Supporting Information

Mn(III)-BASED OXIDATIVE RADICAL RING-EXPANSION REACTION USING SQUARATE DERIVATIVES: SELECTIVE SYNTHESIS OF BIS(BUTANOLIDE)S AND THE ACETATE MONOMERS

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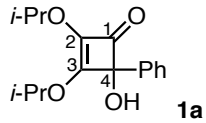
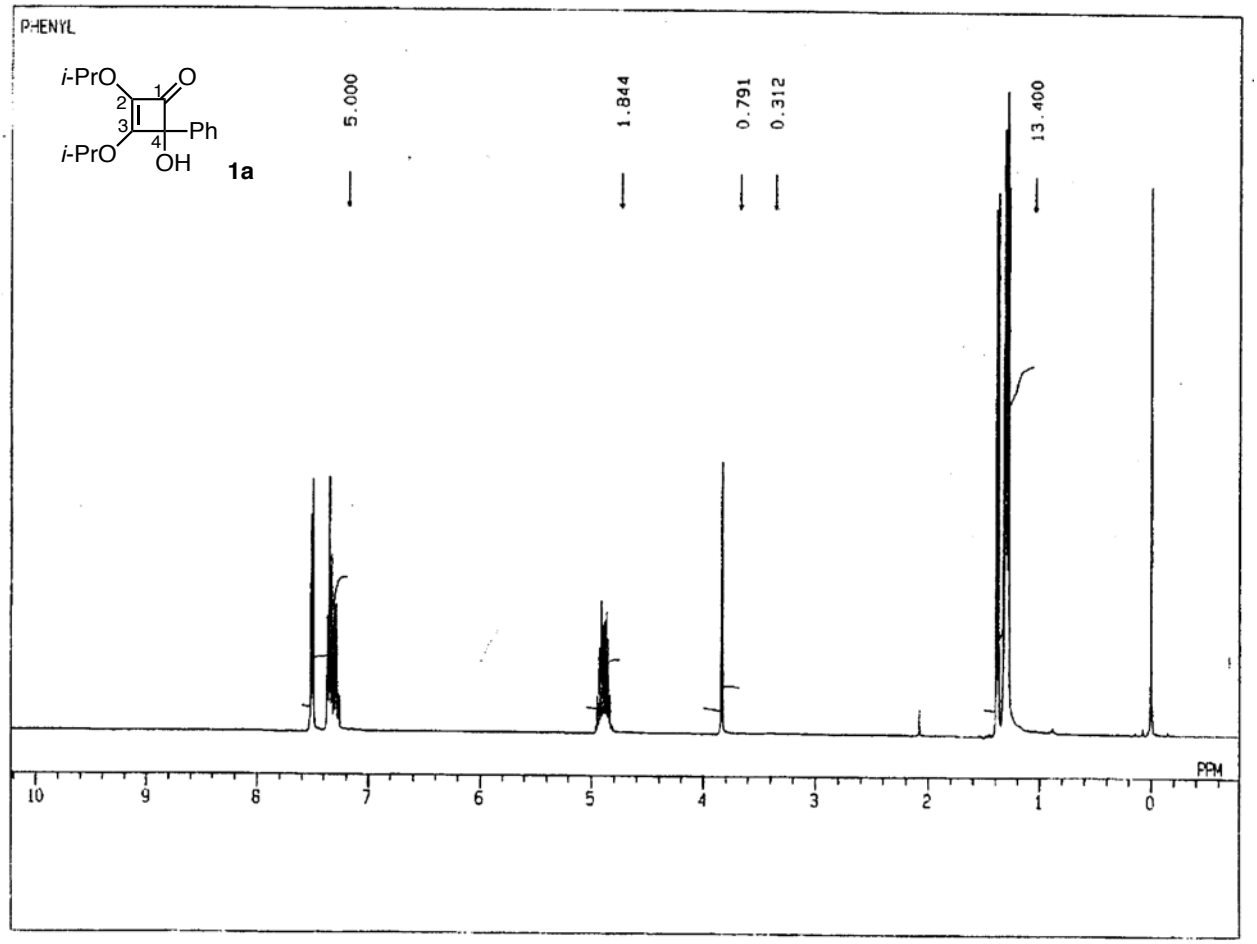
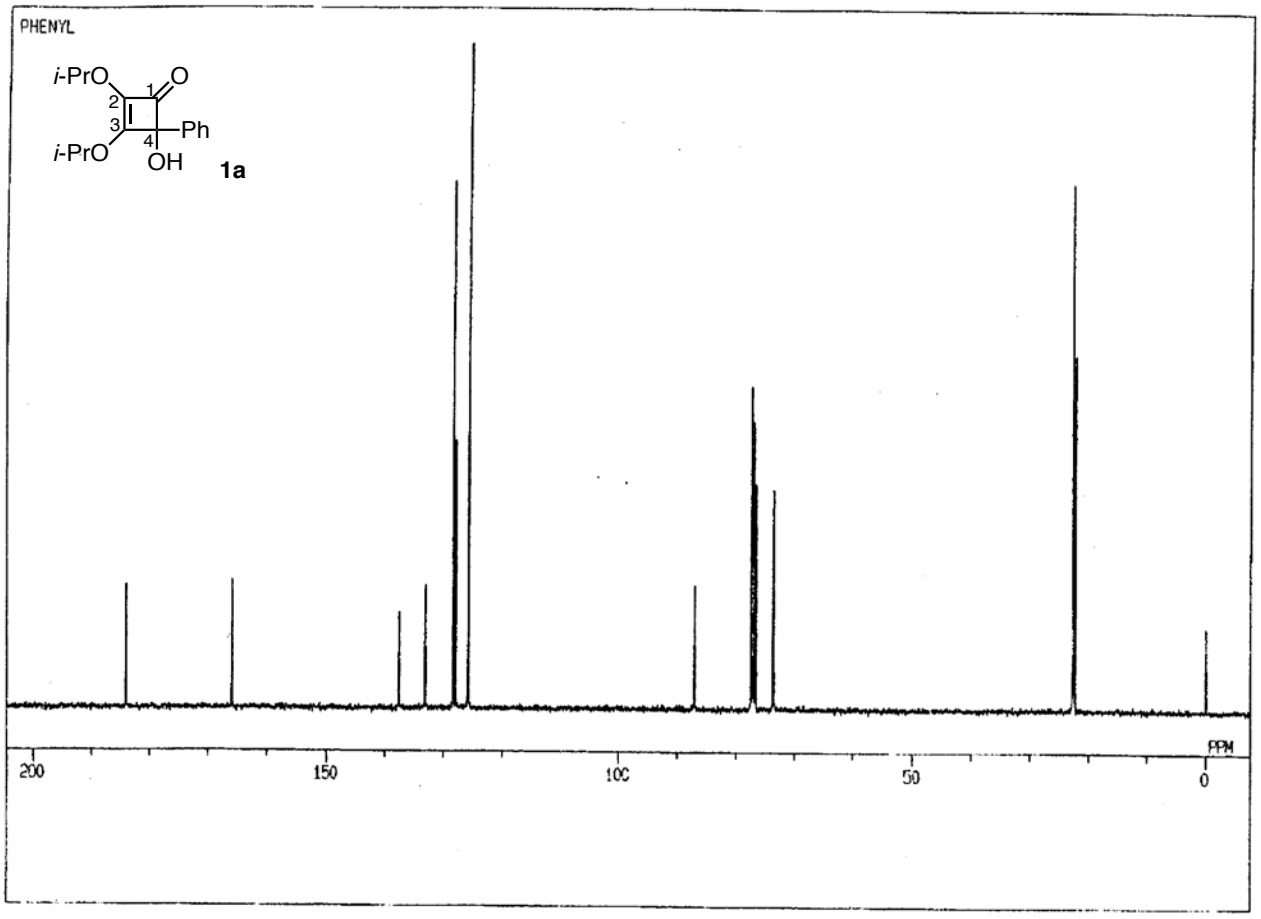
Spectral Data, and ^{1}H and ^{13}C NMR spectra of the Starting Materials 1a-l.

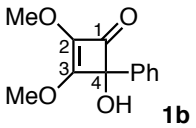


1a

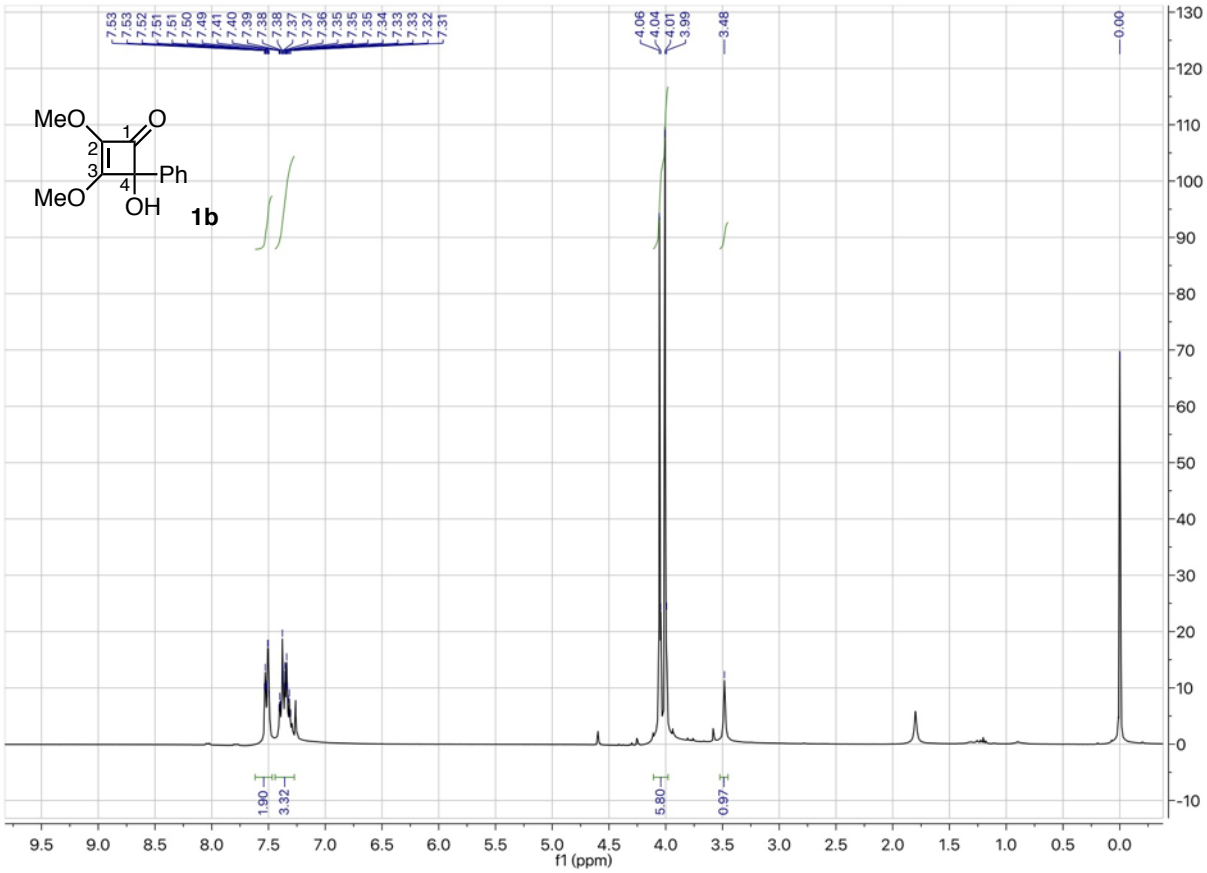
4-Hydroxy-2,3-diisopropoxy-4-phenylcyclobut-2-en-1-one (1a)[9a]: yellowish oil; IR ($CHCl_3$) ν 3400 (OH), 1775 (C=O), 1625 (>C=C<); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.26 (5H, m, arom H), 4.94 (1H, sept, J = 6.1 Hz, >CH-O), 4.84 (1H, sept, J = 6.1 Hz, >CH-O), 3.83 (1H, s, OH), 1.39 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3), 1.25 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1 (C-1), 166.0 (C-3), 137.7 (C-2), 133.2 (arom C), 128.5 (2C), 128.0, 125.9 (2C) (arom CH), 87.2 (C-4), 77.5, 73.7 (>CH-O), 22.7 (2C), 22.5, 22.3 (CH_3).







4-Hydroxy-2,3-dimethoxy-4-phenylcyclobut-2-en-1-one (1b): colorless microcryatals (from MnOH/jexane); mp 95-98 °C (lit,[22] mp 96-98 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.50 (2H, m, arom H), 7.40-7.31 (3H, m, arom H), 4.05 (3H, s, CH_3O), 4.00 (3H, s, CH_3O), 3.48 (1H, s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.1 (C-1), 166.1 (C-3), 137.1 (C-2), 135.3 (arom C), 128.6 (2C), 128.4, 125.9 (2C) (arom CH), 87. 6 (C-4), 60.3, 58.7 (CH_3O).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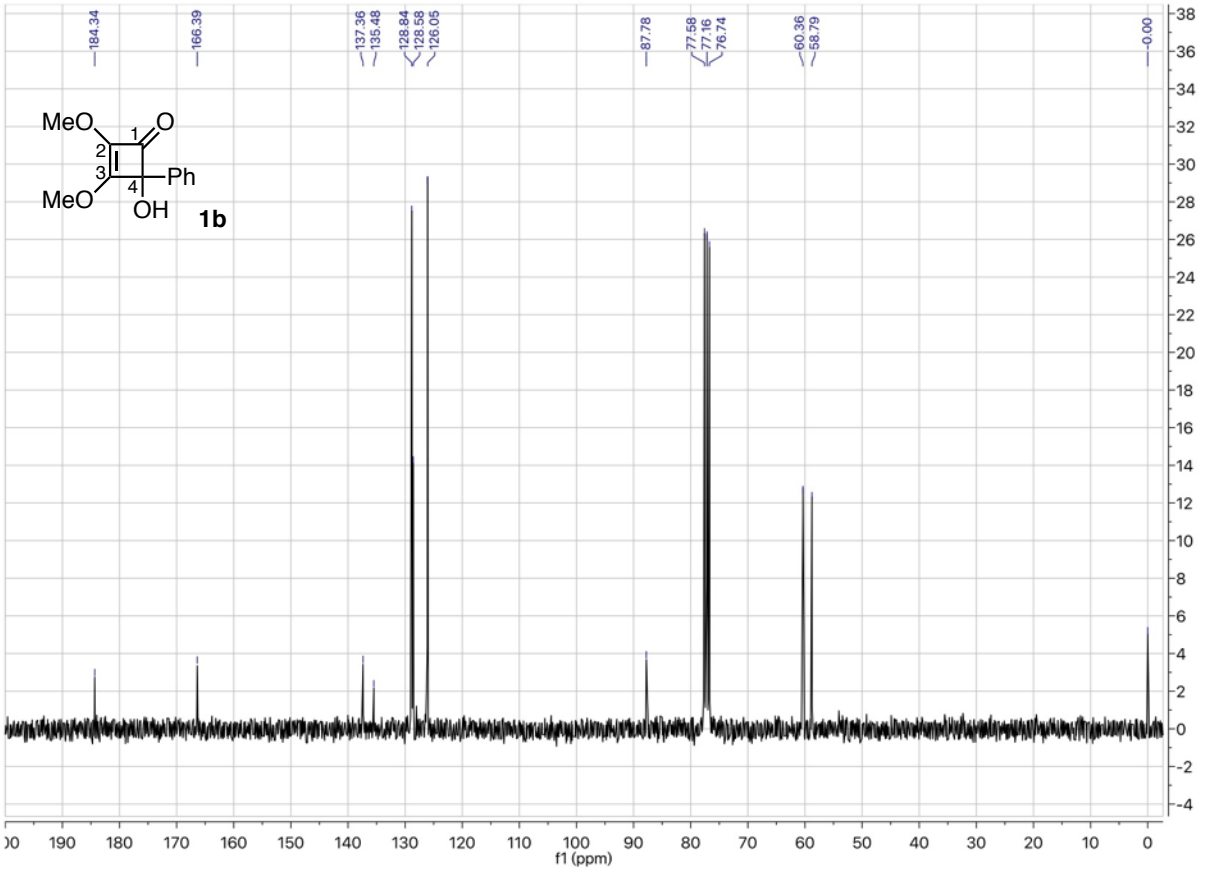
MeO
O
Ph
OH
1b
f1 (ppm)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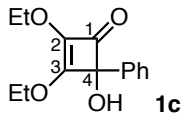
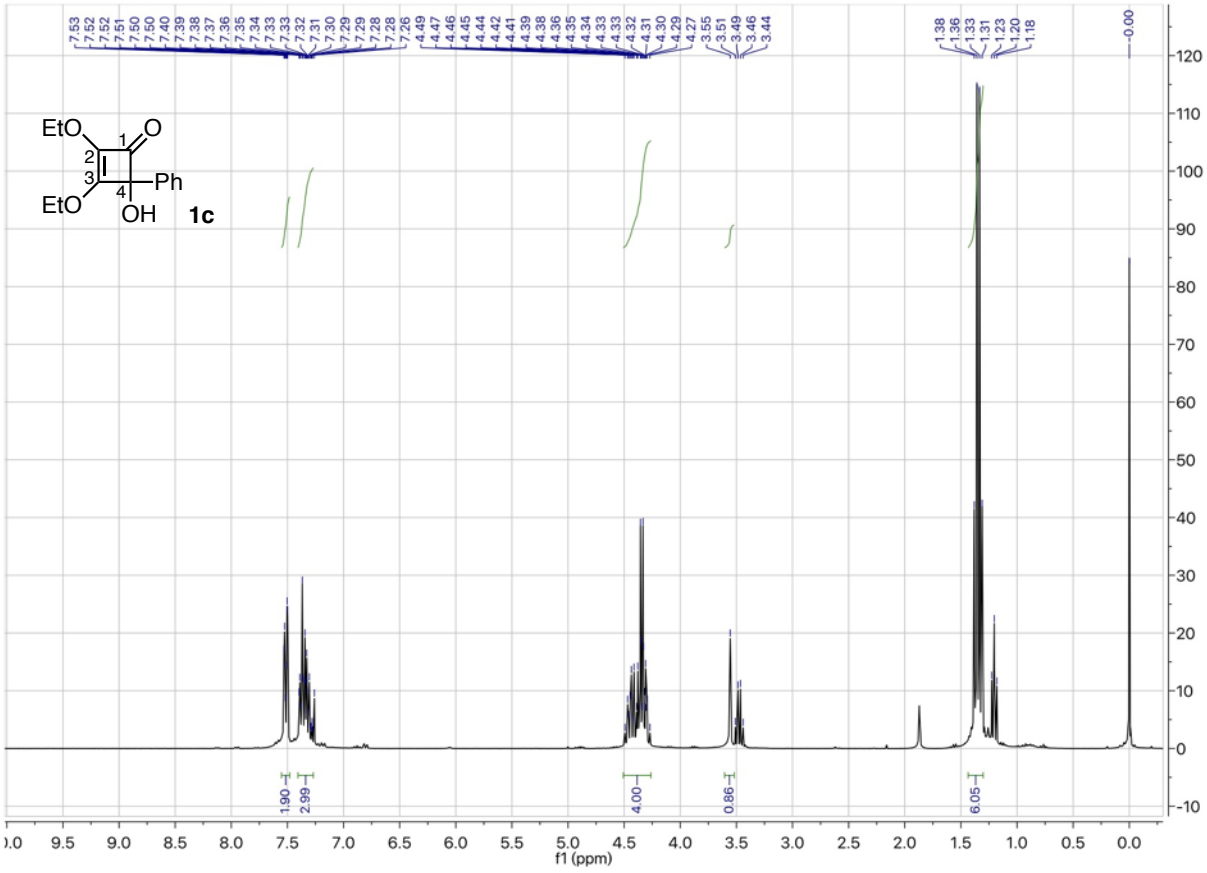
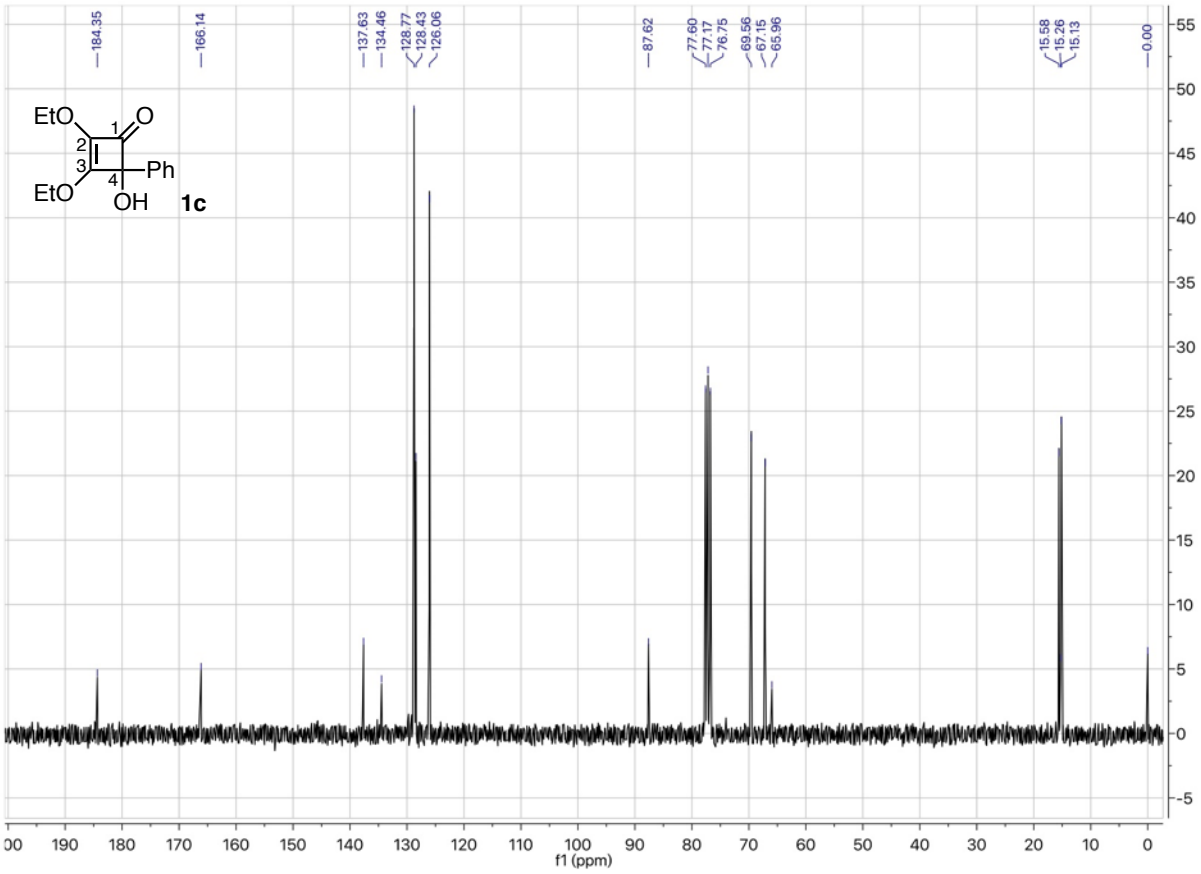
1b
f1 (ppm)

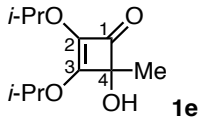


1c

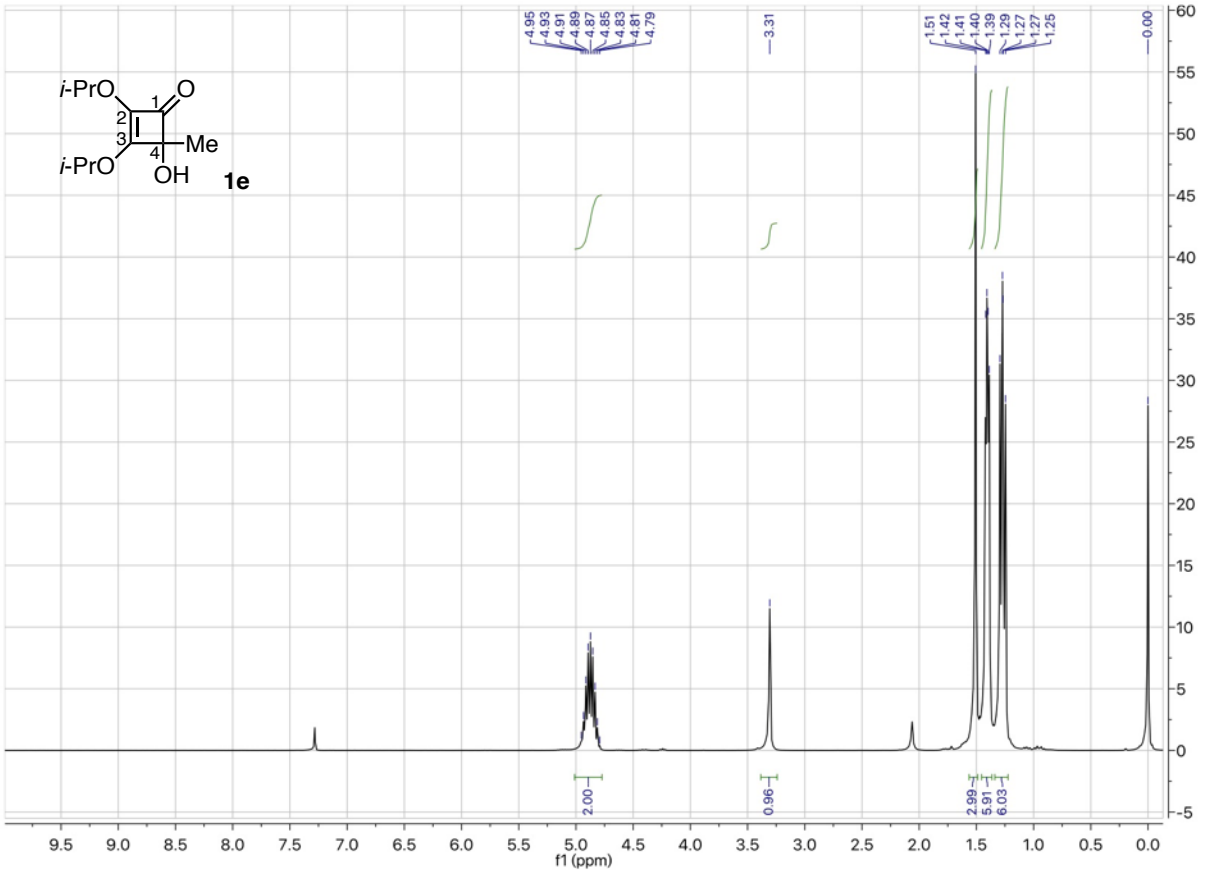
2,3-Diethoxy-4-hydroxy-4-phenylcyclobut-2-en-1-one (1c)[11a]**:** yellowish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.32 (5H, m, arom H), 4.42 (2H, q, J = 6.0 Hz, CH_2O), 4.35 (2H, q, J = 6.0 Hz, CH_2O), 3.55 (1H, s, OH), 1.36 (3H, t, J = 6.0 Hz, CH_3), 1.33 (3H, t, J = 6.0 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7 (C-1), 166.1 (C-3), 137.6 (C-2), 134.5 (arom C), 128.8 (2C), 128.4, 126.1 (2C) (arom CH), 87.6 (C-4), 66.9, 67.2 ($\underline{C}H_2$-O), 15.6, 15.1 (CH_3).







