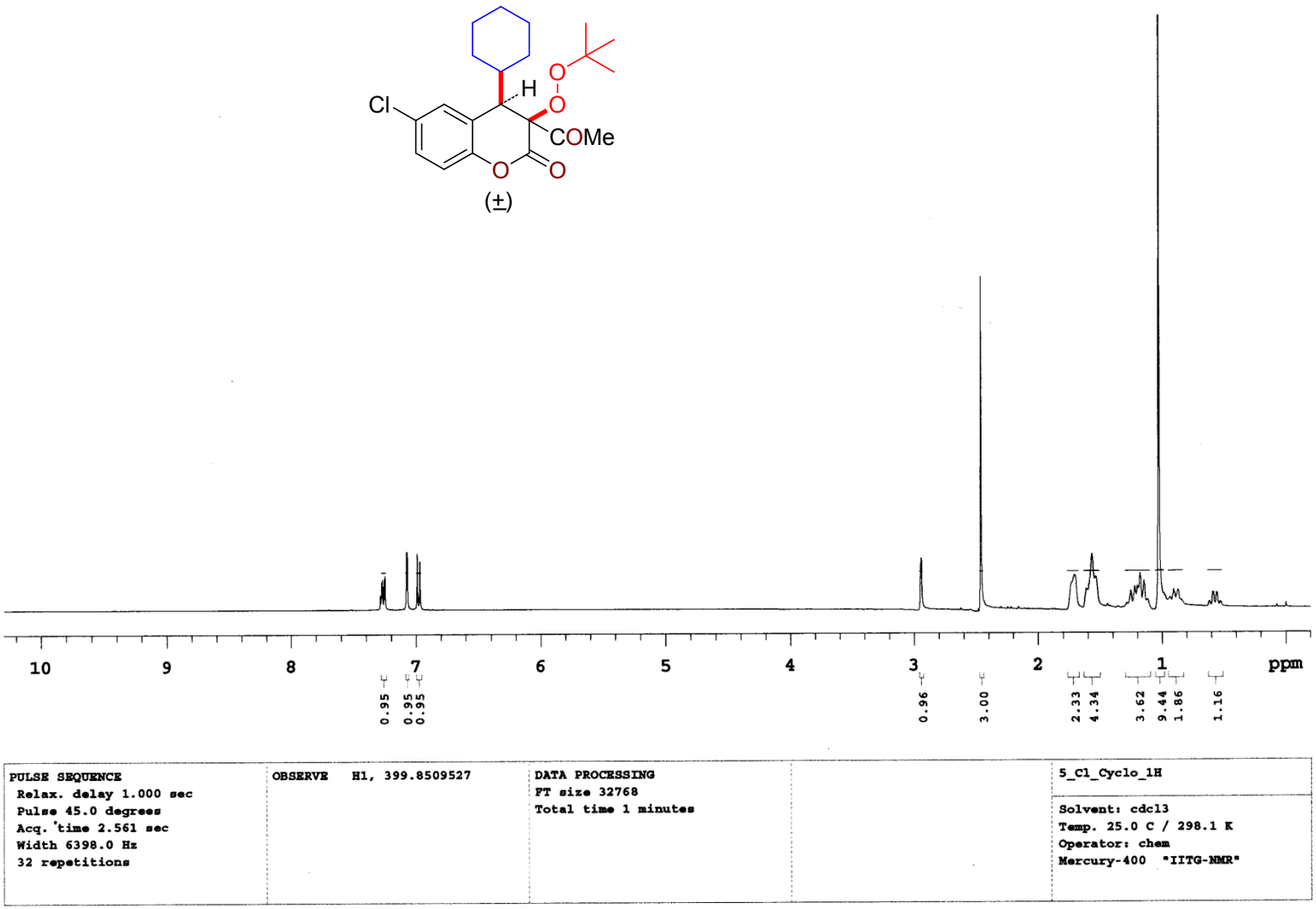
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (1a): ^{13}C NMR ($CDCl_3$, 150 MHz)

AB-COME-CYCLO-13C

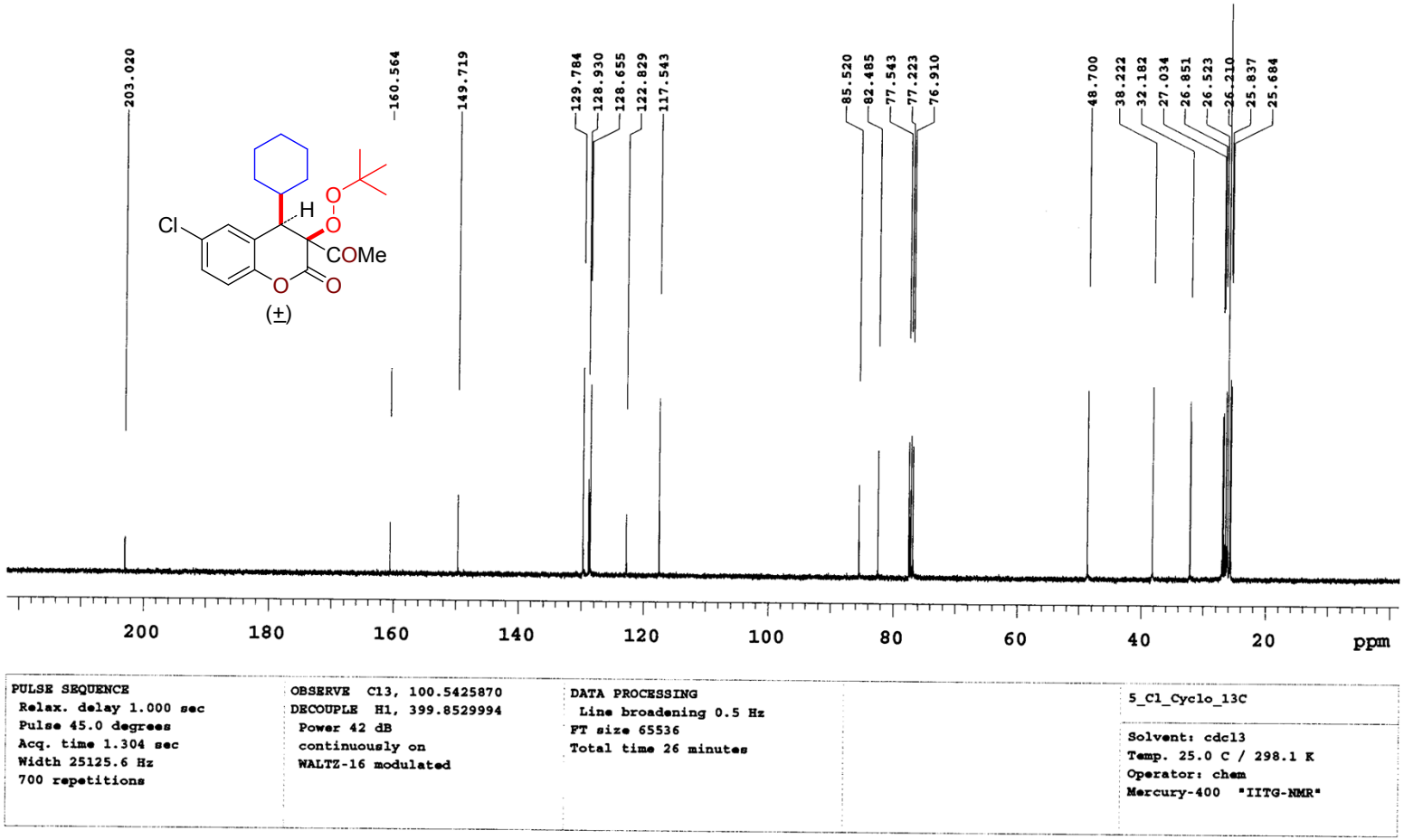



```
Current Data Parameters
NAME      AB-COME-CYCLO-13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20140218
Time              10.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  206
DS                    2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE               300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1               13C
P1               10.50 usec
PLW1        95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        21.00000000 W
PLW12        0.61714000 W
PLW13        0.30239999 W

F2 - Processing parameters
SI                16384
SF          150.9128348 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

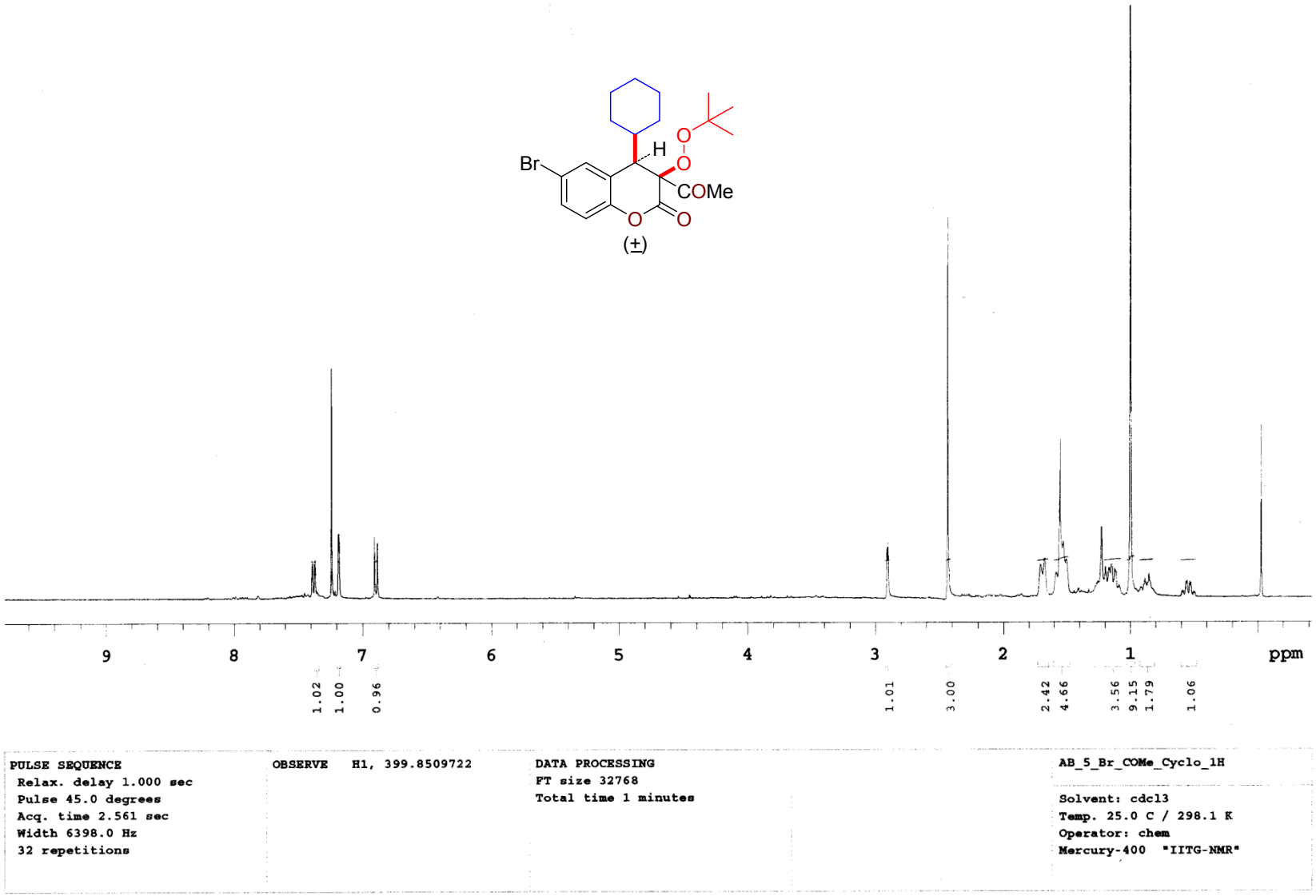
3-Acetyl-3-(*tert*-butylperoxy)-6-chloro-4-cyclohexylchroman-2-one (2a): ^{1}H NMR ($CDCl_3$, 400 MHz)



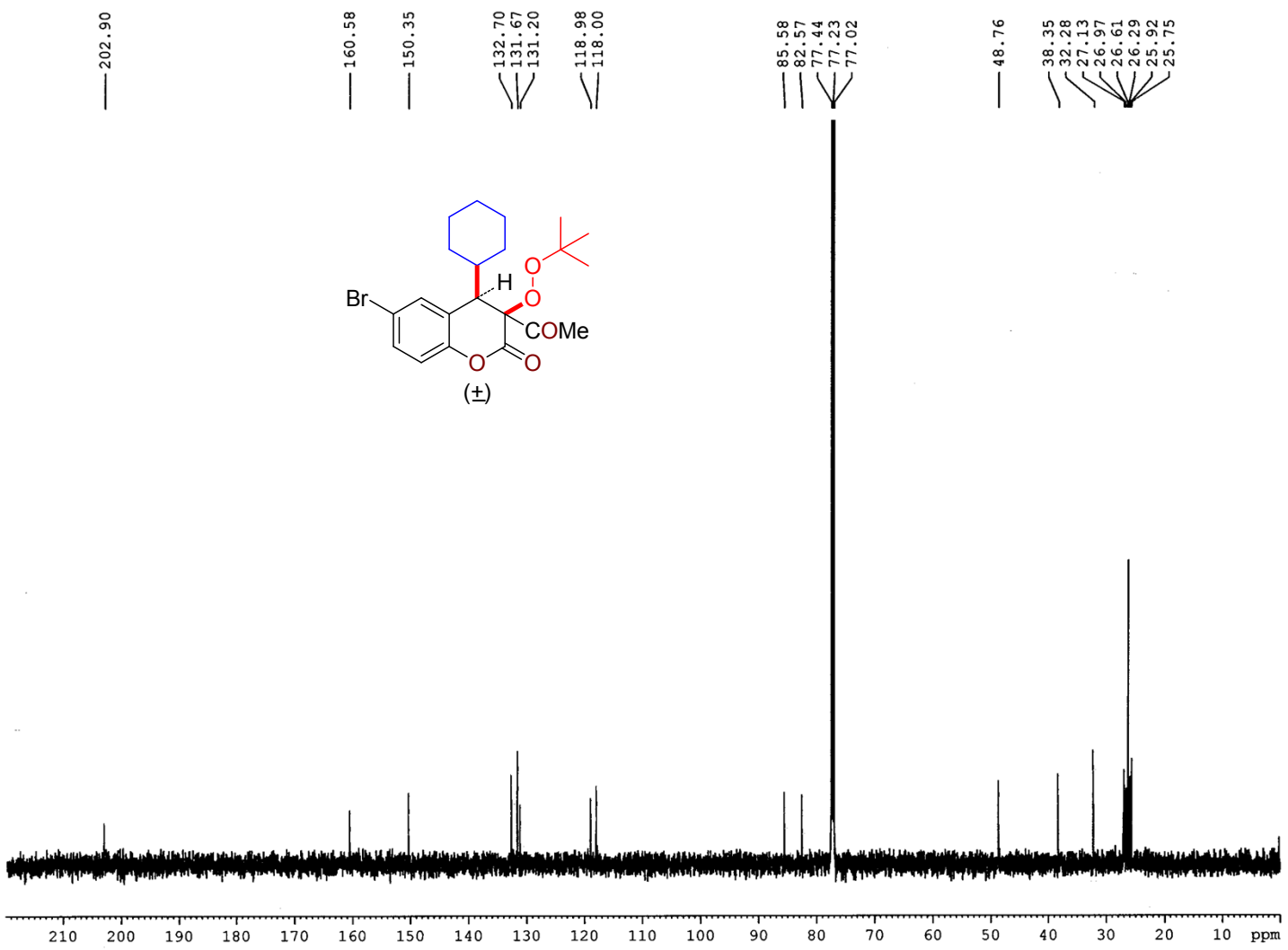
3-Acetyl-3-(*tert*-butylperoxy)-6-chloro-4-cyclohexylchroman-2-one (2a): ^{13}C NMR ($CDCl_3$, 100 MHz)



3-Acetyl-6-bromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (3a): ^{1}H NMR ($CDCl_3$, 400 MHz)



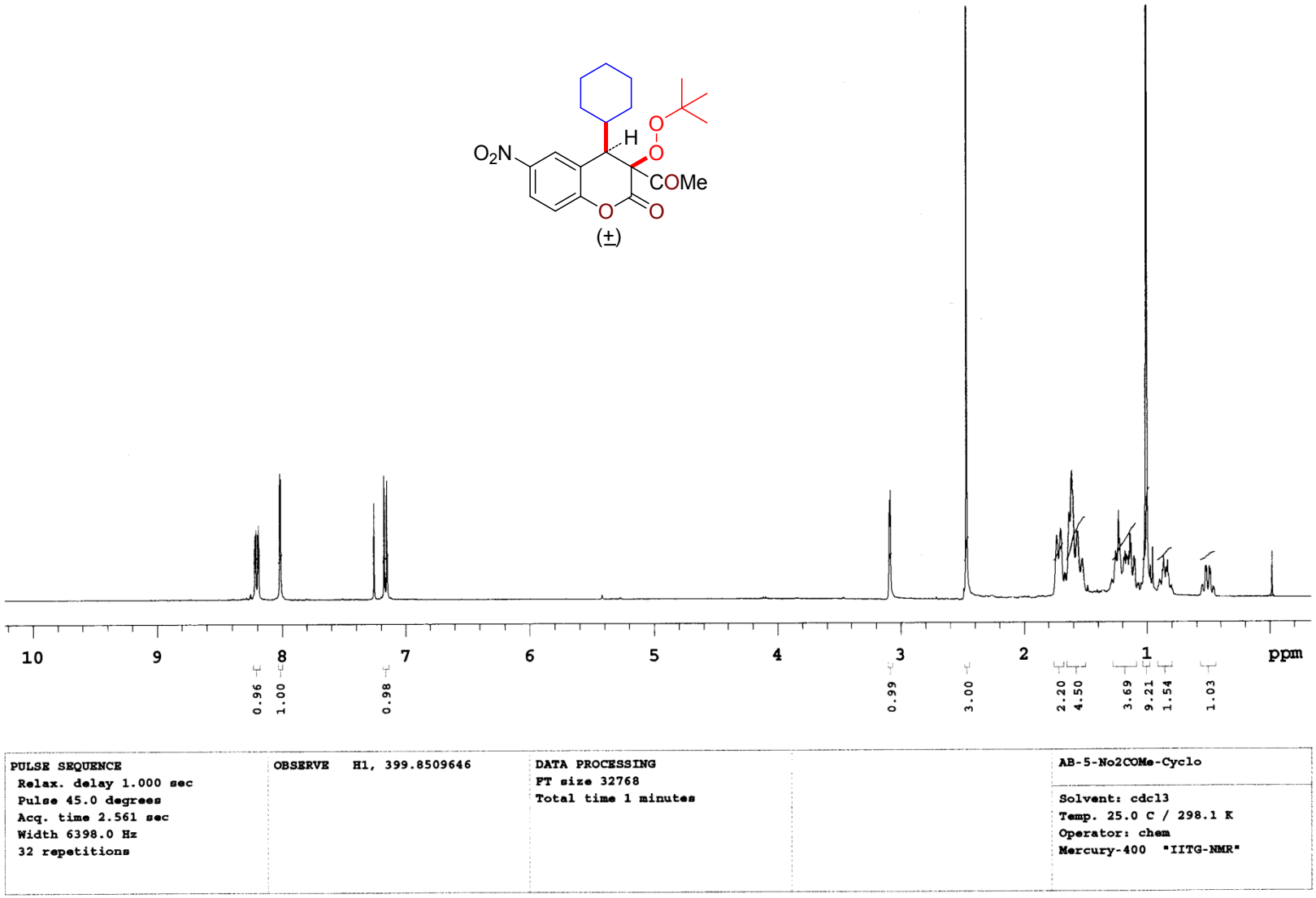
3-Acetyl-6-bromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (3a): ^{13}C NMR ($CDCl_3$, 150 MHz)



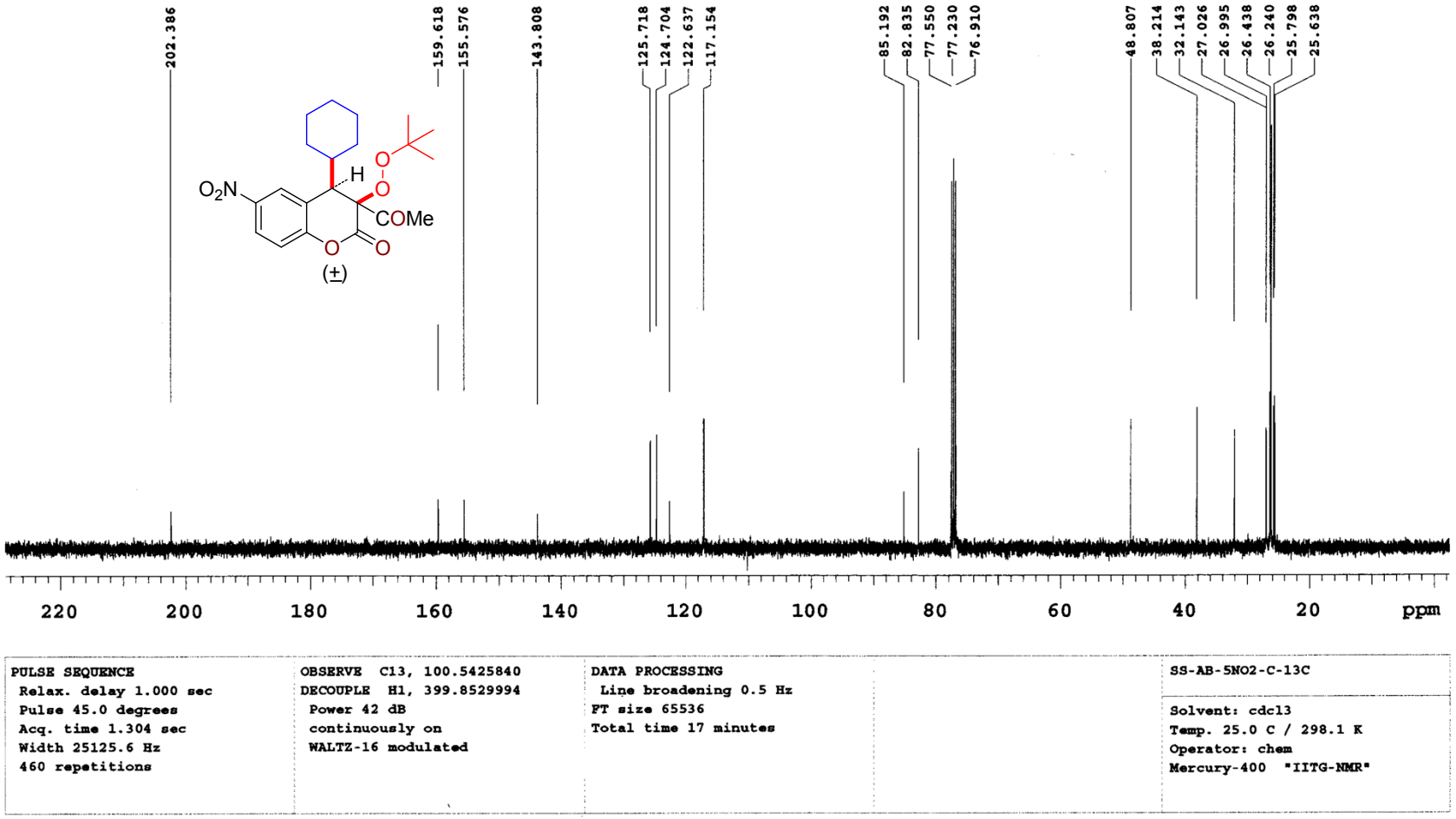
BRUKER

```
Current Data Parameters
NAME      AB-5BR-CYCLO1-13C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140128
Time                  11.43
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     426
DS                       2
SWH              36057.691 Hz
FIDRES            1.100393 Hz
AQ                0.4543829 sec
RG                    65.24
DW                   13.867 usec
DE                    6.50 usec
TE                   298.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                   13C
P1                   10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                    16384
SF            150.9128332 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-6-nitrochroman-2-one (4a): ^{1}H NMR ($CDCl_3$, 400 MHz)

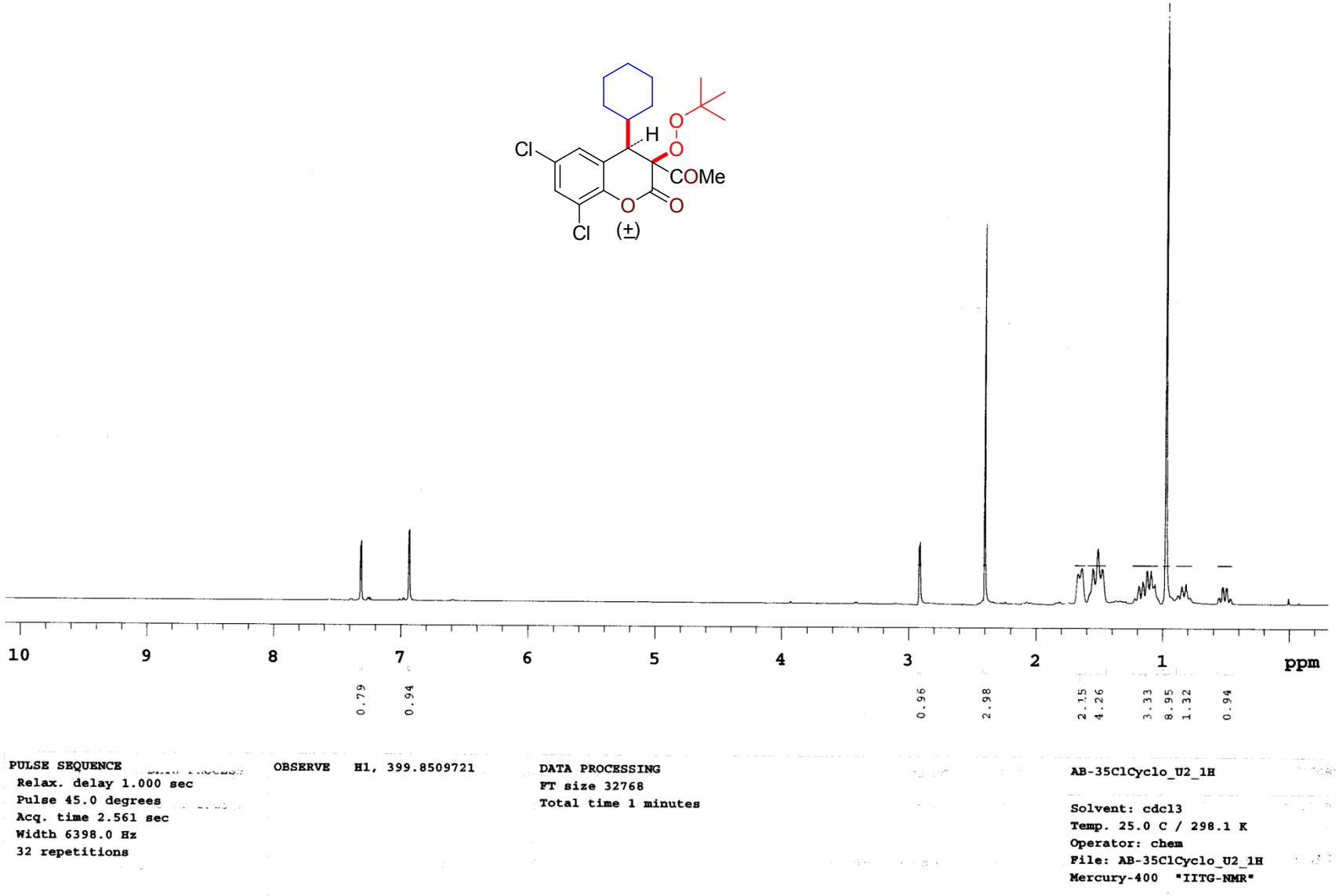


3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-6-nitrochroman-2-one (4a): ^{13}C NMR ($CDCl_3$, 100 MHz)