4-Hydroxy-2,3-diisopropoxy-4-methylcyclobut-2-en-1-one (1e)[9a]**:** R_f = 0.35 (7:3 Et_2O/hexane v/v); yield 72%; colorless solid; mp 35-36 °C; IR ($CHCl_3$) ν 3370 (OH), 1766 (C=O), 1620 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88 (2H, sept, J = 6.1 Hz, >CH-O ×2), 3.31 (1H, s, OH), 1.51 (3H, s, CH_3), 1.41 (3H, d, J = 6.1 Hz, CH_3), 1.40 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.6 (C-1), 168.5 (C-2), 130.7 (C-3), 83.1 (C-4), 76.8, 73.2 (>CH-O), 22.7 (2C), 22.5, 22.4, 19.2 (CH_3).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4.83
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4.79
3.31
1.51
1.42
1.41
1.40
1.39
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1.27
1.27
1.25
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0.96
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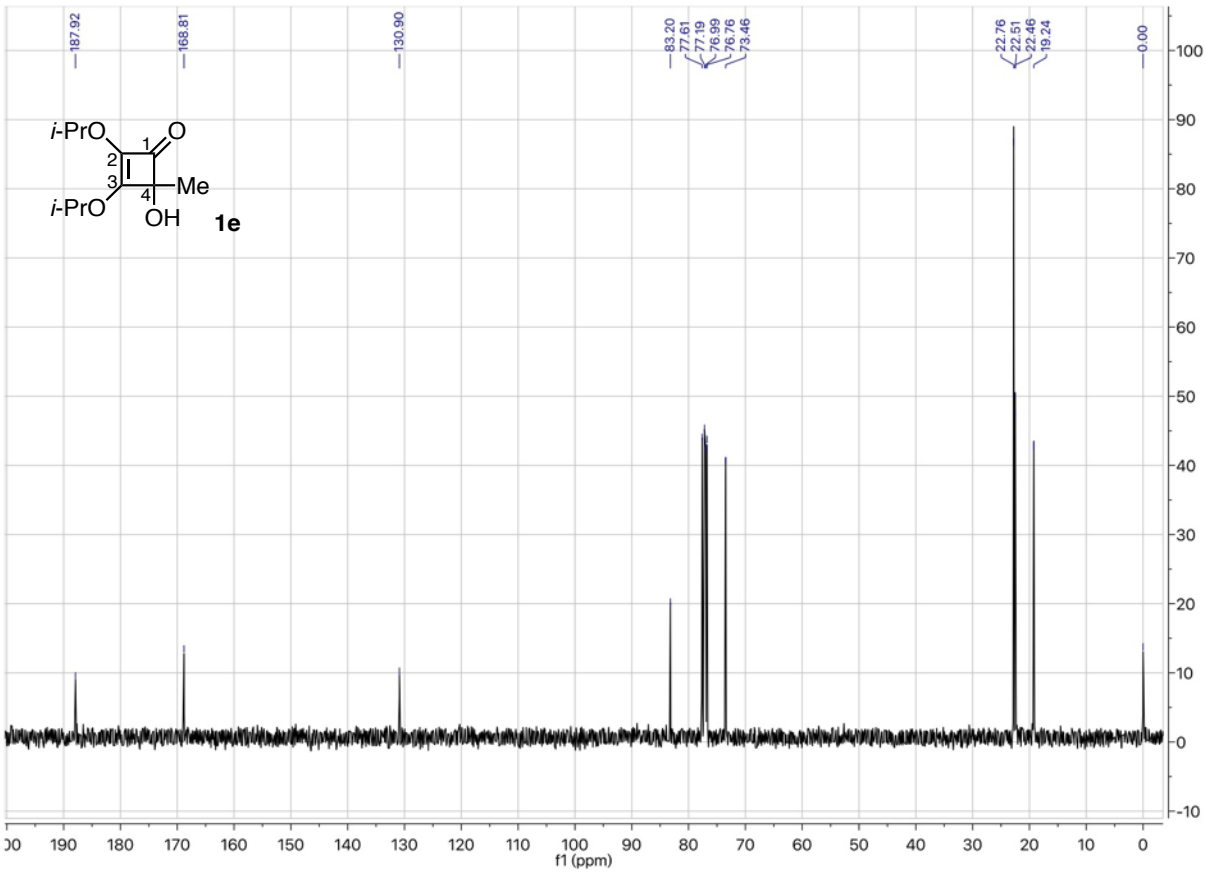
6.03
f1 (ppm)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22.51
22.46
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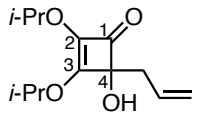
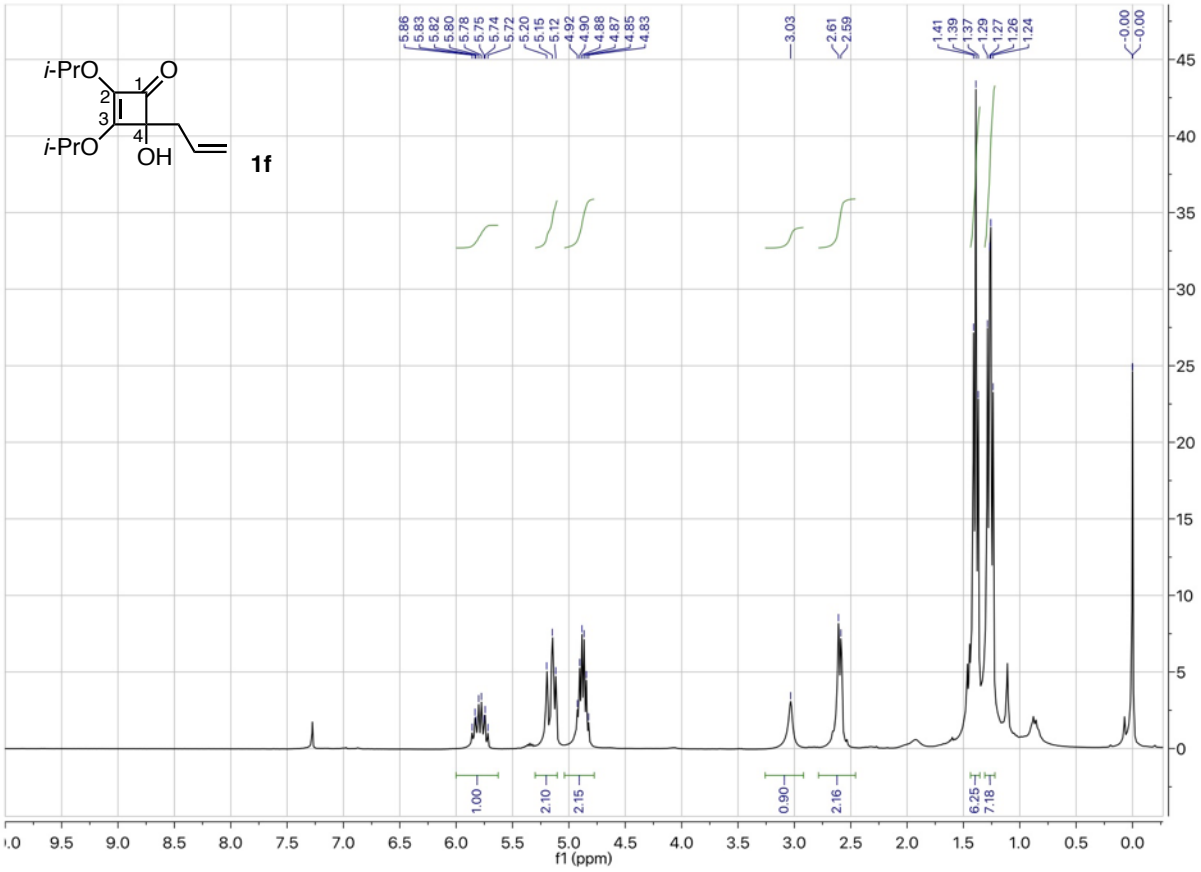
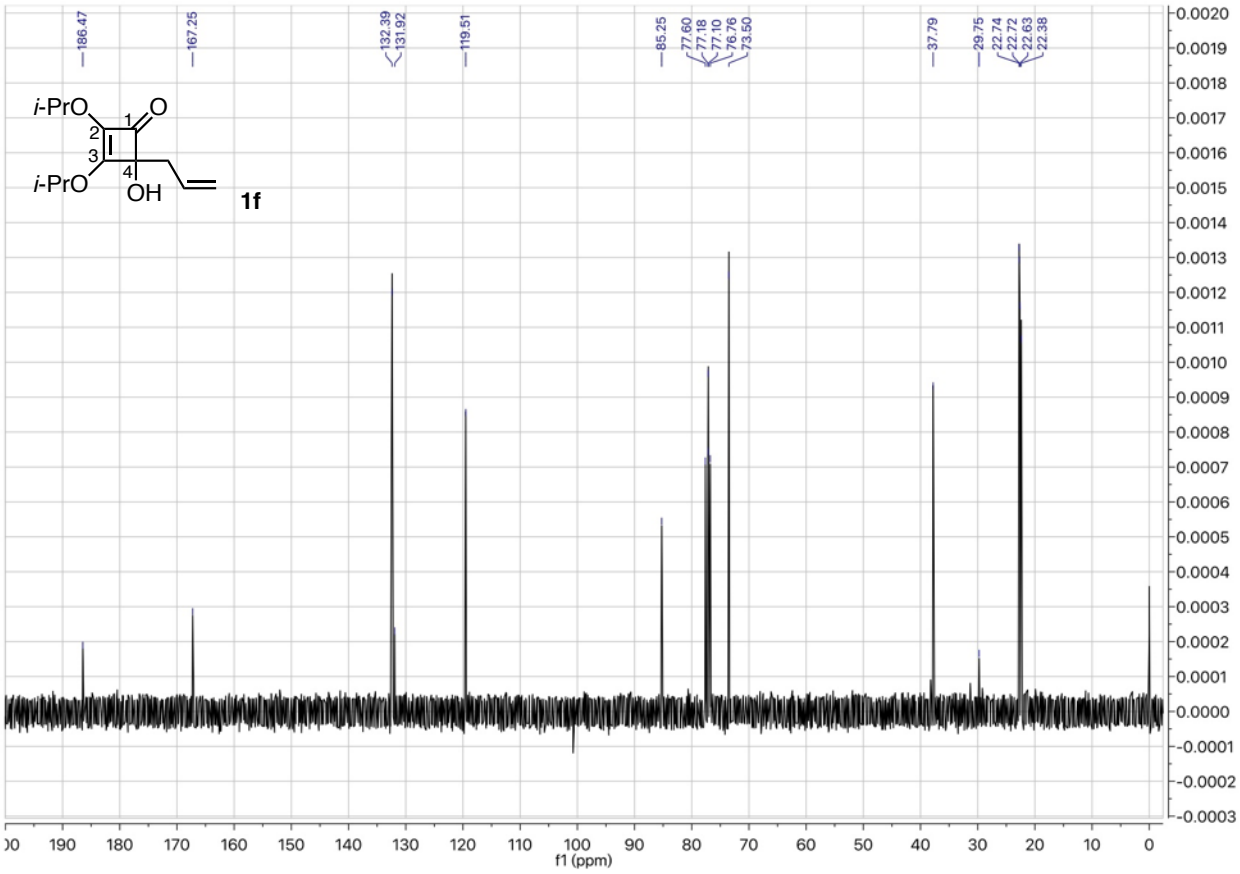
0.00
f1 (ppm)

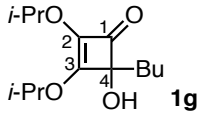


1f

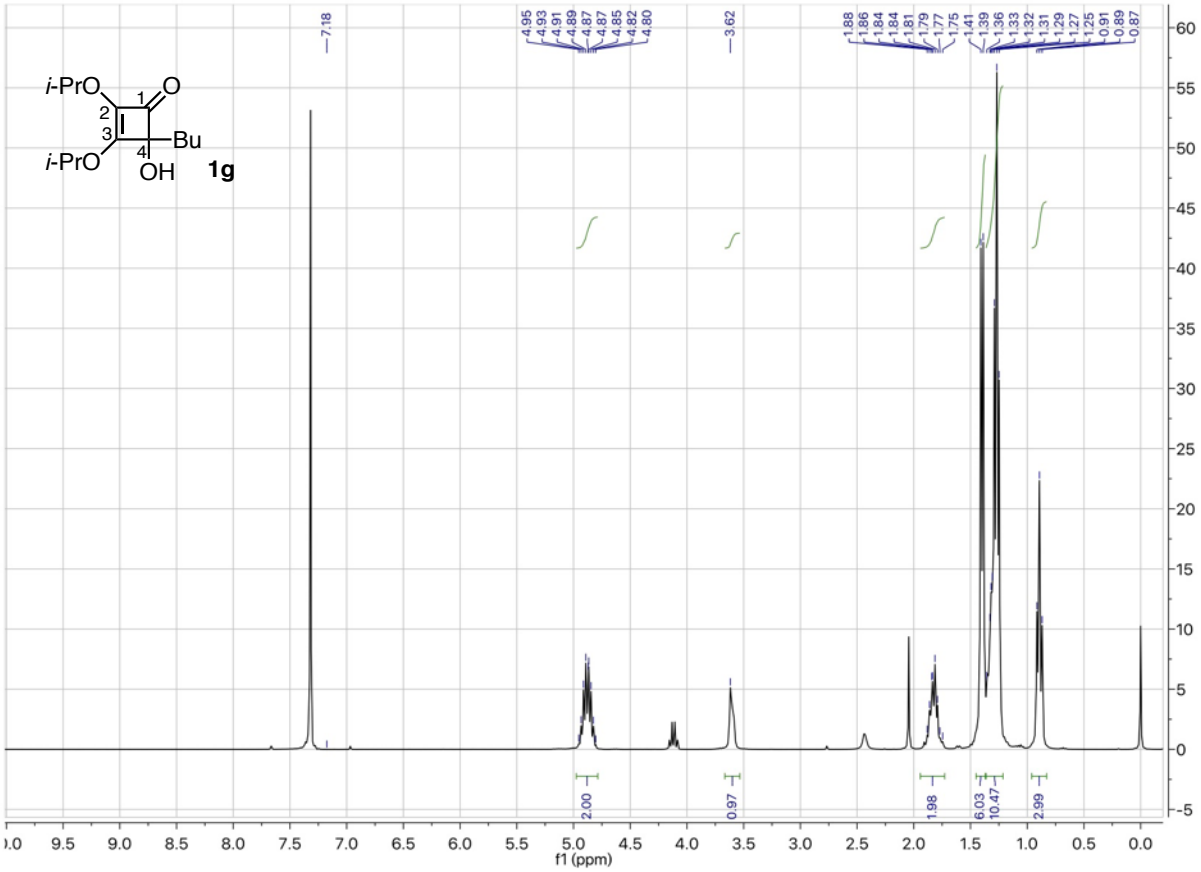
4-Allyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1f): R_f = 0.29 (7:3 Et_2O/hexane v/v); yellow solid; mp 37-38 °C; IR ($CHCl_3$) ν 3373 (OH), 1767 (C=O), 1620 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86-5.72 (1H, m, -CH=), 5.17 (1H, d, J = 17.1 Hz, =C$\underline{H}_{trans}H_{cis}$), 5.13 (1H, d, J = 10.7 Hz, =C$H_{trans}\underline{H}_{cis}$), 4.88 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 3.03 (1H, s, OH), 2.60 (2H, d, J = 6.4 Hz, -CH_2-), 1.40 (3H, d, J = 6.1 Hz, CH_3), 1.38 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3), 1.25 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5 (C-1), 167.3 (C-3), 132.4 (-CH=), 131.9 (C-2), 119.5 (=CH_2), 85.3 (C-4), 77.1, 73.5 (>CH-O), 37.8 (-CH_2-), 22.74, 22.72, 22.6, 22.4 (CH_3).







4-Butyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1g)[9a]**:** R_f = 0.15 ($CHCl_3$); yield 83%; yellow oil; IR ($CHCl_3$) ν 3370 (OH), 1765 (C=O), 1616 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 3.62 (1H, s, OH), 1.88-1.75 (2H, m, -CH_2-), 1.41 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.27 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3), 1.39-1.28 (4H, m, -CH_2- ×2), 0.89 (3H, t, J = 6.9 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.8 (C-1), 168.1 (C-3), 131.8 (C-2), 86.4 (C-4), 76.99, 73.4 (>CH-O), 32.4, 27.2, 22.9 (-CH_2-), 22.7 (2C), 22.6, 22.4, 13.95 (CH_3).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O
1
2
3
Bu
4
i-PrO
OH
1g
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1.77
1.75
1.41
1.39
1.36
1.33
1.32
1.31
1.29
1.27
1.25
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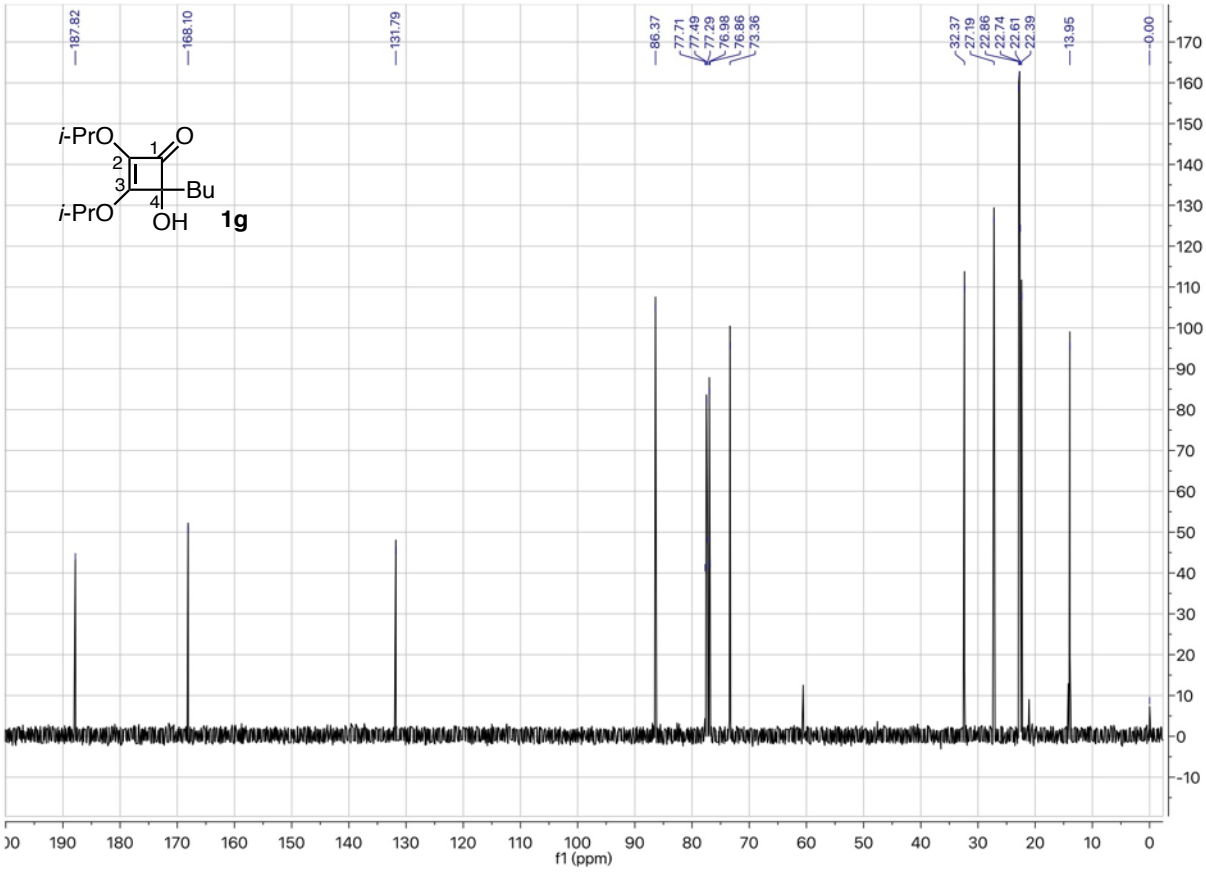
0.89
0.87
2.00
0.97
1.98
6.03
10.47
2.99
f1 (ppm)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2
3
Bu
4
i-PrO
OH
1g
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77.29
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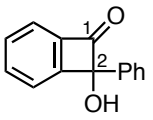
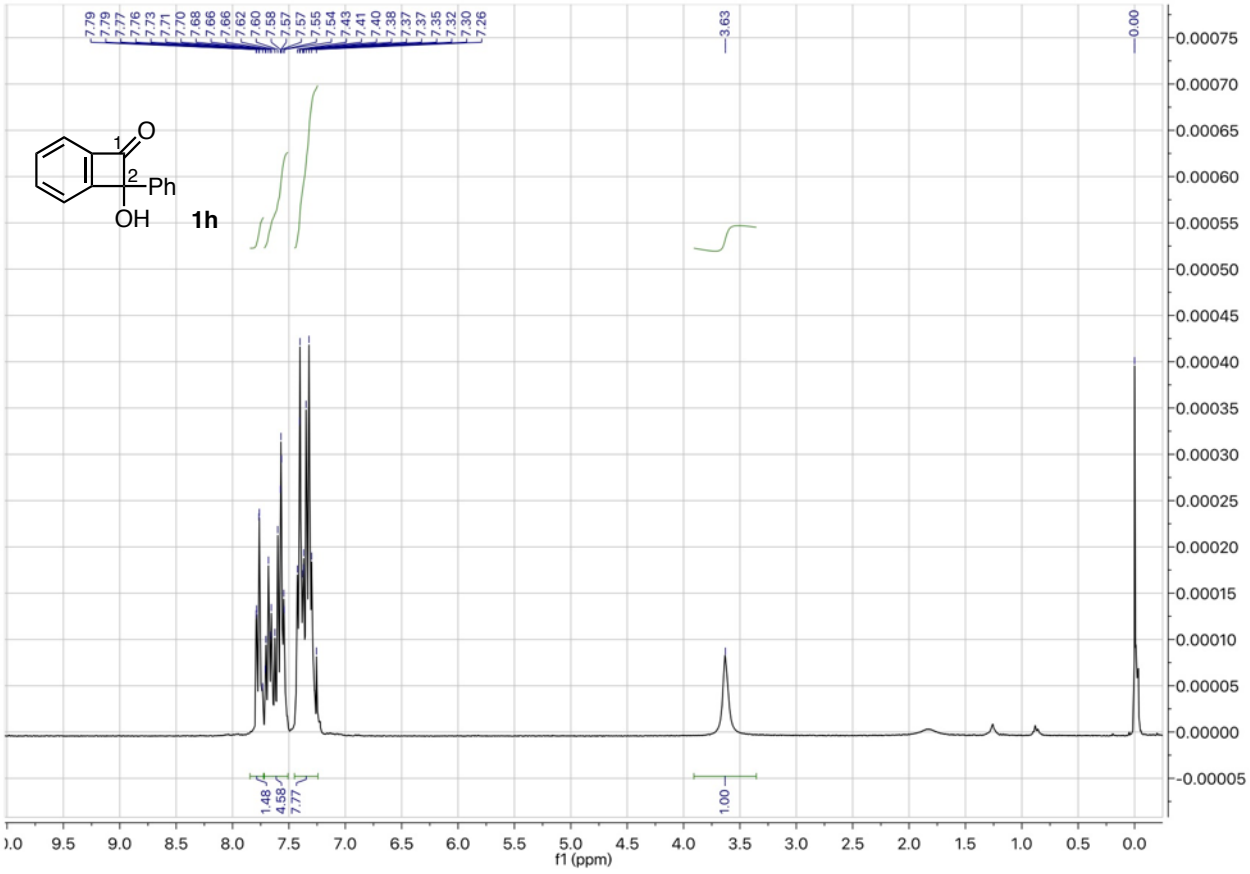
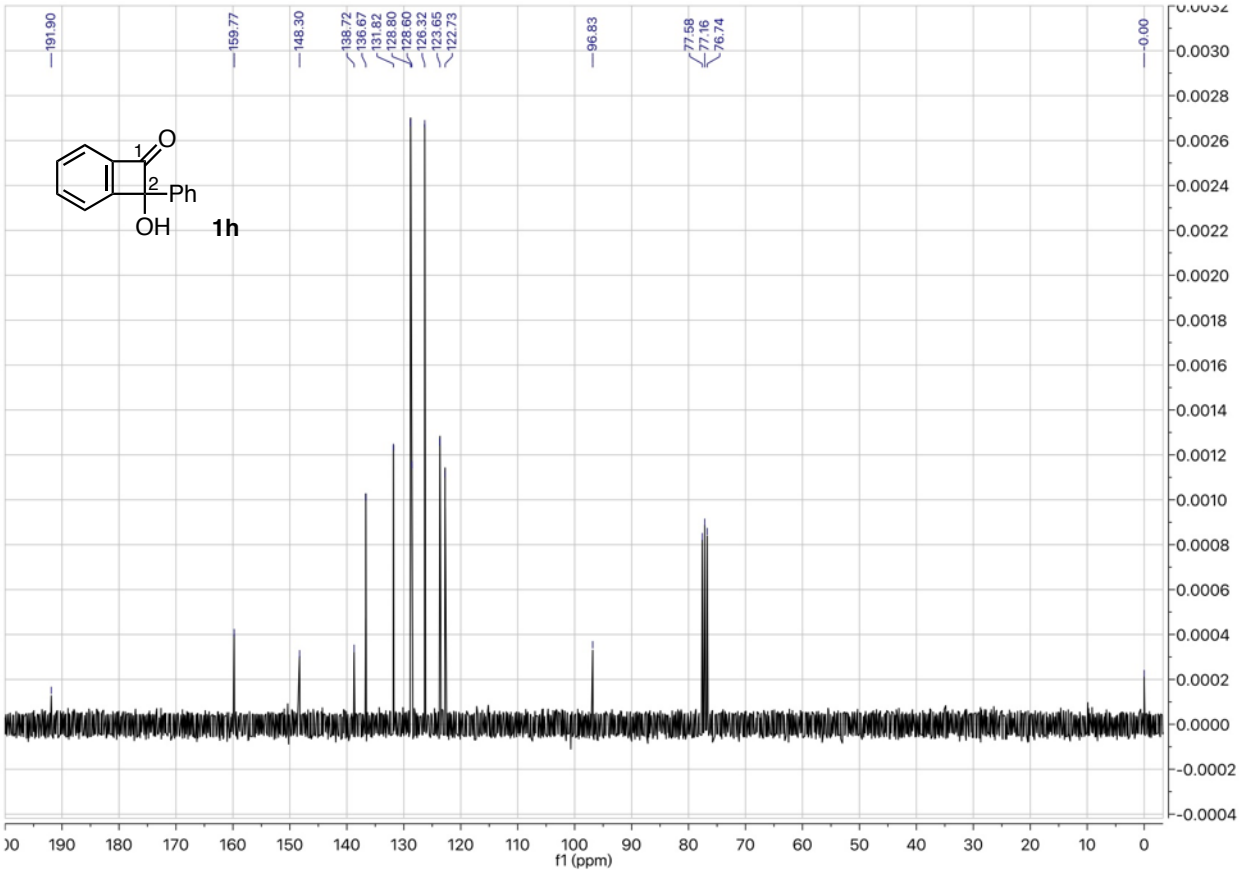
22.61
22.39
13.95
0.00
f1 (ppm)