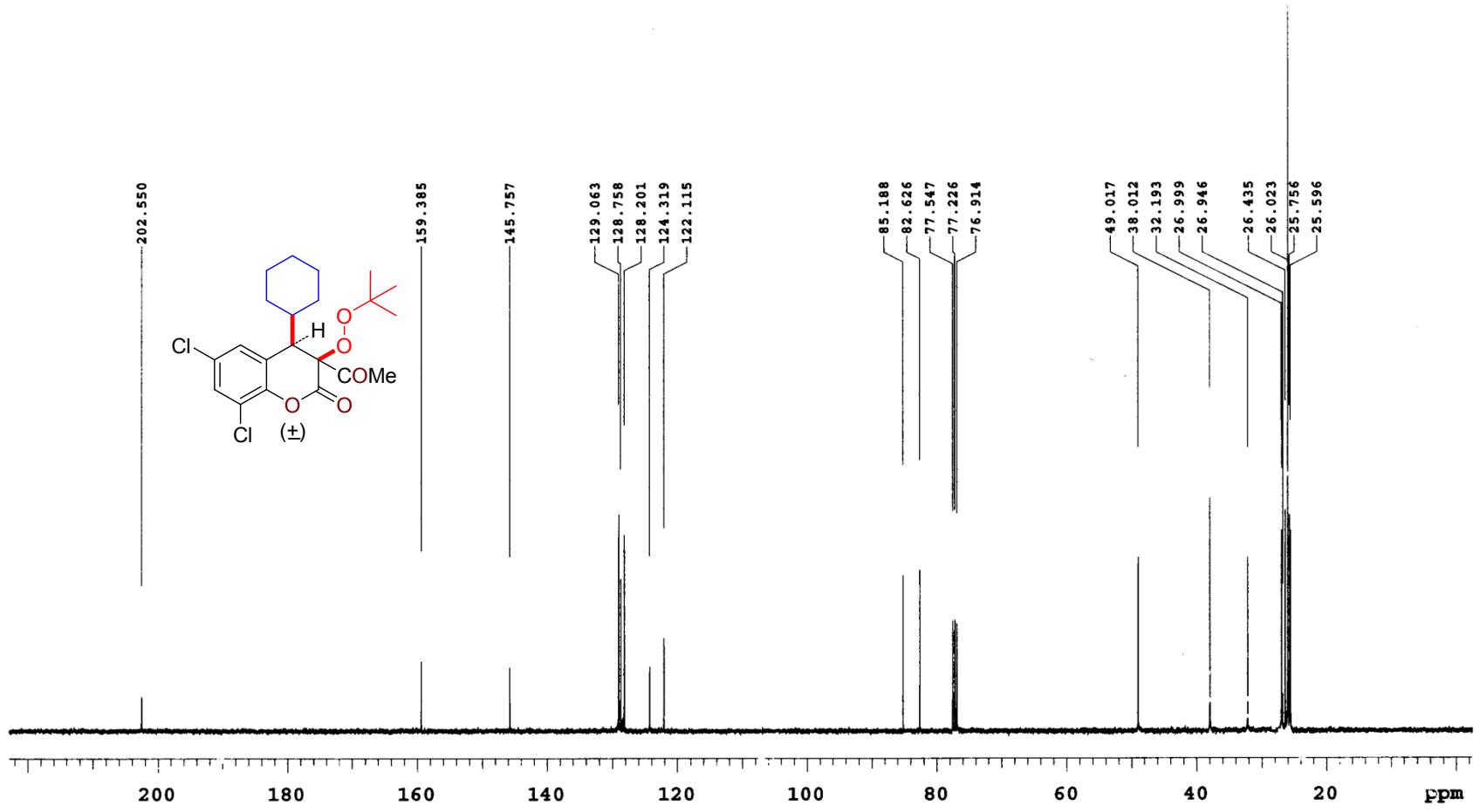


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.304 sec Width 25125.6 Hz 460 repetitions	OBSERVE C13, 100.5425840 DECOUPLE H1, 399.8529994 Power 42 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 17 minutes	SS-AB-5NO2-C-13C Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

3-Acetyl-3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexylchroman-2-one (5a): ^{1}H NMR ($CDCl_3$, 400 MHz)



3-Acetyl-3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexylchroman-2-one (5a): ^{13}C NMR ($CDCl_3$, 100 MHz)



PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
320 repetitions

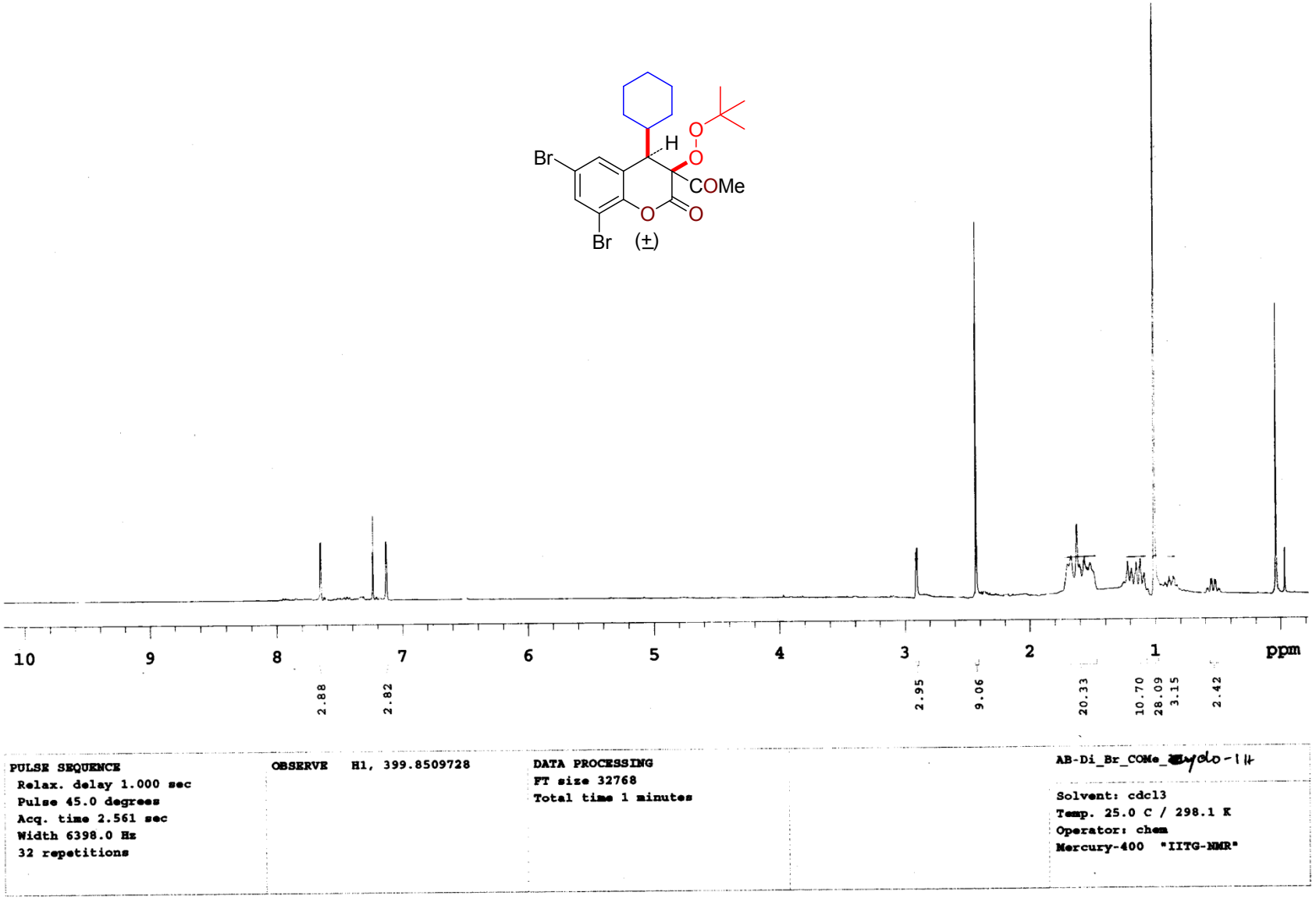
OBSERVE C13, 100.5425912
DECOUPLE H1, 399.8529994
Power 42 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 minutes

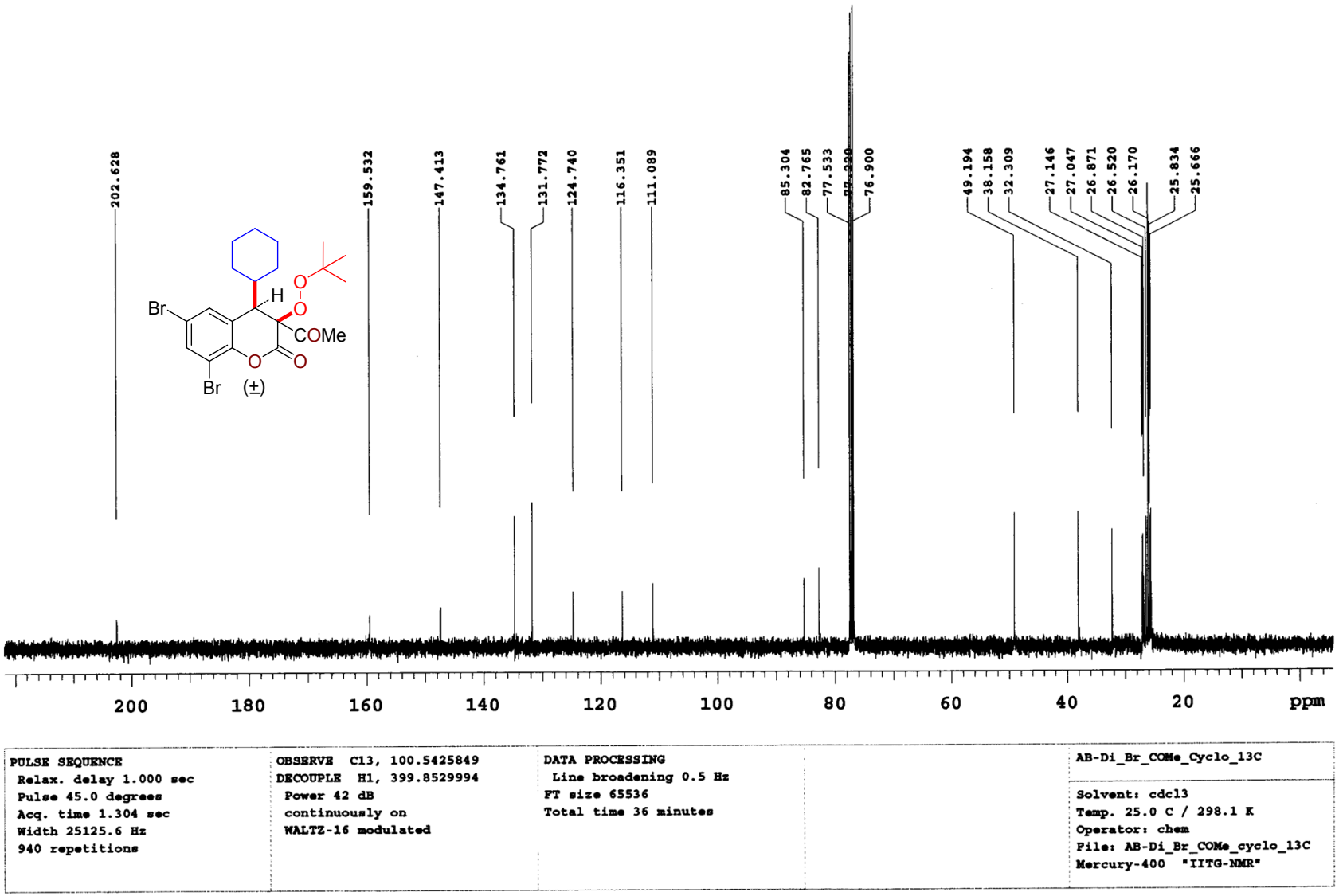
AB-35ClCyclo_U2_13C

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
File: AB-35ClCyclo_U2_13C
Mercury-400 "IITG-NMR"

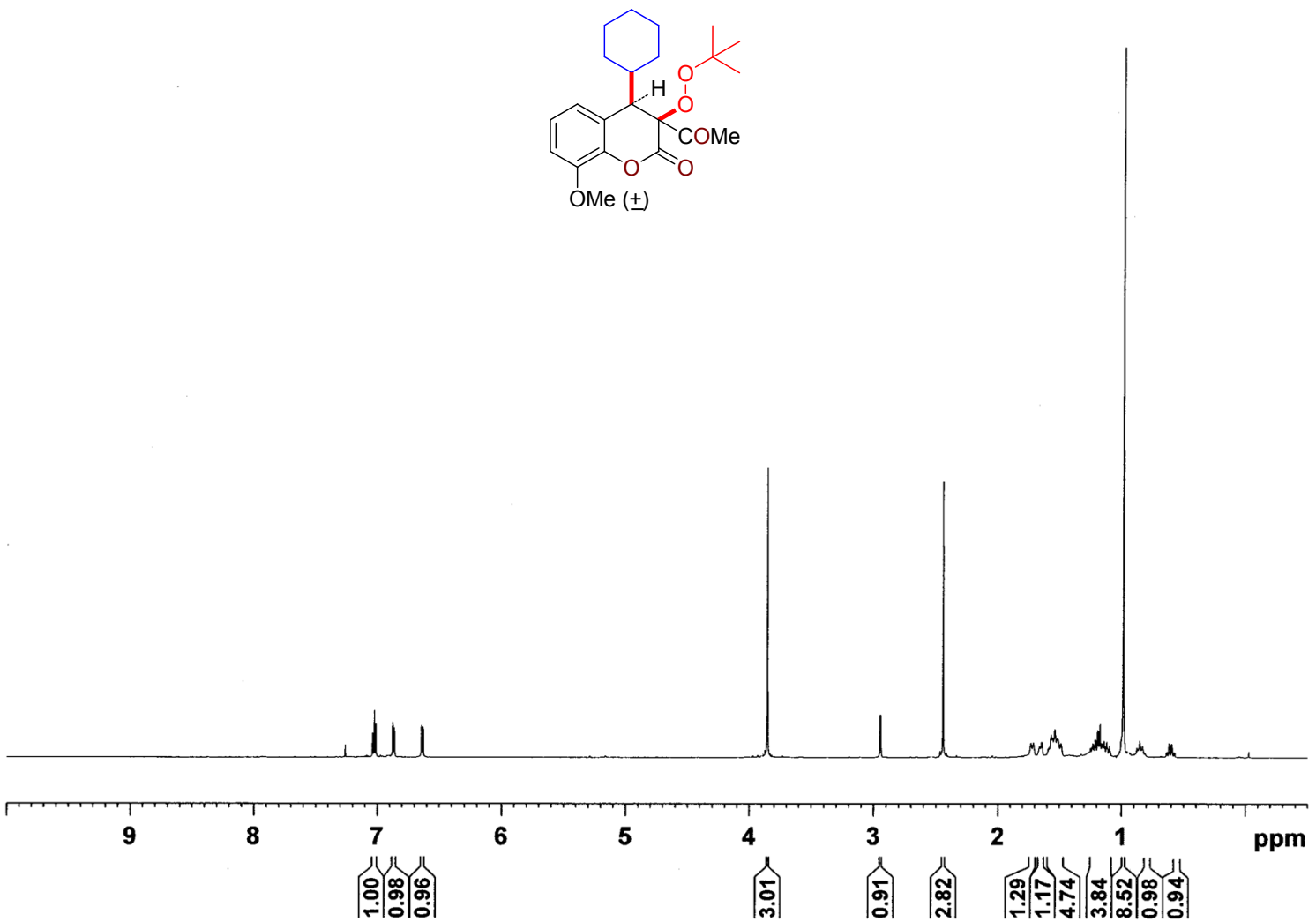
3-Acetyl-6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (6a): ^{1}H NMR ($CDCl_3$, 400 MHz)



3-Acetyl-6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (6a): ^{13}C NMR ($CDCl_3$, 100 MHz)

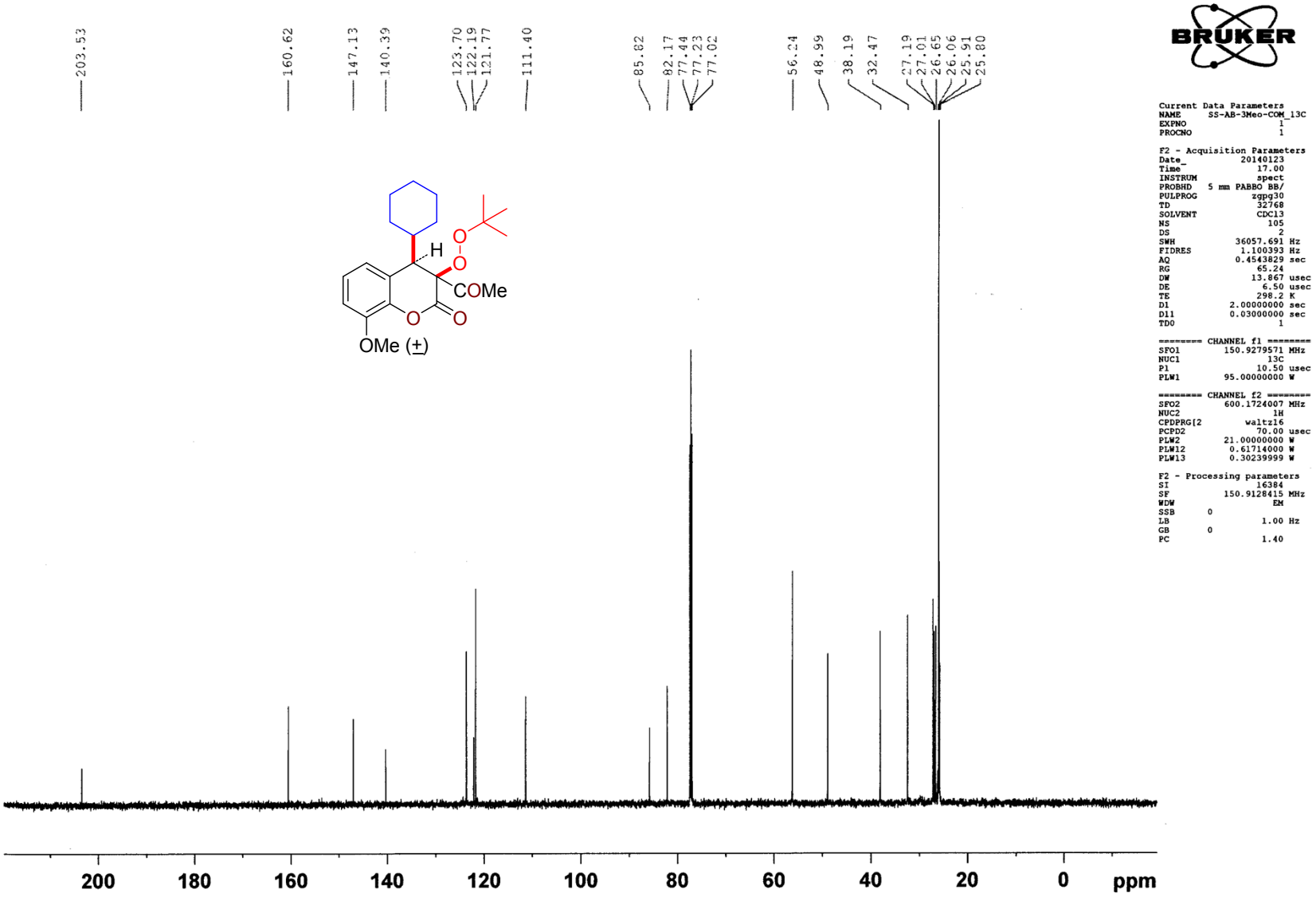


3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxychroman-2-one (7a): ^{1}H NMR ($CDCl_3$, 600 MHz)




```
Current Data Parameters
NAME      AB-3-Ome-cyclo_1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20140124
Time               12.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12019.230 Hz
FIDRES          0.366798 Hz
AQ              1.3631488 sec
RG                 22.18
DW                41.600 usec
DE                 6.50 usec
TE                298.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1737063 MHz
NUC1                   1H
P1                 12.00 usec
PLW1         21.00000000 W

F2 - Processing parameters
SI                 16384
SF           600.1700148 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

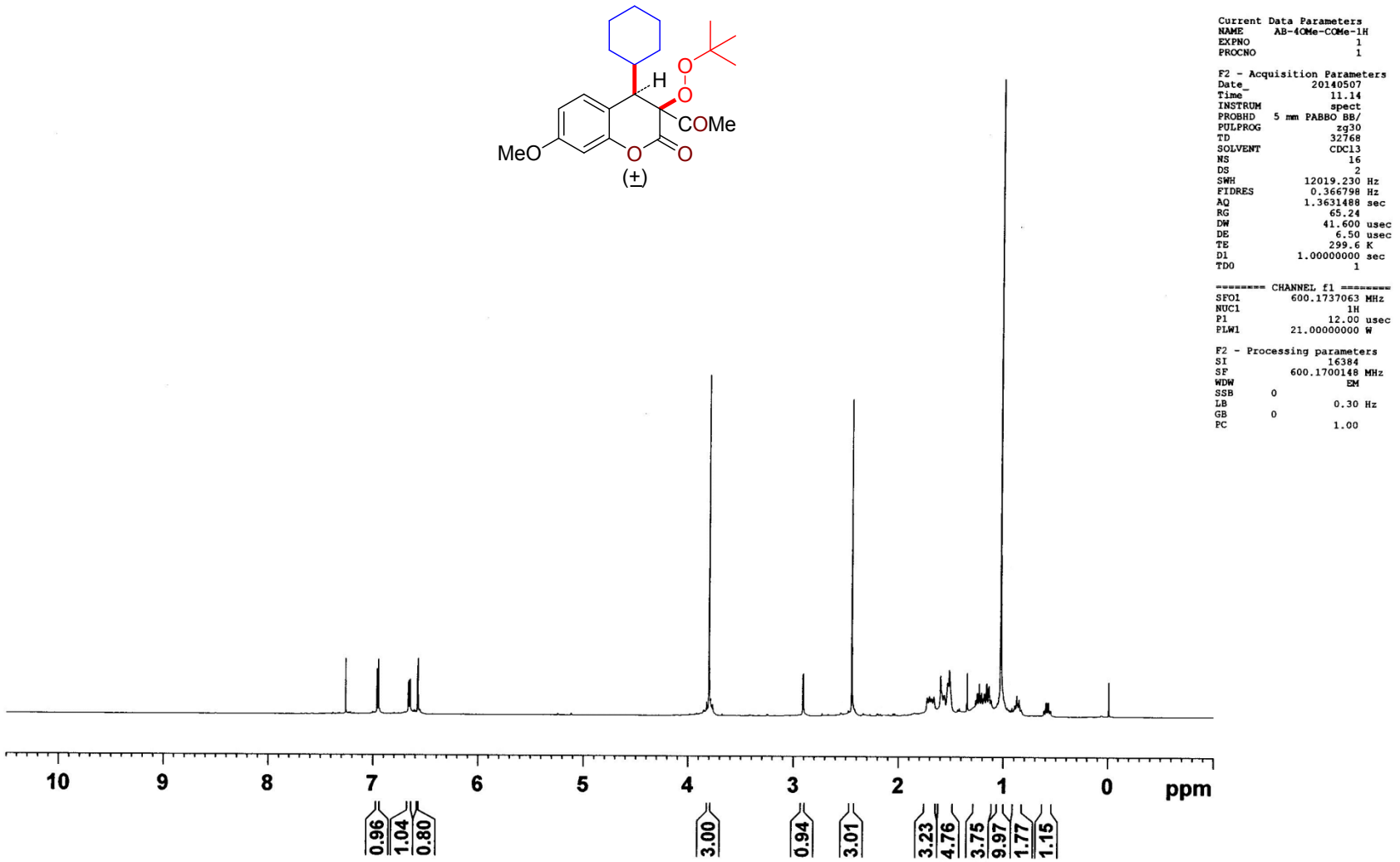
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxychoman-2-one (7a): ^{13}C NMR ($CDCl_3$, 150 MHz)




```
Current Data Parameters
NAME        SS-AB-3Meo-COM_13C
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20140123
Time                     17.00
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                zgpg30
TD                      32768
SOLVENT                 CDCl3
NS                        105
DS                          2
SWH                 36057.691 Hz
FIDRES               1.100393 Hz
AQ                   0.4543829 sec
RG                       65.24
DW                      13.867 usec
DE                        6.50 usec
TE                      298.2 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               150.9279571 MHz
NUC1                       13C
P1                       10.50 usec
PLW1               95.00000000 W

======== CHANNEL f2 ========
SFO2               600.1724007 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                    70.00 usec
PLW2               21.00000000 W
PLW12               0.61714000 W
PLW13               0.30239999 W

F2 - Processing parameters
SI                       16384
SF                 150.9128415 MHz
WDW                         EM
SSB                  0
LB                       1.00 Hz
GB                   0
PC                       1.40
```

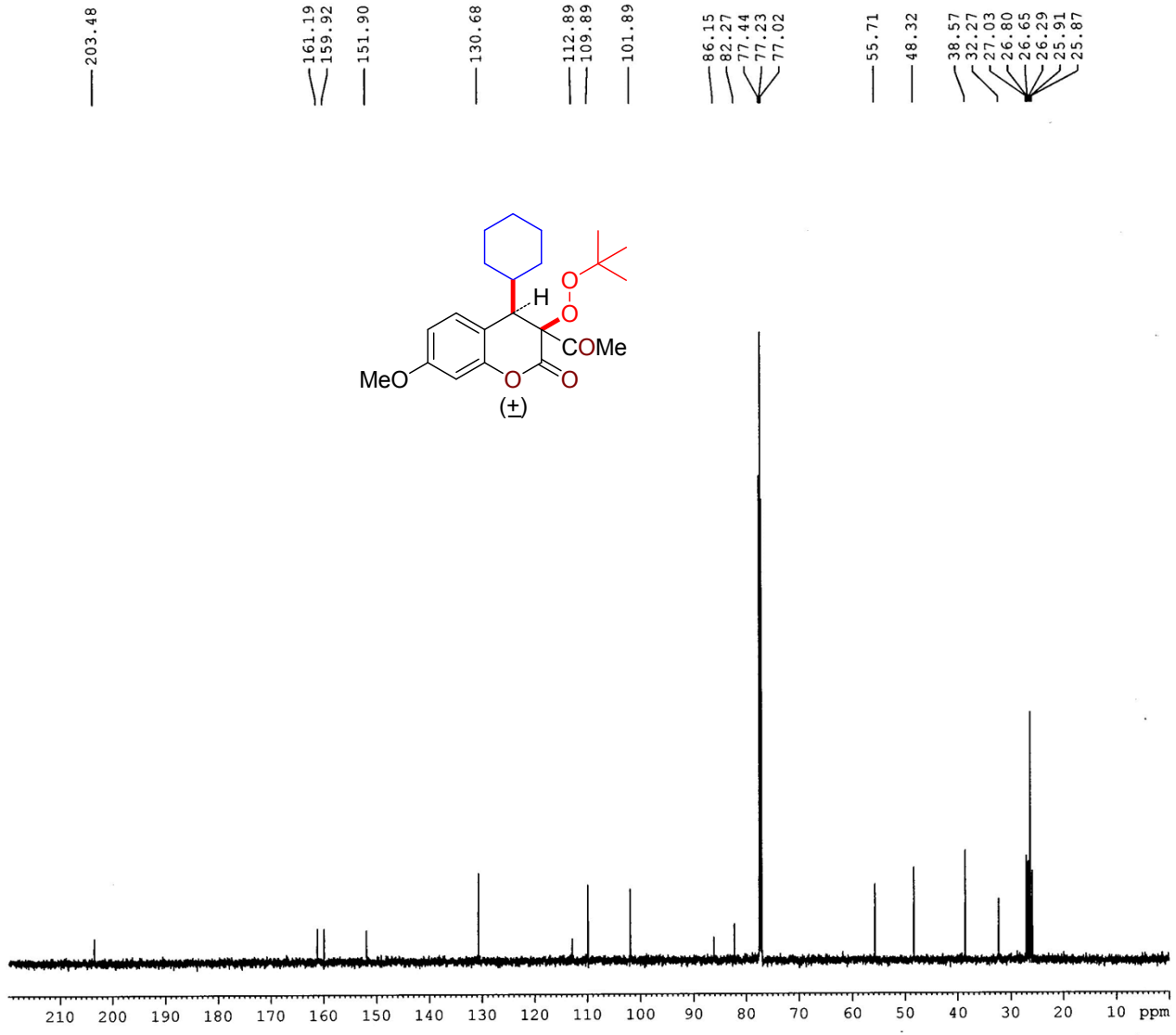
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-7-methoxychroman-2-one (8a): ^{1}H NMR ($CDCl_3$, 600 MHz)

AB-4OMe-COMe-1H




```
Current Data Parameters
NAME      AB-4OMe-COMe-1H
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140507
Time                11.14
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12019.230 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                 65.24
DW                41.600 usec
DE                 6.50 usec
TE                299.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          600.1737063 MHz
NUC1                  1H
P1                 12.00 usec
PLW1          21.00000000 W

F2 - Processing parameters
SI                 16384
SF            600.1700148 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

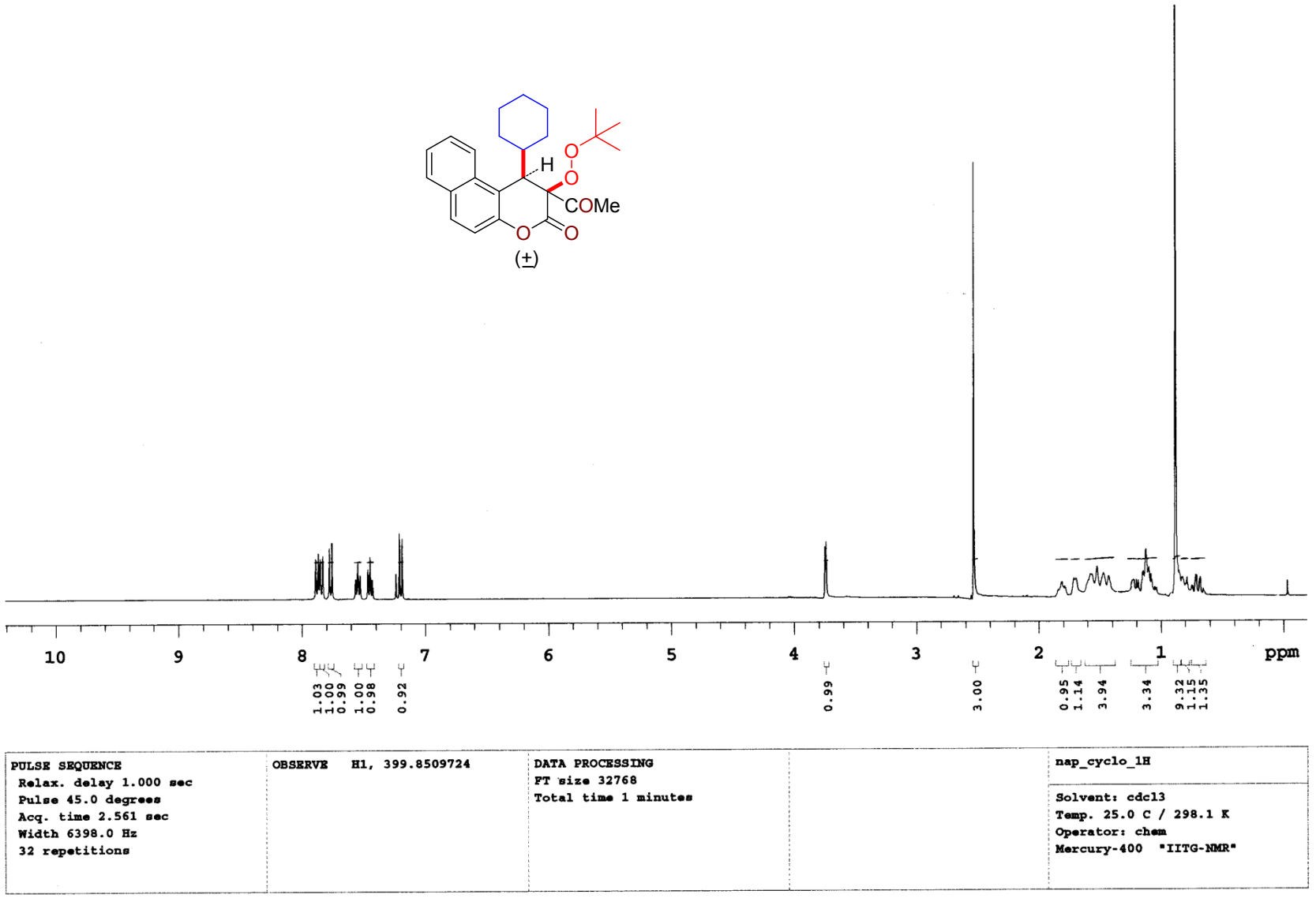
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclohexyl-7-methoxychroman-2-one (8a): ^{13}C NMR ($CDCl_3$, 150 MHz)



BRUKER

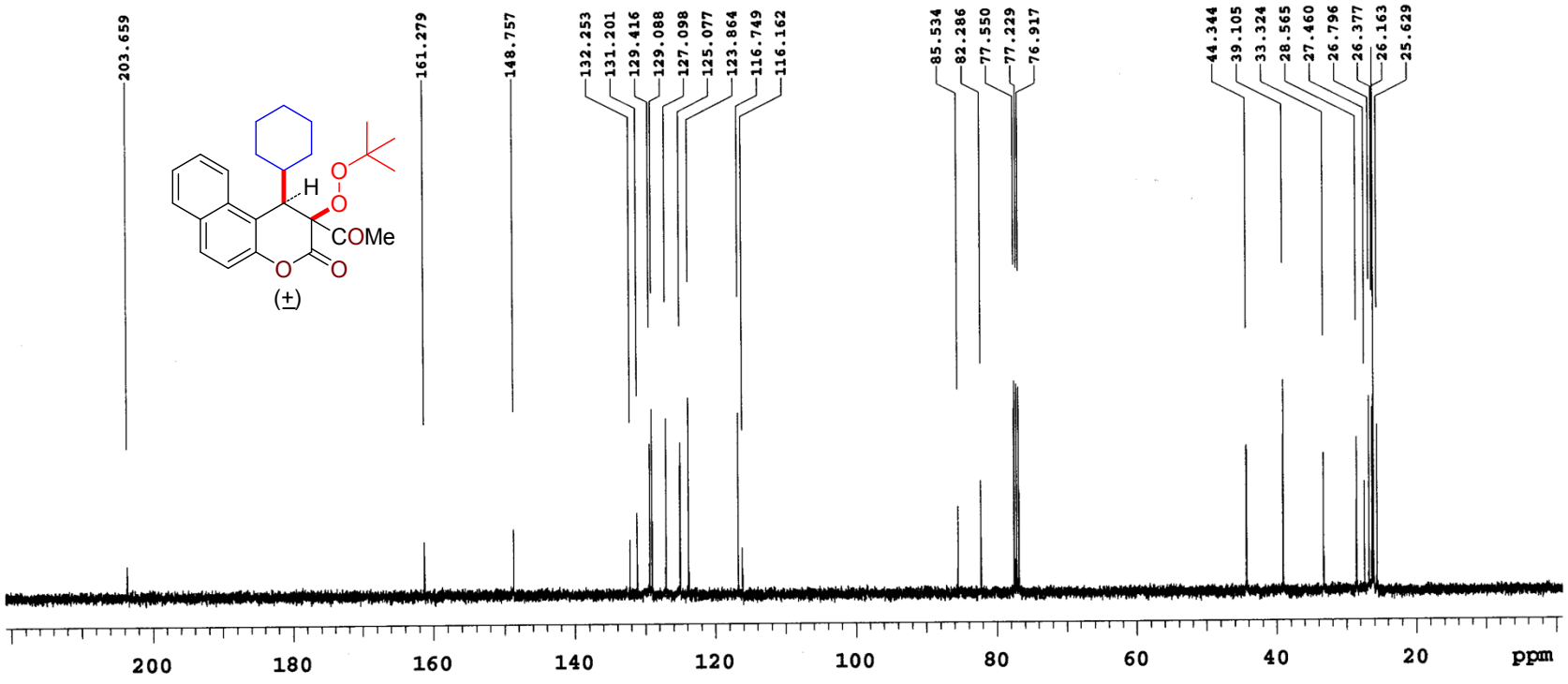
```
Current Data Parameters
NAME      AB-4OMe-COMe-13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140507
Time                 11.04
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     143
DS                       2
SWH              36057.691 Hz
FIDRES            1.100393 Hz
AQ               0.4543829 sec
RG                   65.24
DW                  13.867 usec
DE                    6.50 usec
TE                  299.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                   13C
P1                   10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                   16384
SF            150.9128348 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

2-Acetyl-2-(*tert*-butylperoxy)-1-cyclohexyl-1H-benzo[*f*]chromen-3(2H)-one (9a): ^{1}H NMR ($CDCl_3$, 400 MHz)



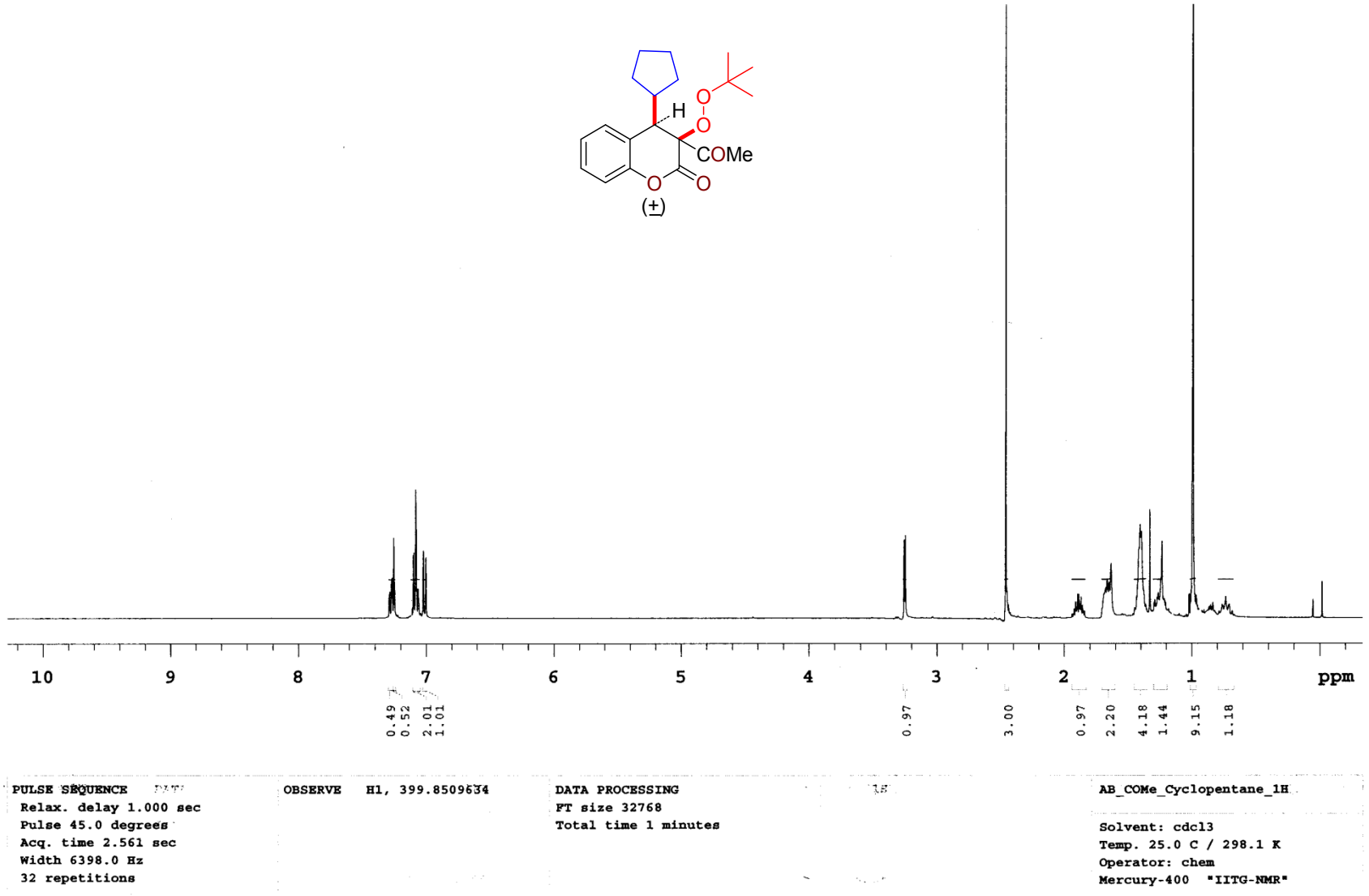
PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.561 sec Width 6398.0 Hz 32 repetitions	OBSERVE H1, 399.8509724	DATA PROCESSING FT size 32768 Total time 1 minutes		nap_cyclo_1H Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

2-Acetyl-2-(*tert*-butylperoxy)-1-cyclohexyl-1H-benzo[*f*]chromen-3(2H)-one (9a): ^{13}C NMR ($CDCl_3$, 100 MHz)

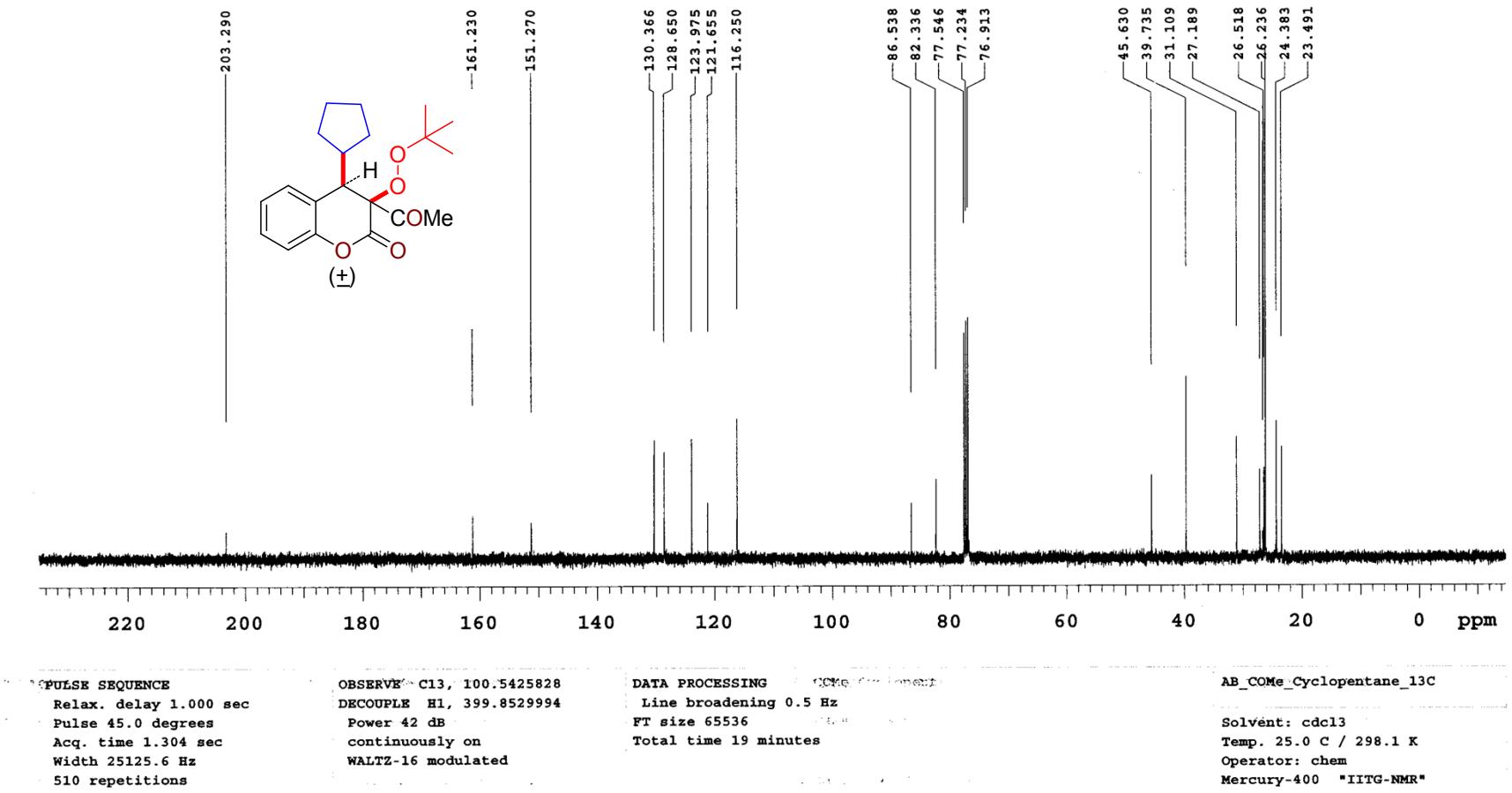


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.304 sec Width 25125.6 Hz 350 repetitions	OBSERVE C13, 100.5425856 DECOUPLE H1, 399.8529994 Power 42 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 13 minutes		nap_cyclo_13C Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

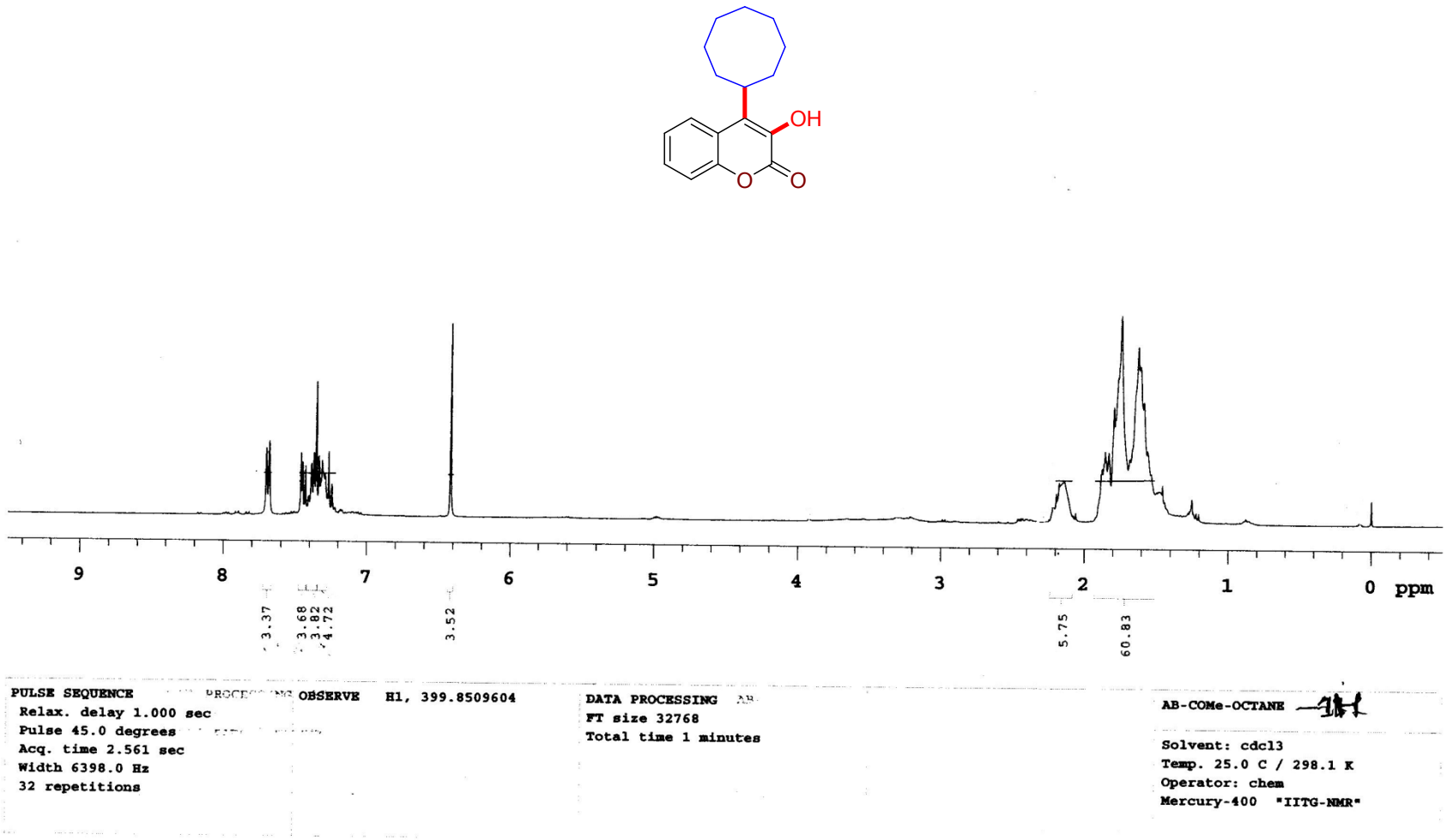
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclopentylchroman-2-one (1b): ^{1}H NMR ($CDCl_3$, 400 MHz)



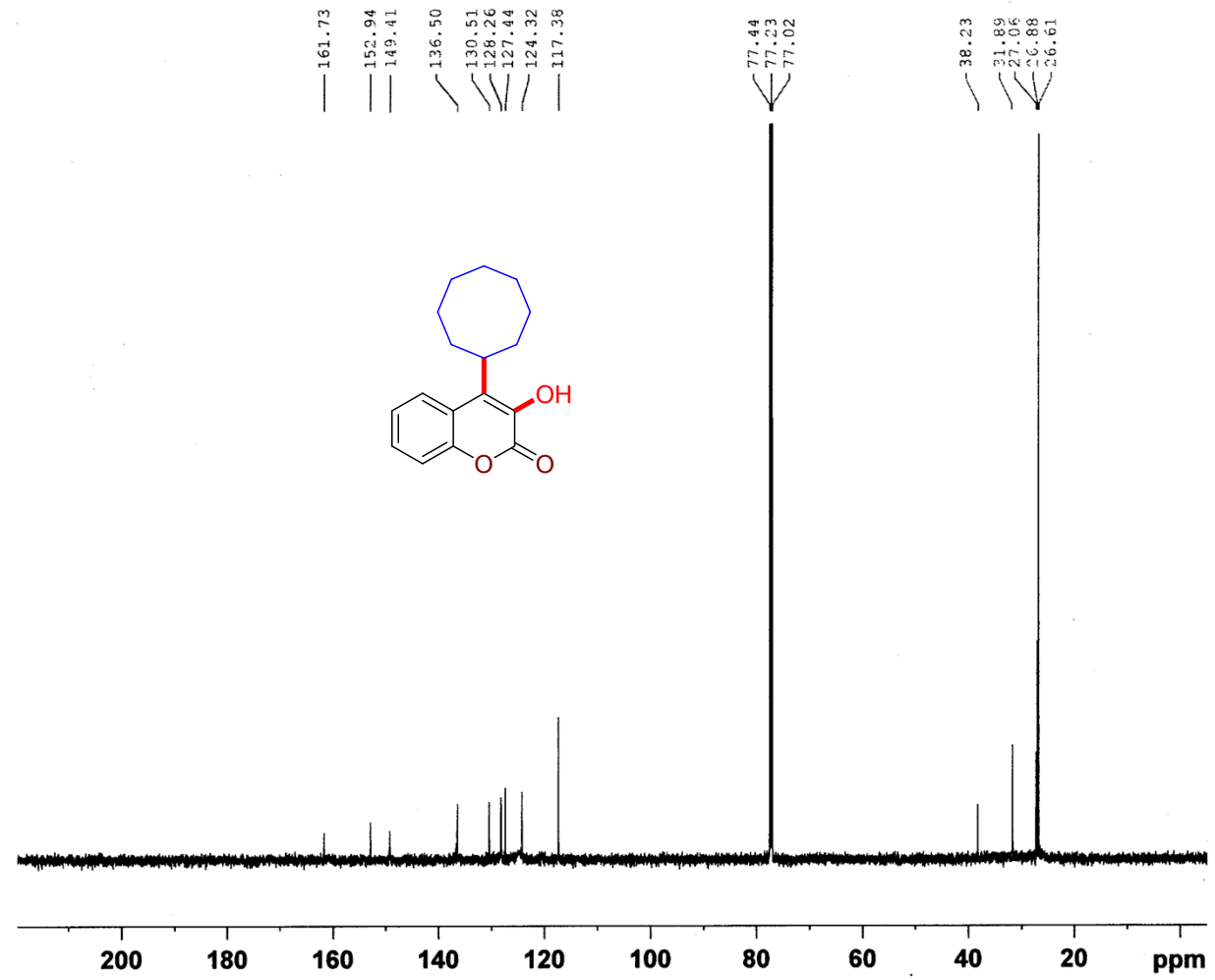
3-Acetyl-3-(*tert*-butylperoxy)-4-cyclopentylchroman-2-one (1b): ^{13}C NMR ($CDCl_3$, 100 MHz)



4-Cyclooctyl-3-hydroxy-2H-chromen-2-one (1c'): ^{1}H NMR ($CDCl_3$, 400 MHz)



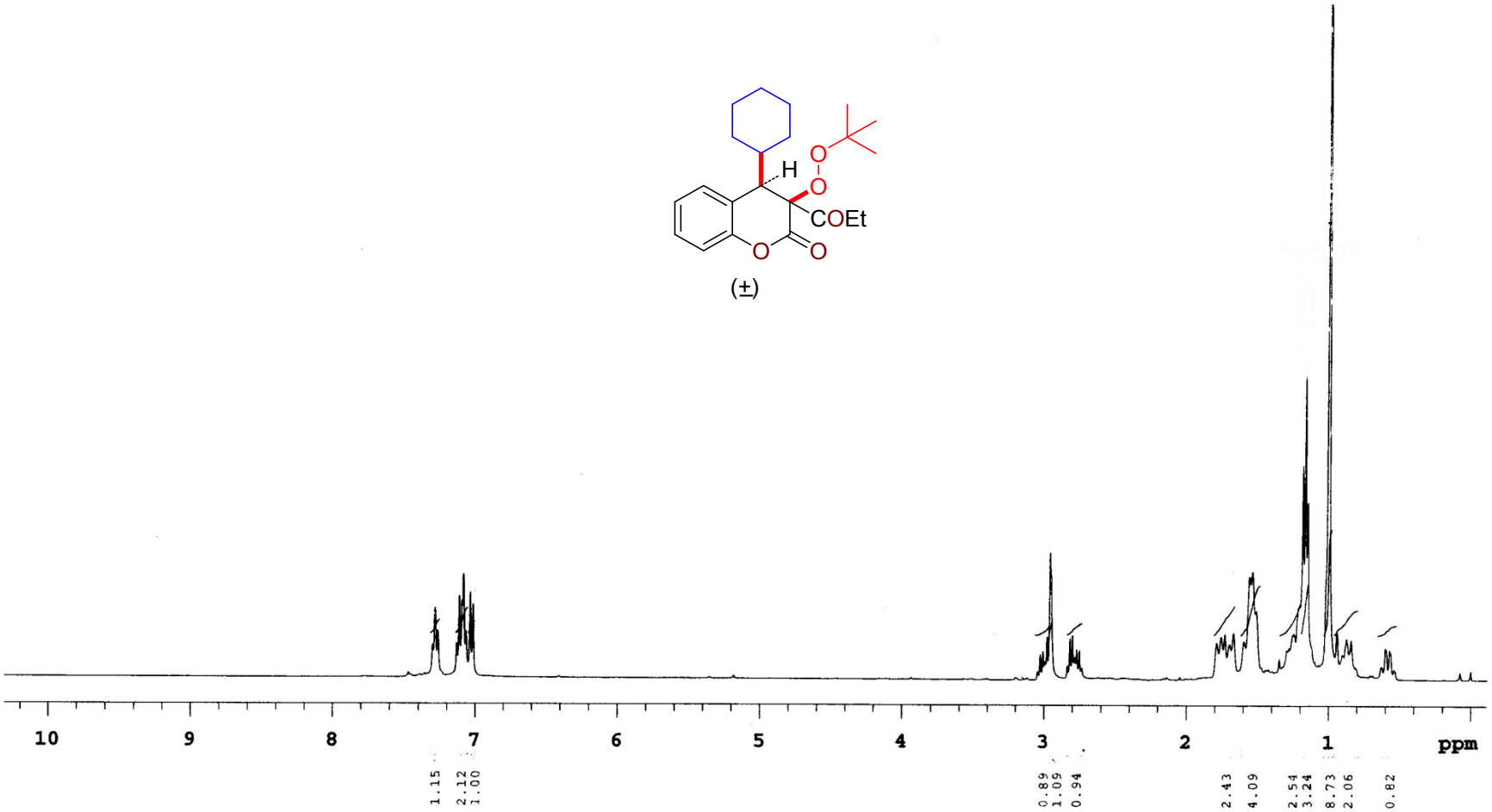
4-Cyclooctyl-3-hydroxy-2H-chromen-2-one (1c'): ^{13}C NMR ($CDCl_3$, 150 MHz)



BRUKER