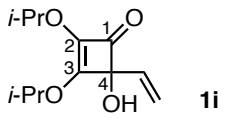


1h

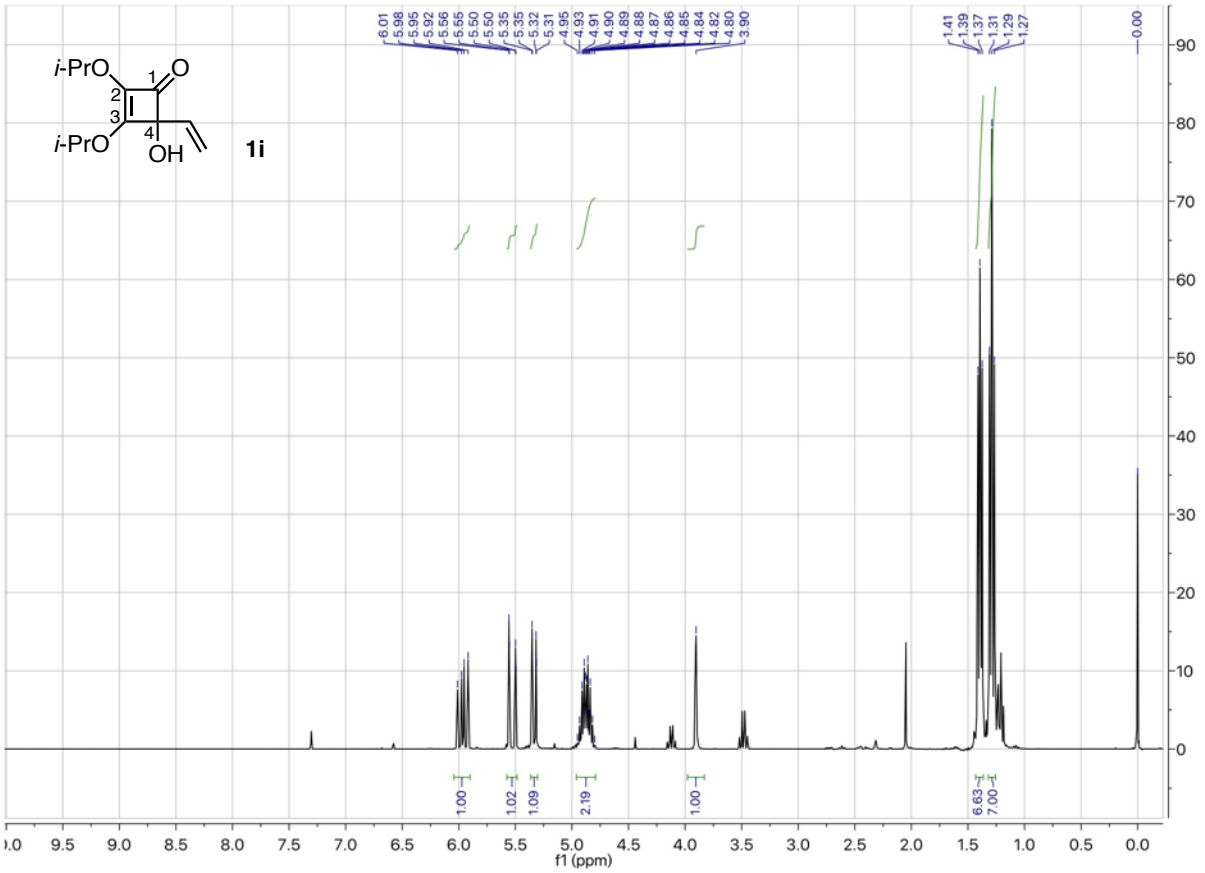
2-Hydroxy-2-phenylbenzocyclobuten-1(2*H*)-one (1h)[18]**:** R_f= 0.09 ($CHCl_3$); colorless microcrystals (from $CHCl_3$/hexane); mp 102-103 °C; IR (KBr) ν 3400-3200 (OH), 1760 (>C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.73 (1H, m, arom H), 7.70-7.54 (3H, m, arom H), 7.43-7.30 (5H, m, arom H), 3.63 (1H, s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9 (>C=O), 159.8, 148.3, 138.7 (arom C), 136.7, 131.8, 128.8, 128.6, 126.3, 123.7, 122.7 (arom CH), 96.8 (C-OH).







4-Hydroxy-2,3-diisopropoxy-4-vinylcyclobut-2-en-1-one (1i)[25]**:** R_f = 0.47 (7:3 Et_2O/hexane v/v); yield 60%; yellow oil; IR ($CHCl_3$) *v* 3375 (OH), 1768 (C=O), 1619 (>C=C<); ^1H NMR (300 MHz, $CDCl_3$) δ 5.97 (1H, dd, J = 17.3, 10.7 Hz, -CH=), 5.53 (1H, dd, J =17.3, 0.9 Hz, =C$\underline{H}_{trans}H_{cis}$), 5.34 (1H, dd, J = 10.7, 0.9 Hz, =C$H_{trans}\underline{H}_{cis}$), 4.95-4.80 (2H, m, >CH-O), 3.90 (1H, s, OH), 1.40 (3H, d, J = 6.1 Hz, CH_3), 1.38 (3H, d, J = 6.1 Hz, CH_3), 1.30 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2 (C-1), 166.9 (C-3), 135.0 (-CH=), 132.5 (C-2), 118.2 (=CH_2), 86.7 (C-4), 77.5, 73.7 (>CH-O), 22.7, 22.69, 22.55, 22.5 (CH_3).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4.87
4.86
4.85
4.84
4.82
4.80
3.90
1.41
1.39
1.37
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1.00
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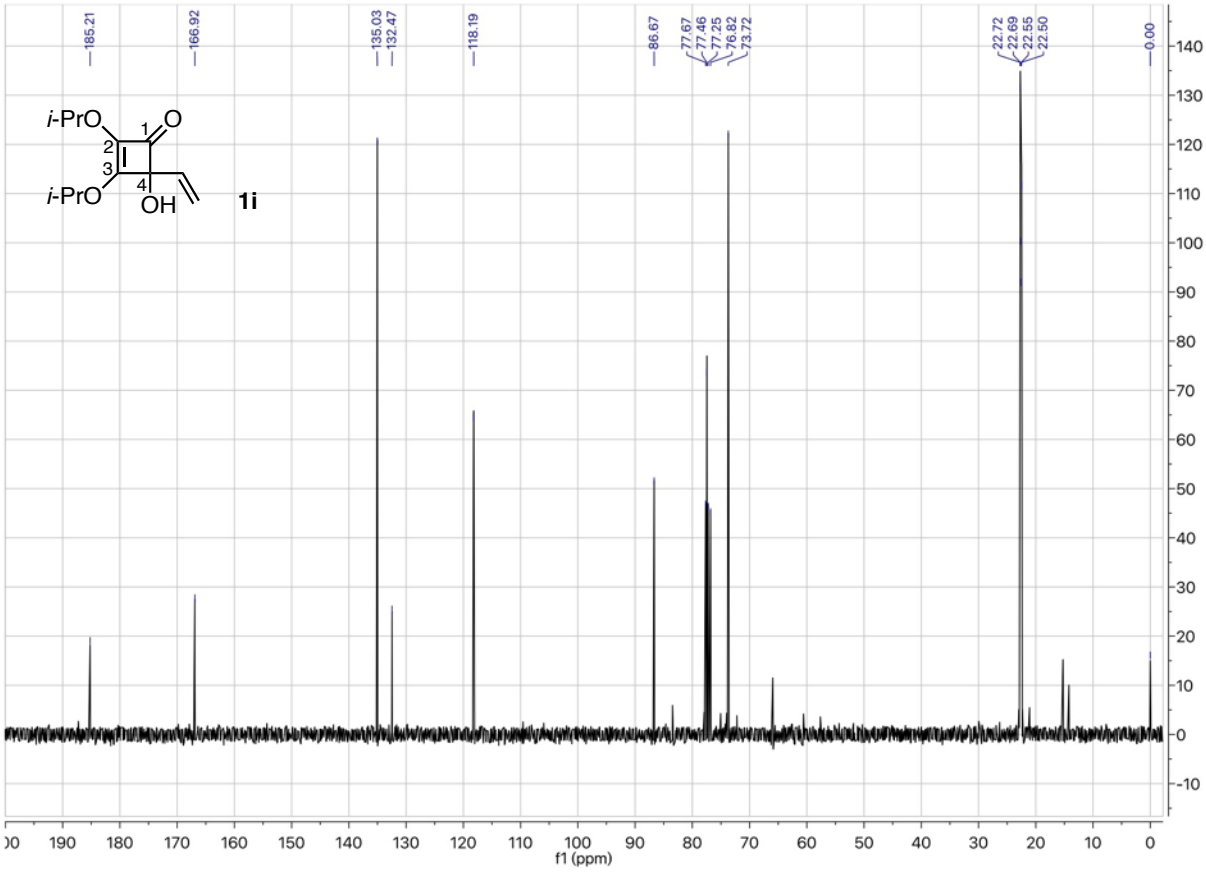
7.00
f1 (ppm)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1
2
3
4
i-PrO
OH
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135.03
132.47
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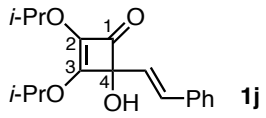
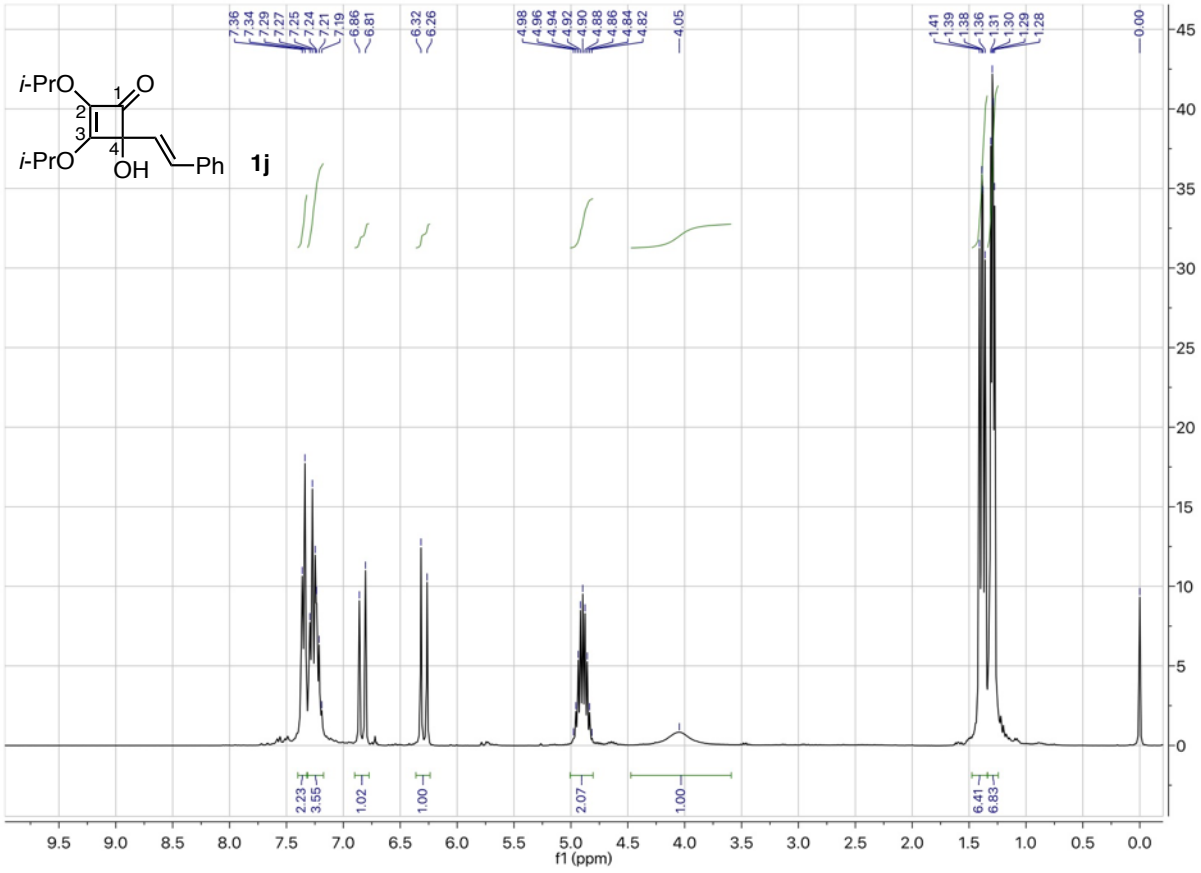
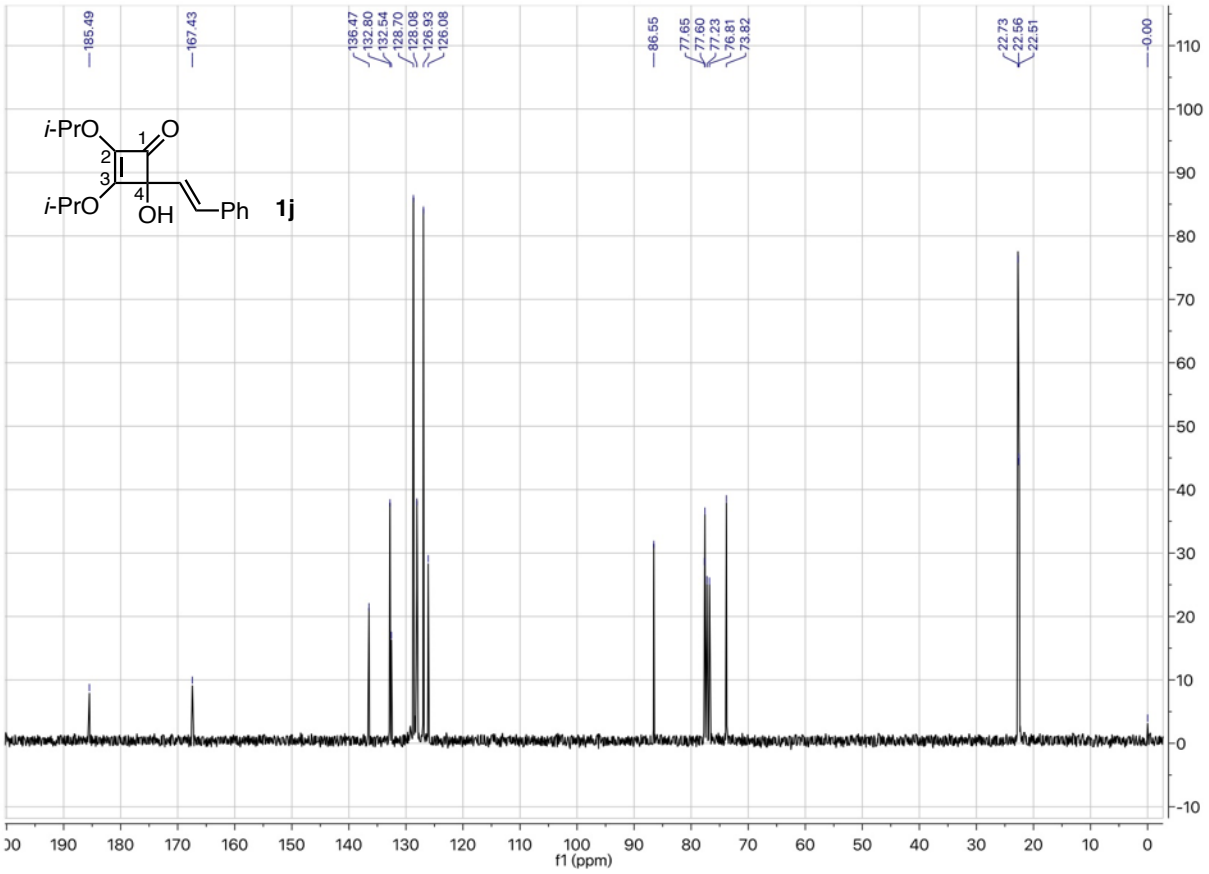
22.69
22.55
22.50
0.00
f1 (ppm)

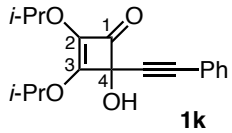


1j

(*E*)-4-Hydroxy-2,3-diisopropoxy-4-styrylcyclobut-2-en-1-one (1j): R_f = 0.55 (7:3 Et_2O/hexane v/v); yellow solid; mp 83-85 °C; IR ($CHCl_3$) ν 3362 (OH), 1767 (C=O), 1618 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.33 (2H, m, arom H), 7.29-7.21 (3H, m, arom H), 6.83 (1H, d, J = 16.2 Hz, -CH=), 6.29 (1H, d, J = 16.2 Hz, -CH=), 4.89 (2H, sept, J = 6.1 Hz, >CH-O ×2), 4.05 (1H, s, OH), 1.40 (3H, d, J = 6.1 Hz, CH_3), 1.37 (3H, d, J = 6.1 Hz, CH_3), 1.30 (3H, d, J = 6.1 Hz, CH_3), 1.29 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.4 (C-1), 167.4 (C-3), 136.5 (C-2), 132.8 (-CH=), 132.5 (arom C), 128.7 (2C) (arom CH), 128.1 (arom CH), 126.9 (2C) (arom CH), 126.1 (-CH=), 86.6 (C-4), 77.7, 73.8 (>CH-O), 22.7 (2C), 22.6, 22.4 (CH_3).

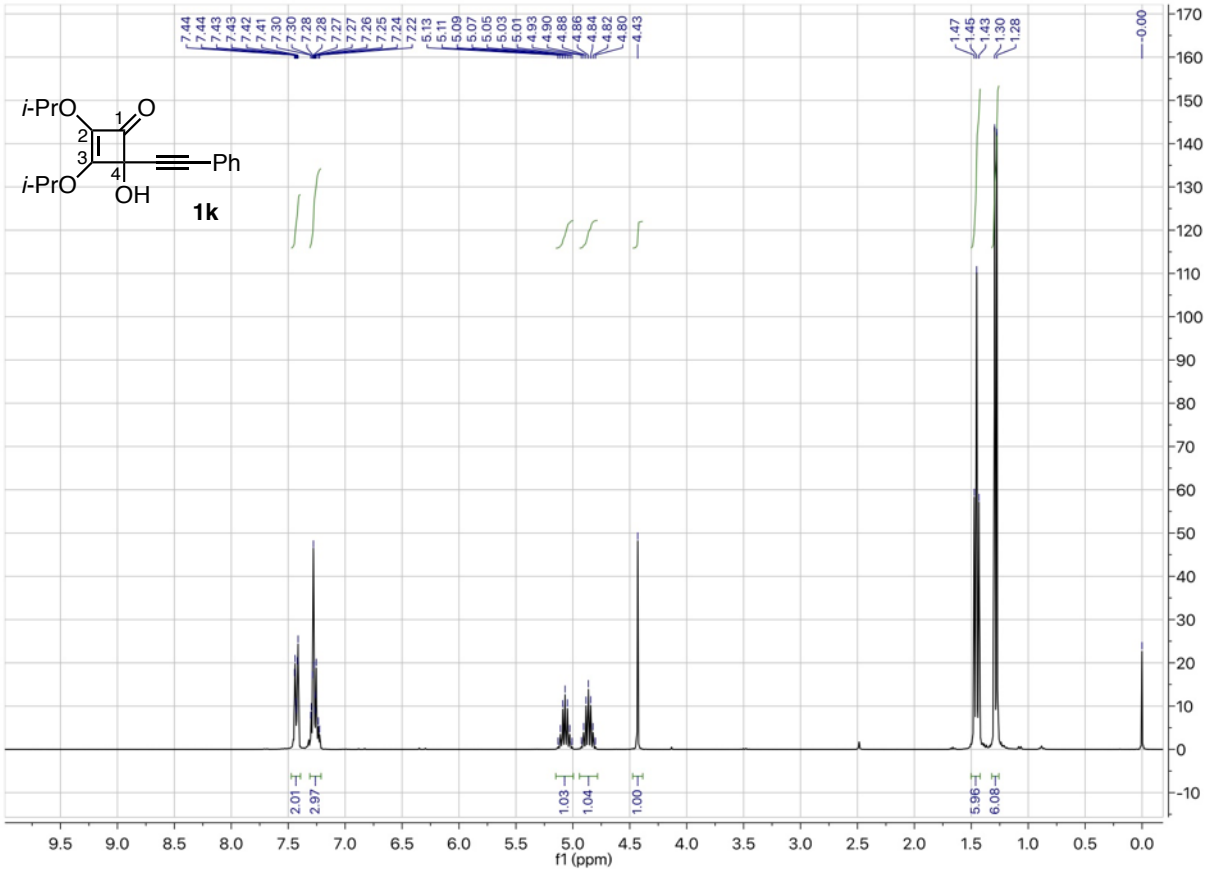


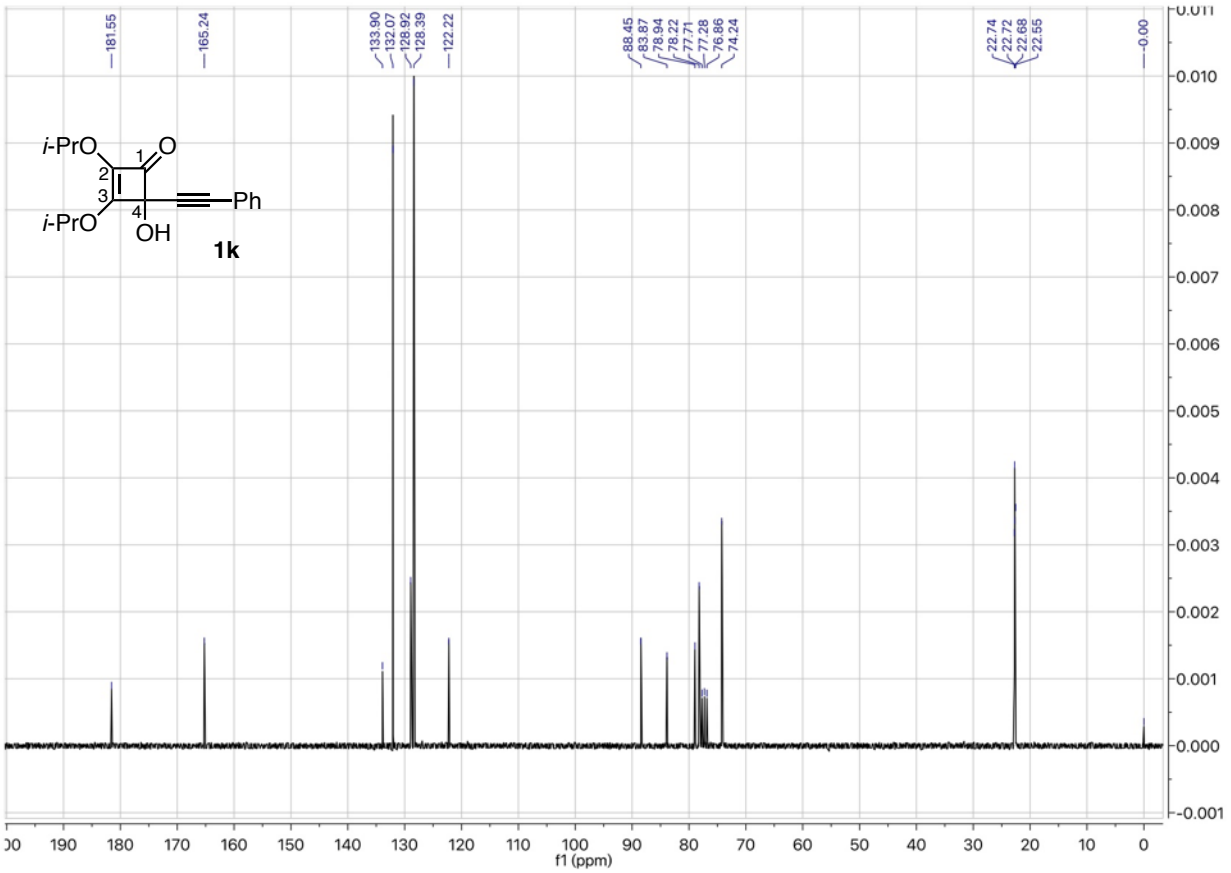


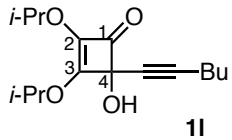


1k

4-Hydroxy-2,3-diisopropoxy-4-(phenylethynyl)cyclobut-2-en-1-one (**1k**)[9a]: R_f = 0.49 (7:3 Et_2O/hexane v/v); yellow microcrystals (from Et_2O-hexane); mp 104-105 °C (lit,[5b] mp 73-7 °C from CH_2Cl_2-hexane); IR ($CHCl_3$) ν 3306 (OH), 2226 (C≡C), 1774 (C=O), 1626 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (2H, m, arom H), 7.30-7.22 (3H, m, arom H), 5.07 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 4.43 (1H, s, OH), 1.46 (3H, d, J = 6.1 Hz, CH_3), 1.44 (3H, d, J = 6.1 Hz, CH_3), 1.28 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.6 (C-1), 165.2 (C-3), 133.9 (C-2), 132.1 (2C), 128.9, 128.4 (2C) (arom CH), 122.2 (arom C), 88.5 (C-4), 83.9 (C≡C), 78.9 (C≡C), 78.2, 74.2 (>CH-O), 22.74, 22.72, 22.68, 22.55 (CH_3).