```
Current Data Parameters
NAME      AB-COME-OCT-13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140218
Time              10.53
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                32768
SOLVENT           CDC13
NS                  198
DS                    2
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.4543829 sec
RG                65.24
DW               13.867 usec
DE                6.50 usec
TE                301.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9279571 MHz
NUC1                13C
P1                10.50 usec
PLW1         95.00000000 W

======== CHANNEL f2 ========
SFO2        600.1724007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2         21.00000000 W
PLW12         0.61714000 W
PLW13         0.30239999 W

F2 - Processing parameters
SI                 16384
SF          150.9128370 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

3-(*tert*-Butylperoxy)-4-cyclohexyl-3-propionylchroman-2-one (10a): ^{1}H NMR ($CDCl_3$, 400 MHz)



PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.561 sec
Width 6398.0 Hz
32 repetitions

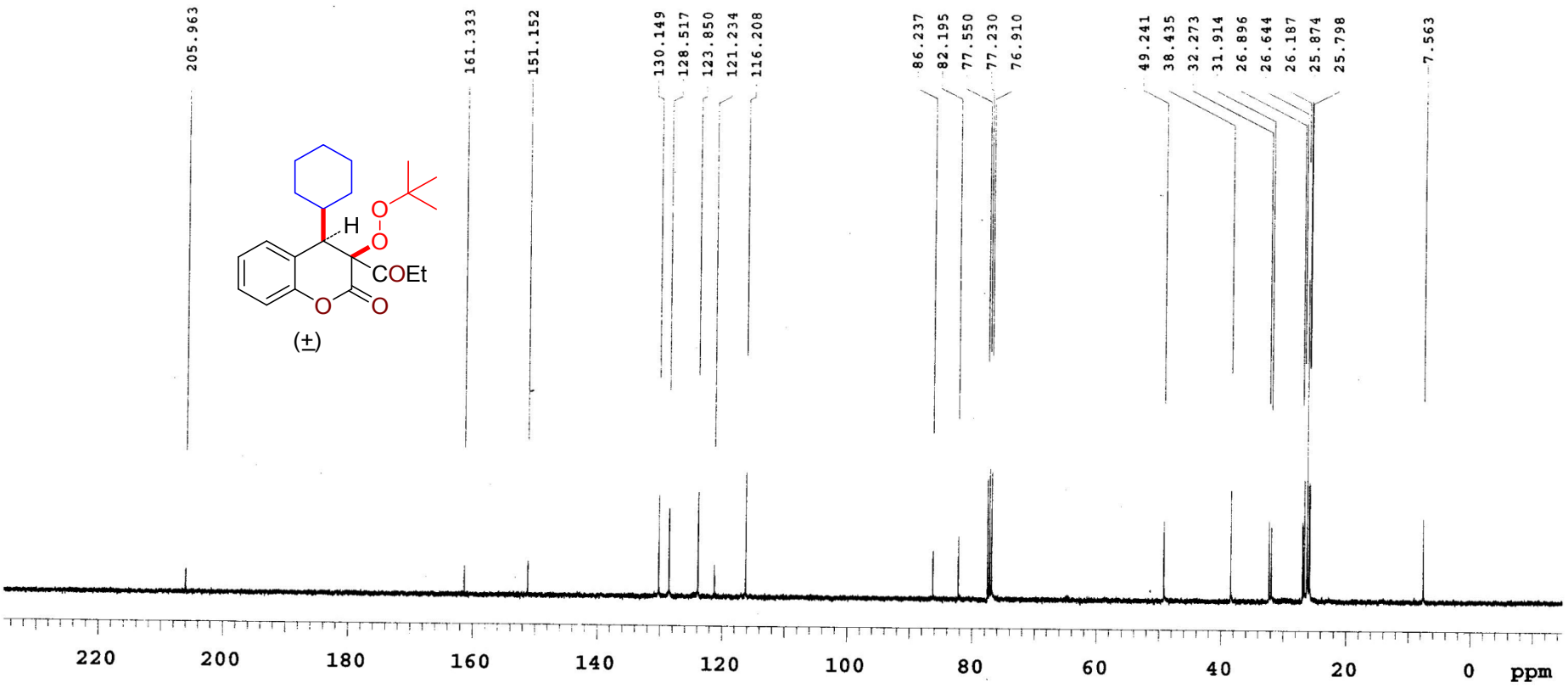
OBSERVE H1, 399.8509531

DATA PROCESSING
FT size 32768
Total time 1 minutes

AB-COEt-Cy-1H

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
Mercury-400 "IITG-NMR"

3-(*tert*-Butylperoxy)-4-cyclohexyl-3-propionylchroman-2-one (10a): ^{13}C NMR ($CDCl_3$, 100 MHz)



PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
500 repetitions

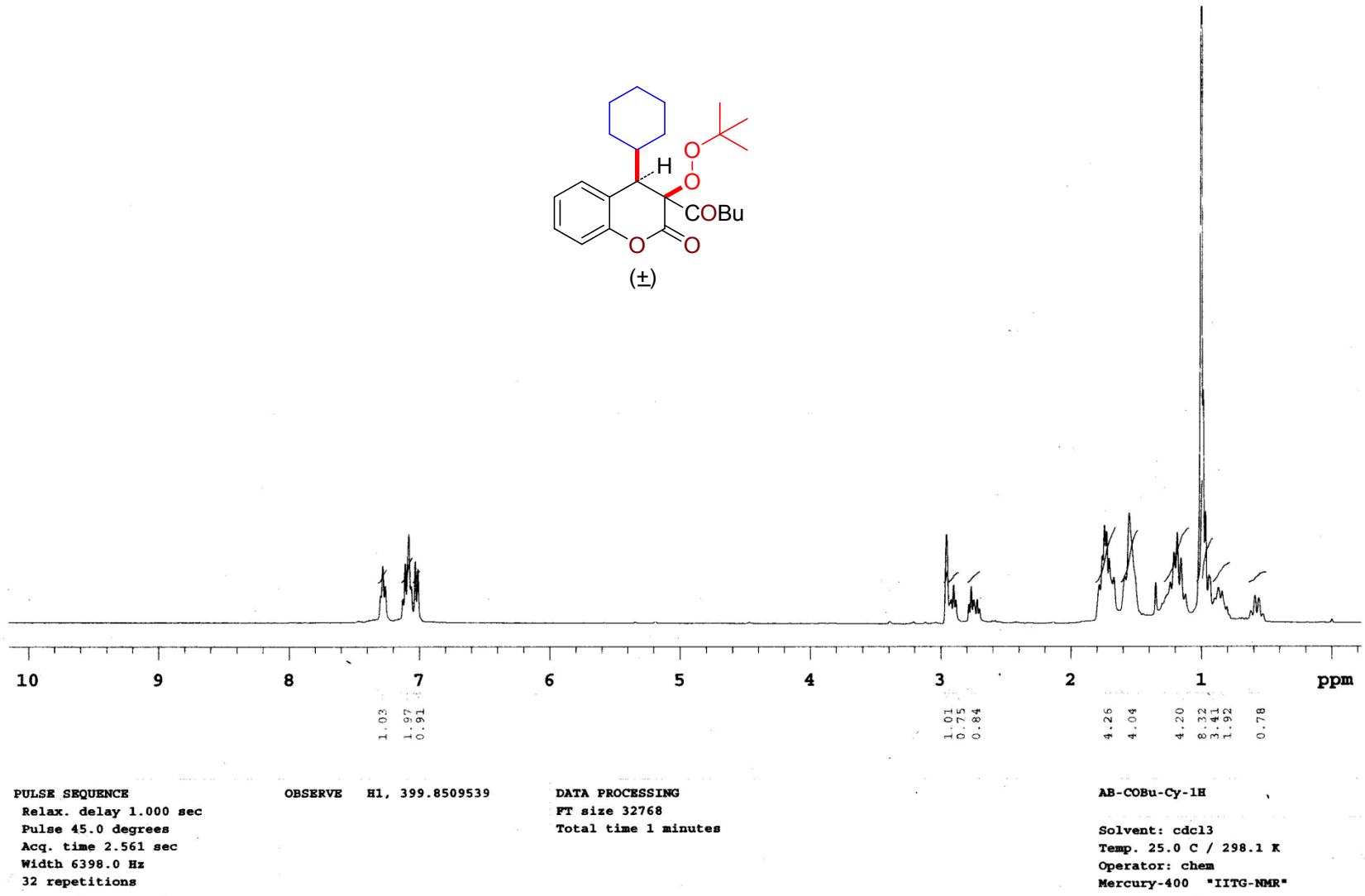
OBSERVE C13, 100.5425855
DECOUPLE H1, 399.8529994
Power 42 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 minutes

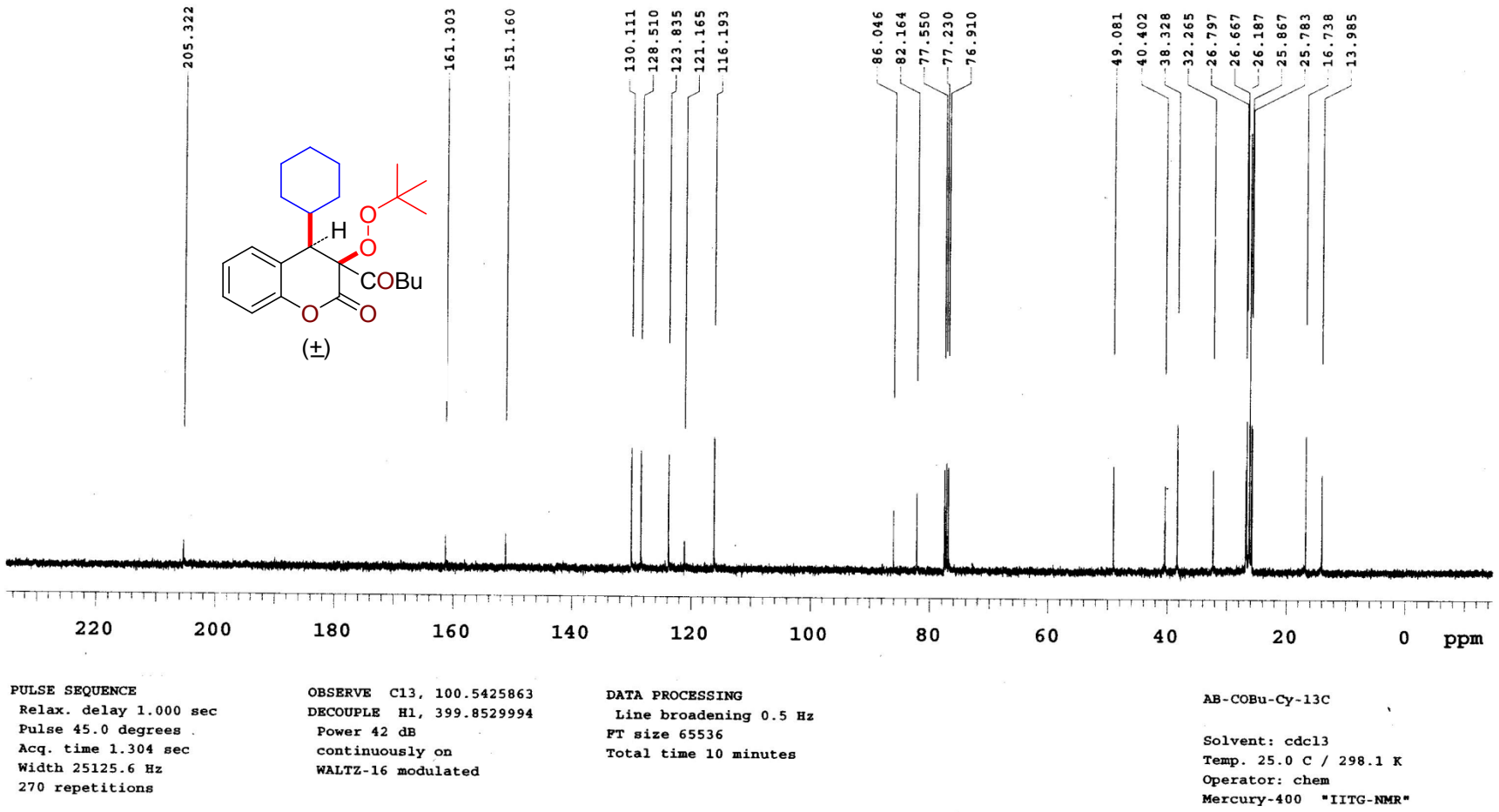
AB-COEt-Cy-13C

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
Mercury-400 "IITG-NMR"

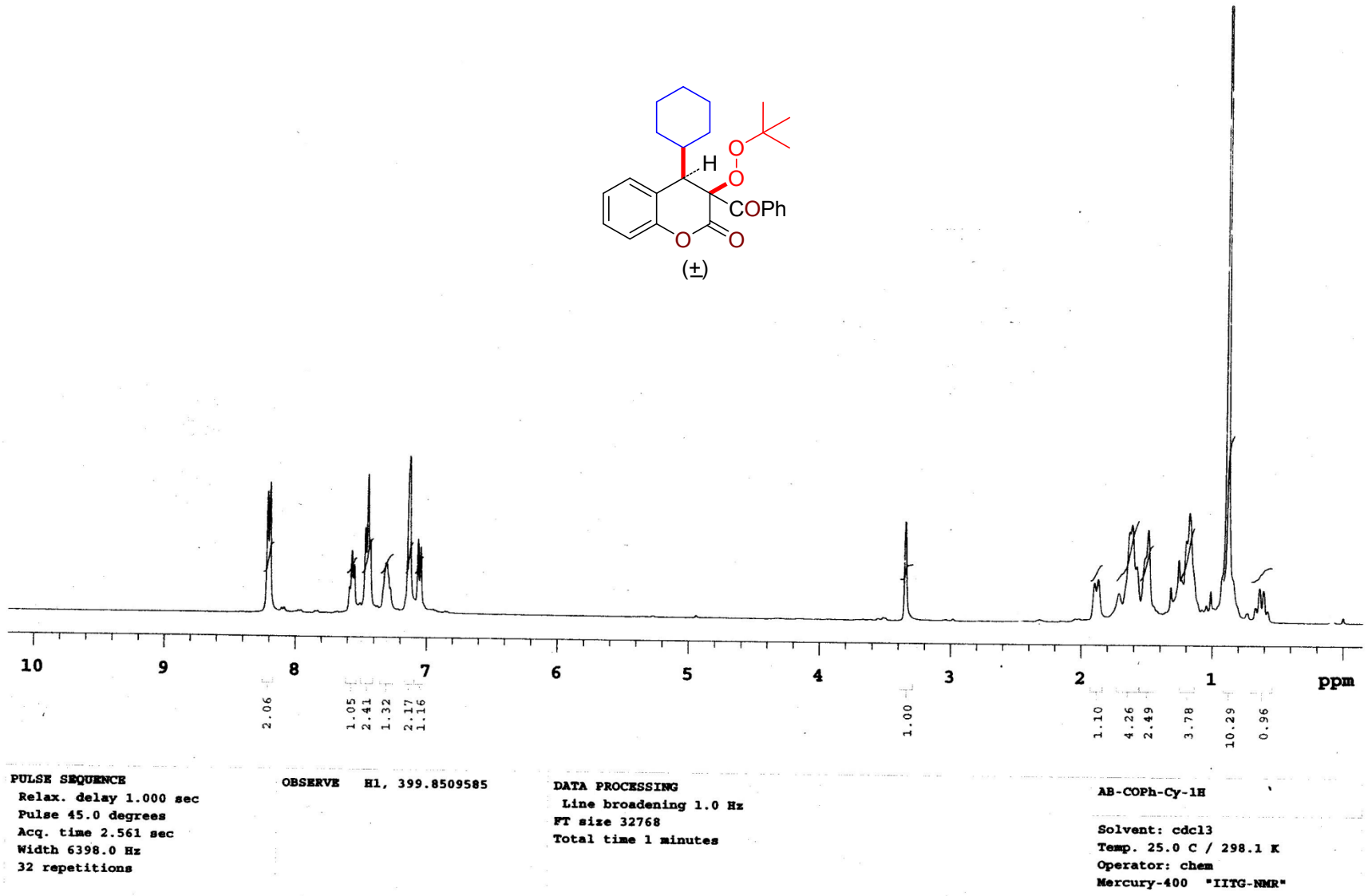
3-(*tert*-Butylperoxy)-4-cyclohexyl-3-pentanoylchroman-2-one (11a): ^{1}H NMR ($CDCl_3$, 400 MHz)



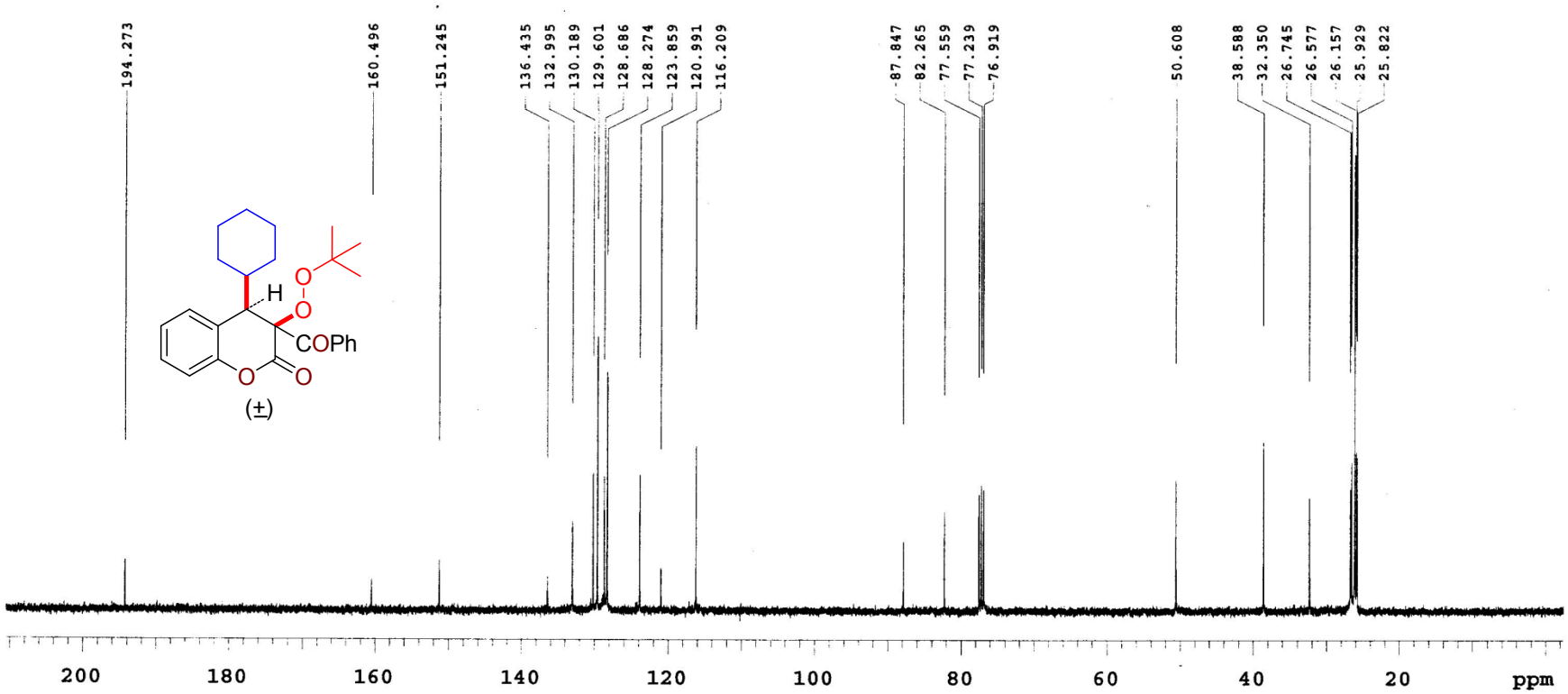
3-(*tert*-Butylperoxy)-4-cyclohexyl-3-pentanoylchroman-2-one (11a): ^{13}C NMR ($CDCl_3$, 100 MHz)



3-Benzoyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (12a): ^{1}H NMR ($CDCl_3$, 400 MHz)



3-Benzoyl-3-(*tert*-butylperoxy)-4-cyclohexylchroman-2-one (12a): ^{13}C NMR ($CDCl_3$, 100 MHz)



PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
410 repetitions

OBSERVE C13, 100.5425861
DECOUPLE H1, 399.8529994
Power 42 dB
continuously on
WALTZ-16 modulated

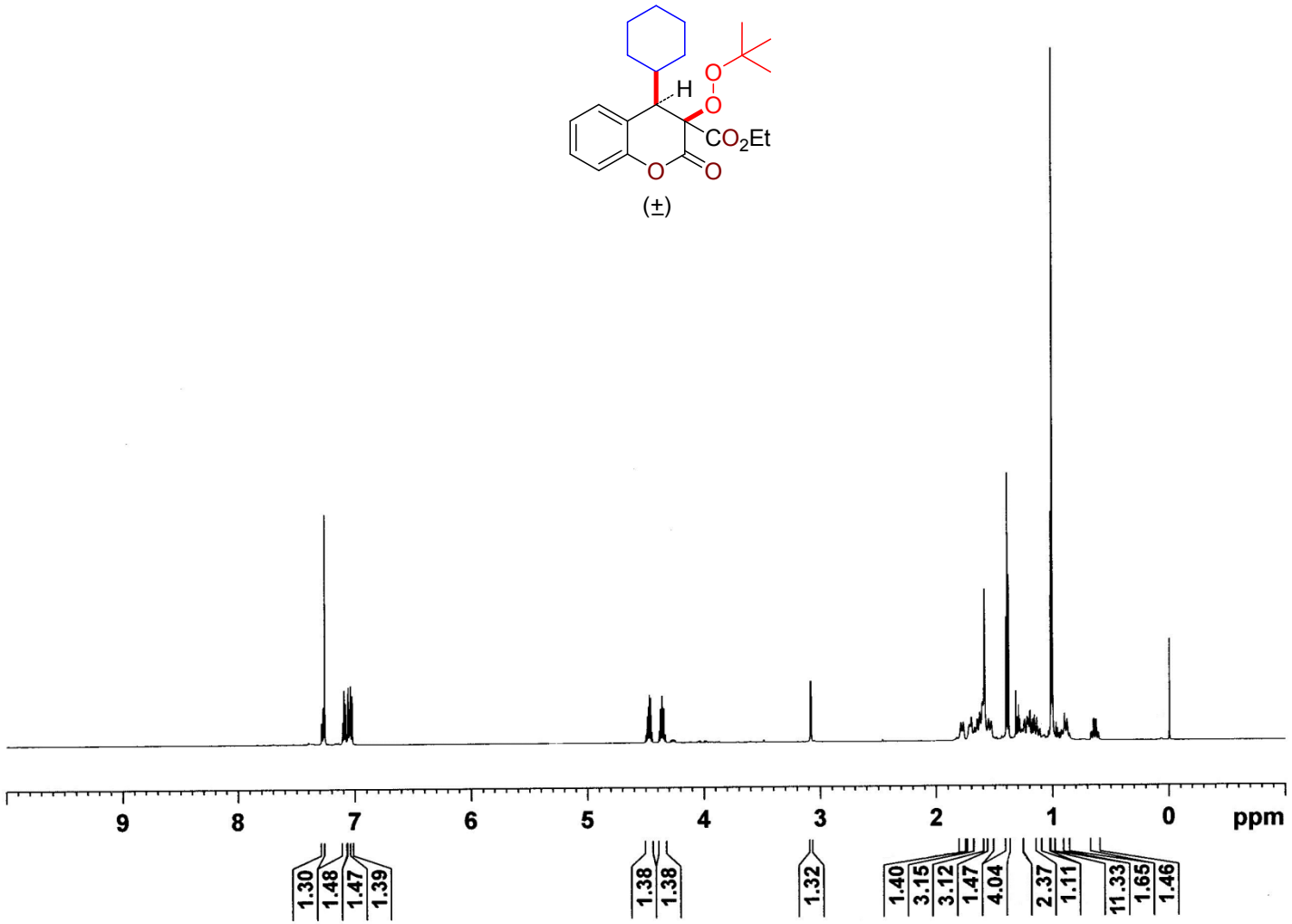
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 15 minutes

AB-COPh-Cy-13C

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
Mercury-400 "IITG-NMR"

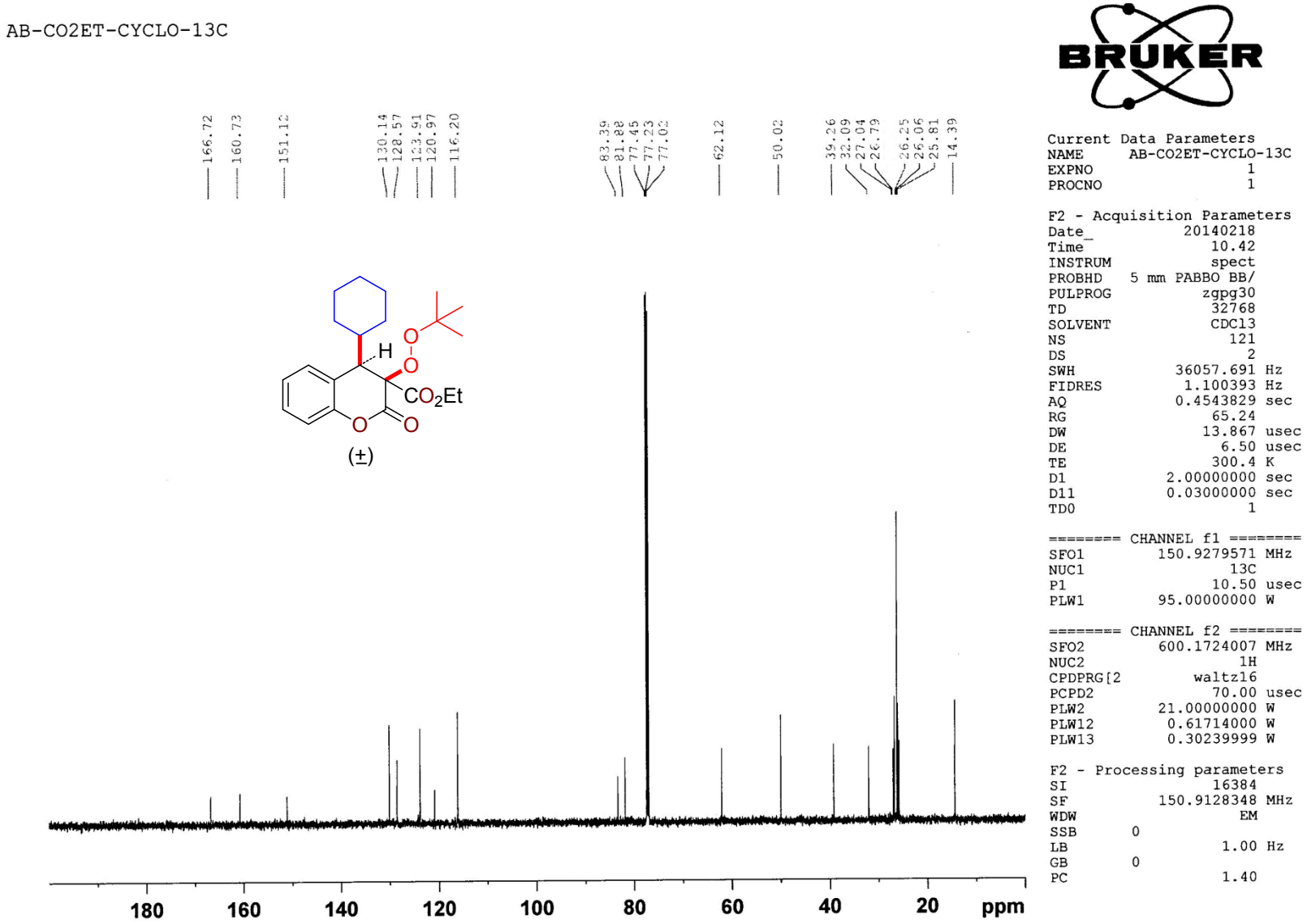
Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (13a): ^{1}H NMR ($CDCl_3$, 600 MHz)

AB-CO2ET-CYCLO_1H



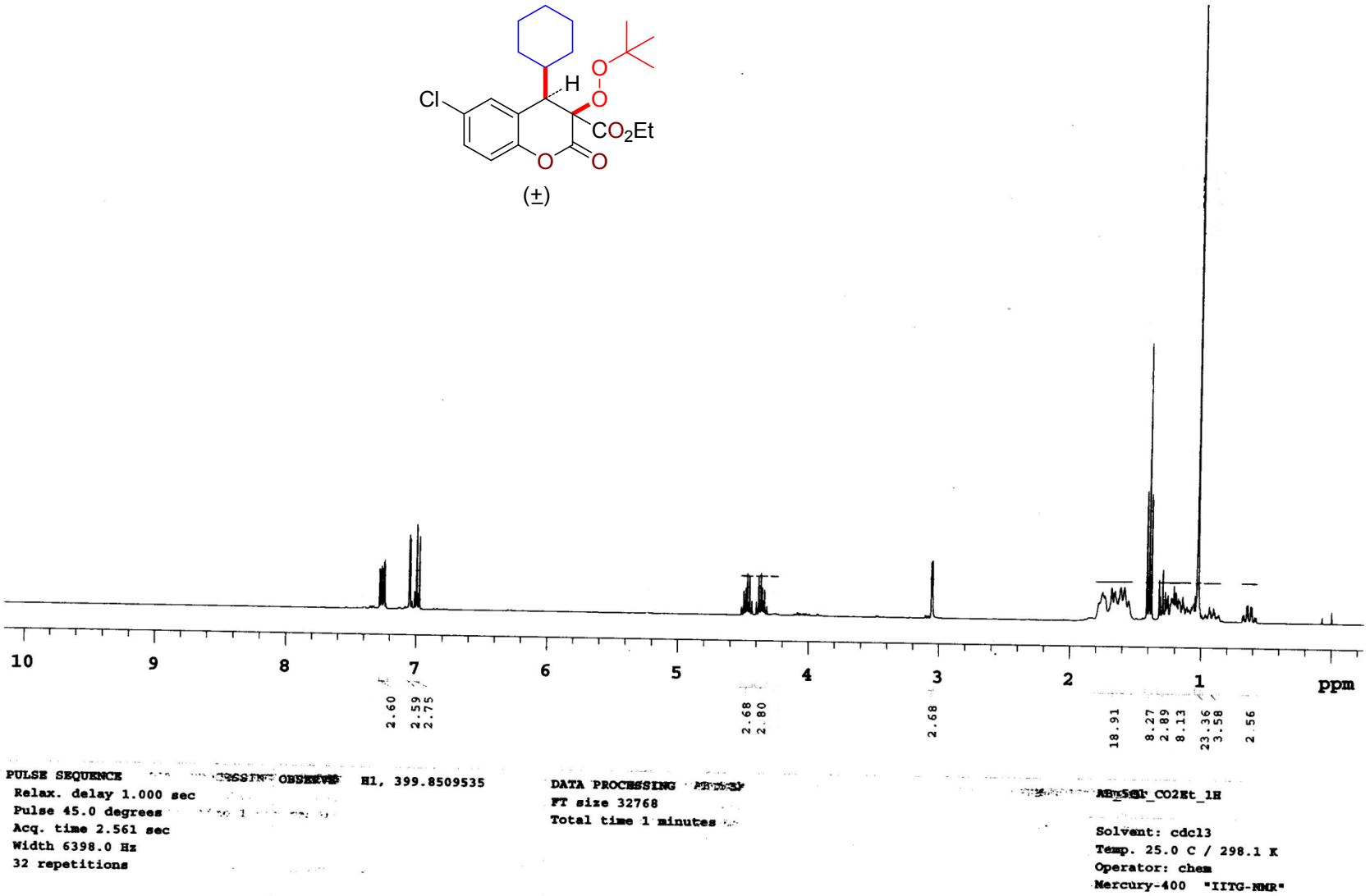

```
Current Data Parameters
NAME      AB-CO2ET-CYCLO_1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140128
Time                 16.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              12019.230 Hz
FIDRES               0.366798 Hz
AQ                1.3631488 sec
RG                    80.22
DW                   41.600 usec
DE                    6.50 usec
TE                   297.7 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          600.1737063 MHz
NUC1                    1H
P1                   12.00 usec
PLW1         21.00000000 W

F2 - Processing parameters
SI                   16384
SF            600.1700147 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (13a): ^{13}C NMR ($CDCl_3$, 150 MHz)

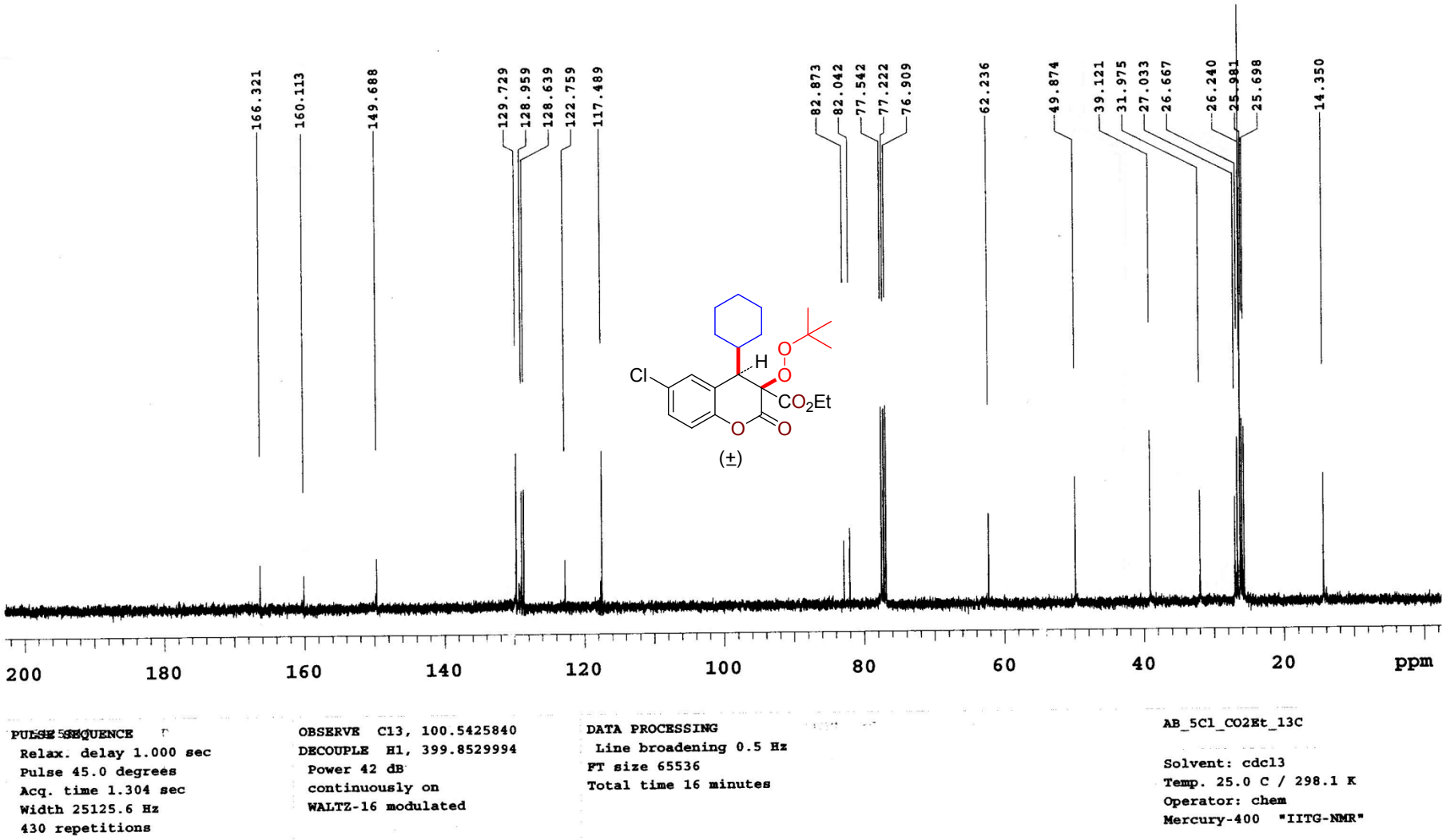



```
Current Data Parameters
NAME      AB-CO2ET-CYCLO-13C
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140218
Time                 10.42
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     121
DS                       2
SWH              36057.691 Hz
FIDRES           1.100393 Hz
AQ               0.4543829 sec
RG                   65.24
DW                 13.867 usec
DE                   6.50 usec
TE                  300.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                  13C
P1                  10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                    16384
SF            150.9128348 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

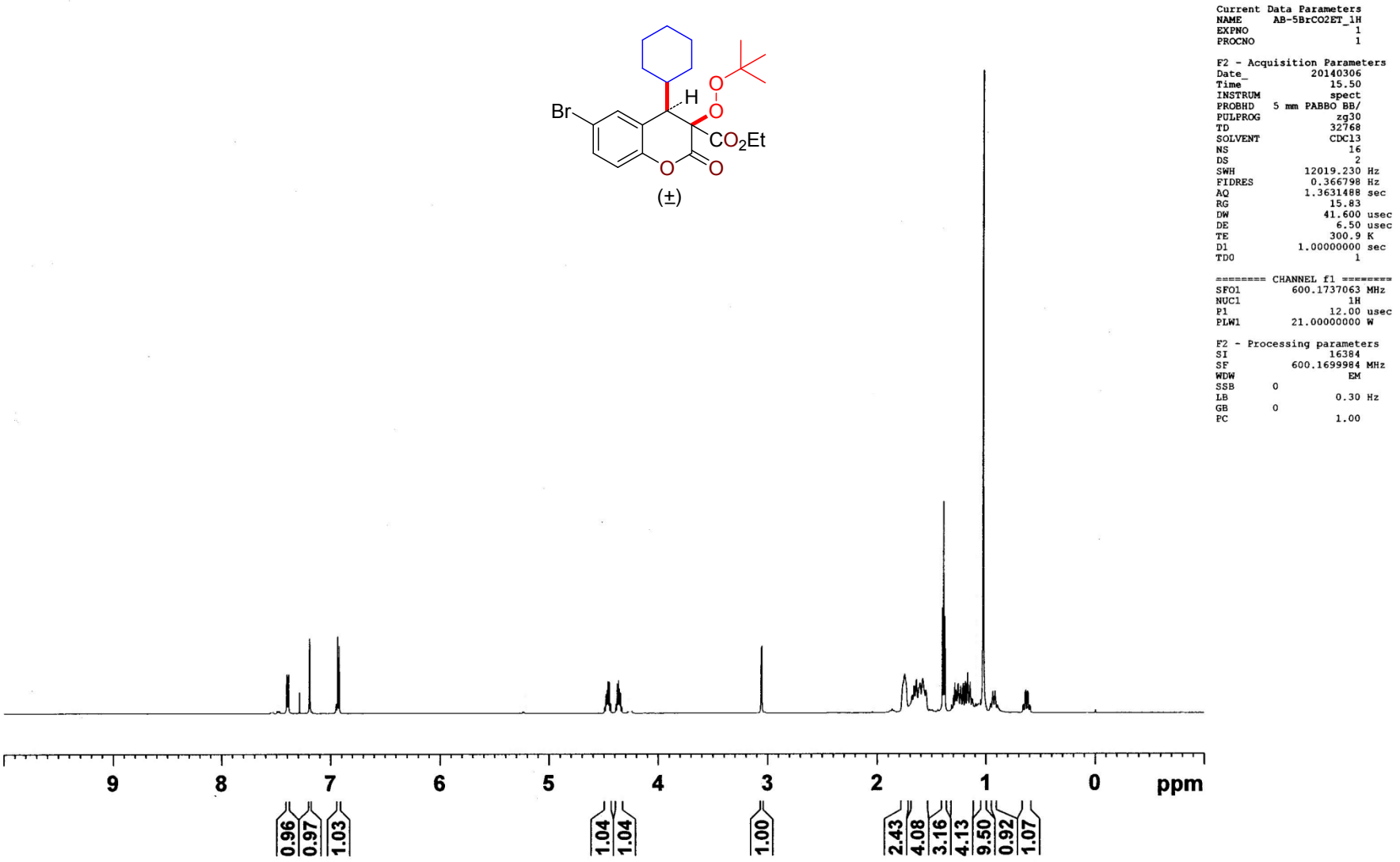
Ethyl 3-(*tert*-butylperoxy)-6-chloro-4-cyclohexyl-2-oxochroman-3-carboxylate (14a): ^{1}H NMR ($CDCl_3$, 400 MHz)



Ethyl 3-(*tert*-butylperoxy)-6-chloro-4-cyclohexyl-2-oxochroman-3-carboxylate (14a): ^{13}C NMR ($CDCl_3$, 100 MHz)

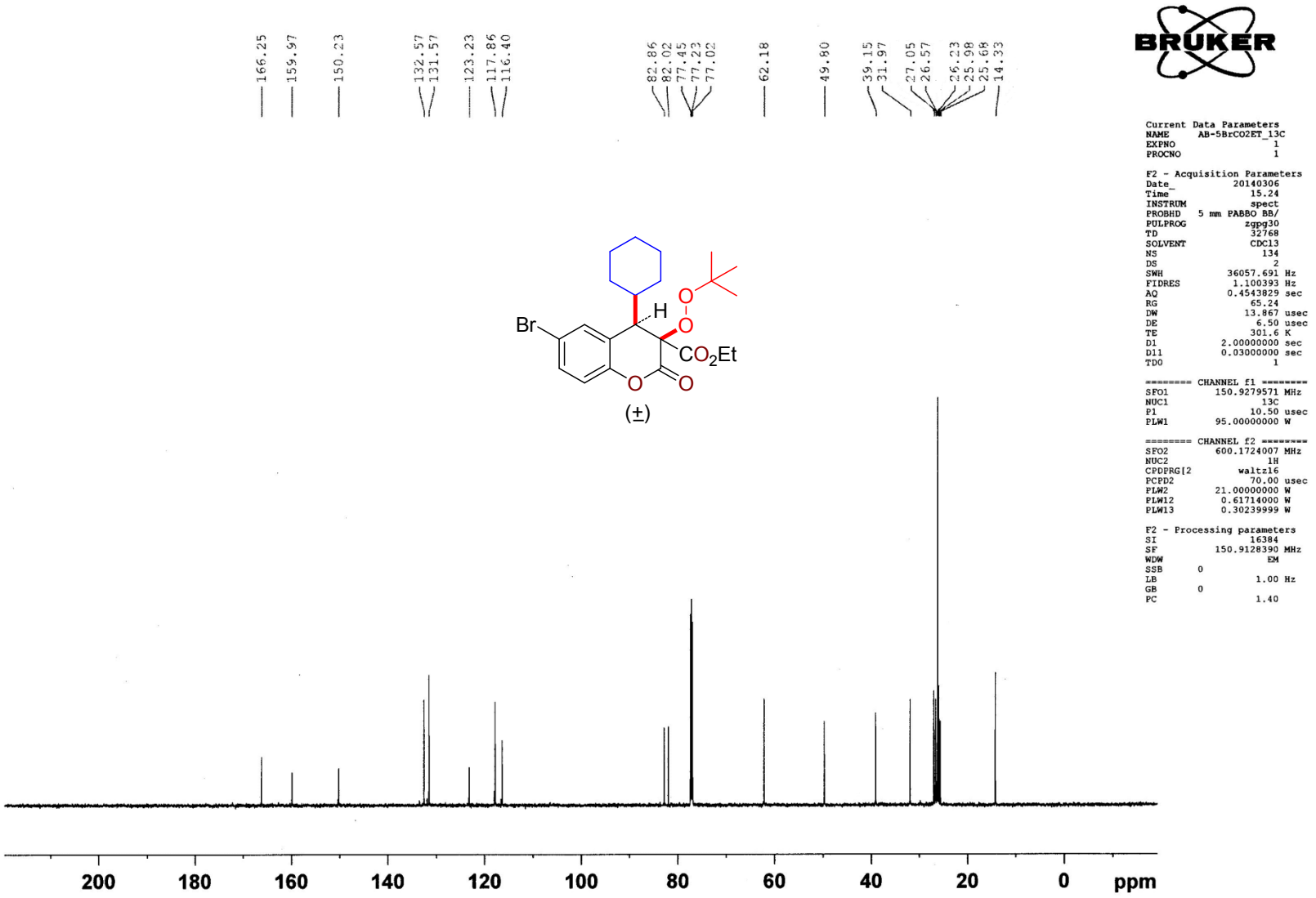


Ethyl 6-bromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (15a): ^{1}H NMR ($CDCl_3$, 600 MHz)



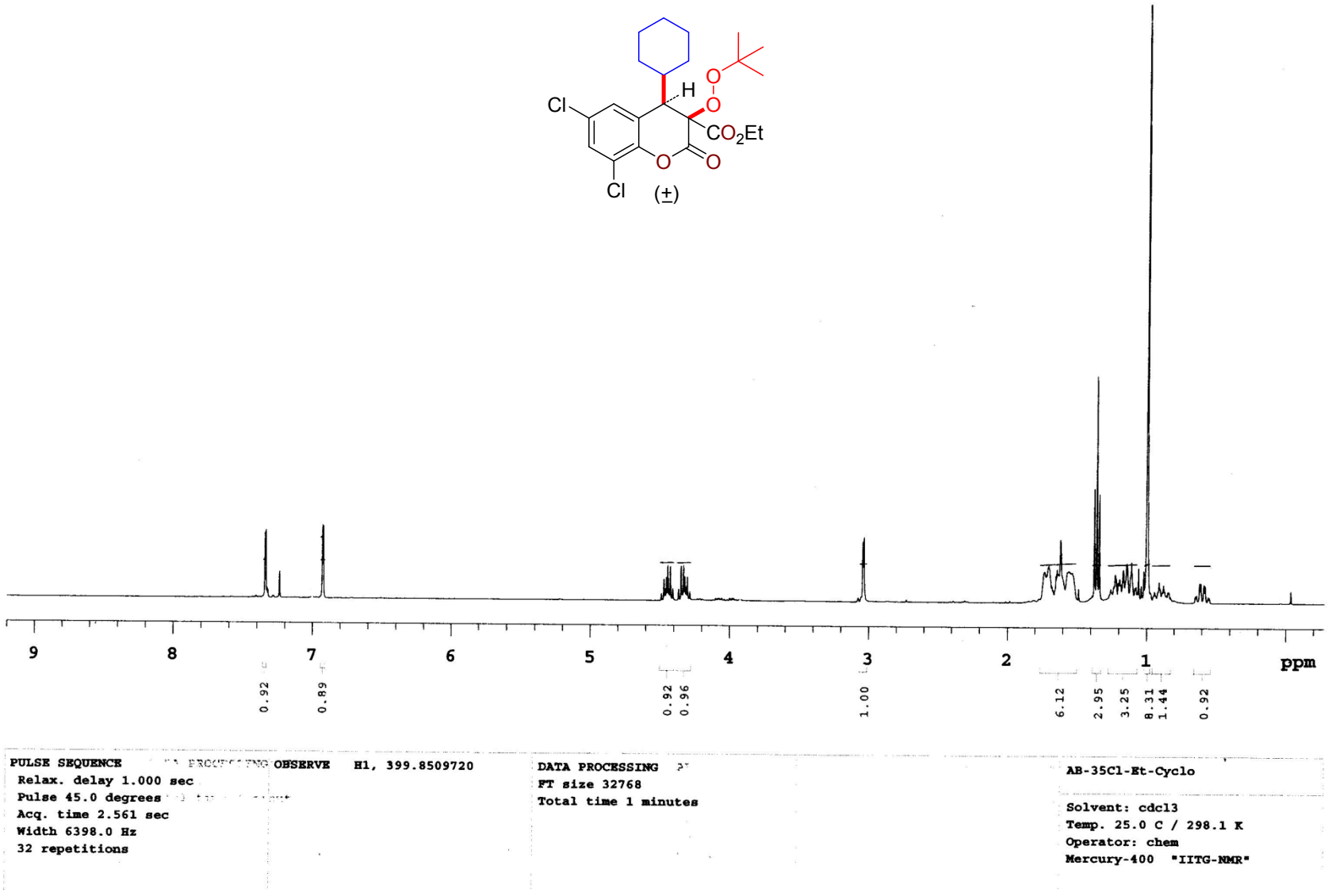

```
Current Data Parameters
NAME      AB-5BrCO2ET_1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140306
Time              15.50
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           12019.230 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                15.83
DW               41.600 usec
DE                6.50 usec
TE               300.9 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        600.1737063 MHz
NUC1                1H
P1                 12.00 usec
PLW1       21.00000000 W

F2 - Processing parameters
SI                 16384
SF          600.1699984 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

Ethyl 6-bromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (15a): ^{13}C NMR ($CDCl_3$, 150 MHz)

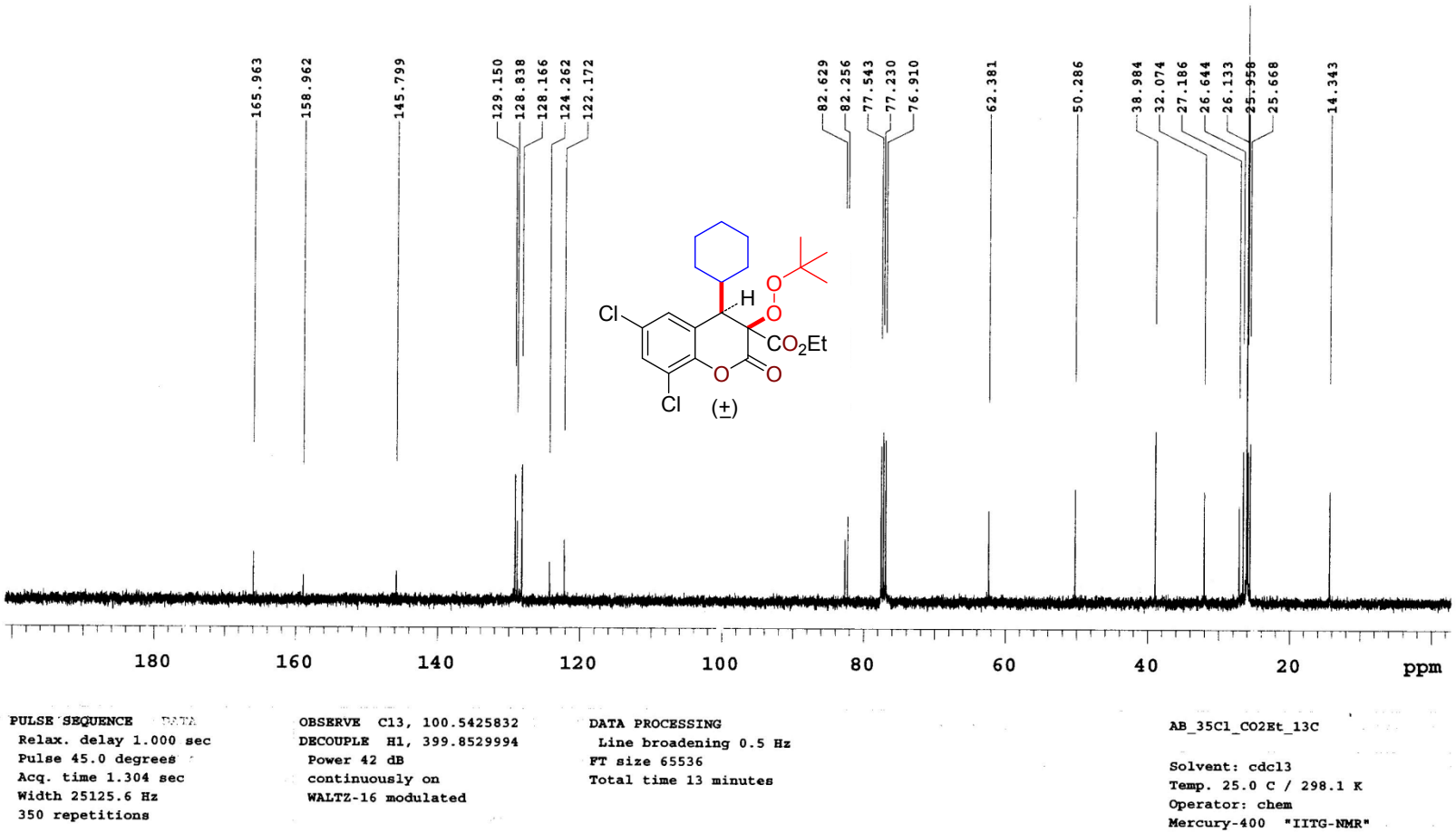