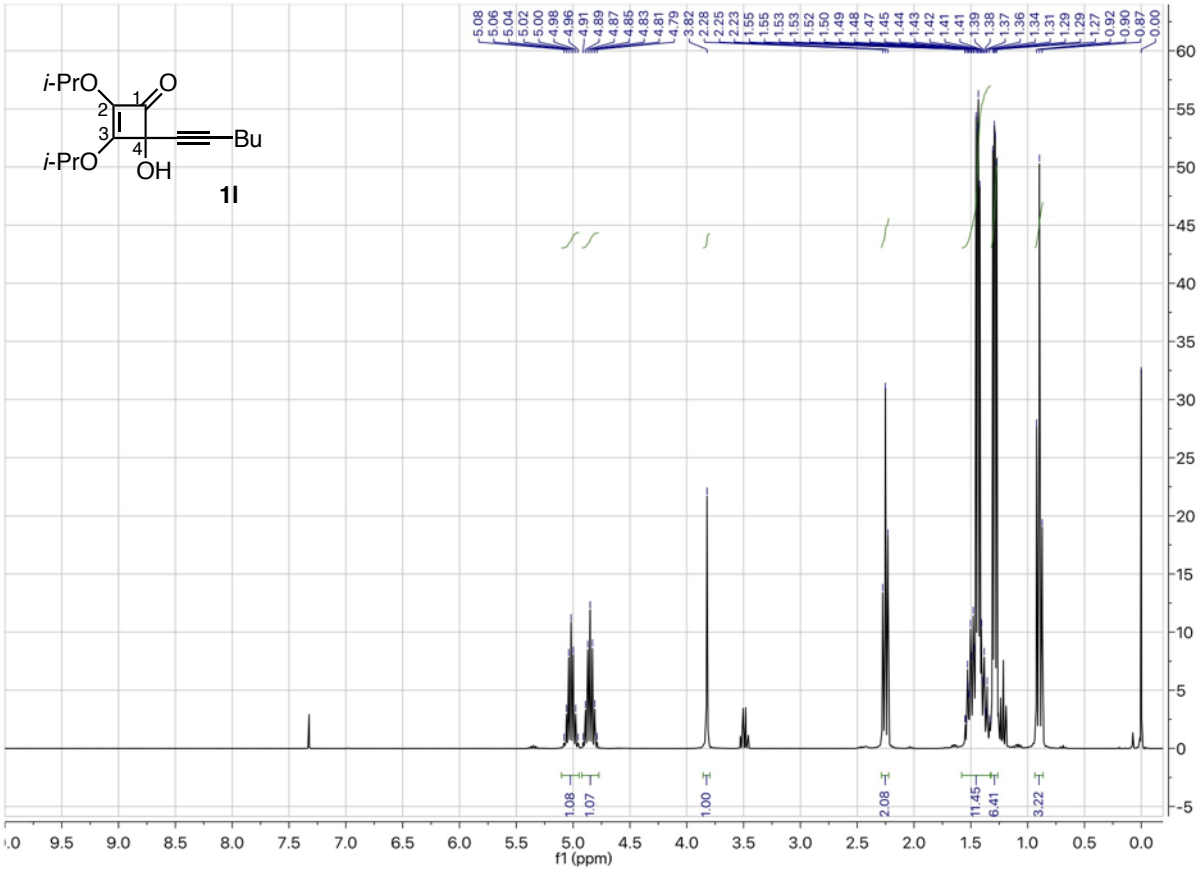

i-PrO
O
1
2
3
4
Ph
i-PrO
OH
1k
f1 (ppm)

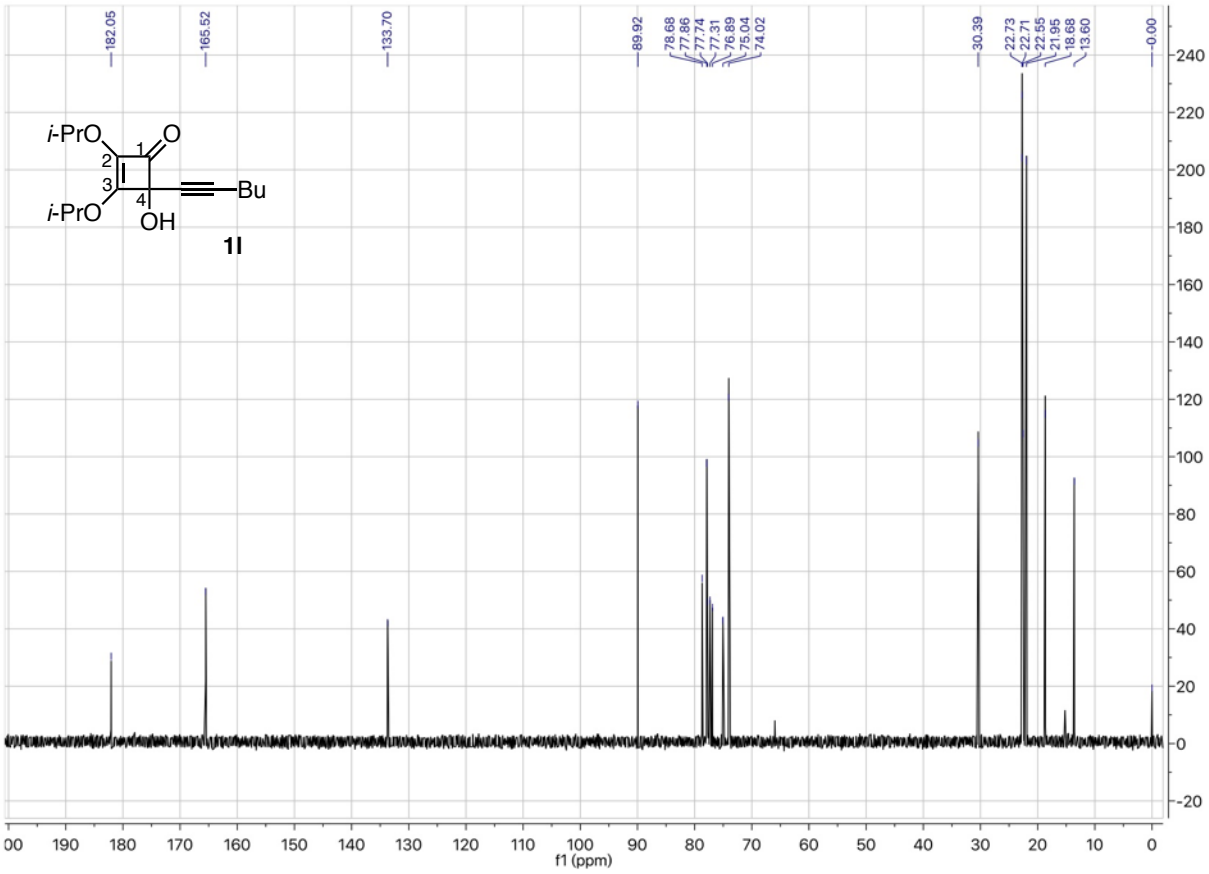

i-PrO
O
1
2
3
4
Ph
i-PrO
OH
1k
f1 (ppm)



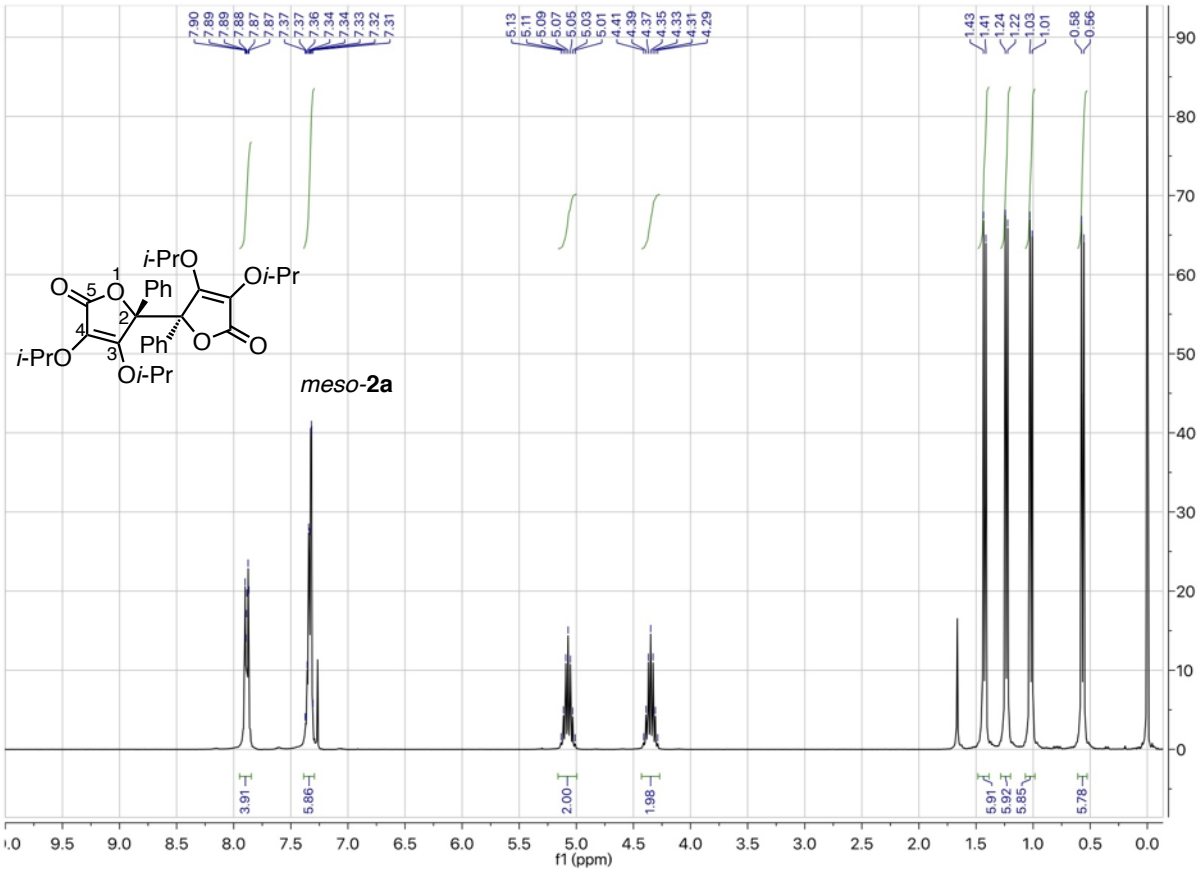
1l

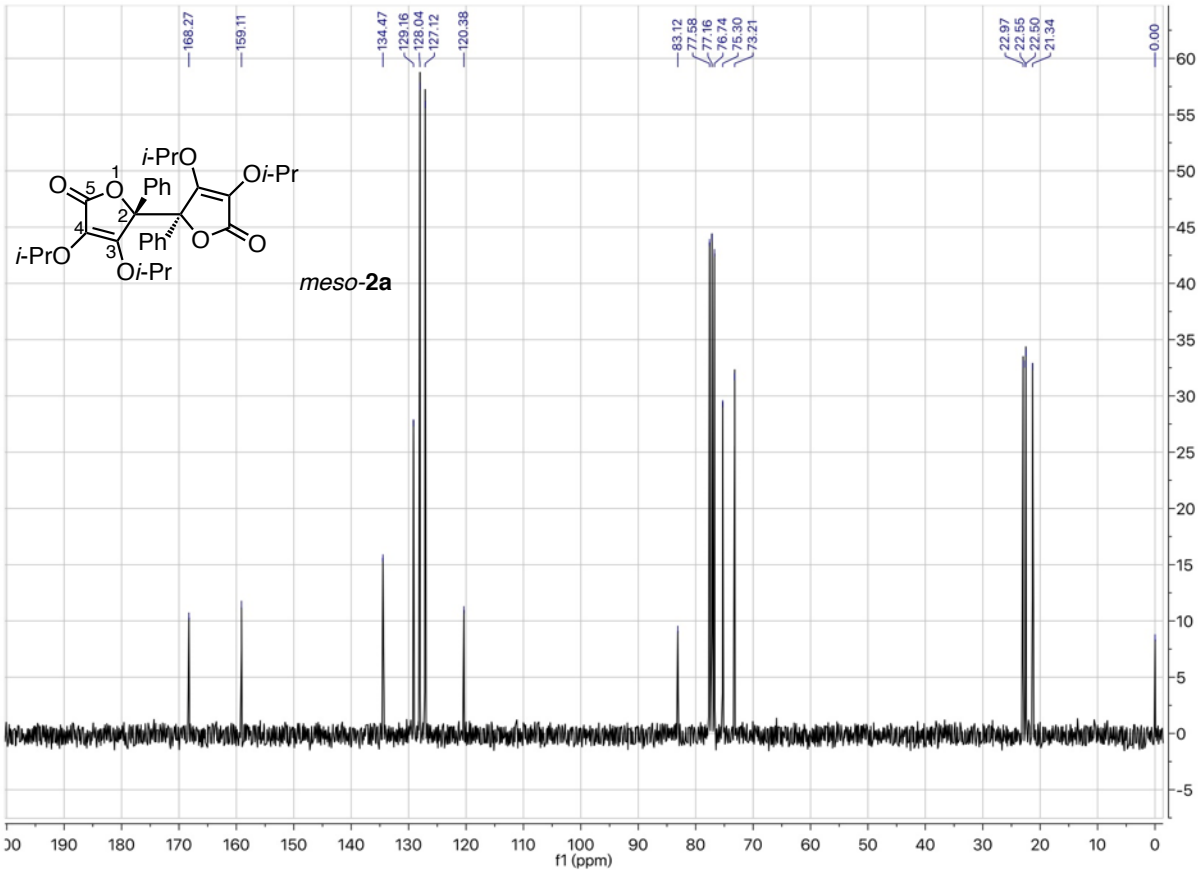
4-(Hex-1-yn-1-yl)-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1l)[9a]**:** R_f = 0.20 ($CHCl_3$); yield 98%; colorless oil; IR ($CHCl_3$) ν 3342 (OH), 2233 (C≡C), 1774 (C=O), 1614 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.02 (1H, sept, J = 6.1 Hz, >CH-O), 4.85 (1H, sept, J = 6.1 Hz, >CH-O), 3.82 (1H, s, OH), 2.25 (2H, t, J = 7.0 Hz, -CH_2-), 1.55-1.33 (4H, m, -CH_2- ×2), 1.44 (3H, d, J = 6.1 Hz, CH_3), 1.43 (3H, d, J = 6.1 Hz, CH_3), 1.30 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3), 0.90 (3H, t, J = 7.0 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.1 (C-1), 165.5 (C-3), 133.7 (C-2), 89.9 (C-4), 78.7 (C≡C), 77.9 (>CH-O), 75.0 (C≡C), 74.0 (>CH-O), 30.4 (-CH_2-), 22.73 (2C), 22.71, 22.6 (CH_3), 22.0, 18.7 (-CH_2-), 13.6 (CH_3).



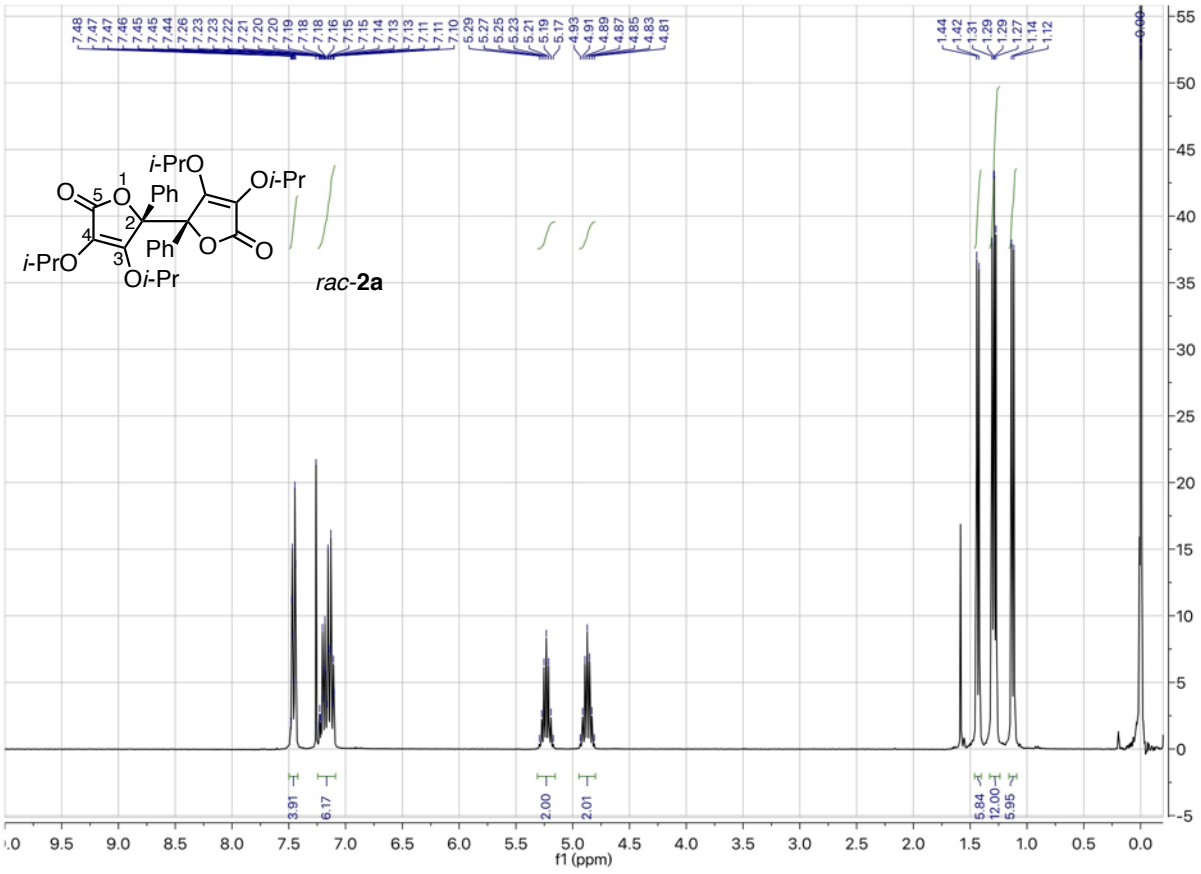

182.05
165.52
133.70
89.92
78.68
77.86
77.74
77.31
76.89
75.04
74.02
30.39
22.73
22.71
22.55
21.95
18.68
13.60
0.00
i-PrO
O
1
2
3
4
Bu
i-PrO
OH
1l
f1 (ppm)

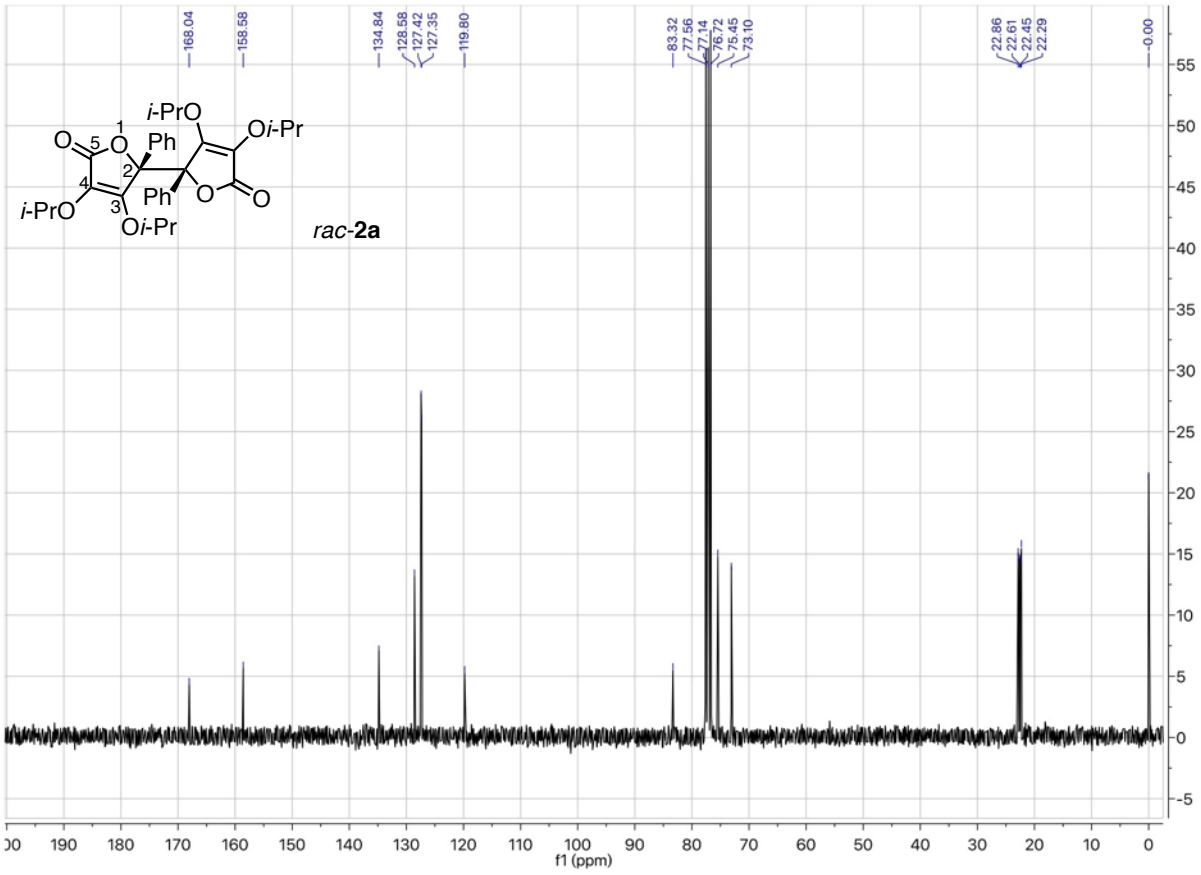
***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2a):**



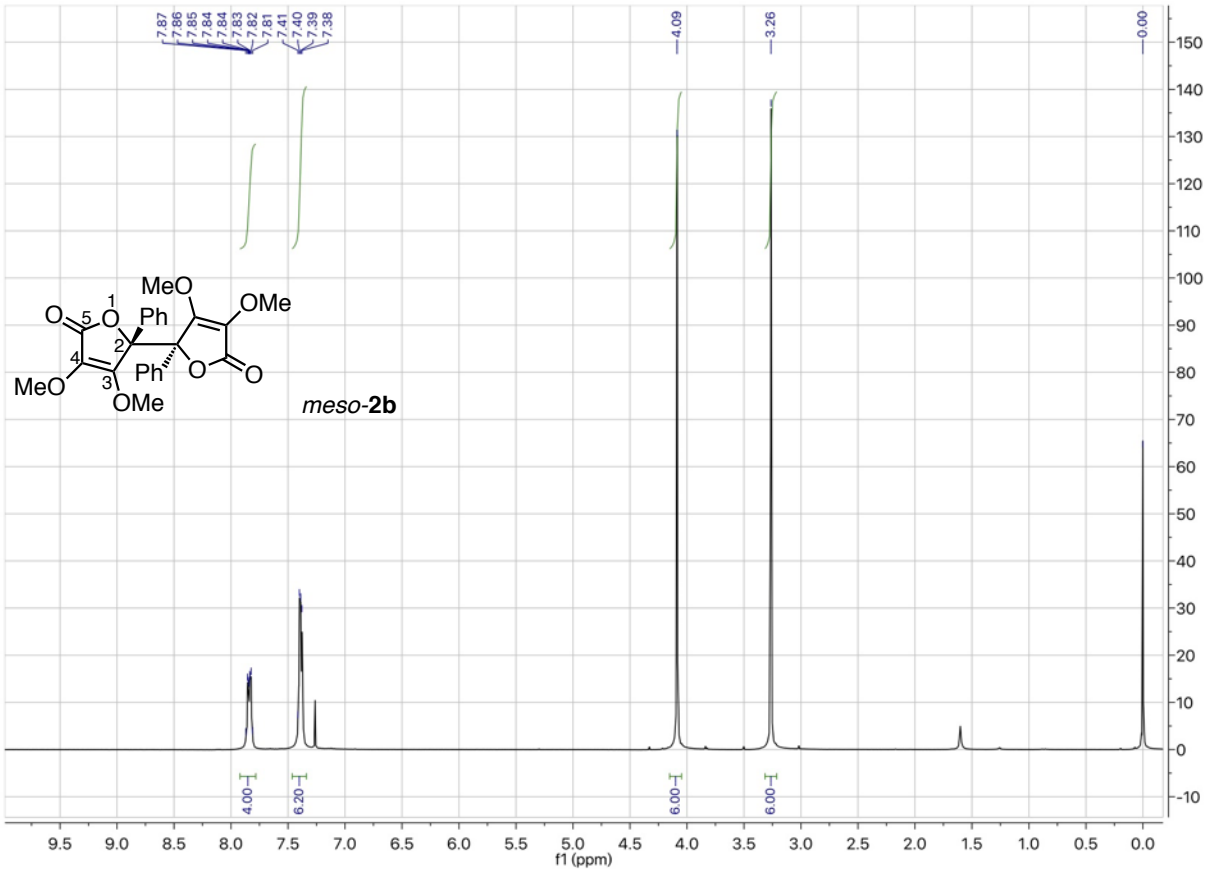


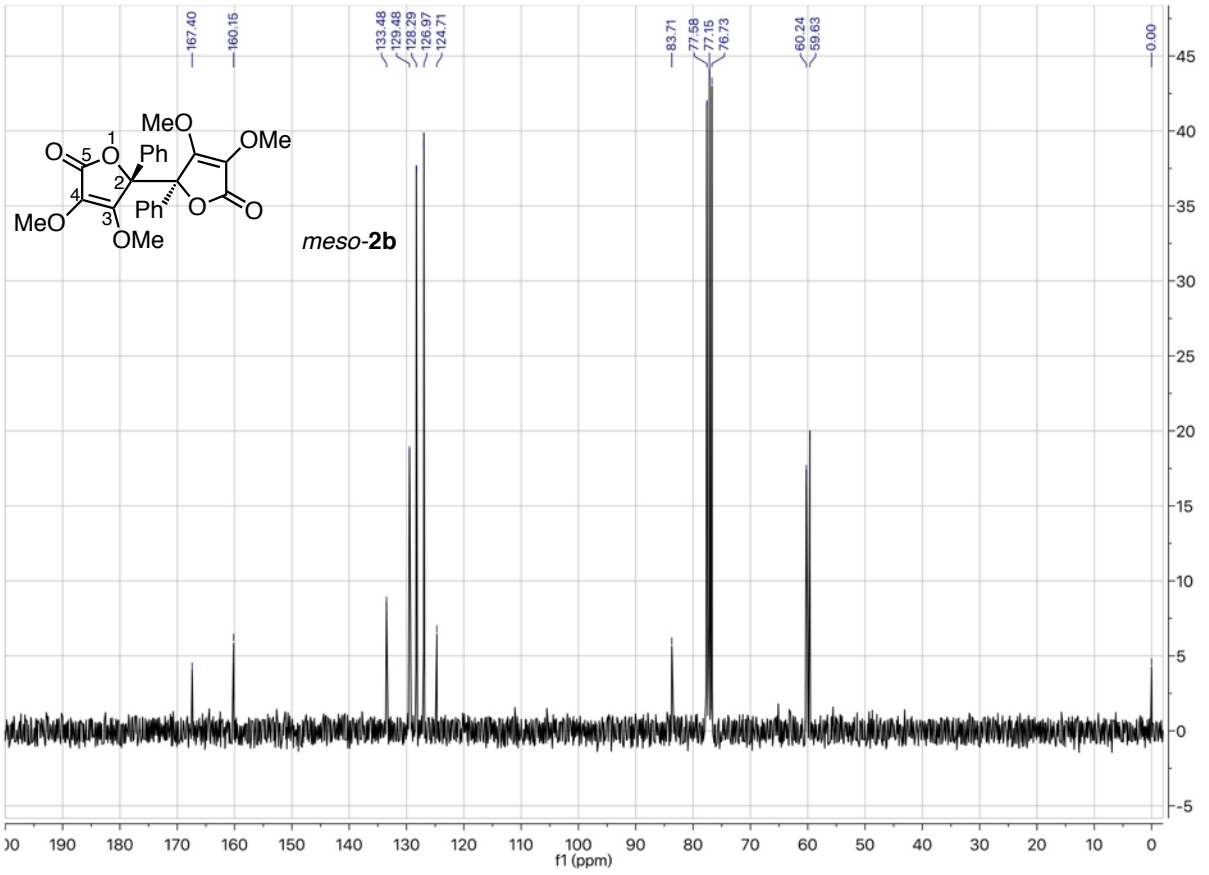
***rac*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2a):**



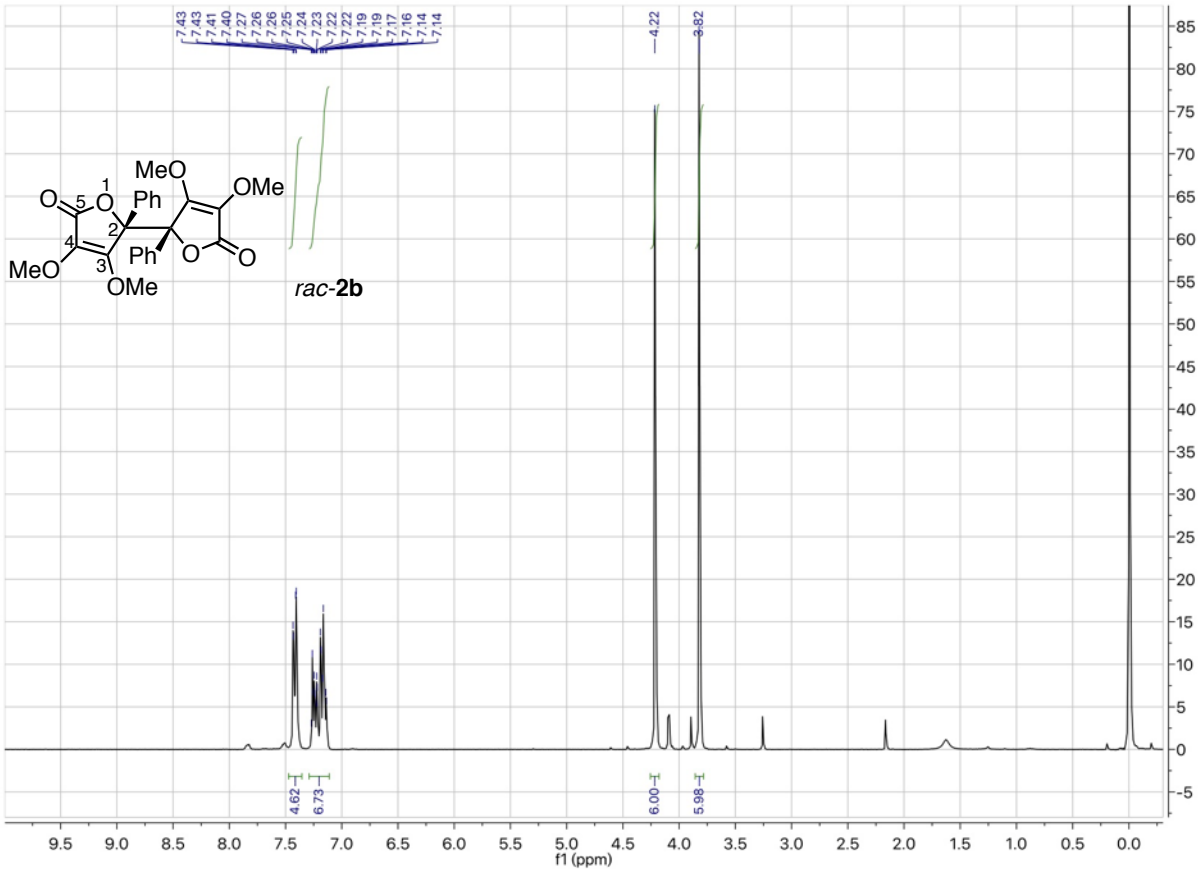


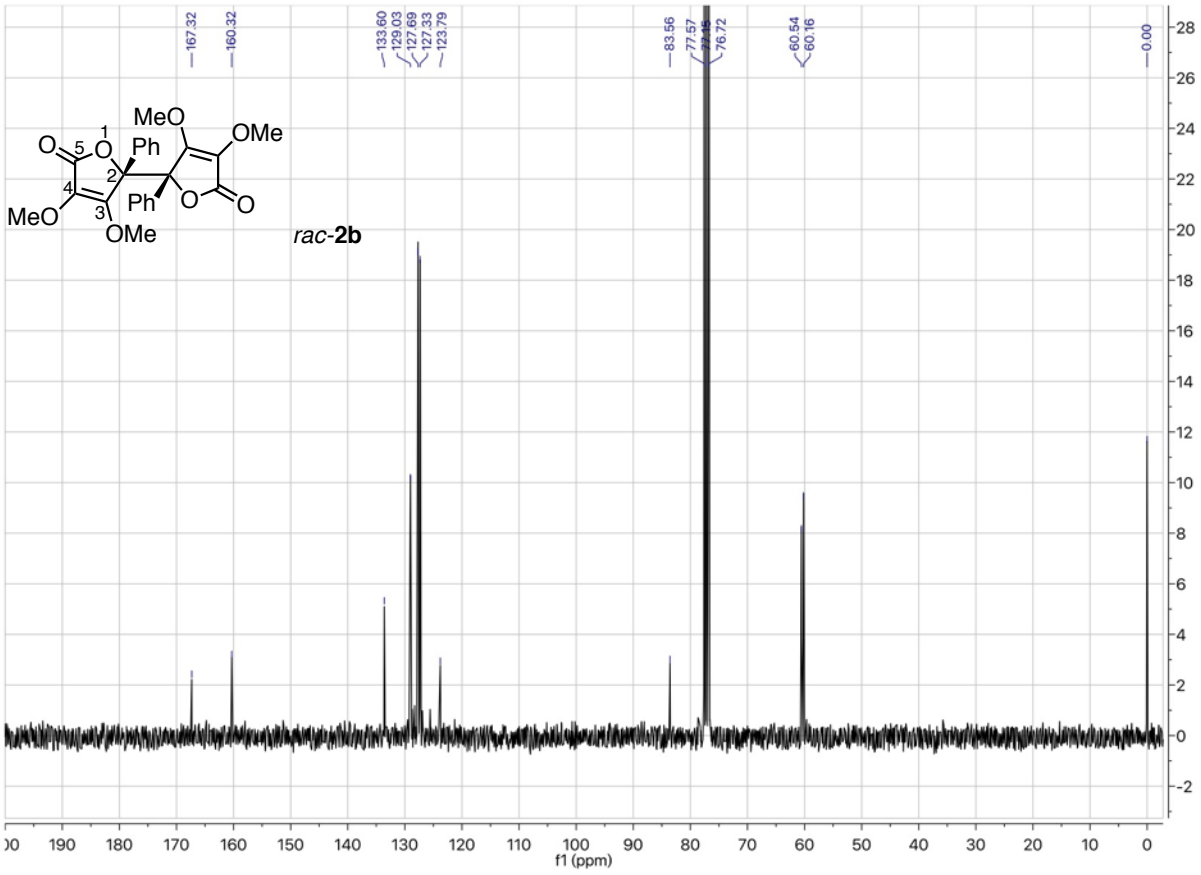
***meso*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2b):**



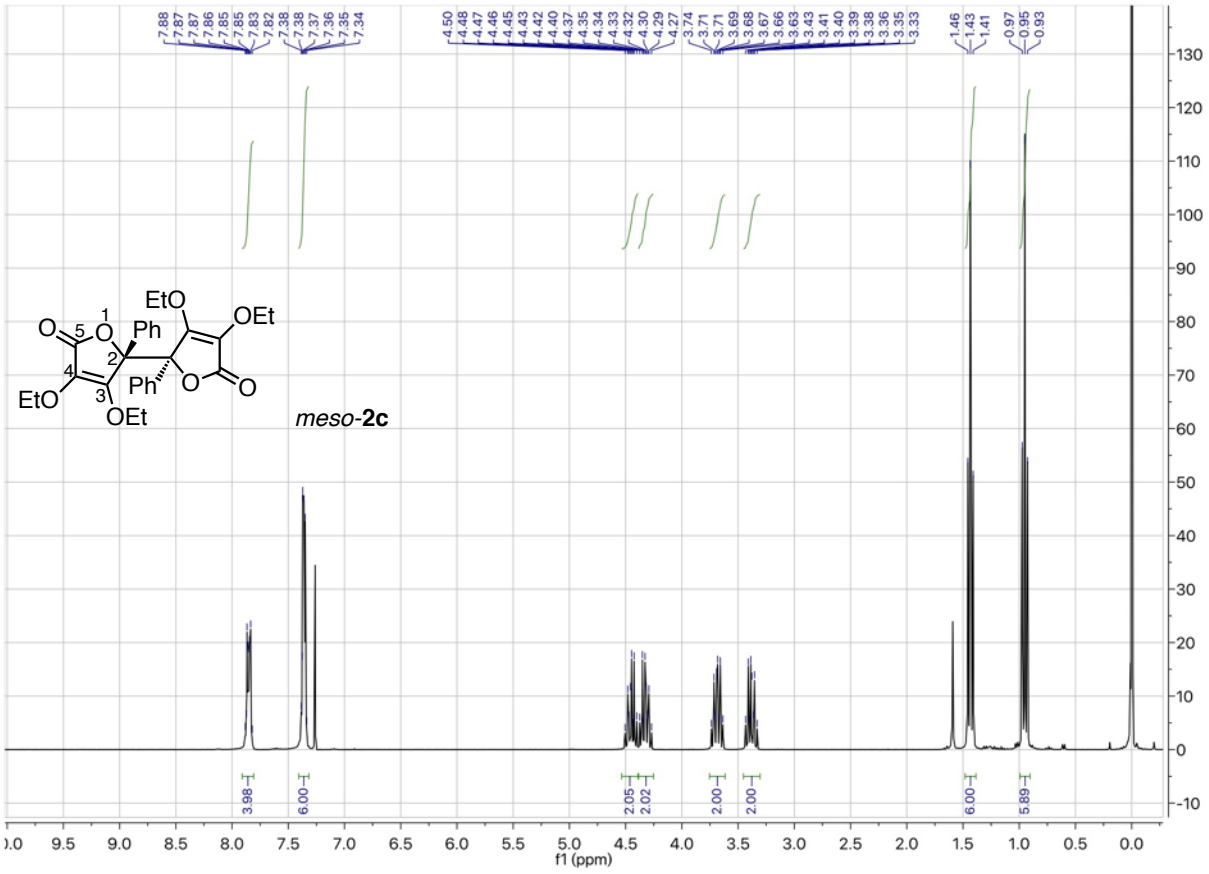


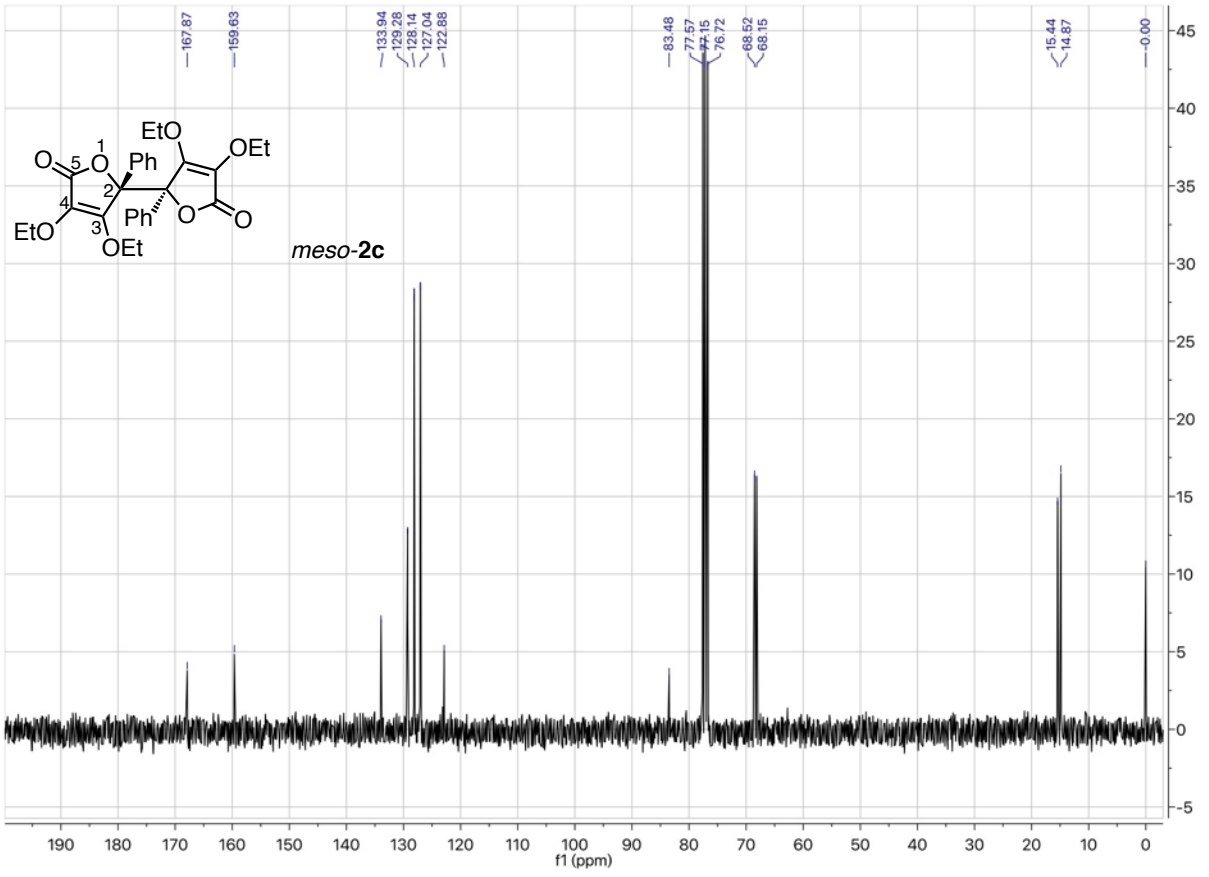
***rac*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2b):**



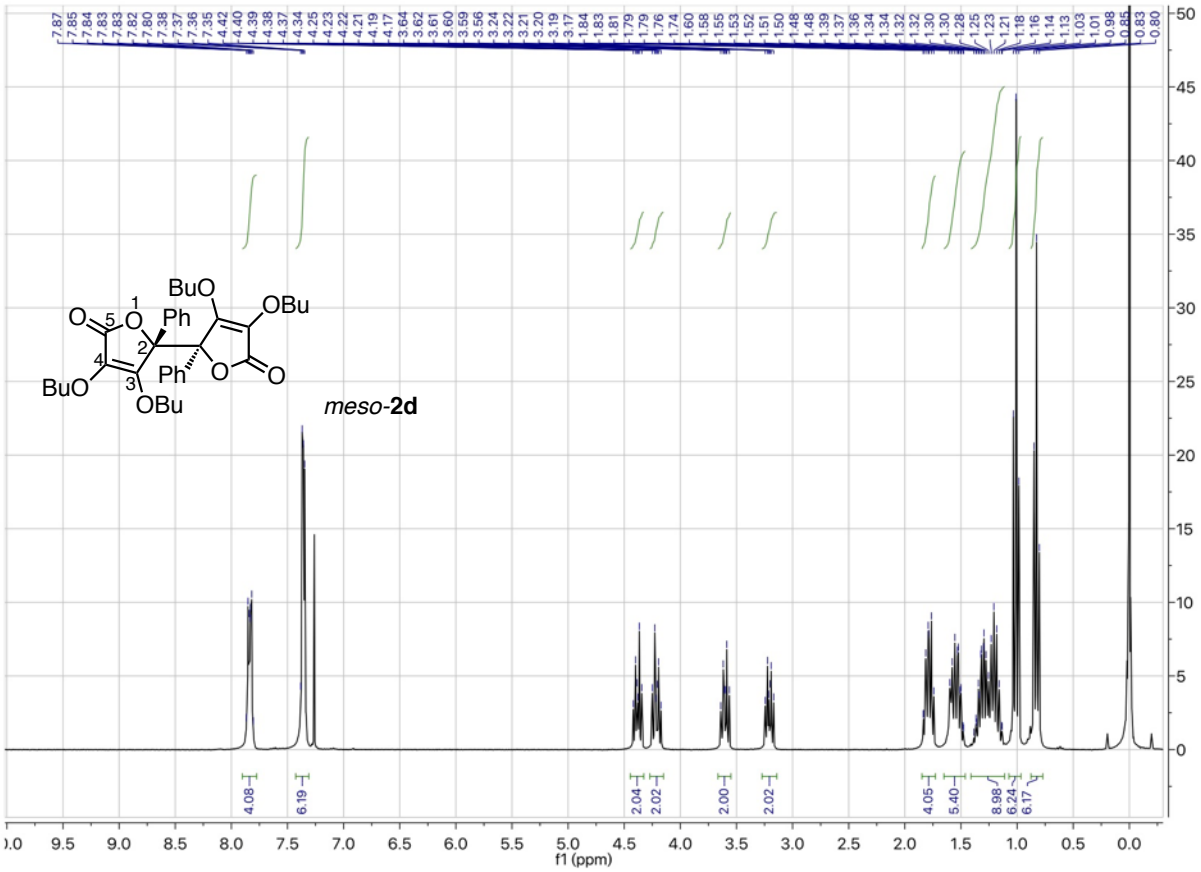


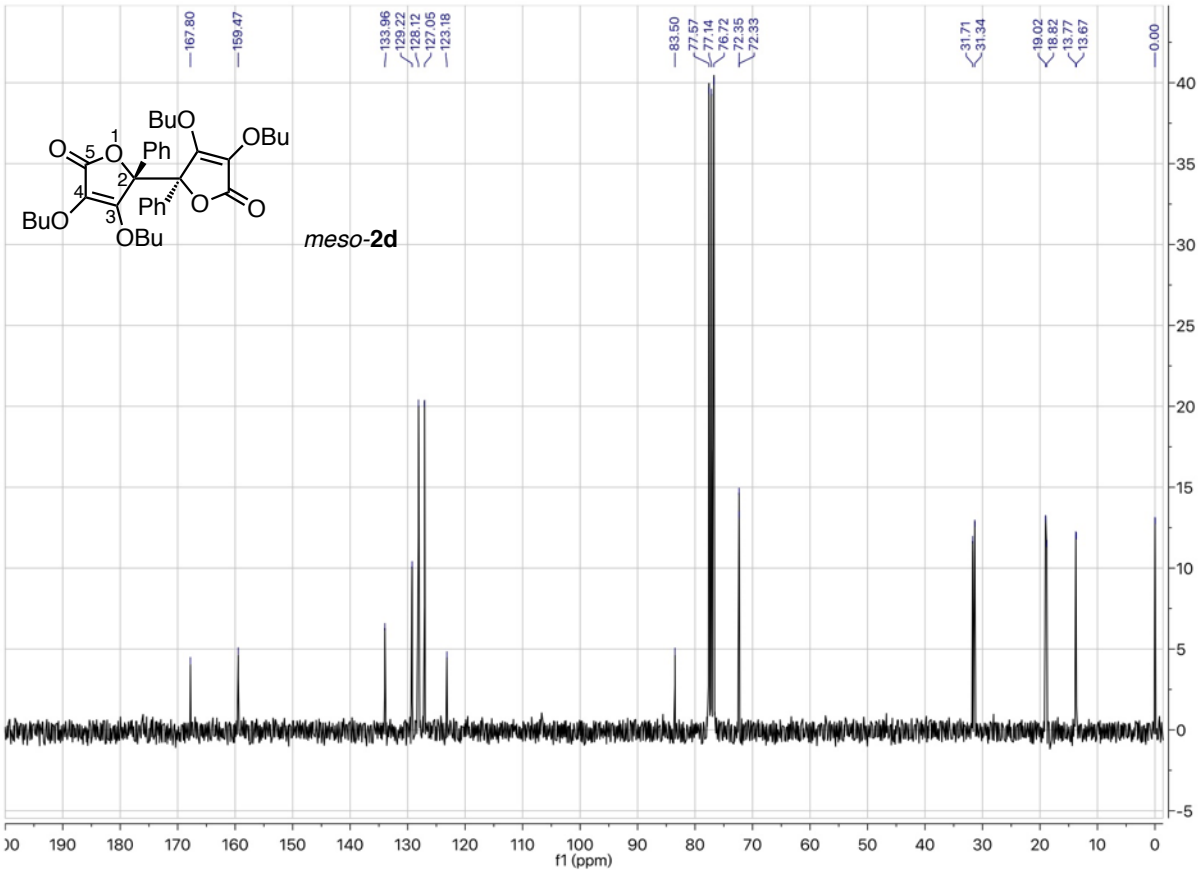
***meso*-3,3',4,4'-Tetraethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2c):**

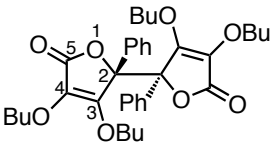




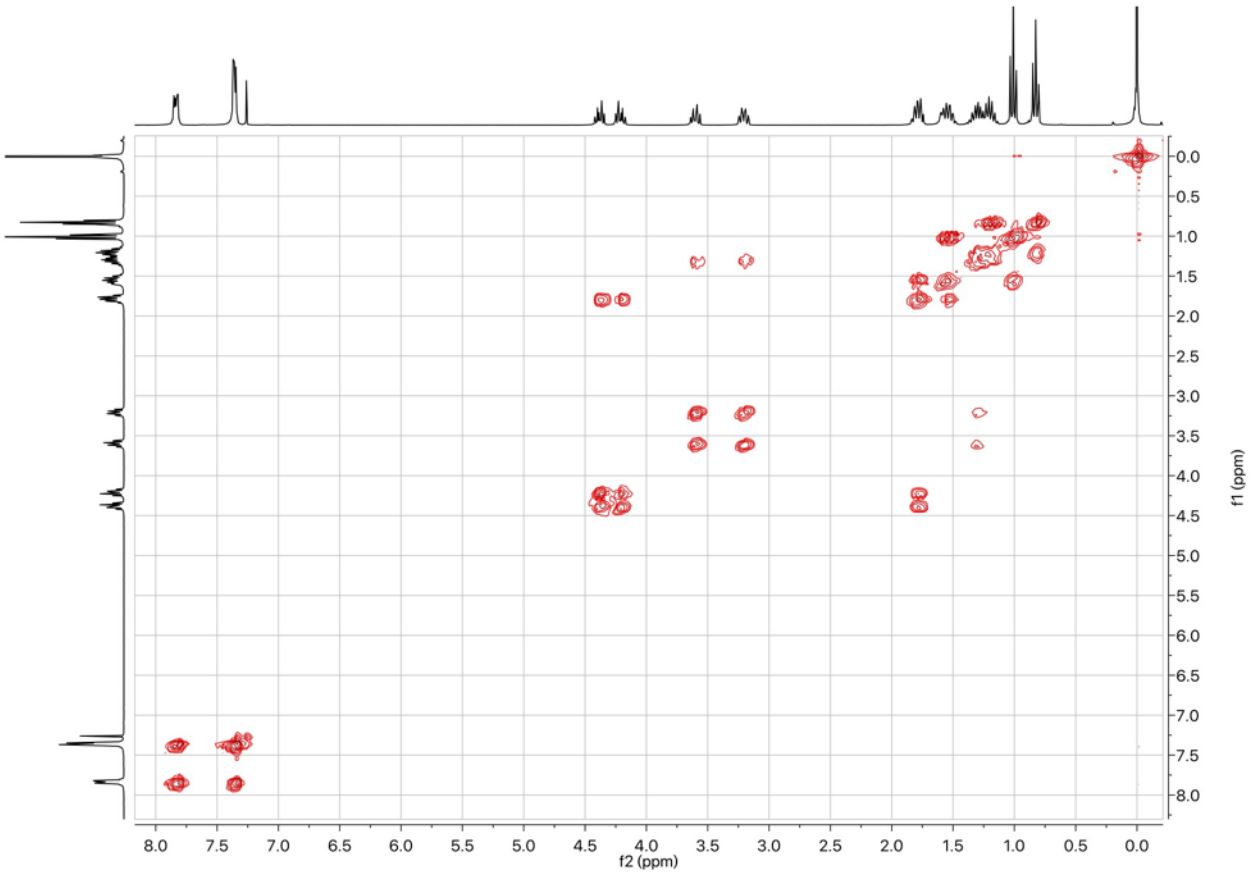
***meso*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2d):**