```
Current Data Parameters
NAME      AB-5BrCO2ET_13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140306
Time                15.24
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   134
DS                     2
SWH            36057.691 Hz
FIDRES          1.100393 Hz
AQ              0.4543829 sec
RG                  65.24
DW                 13.867 usec
DE                   6.50 usec
TE                  301.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9279571 MHz
NUC1                   13C
P1                   10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2         600.1724007 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                   16384
SF           150.9128390 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

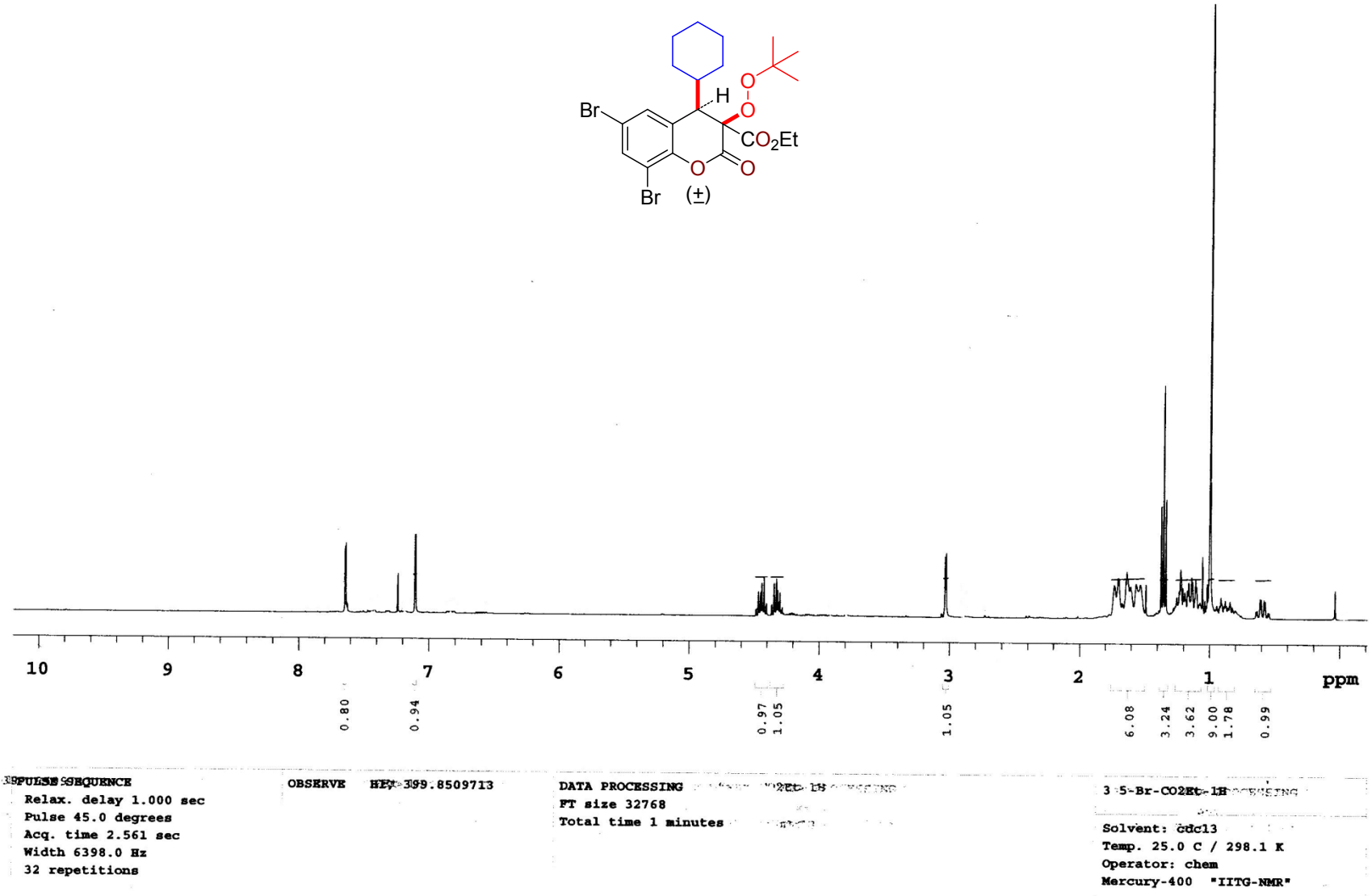
Ethyl 3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexyl-2-oxochroman-3-carboxylate (16a): ^{1}H NMR ($CDCl_3$, 400 MHz)



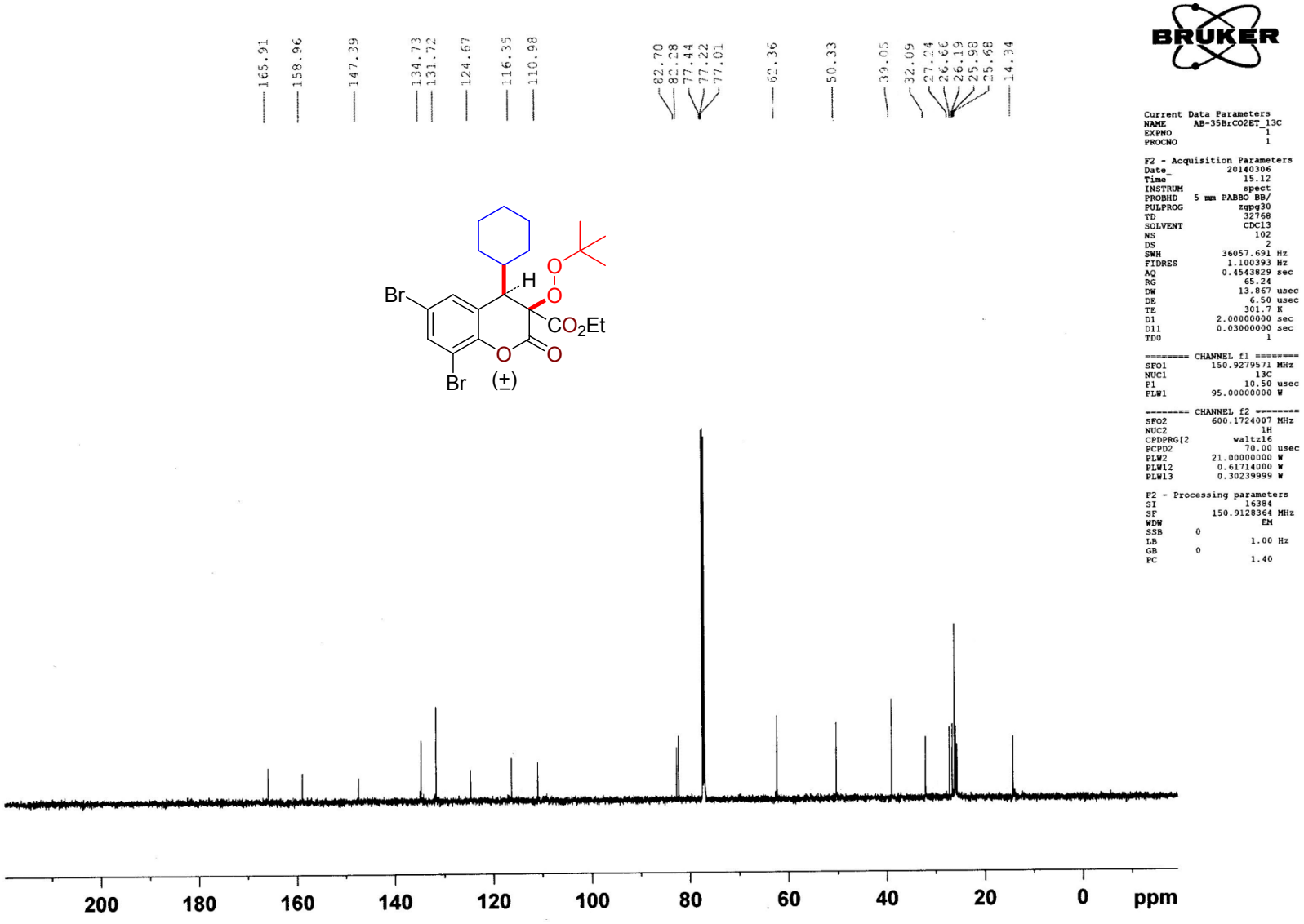
Ethyl 3-(*tert*-butylperoxy)-6,8-dichloro-4-cyclohexyl-2-oxochroman-3-carboxylate (16a): ^{13}C NMR ($CDCl_3$, 100 MHz)



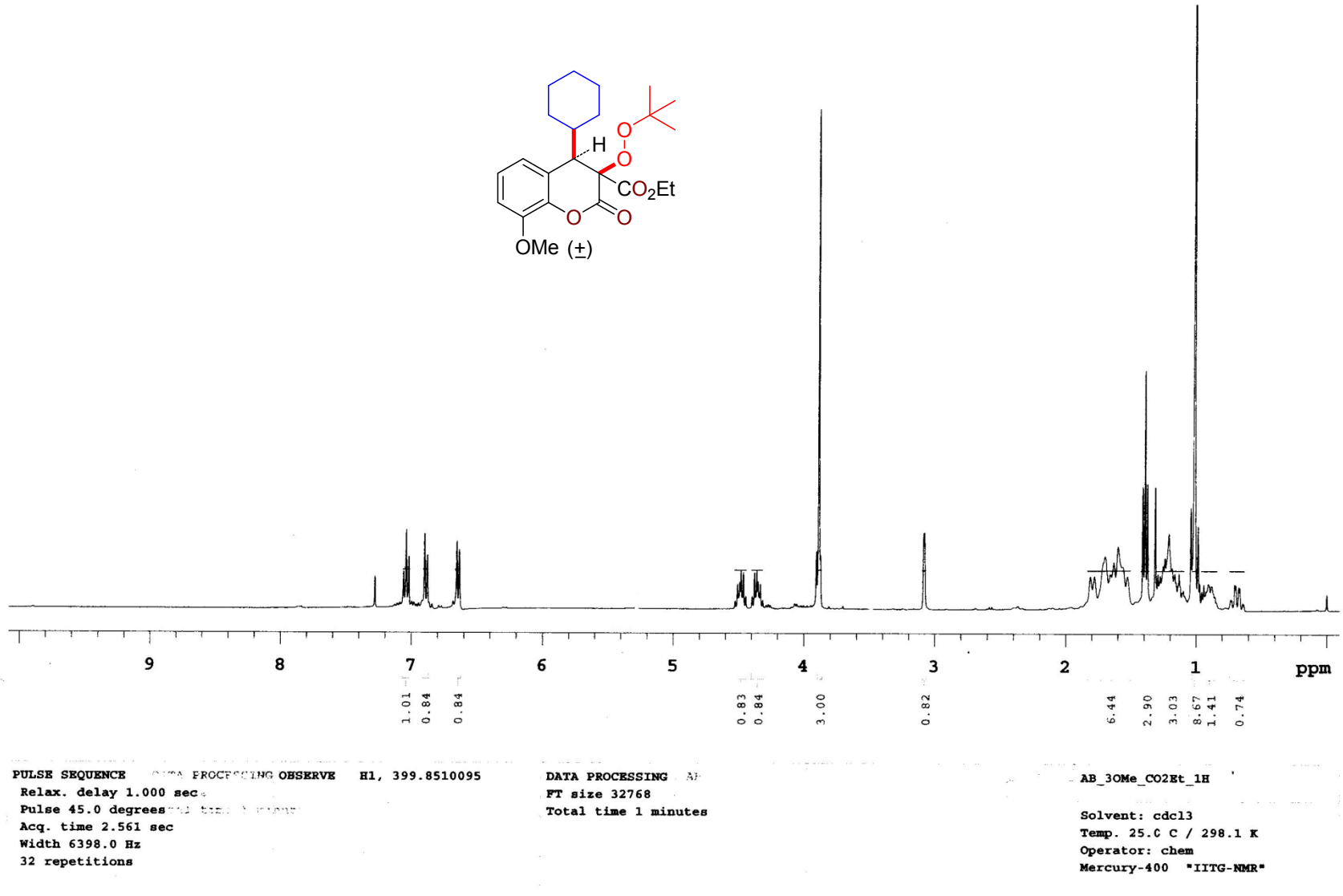
Ethyl 6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (17a): ^{1}H NMR ($CDCl_3$, 400 MHz)



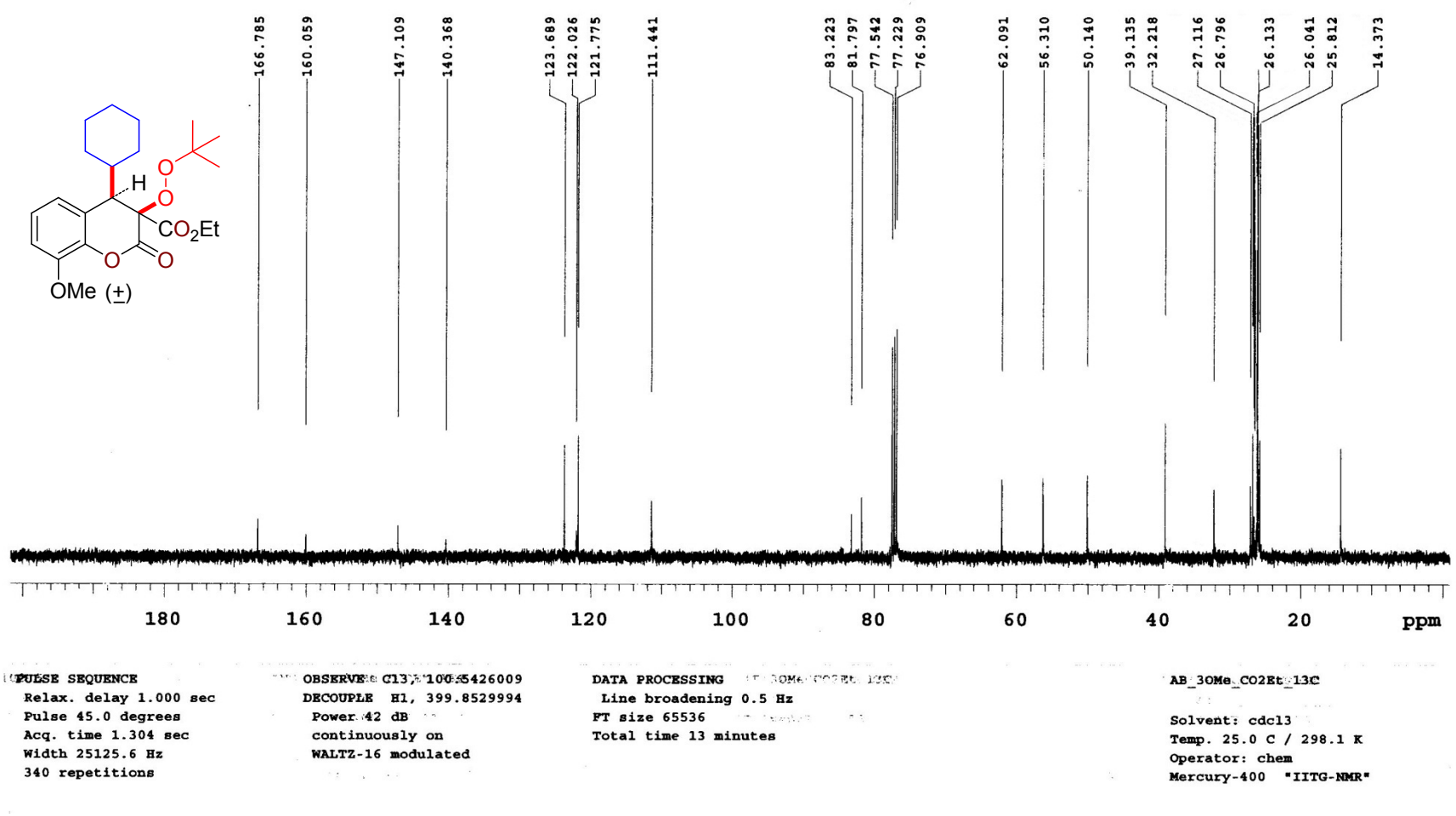
Ethyl 6,8-dibromo-3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (17a): ^{13}C NMR ($CDCl_3$, 150 MHz)



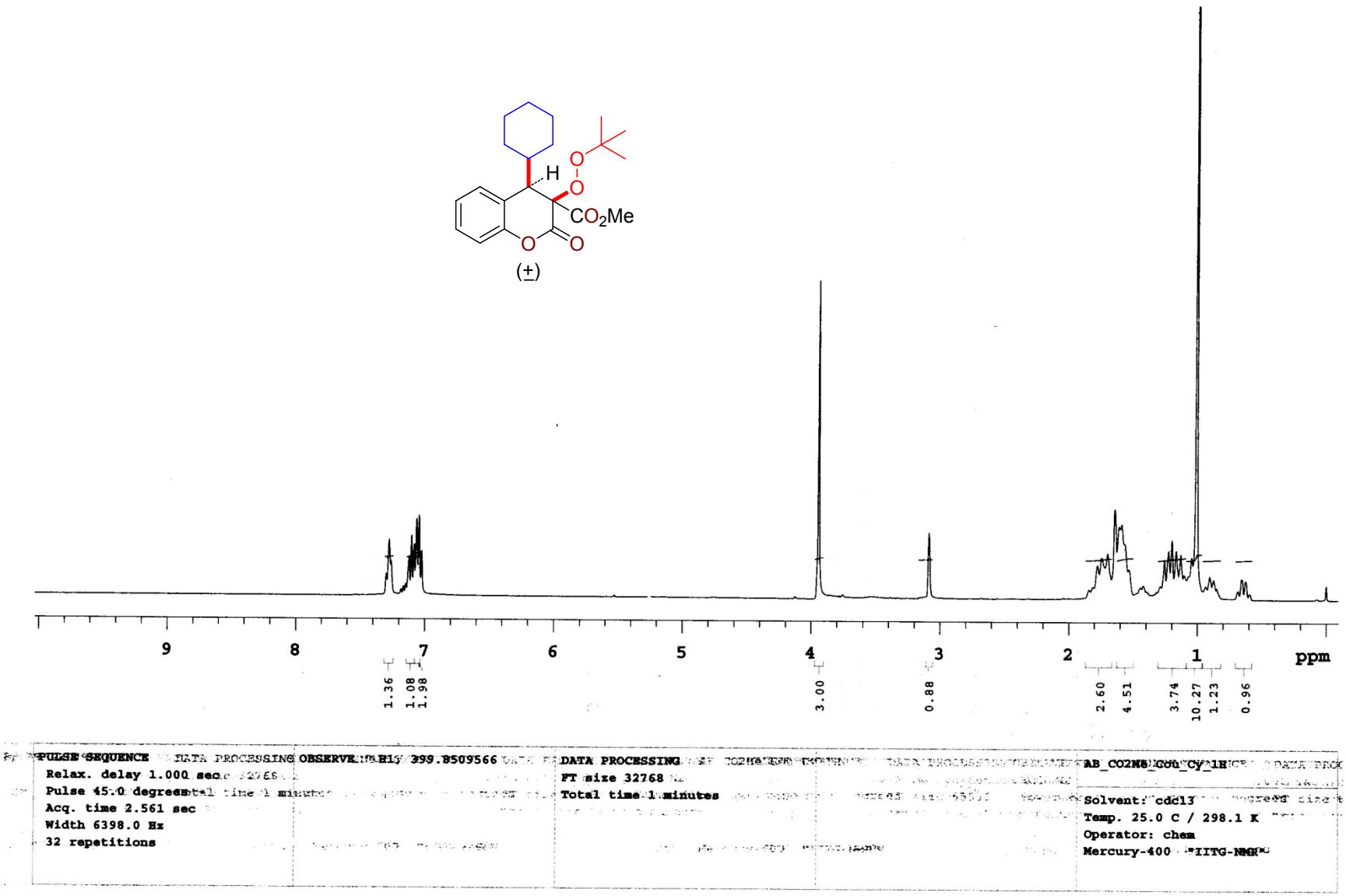
Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxy-2-oxochroman-3-carboxylate (18a): ^{1}H NMR ($CDCl_3$, 400 MHz)



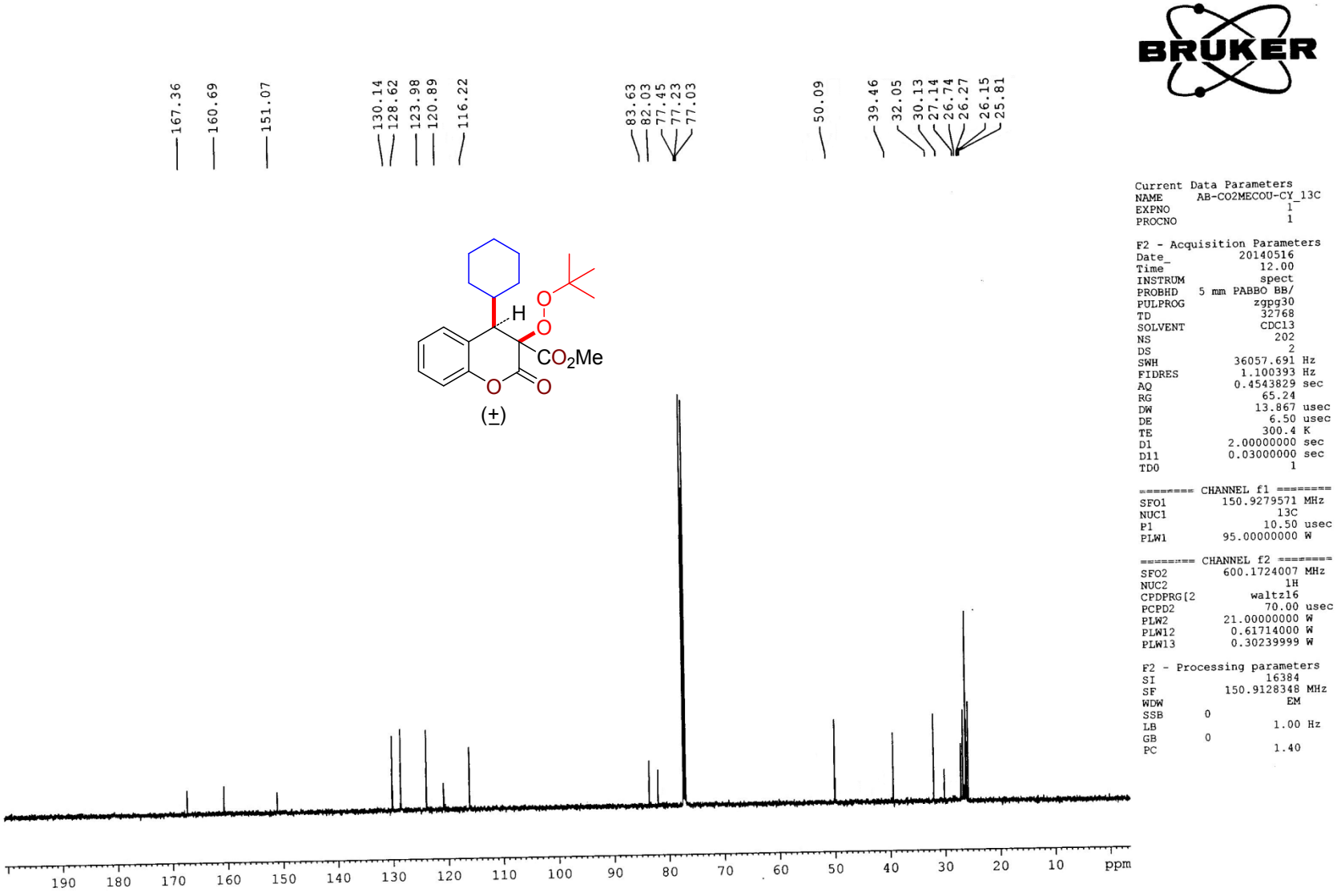
Ethyl 3-(*tert*-butylperoxy)-4-cyclohexyl-8-methoxy-2-oxochroman-3-carboxylate (18a): ^{13}C NMR ($CDCl_3$, 100 MHz)