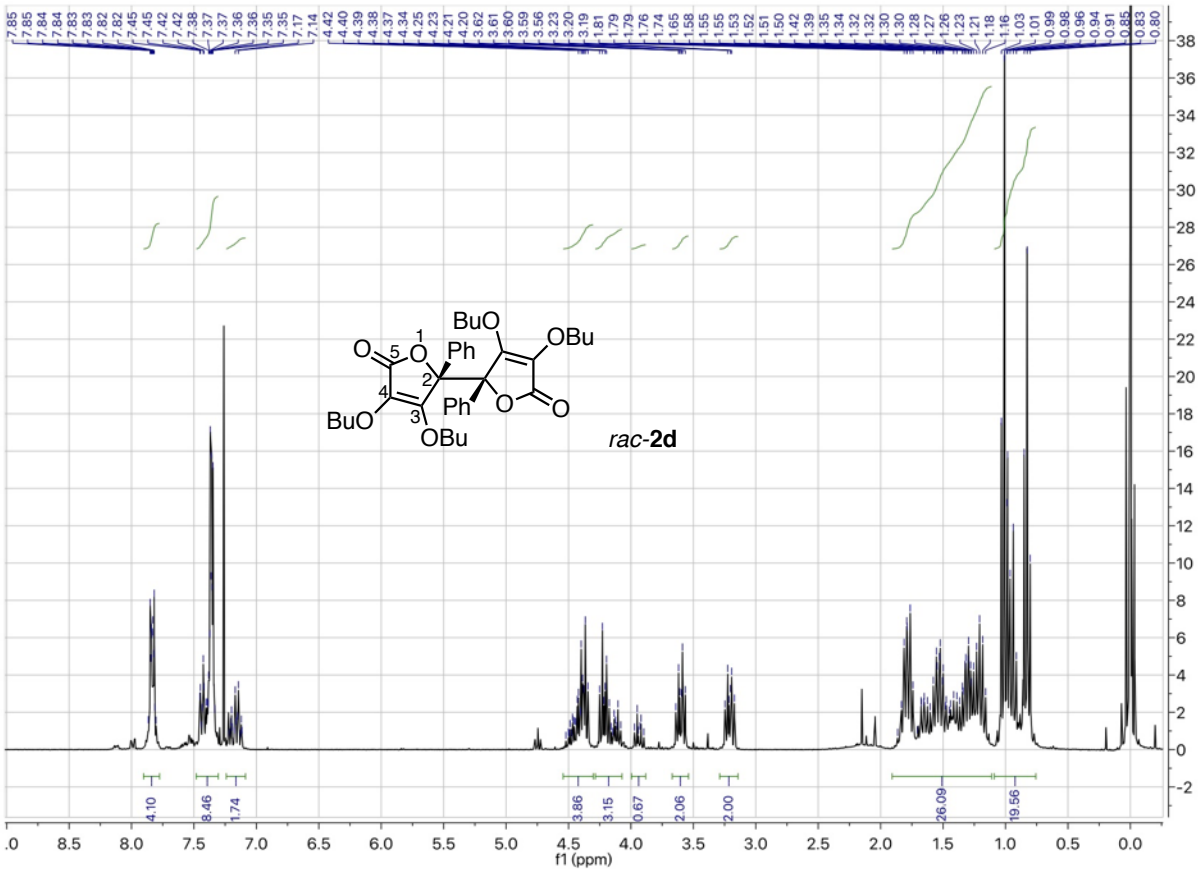


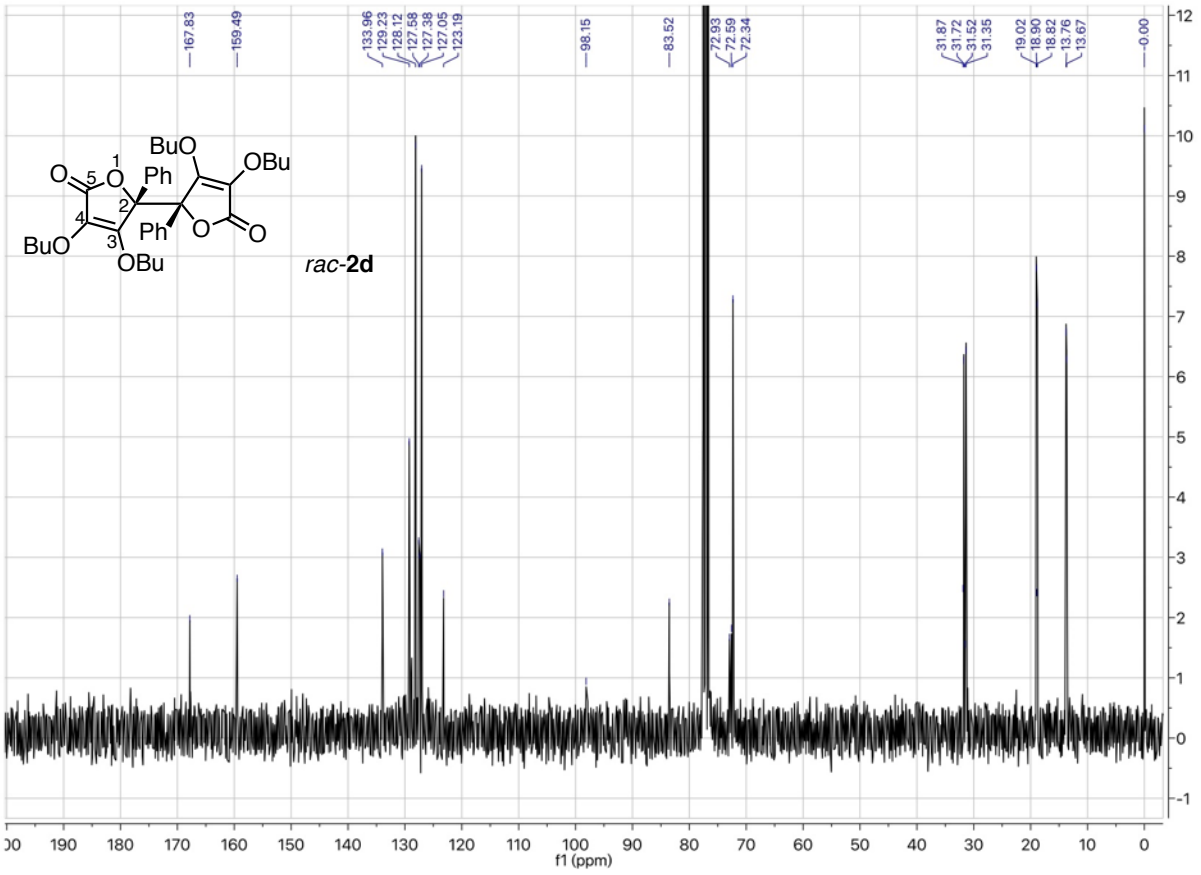


meso-**2d**

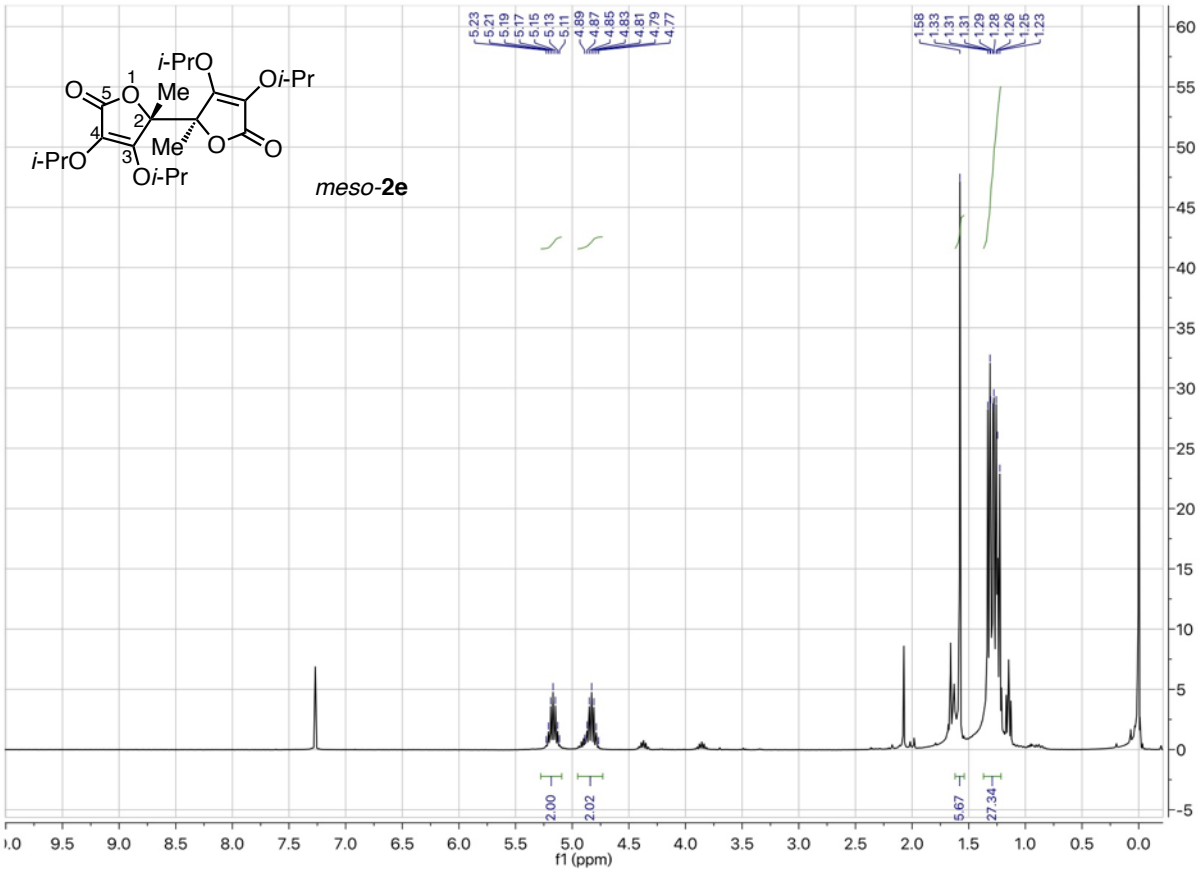


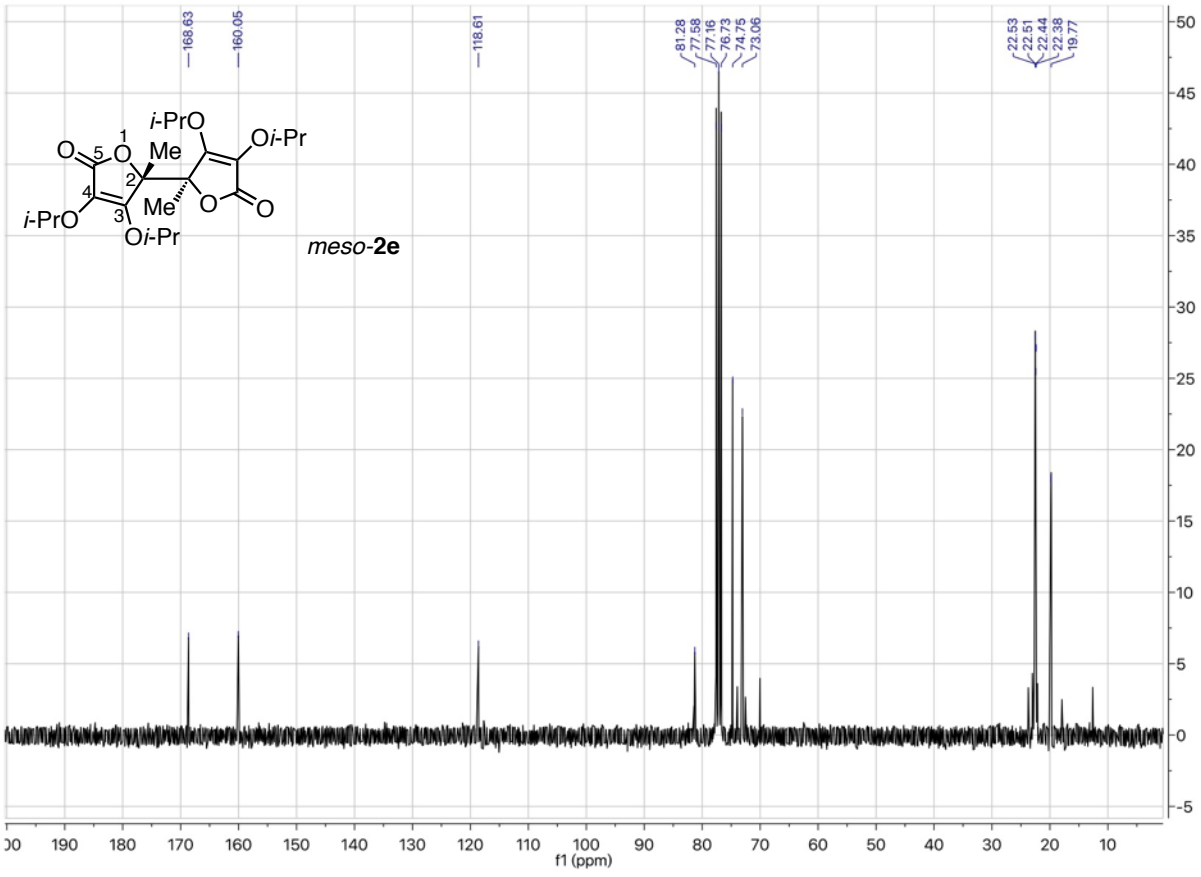
***rac*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2d):**



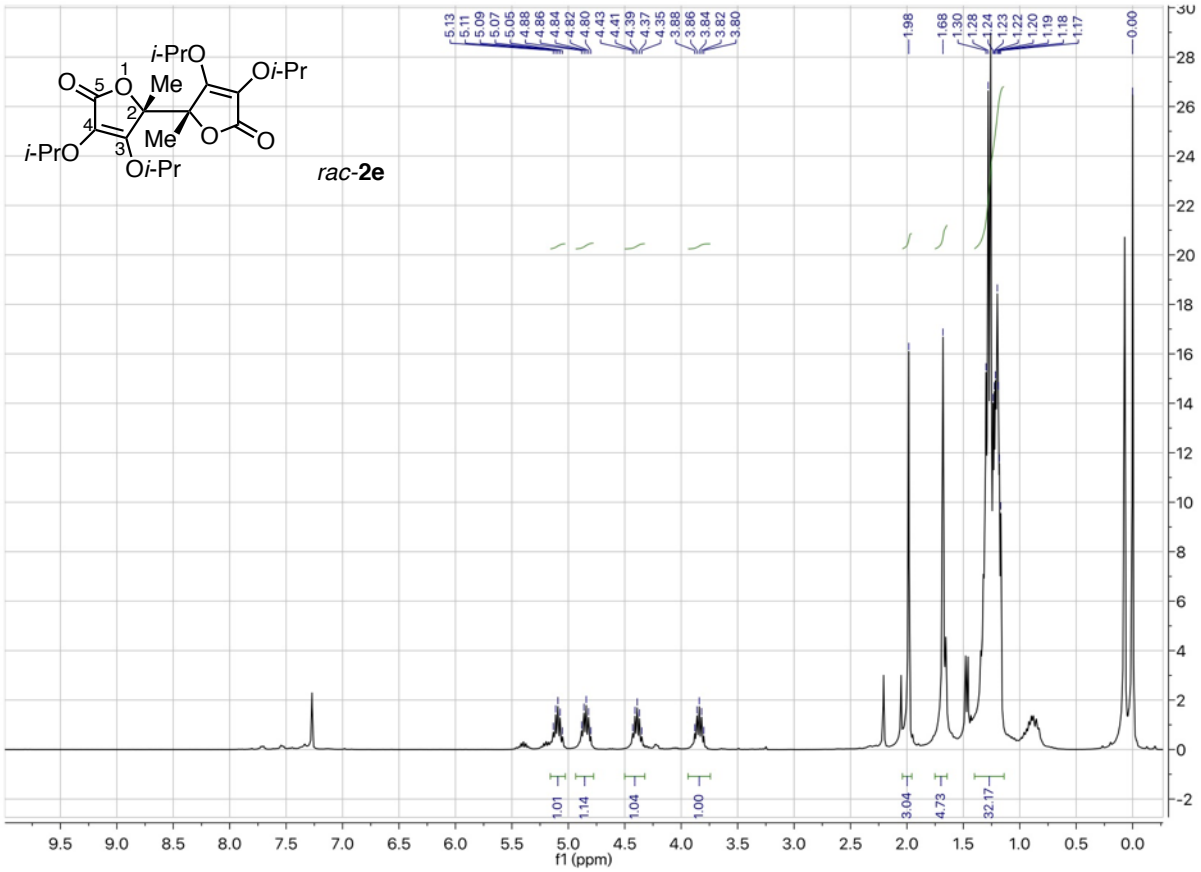


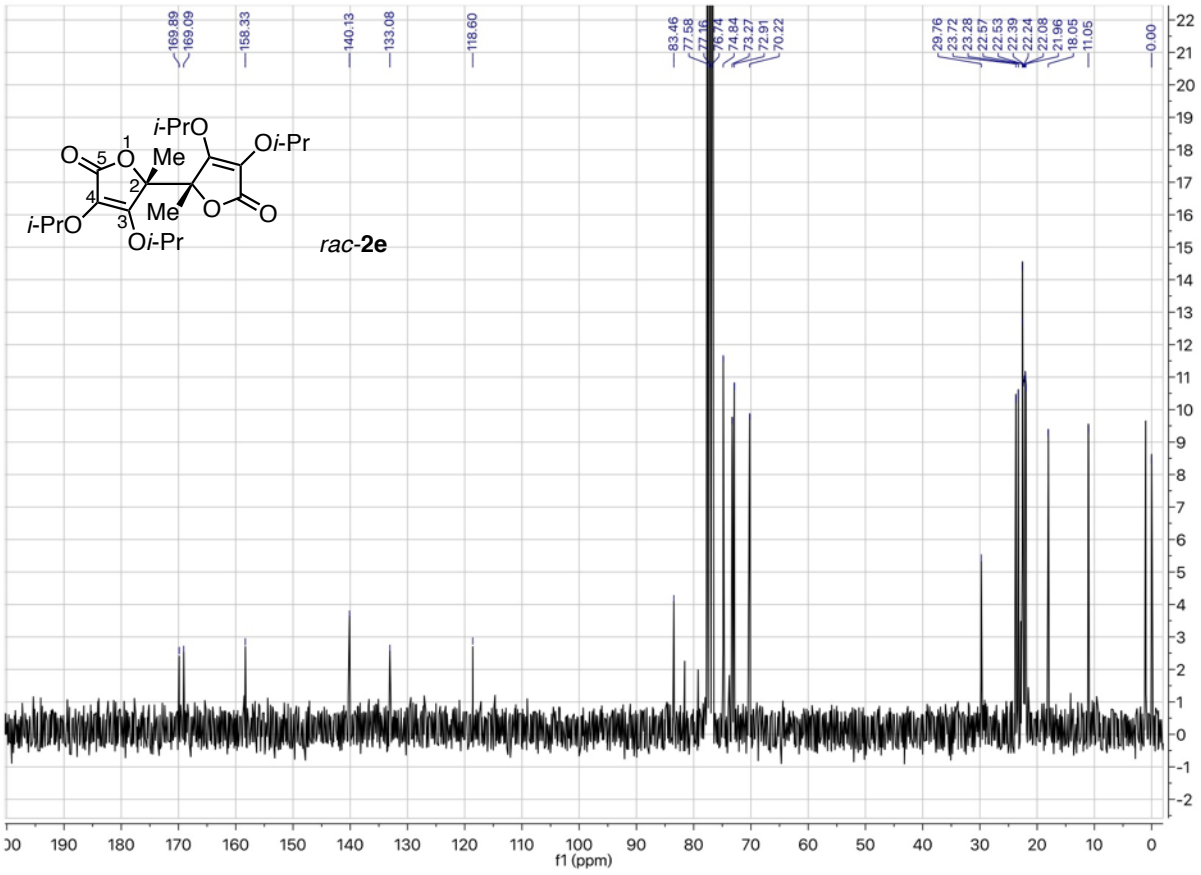
***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2e):**



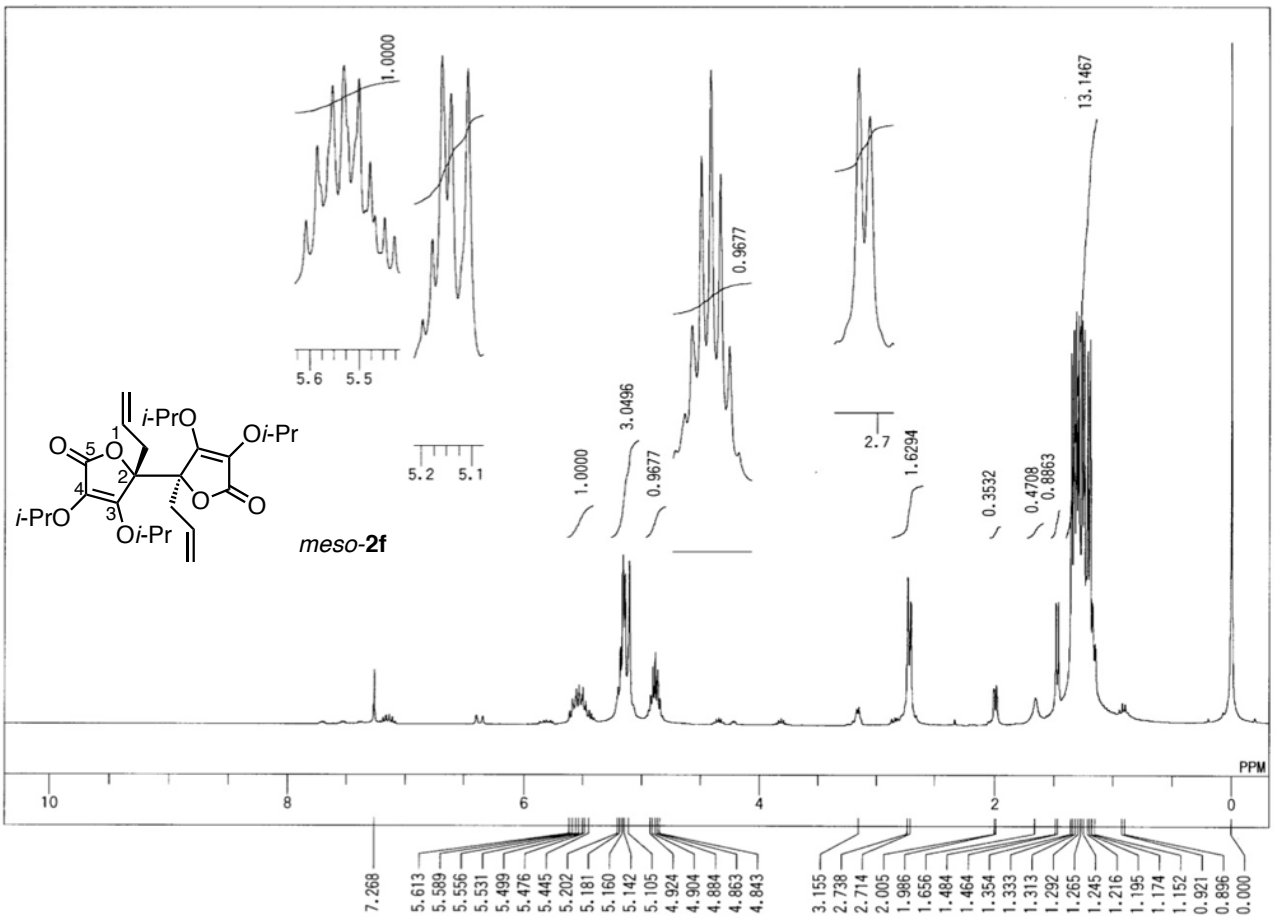


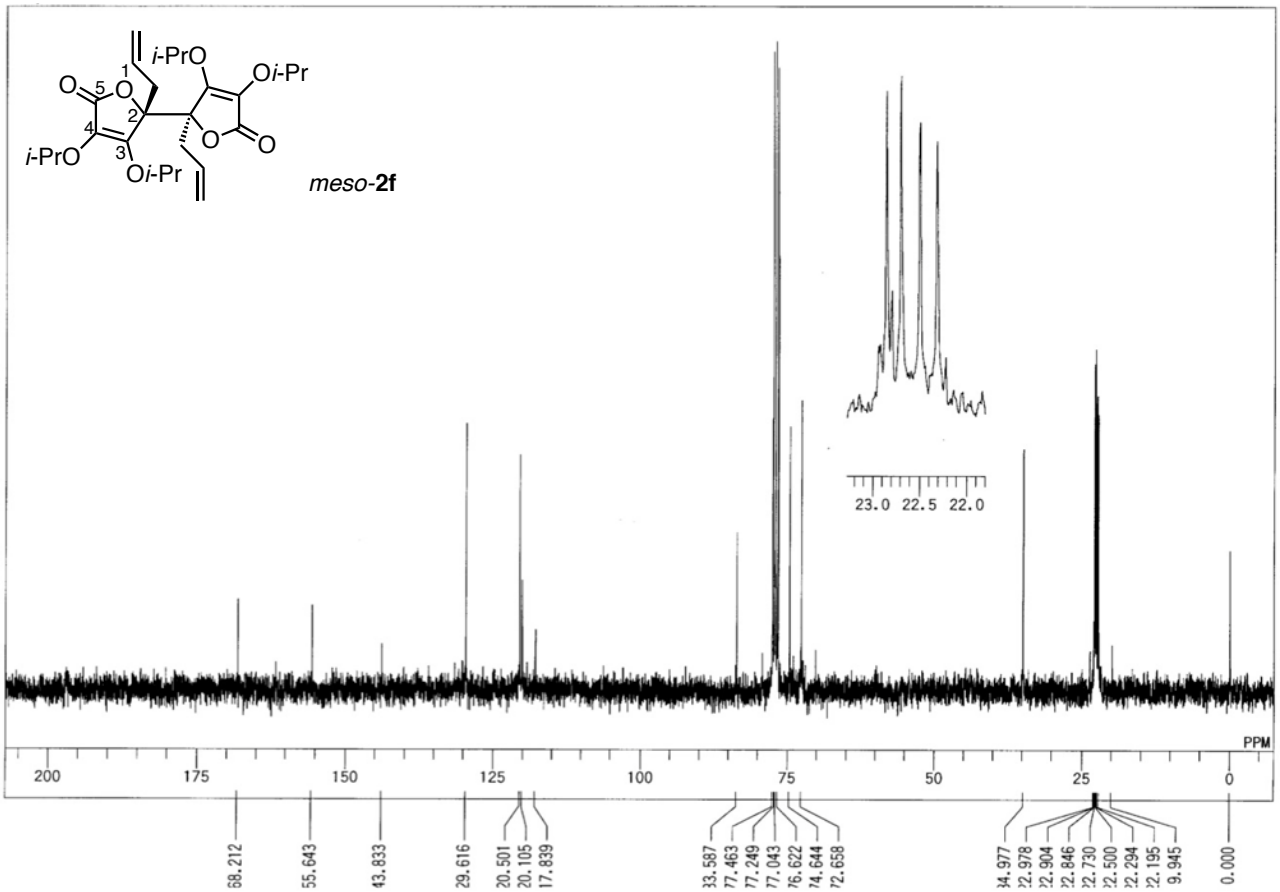
***rac*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2e):**



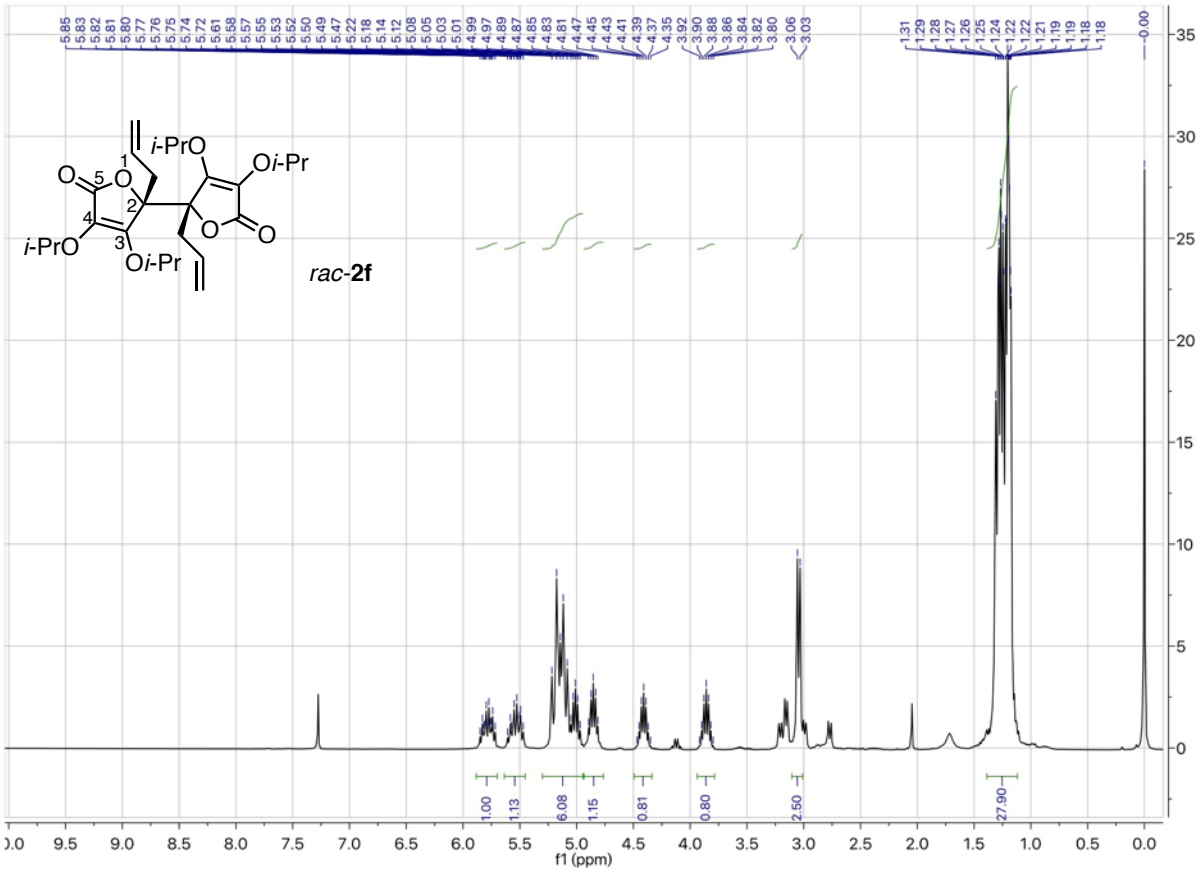


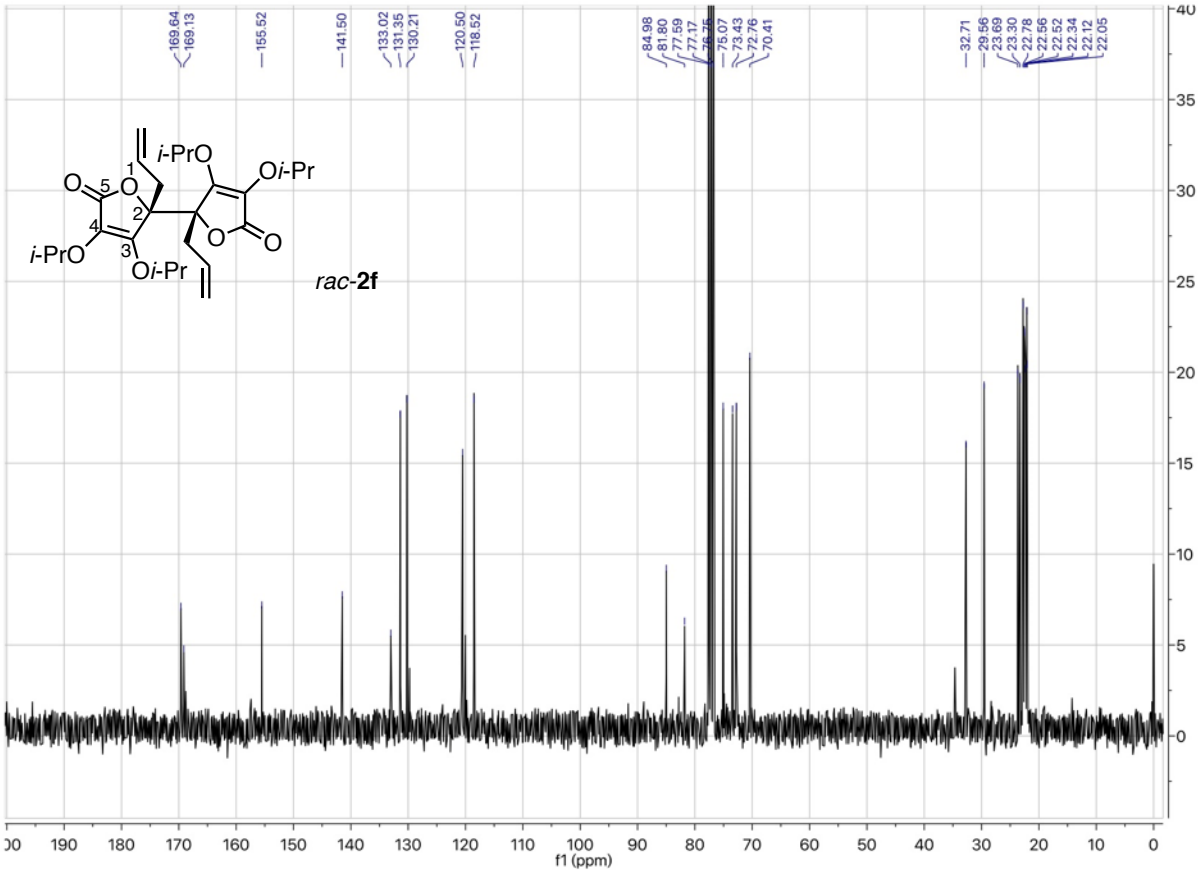
***meso*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2f):**



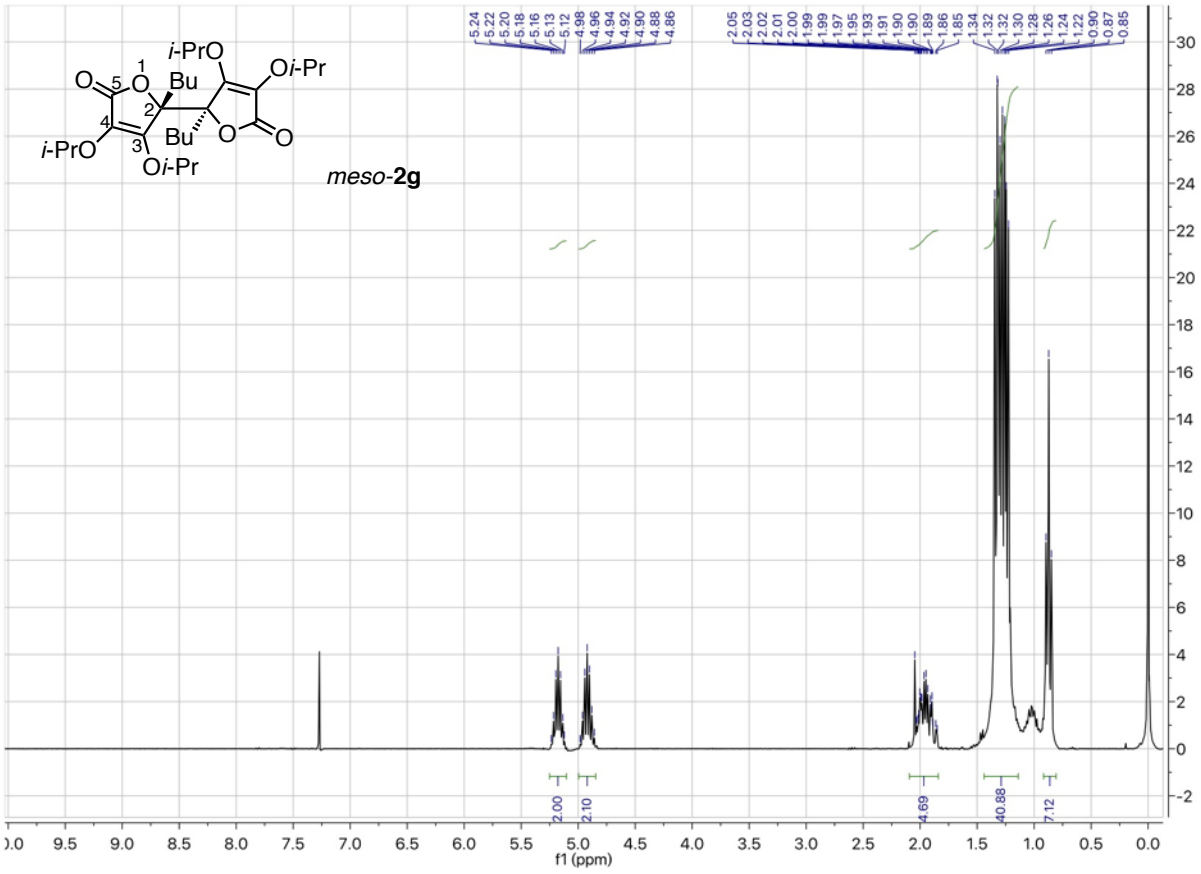


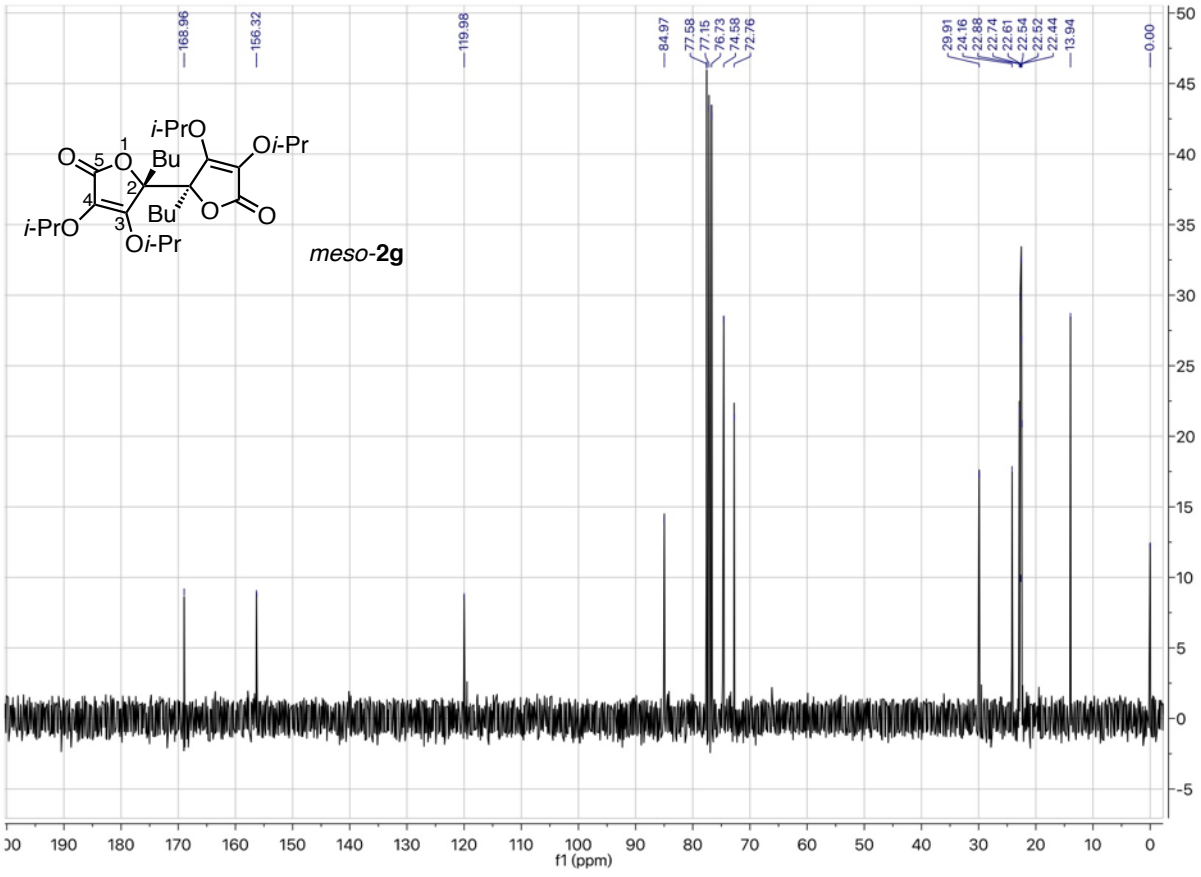
***rac*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2f):**



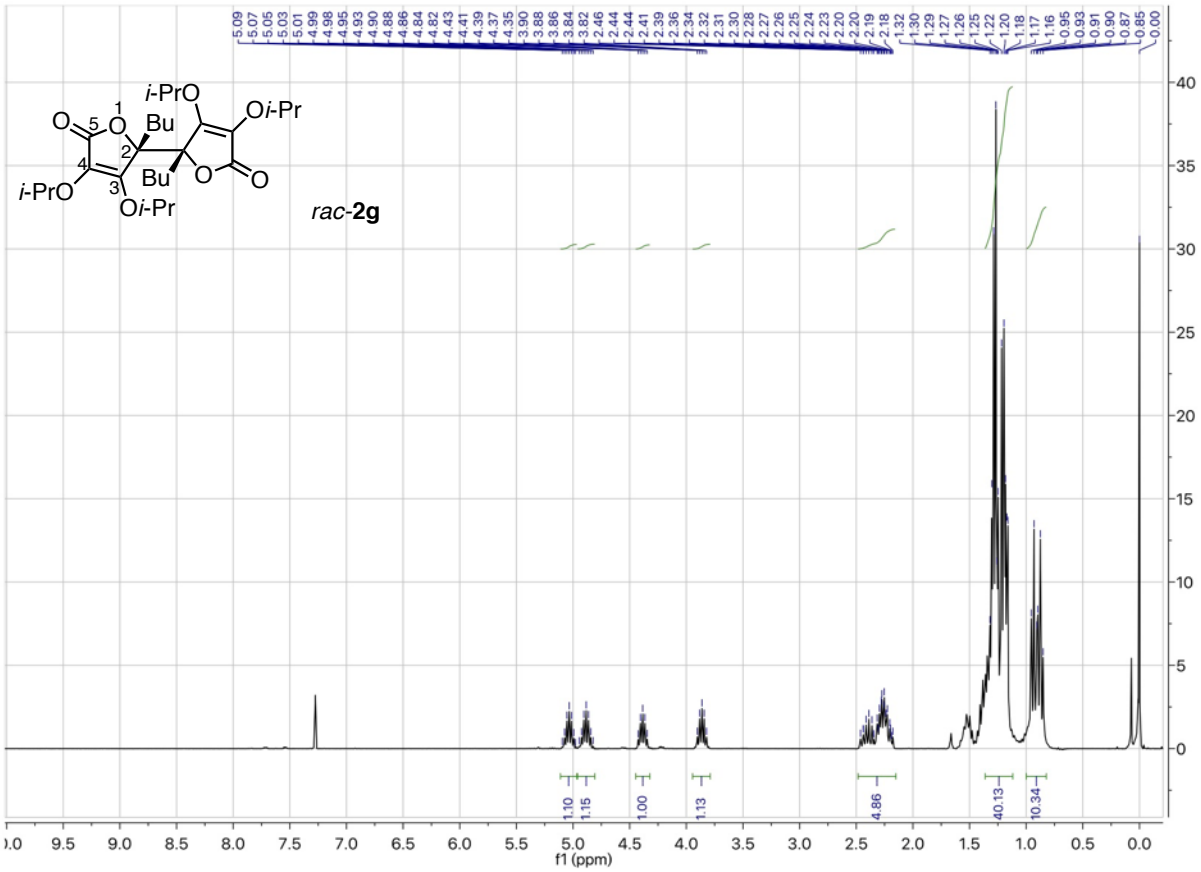


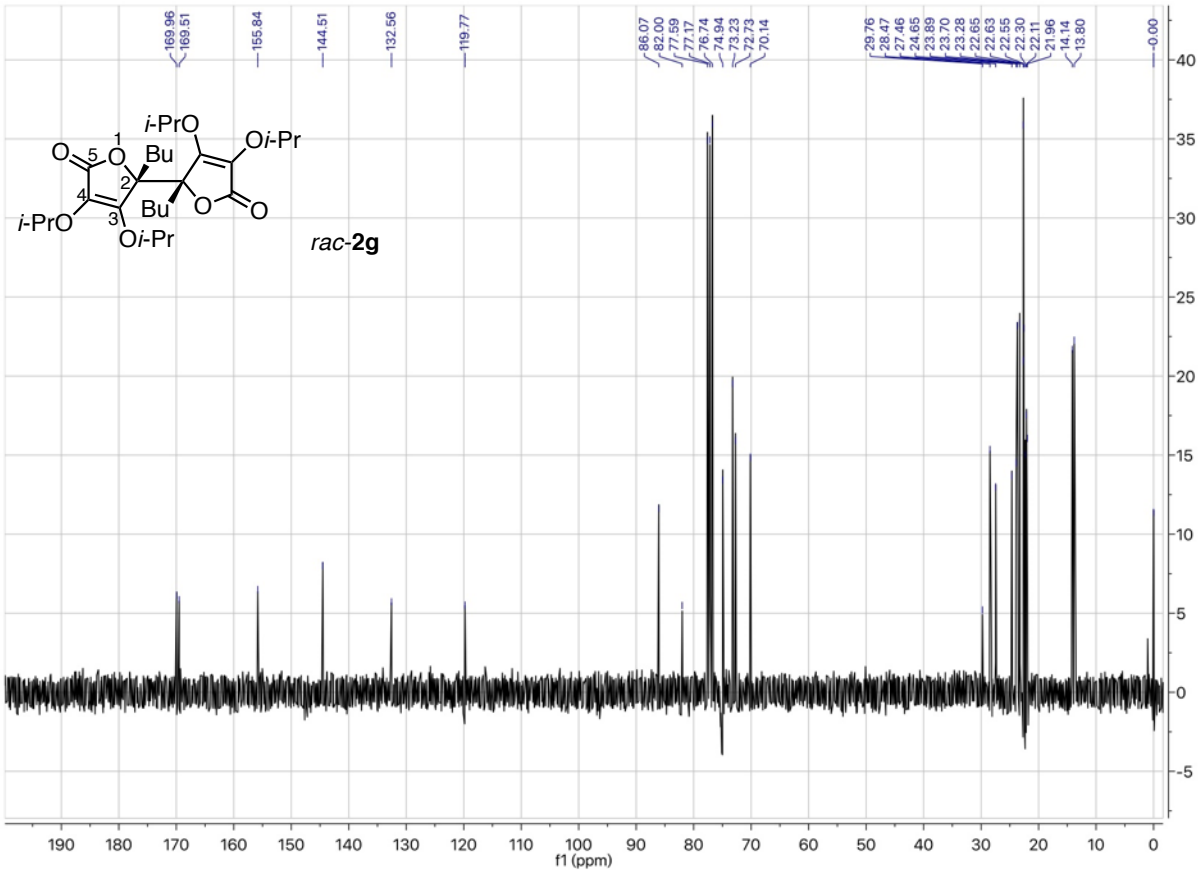
***meso*-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2g):**



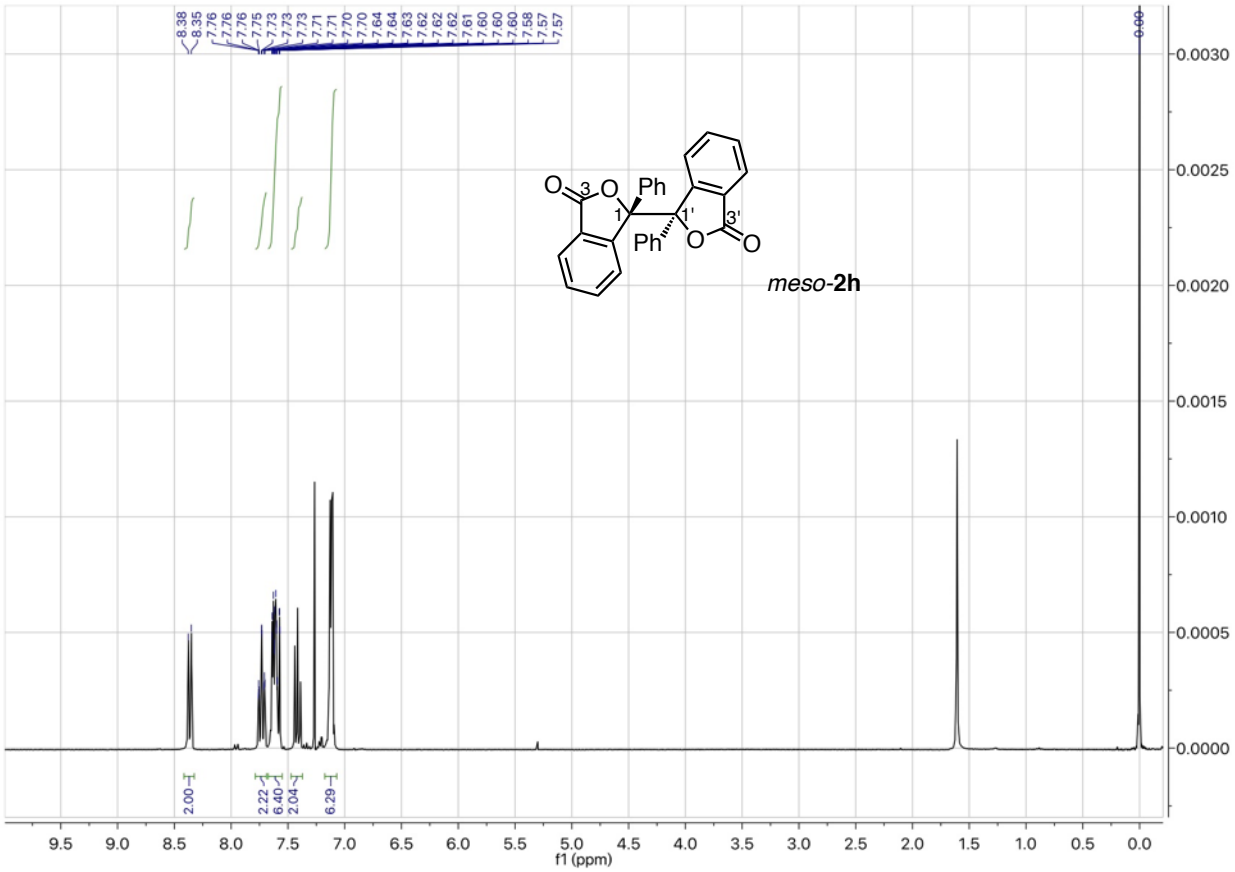


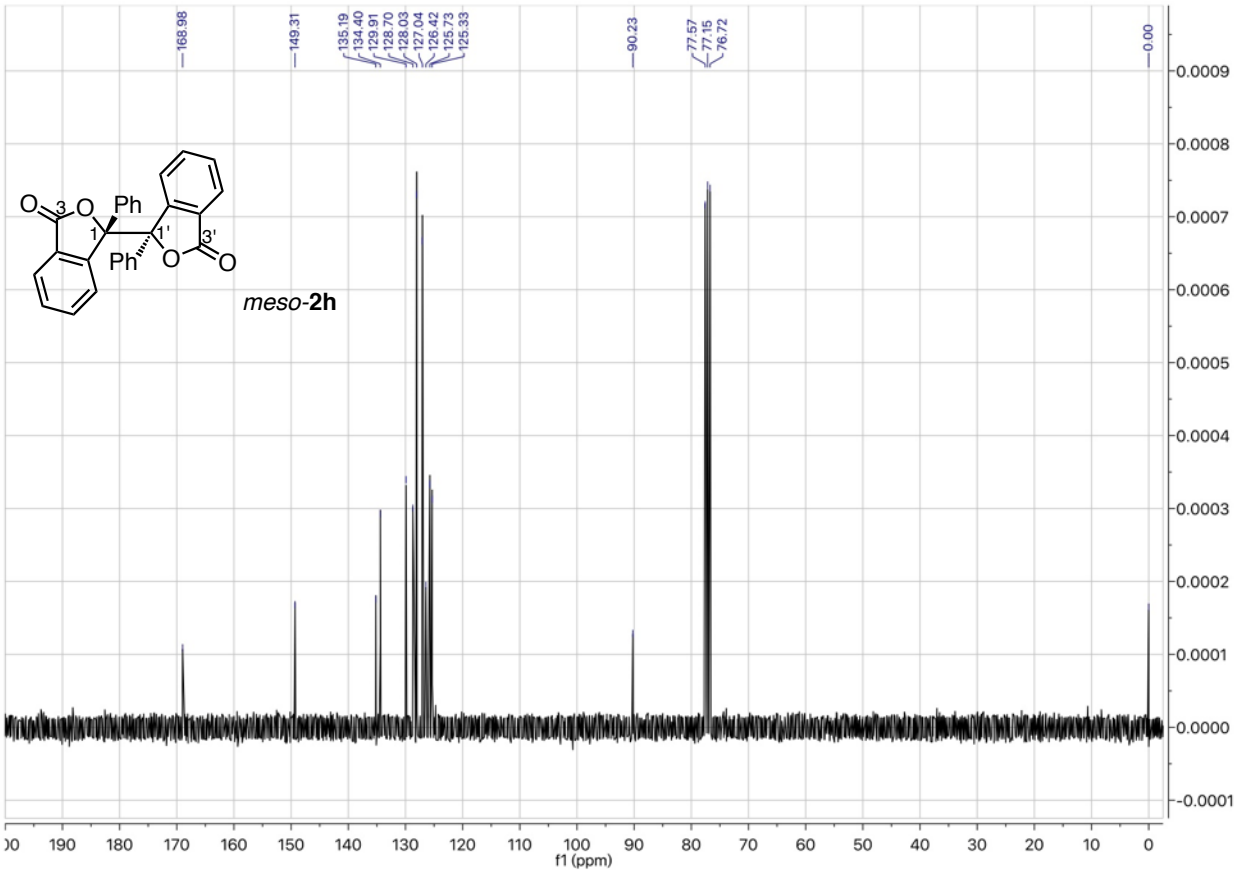
***rac*-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2g):**