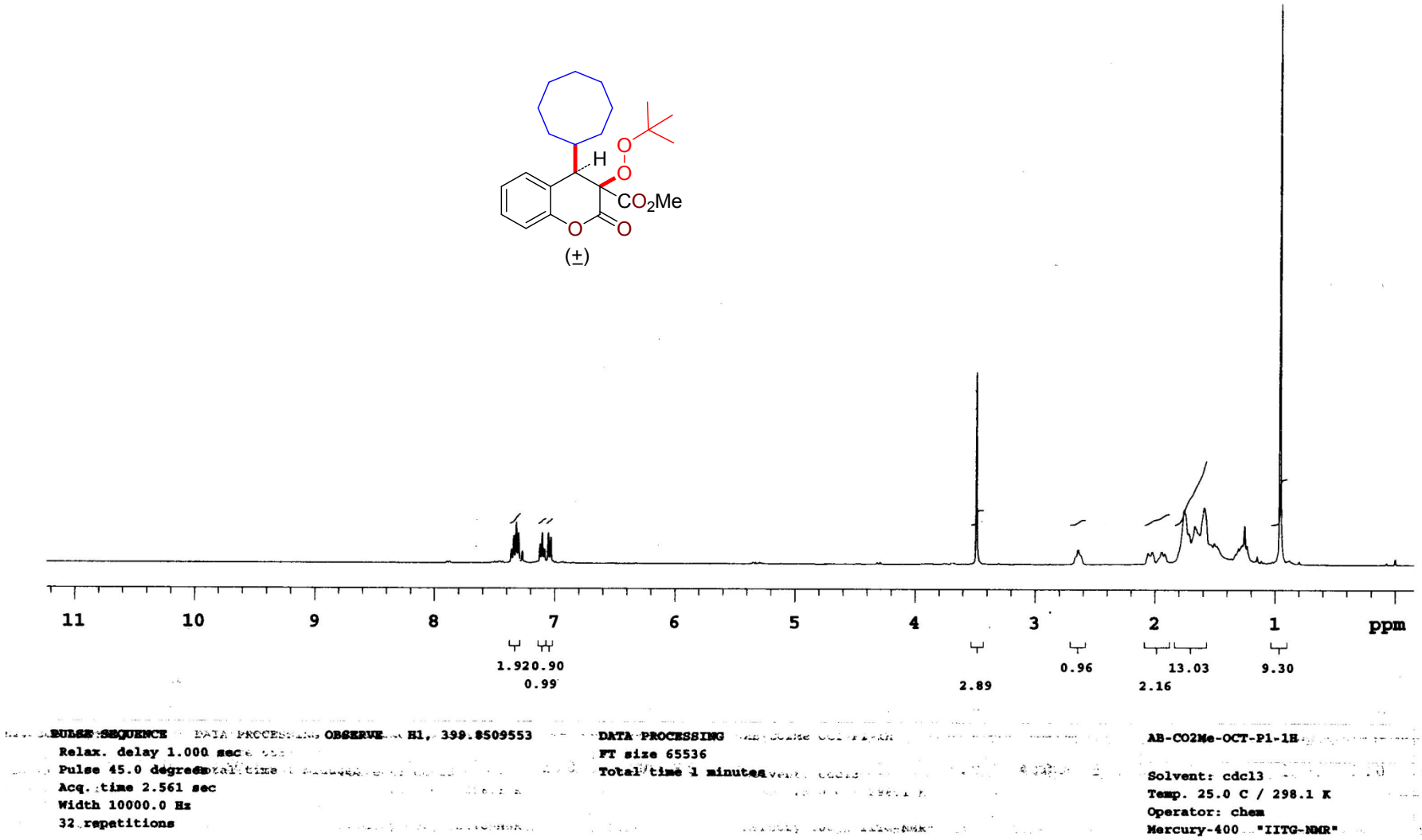
Methyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (19a): ^{1}H NMR ($CDCl_3$, 400 MHz)



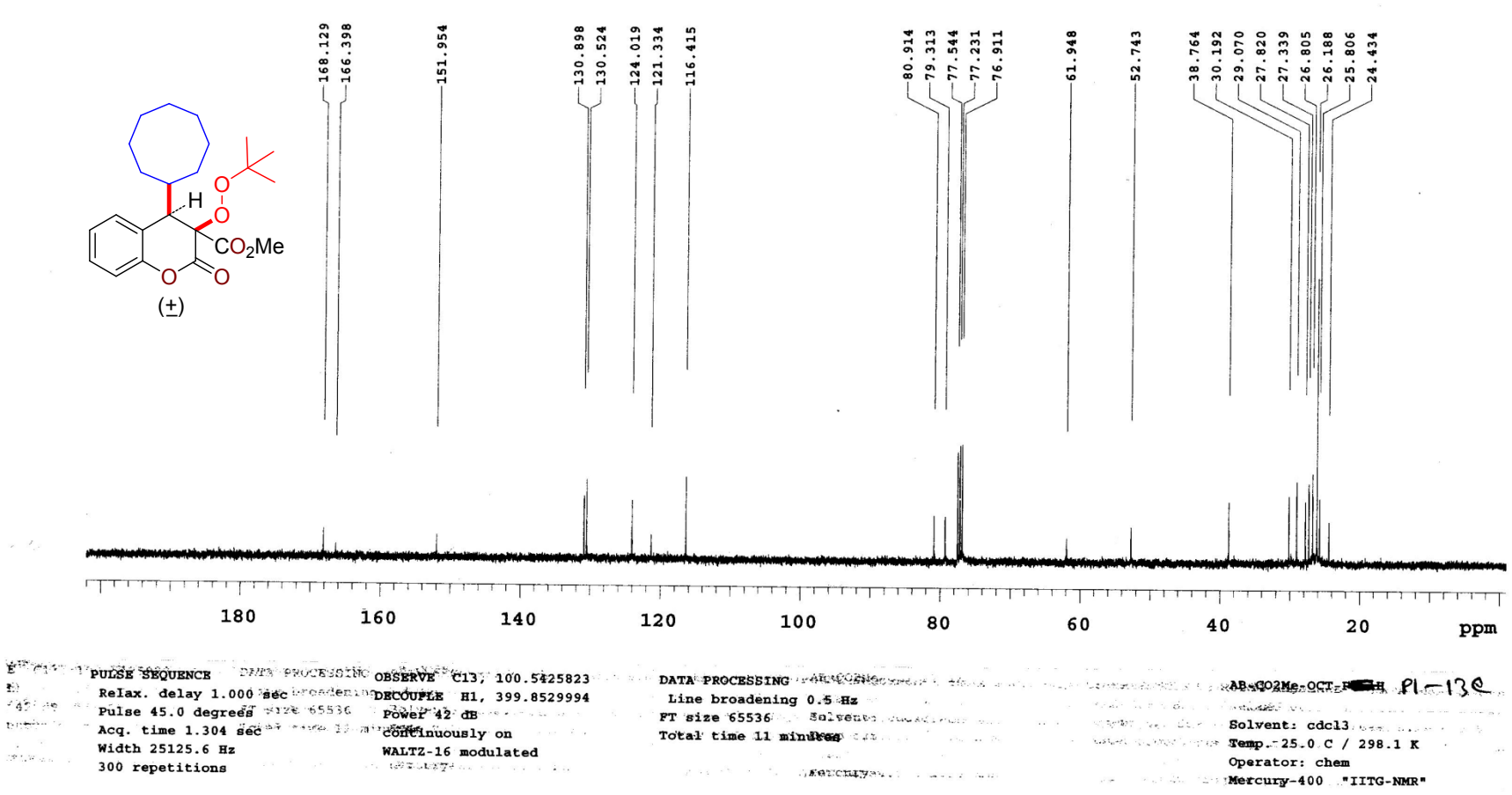
Methyl 3-(*tert*-butylperoxy)-4-cyclohexyl-2-oxochroman-3-carboxylate (19a): ^{13}C NMR ($CDCl_3$, 150 MHz)



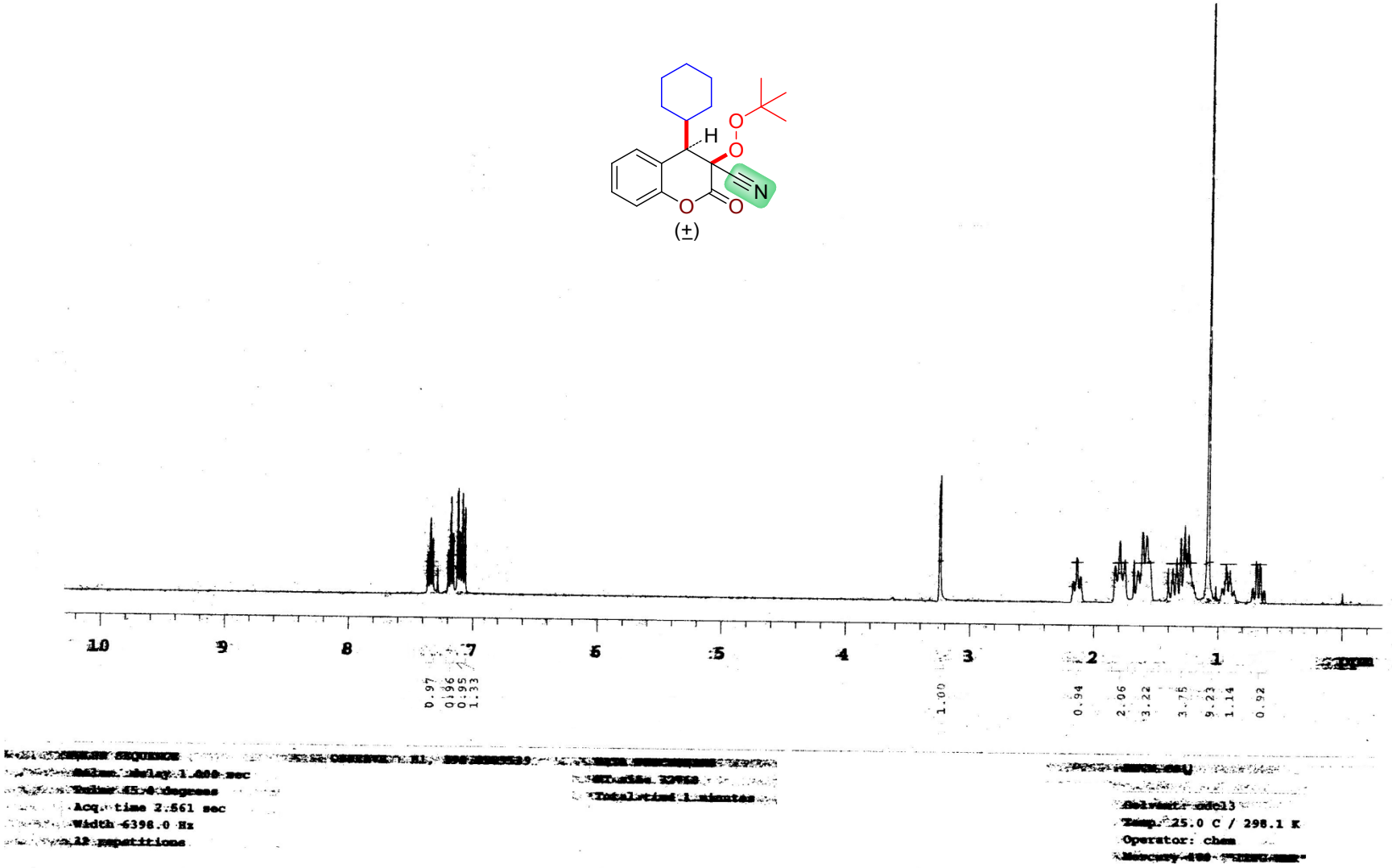
Methyl 3-(*tert*-butylperoxy)-4-cyclooctyl-2-oxochroman-3-carboxylate (19c): ^{1}H NMR ($CDCl_3$, 400 MHz)



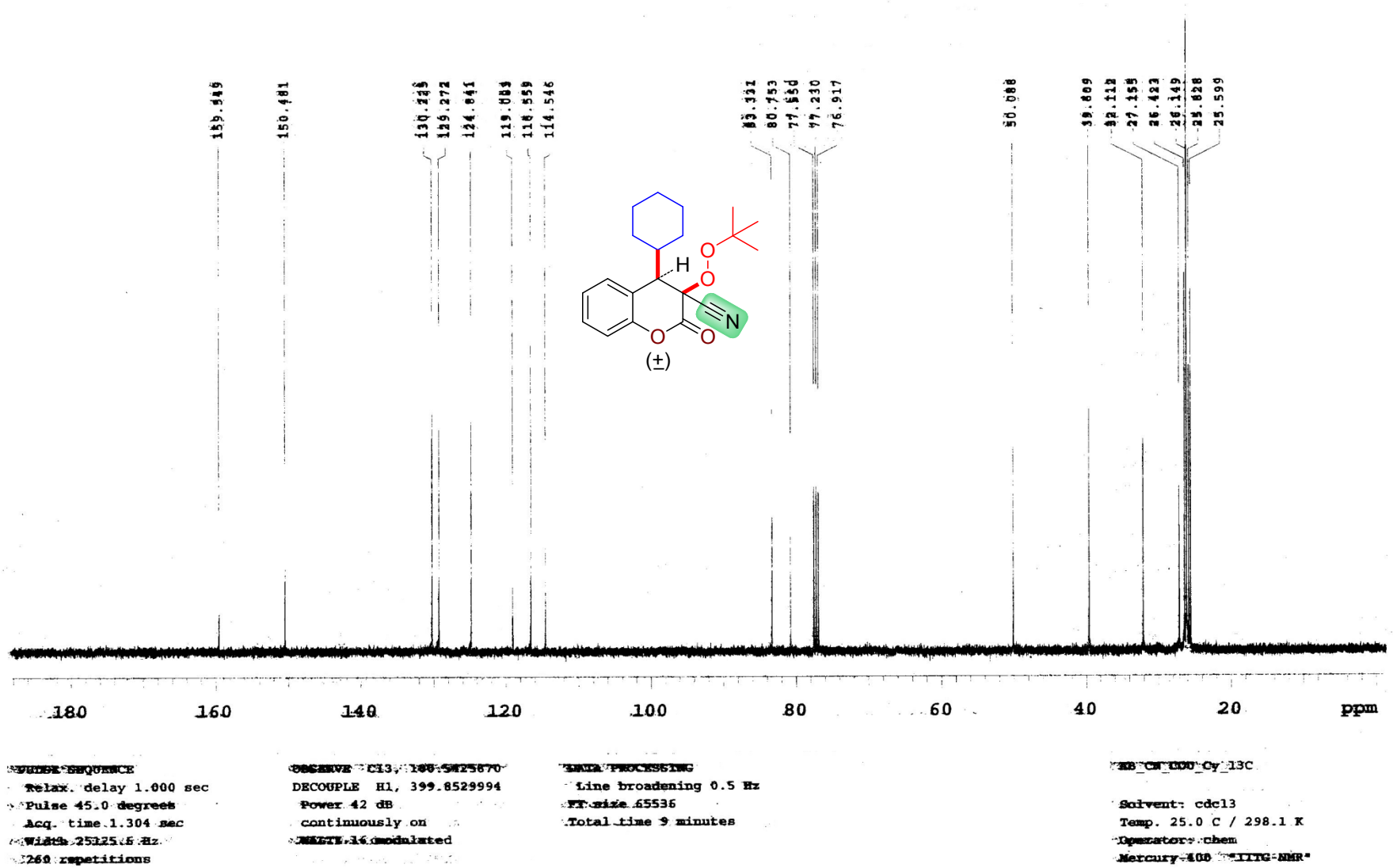
Methyl 3-(*tert*-butylperoxy)-4-cyclooctyl-2-oxochroman-3-carboxylate (19c): ^{13}C NMR ($CDCl_3$, 100 MHz)



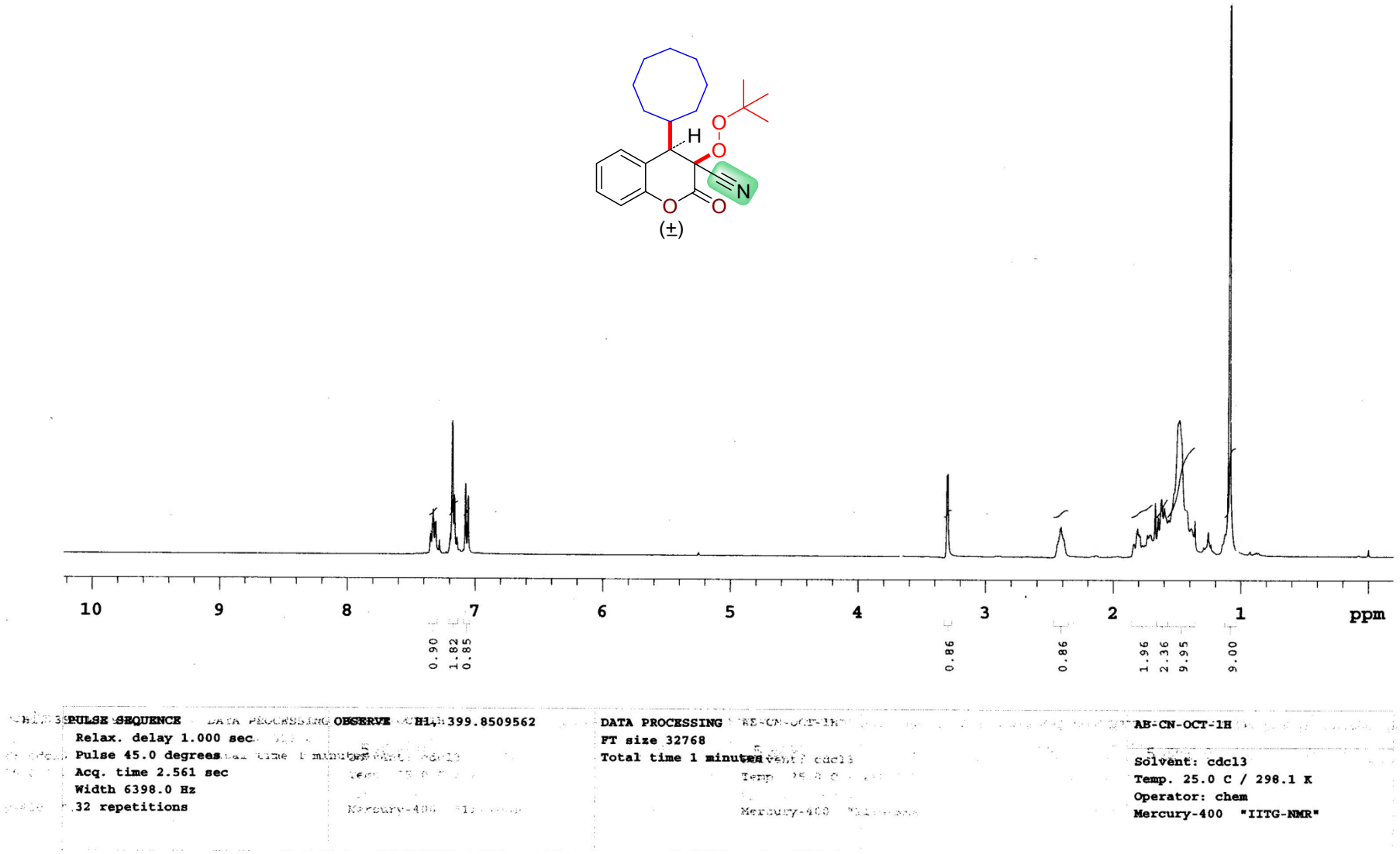
3-(*tert*-Butylperoxy)-4-cyclohexyl-2-oxochroman-3-carbonitrile (20a): ^{1}H NMR ($CDCl_3$, 400 MHz)



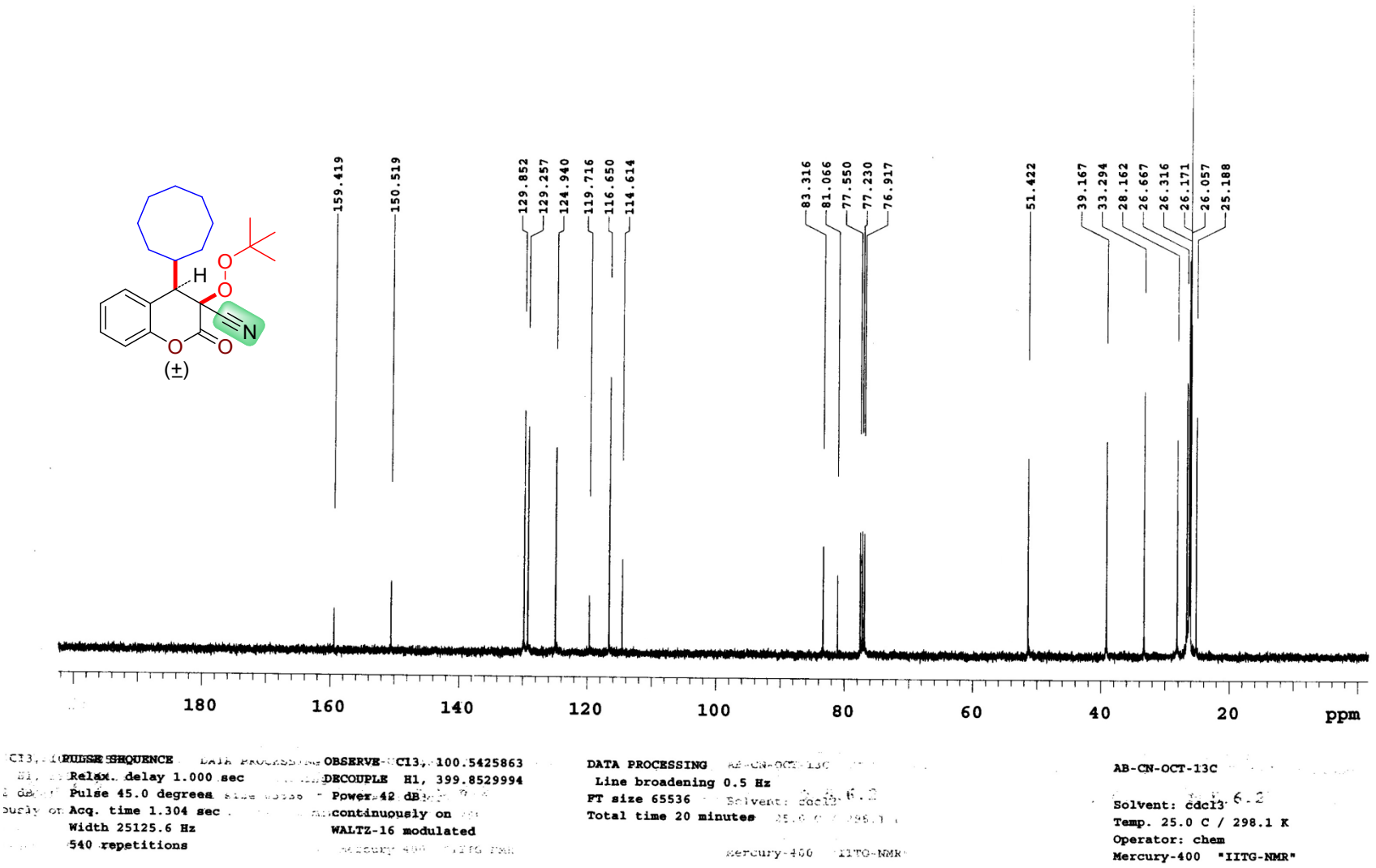
3-(*tert*-Butylperoxy)-4-cyclohexyl-2-oxochroman-3-carbonitrile (20a): ^{13}C NMR ($CDCl_3$, 100 MHz)



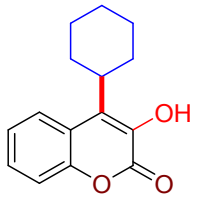
3-(*tert*-Butylperoxy)-4-cyclooctyl-2-oxochroman-3-carbonitrile (20c): ^{1}H NMR ($CDCl_3$, 400 MHz)

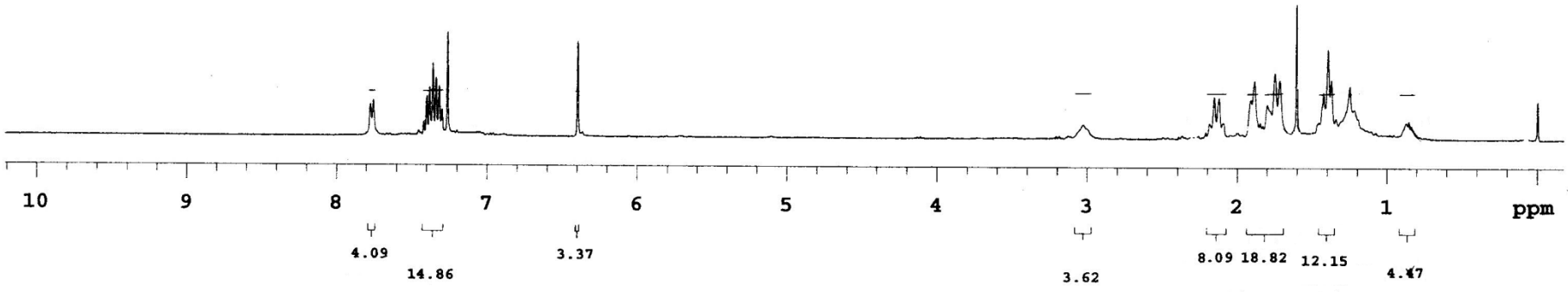


3-(*tert*-Butylperoxy)-4-cyclooctyl-2-oxochroman-3-carbonitrile (20c): ^{13}C NMR ($CDCl_3$, 100 MHz)



4-Cyclohexyl-3-hydroxy-2H-chromen-2-one (1a'): ^{1}H NMR ($CDCl_3$, 400 MHz)





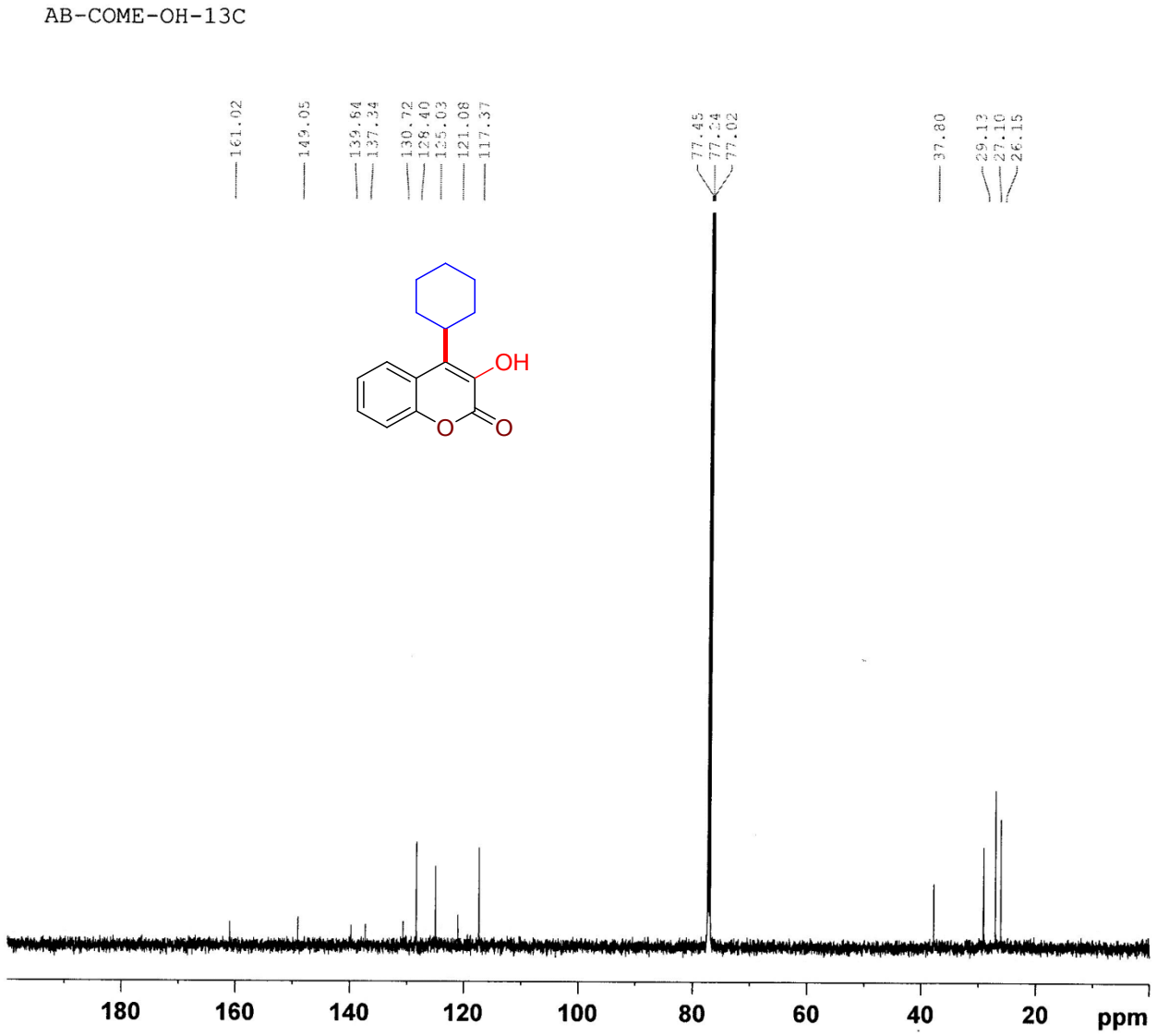
PULSE SEQUENCE DATA PROCESS OBSERVE H1, 399.8509617
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.561 sec
Width 6398.0 Hz
32 repetitions

DATA PROCESSING
FT size 32768
Total time 1 minutes

AB_COMe_DProline-1H

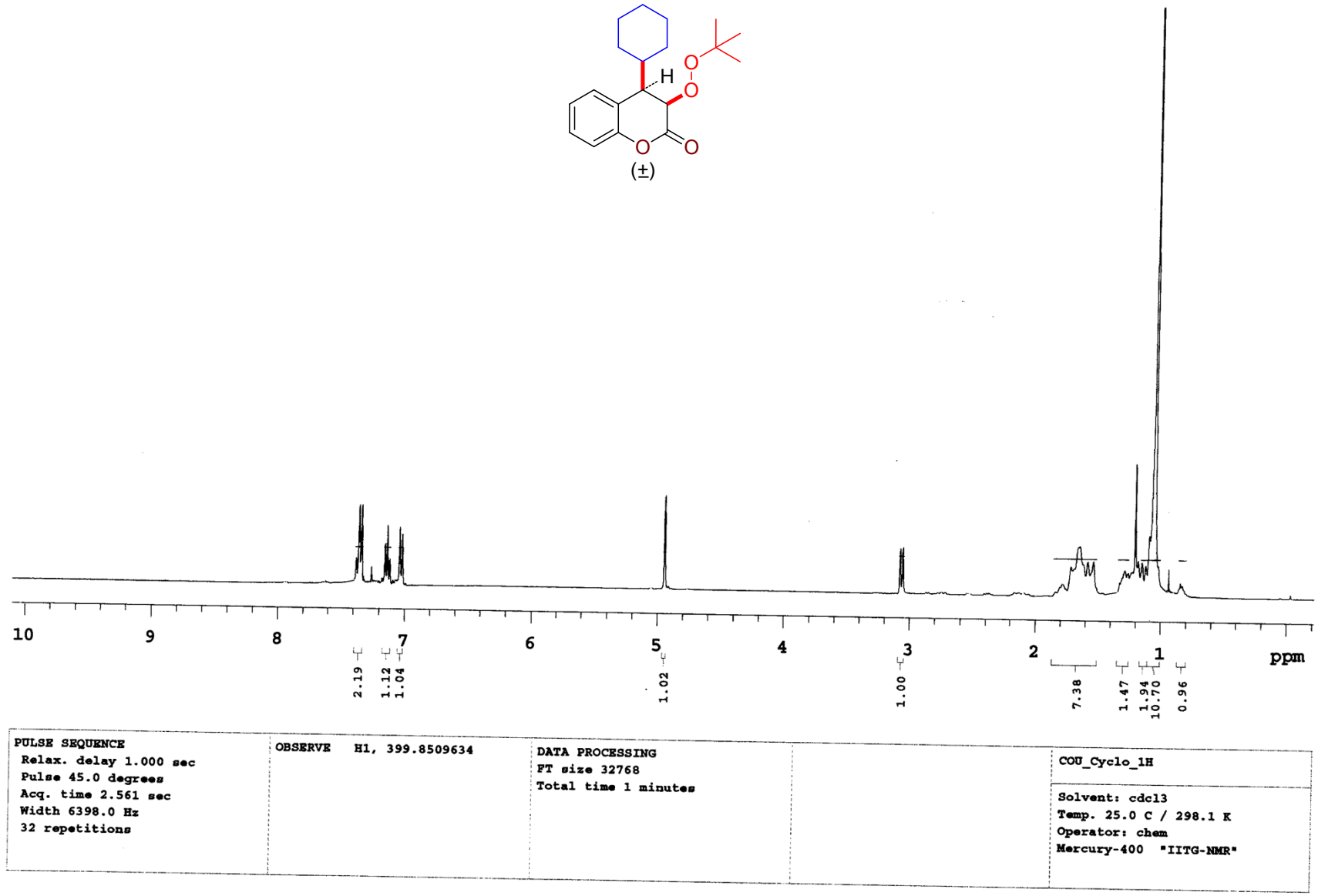
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
Mercury-400 "IITG-NMR"

4-Cyclohexyl-3-hydroxy-2H-chromen-2-one (1a'): ^{13}C NMR ($CDCl_3$, 150 MHz)

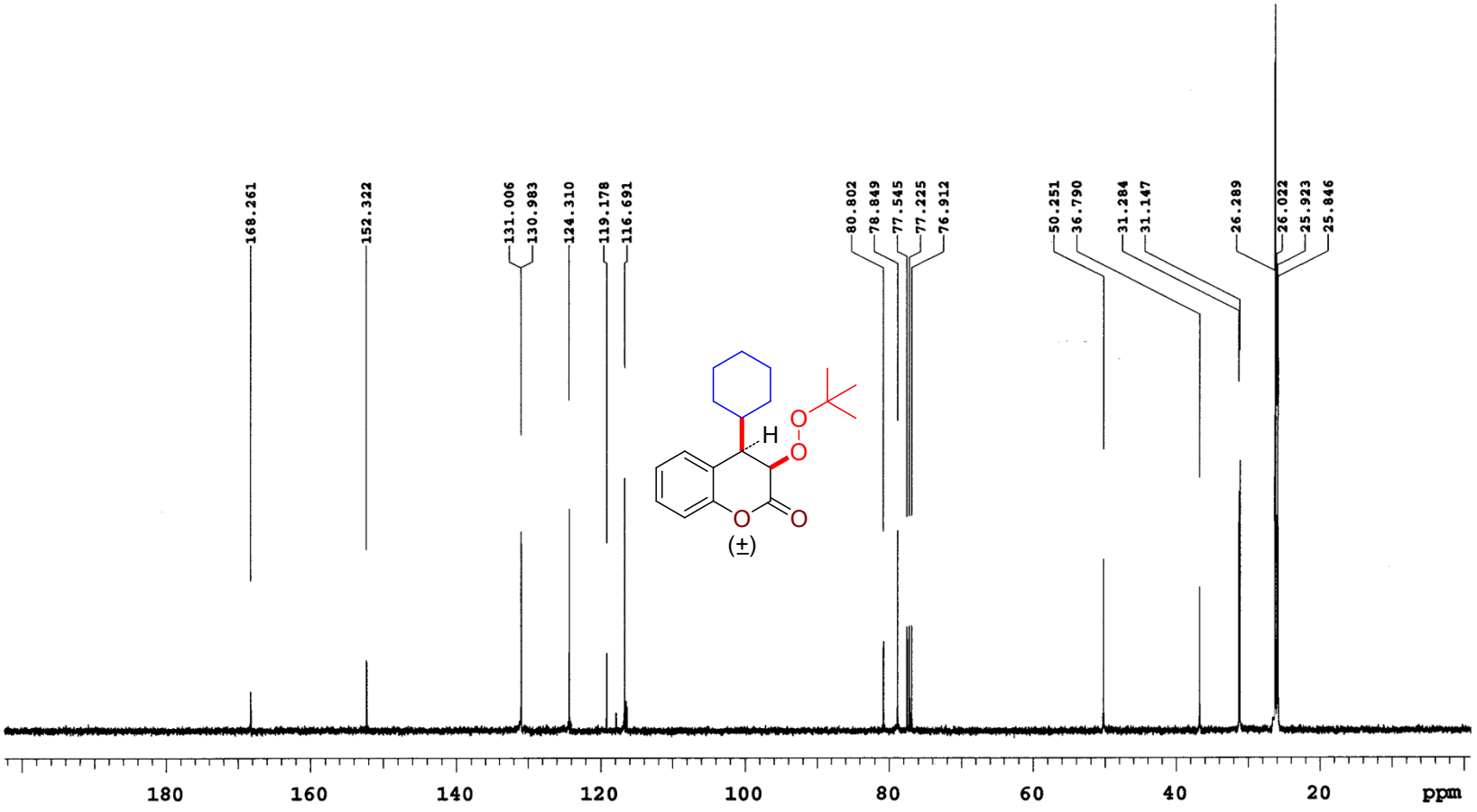



```
Current Data Parameters
NAME      AB-COME-OH-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140416
Time                15.22
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   634
DS                     2
SWH            36057.691 Hz
FIDRES          1.100393 Hz
AQ             0.4543829 sec
RG                 65.24
DW                13.867 usec
DE                 6.50 usec
TE                301.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9279571 MHz
NUC1                 13C
P1                10.50 usec
PLW1         95.00000000 W

======== CHANNEL f2 ========
SFO2         600.1724007 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2         21.00000000 W
PLW12         0.61714000 W
PLW13         0.30239999 W

F2 - Processing parameters
SI                  16384
SF           150.9128325 MHz
WDW                    EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

3-(*tert*-Butylperoxy)-4-cyclohexylchroman-2-one (21a): **^{1}H NMR ($CDCl_3$, 400 MHz)**

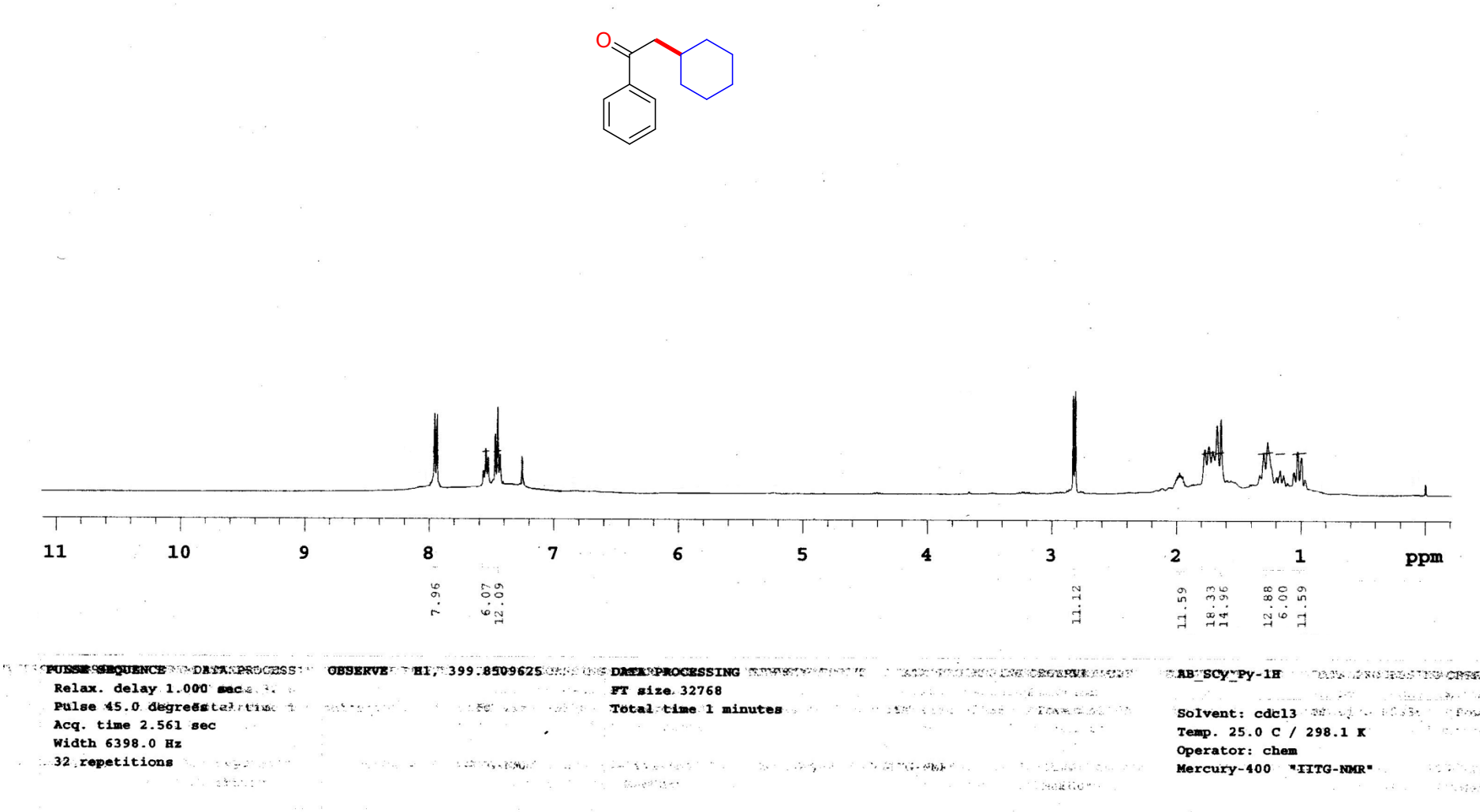


3-(*tert*-Butylperoxy)-4-cyclohexylchroman-2-one (21a): **^{13}C NMR ($CDCl_3$, 100 MHz)**

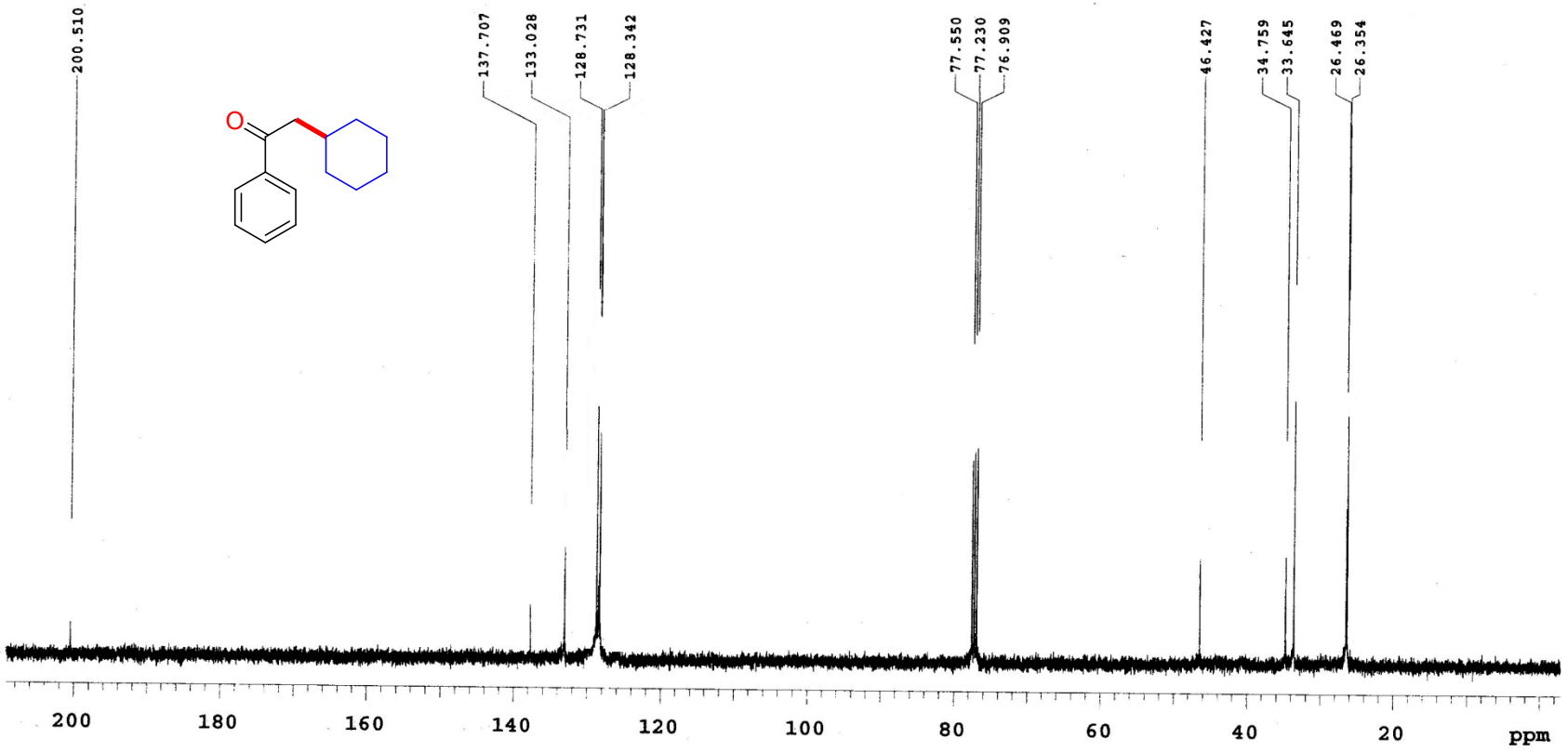


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.304 sec Width 25125.6 Hz 290 repetitions	OBSERVE C13, 100.5425898 DECOUPLE H1, 399.8529994 Power 42 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 11 minutes		COU_Cyclo_13C Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: chem Mercury-400 "IITG-NMR"

2-Cyclohexyl-1-phenylethanone (1'a): ^{1}H NMR ($CDCl_3$, 400 MHz)



2-Cyclohexyl-1-phenylethanone (1'a): ^{13}C NMR ($CDCl_3$, 100 MHz)



PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
670 repetitions

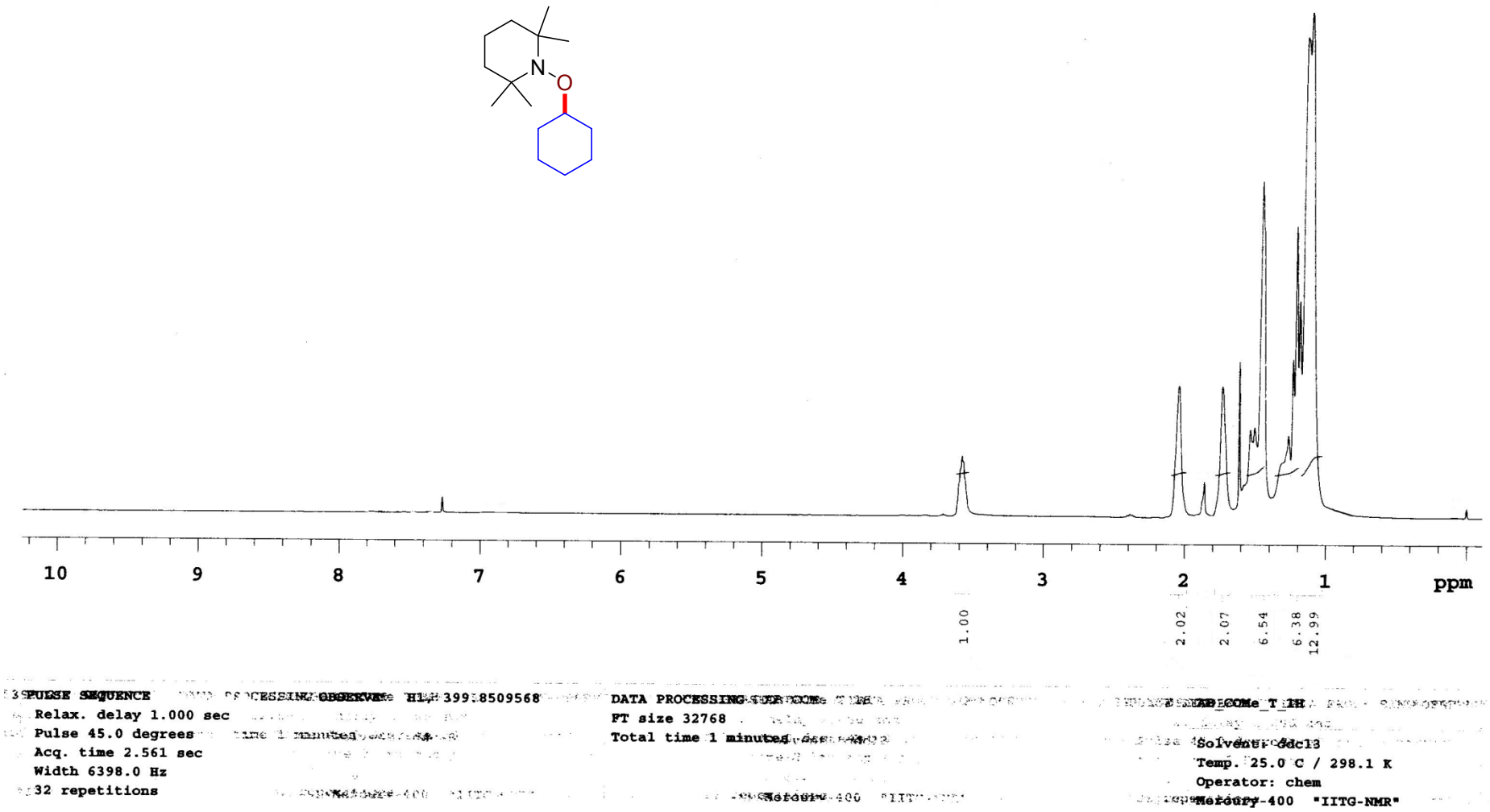
OBSERVE C13, 100.5425848
DECOUPLE H1, 399.8529994
Power 42 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 25 minutes

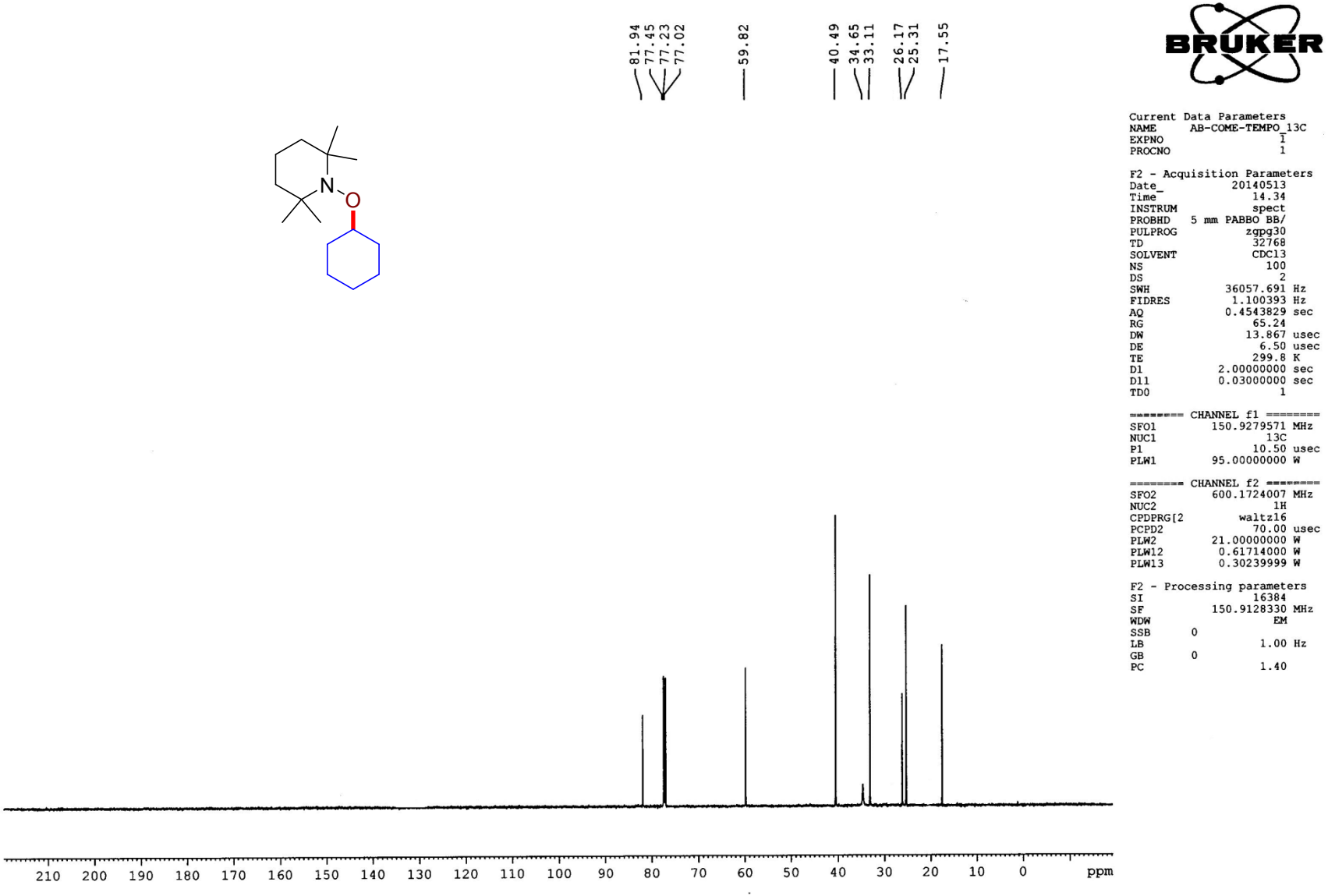
AB_SCy_P1_13C

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: chem
File: AB_SCy_P1_13C
Mercury-400 "IITG-NMR"

1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (1A): ^{1}H NMR ($CDCl_3$, 400 MHz)



1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (1A): ^{13}C NMR ($CDCl_3$, 150 MHz)



BRUKER

```
Current Data Parameters
NAME      AB-COME-TEMPO_13C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20140513
Time                  14.34
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     100
DS                       2
SWH              36057.691 Hz
FIDRES            1.100393 Hz
AQ               0.4543829 sec
RG                   65.24
DW                 13.867 usec
DE                   6.50 usec
TE                  299.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9279571 MHz
NUC1                    13C
P1                   10.50 usec
PLW1          95.00000000 W

======== CHANNEL f2 ========
SFO2          600.1724007 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                70.00 usec
PLW2          21.00000000 W
PLW12          0.61714000 W
PLW13          0.30239999 W

F2 - Processing parameters
SI                      16384
SF            150.9128330 MHz
WDW                        EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```