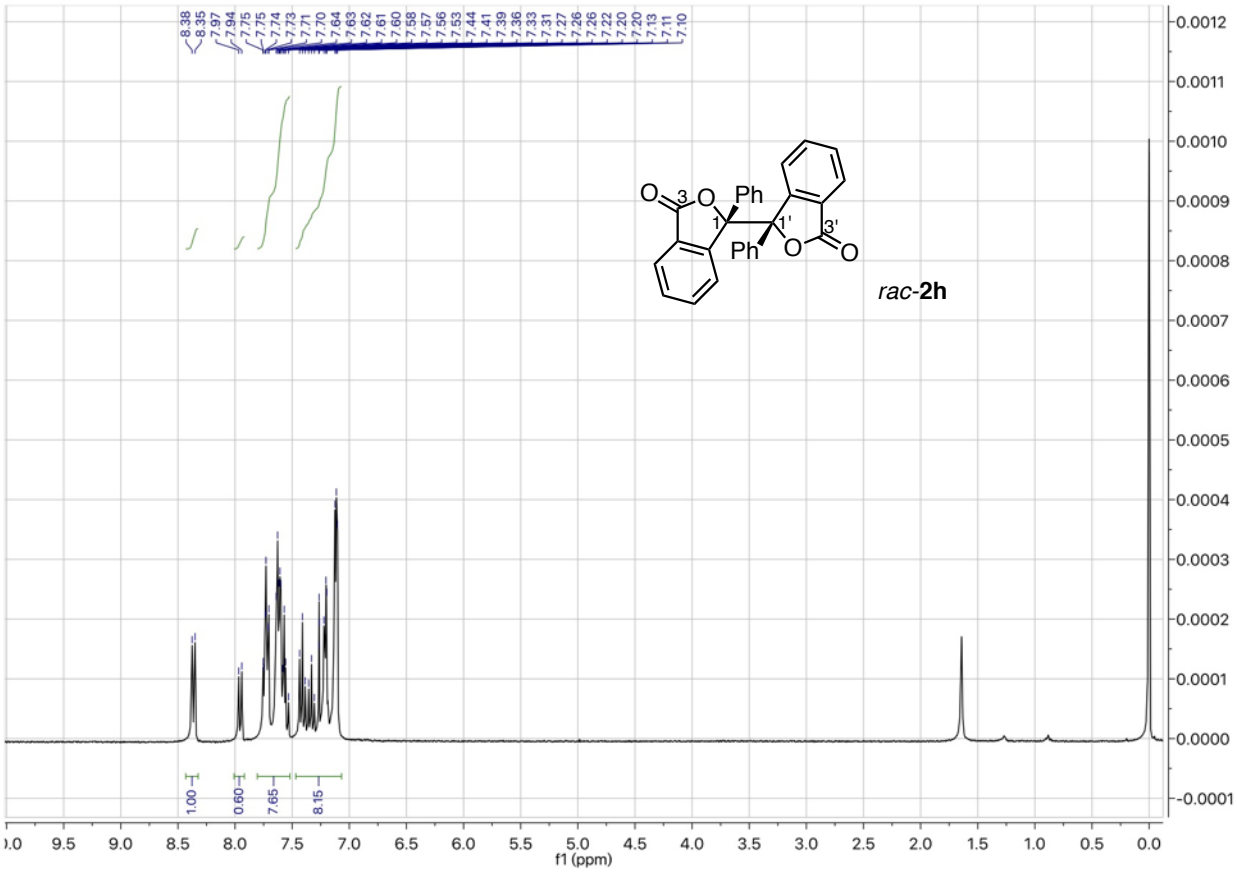


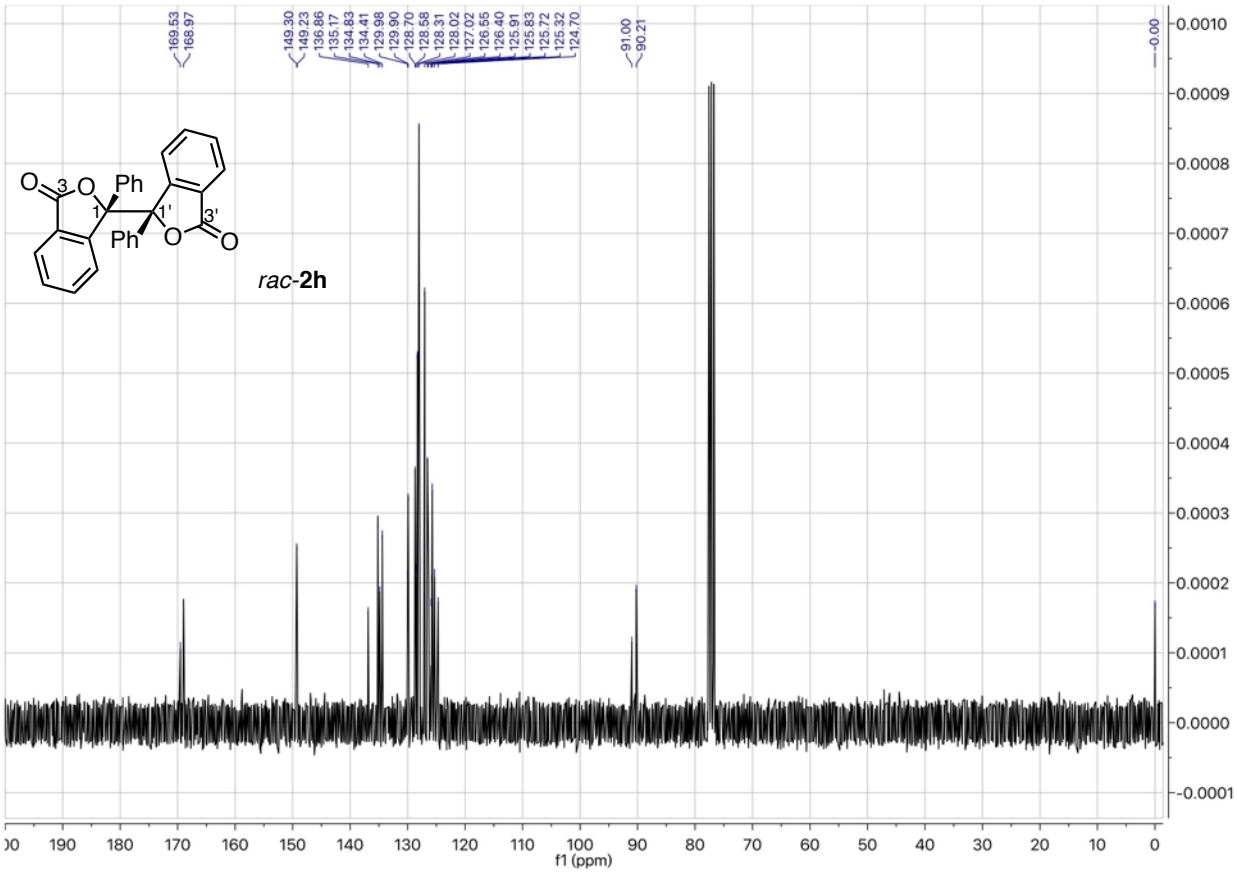
***meso*-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*meso*-2h):**



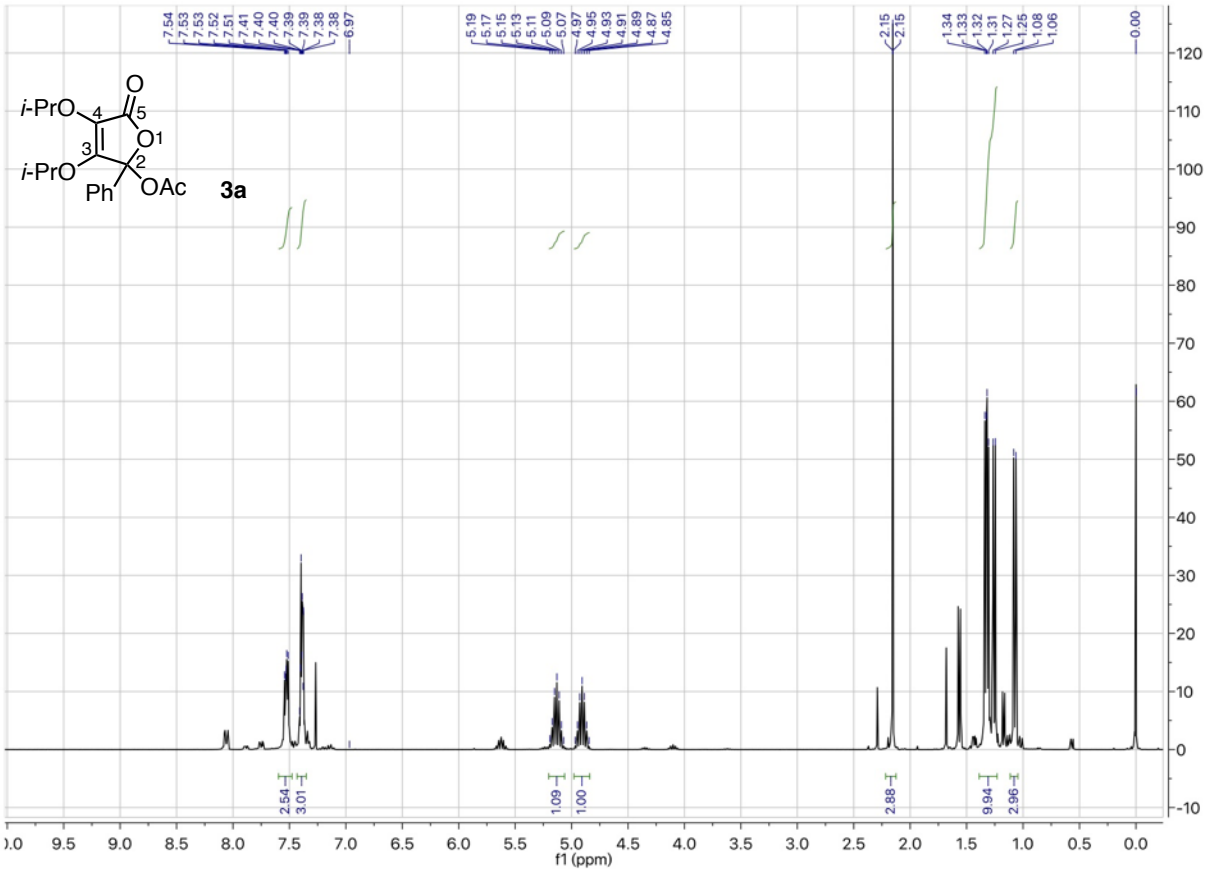


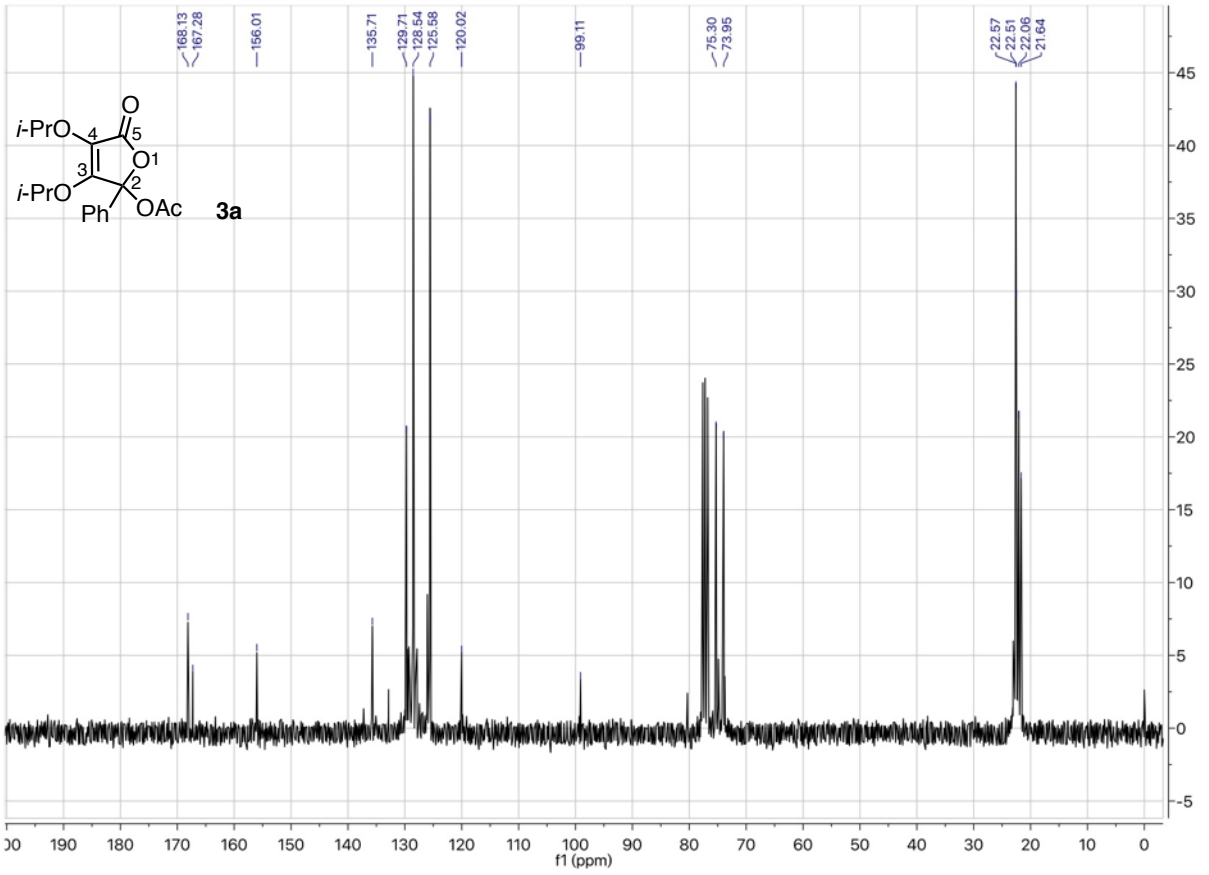
***rac*-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*rac*-2h)[19]:**



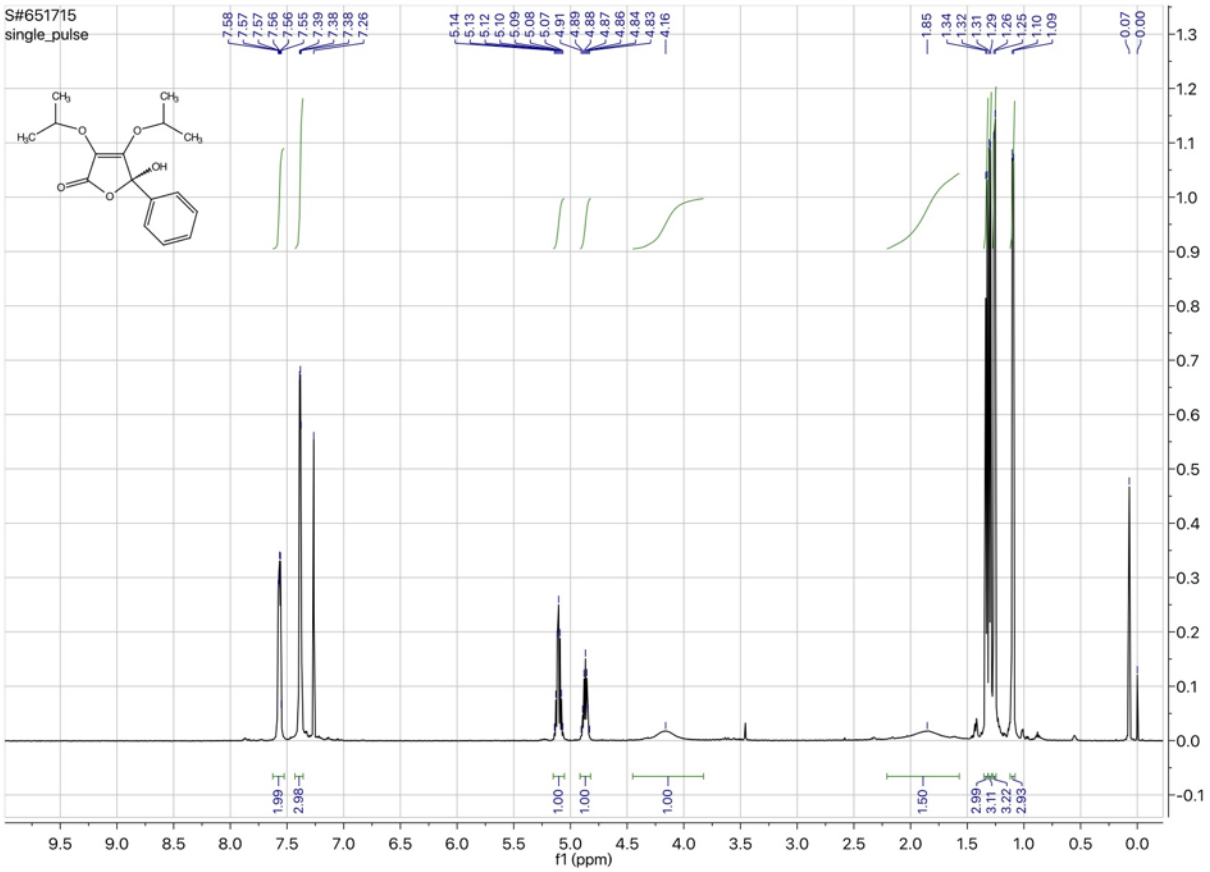


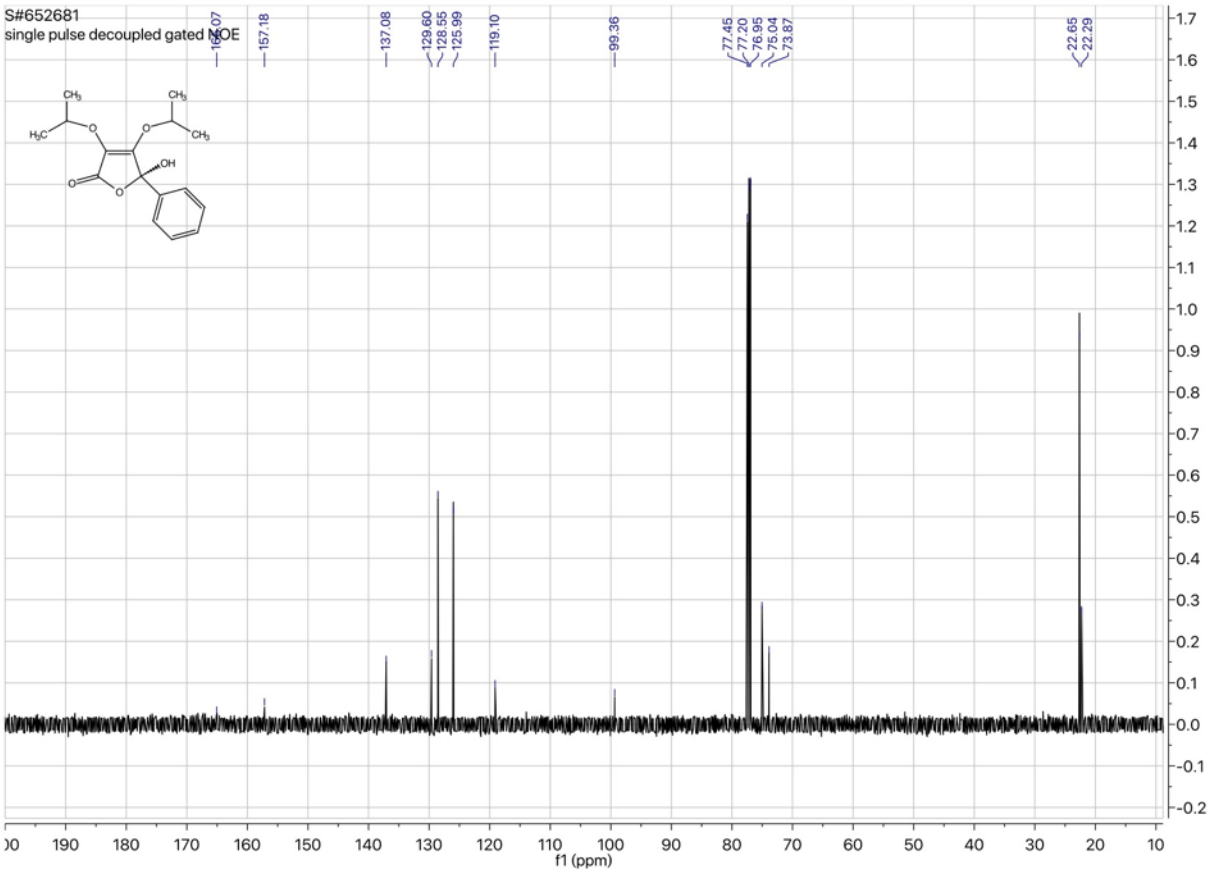
3,4-Diisopropoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3a):



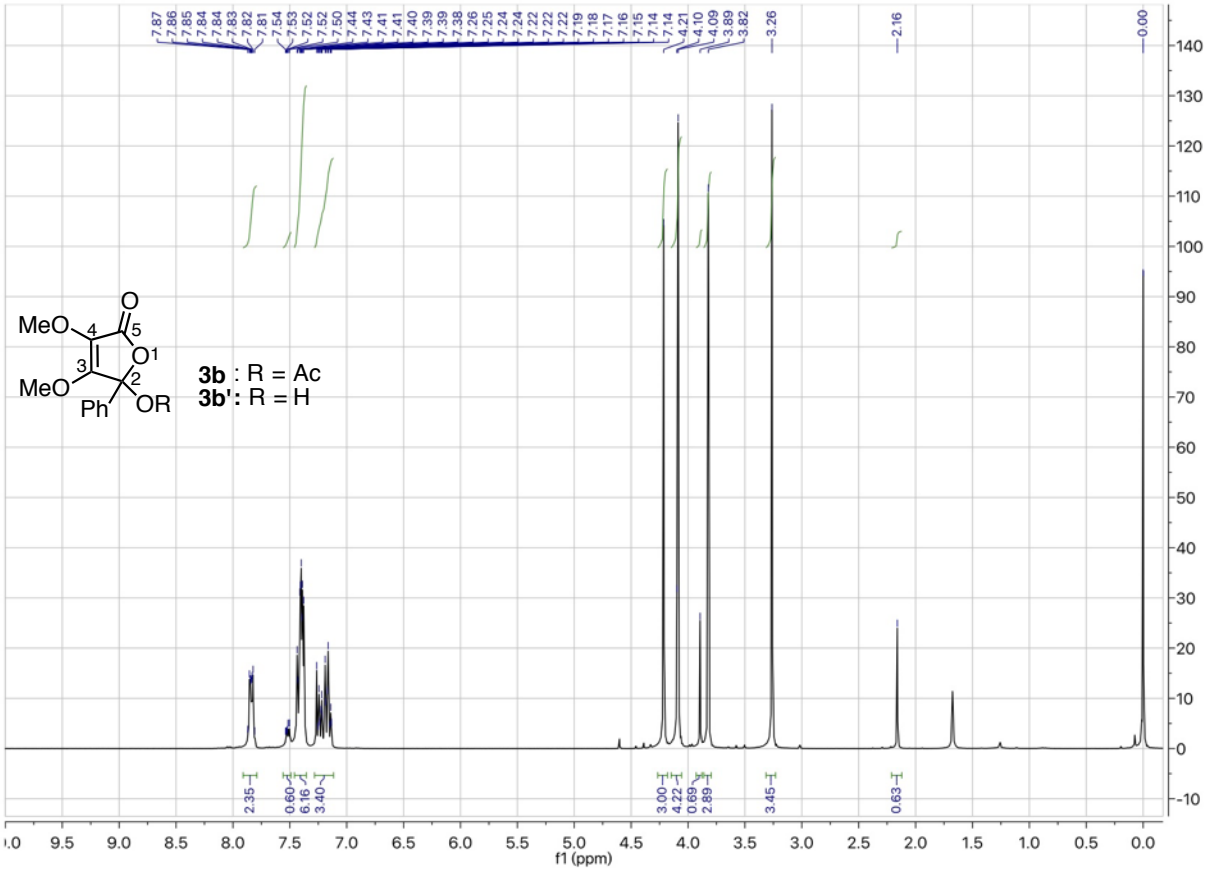


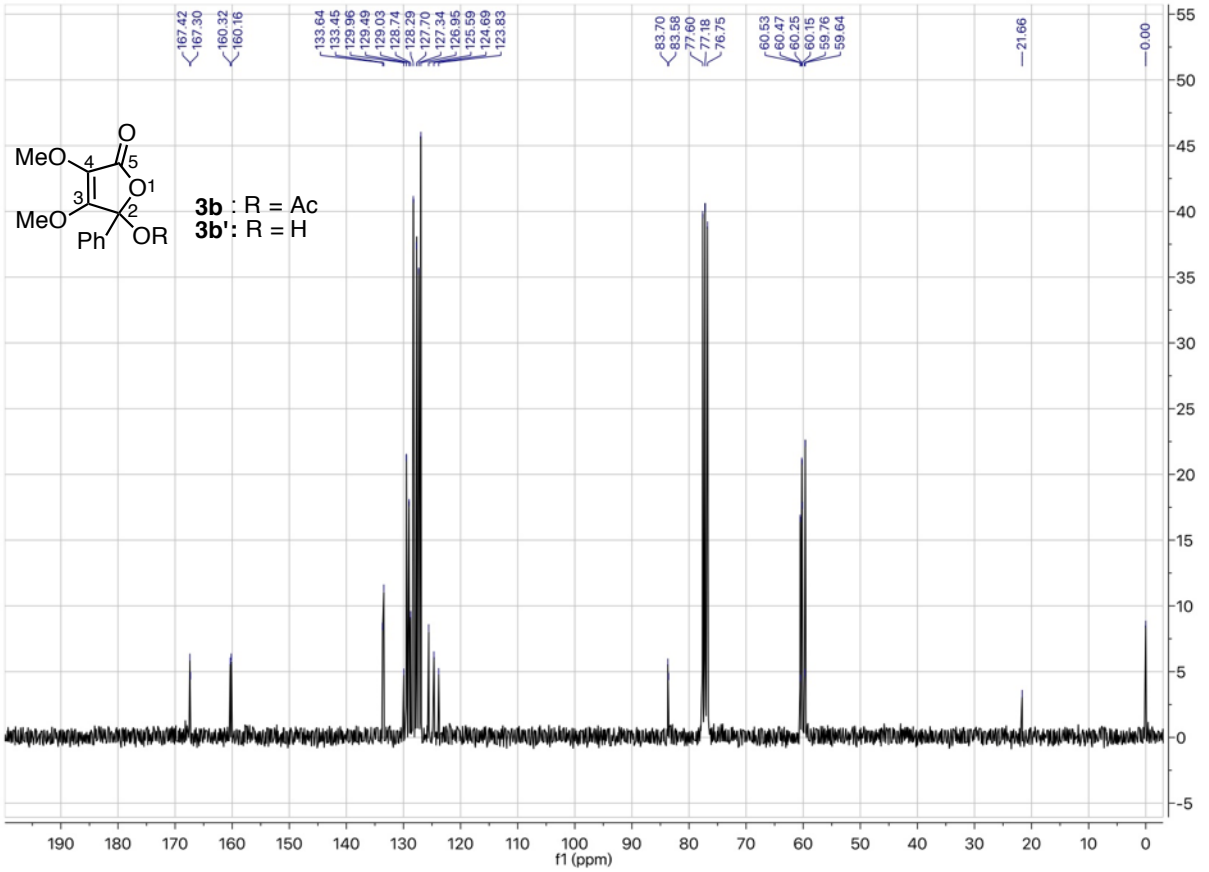
5-Hydroxy-3,4-diisopropoxy-5-phenylfuran-2(5*H*)-one (3a'):



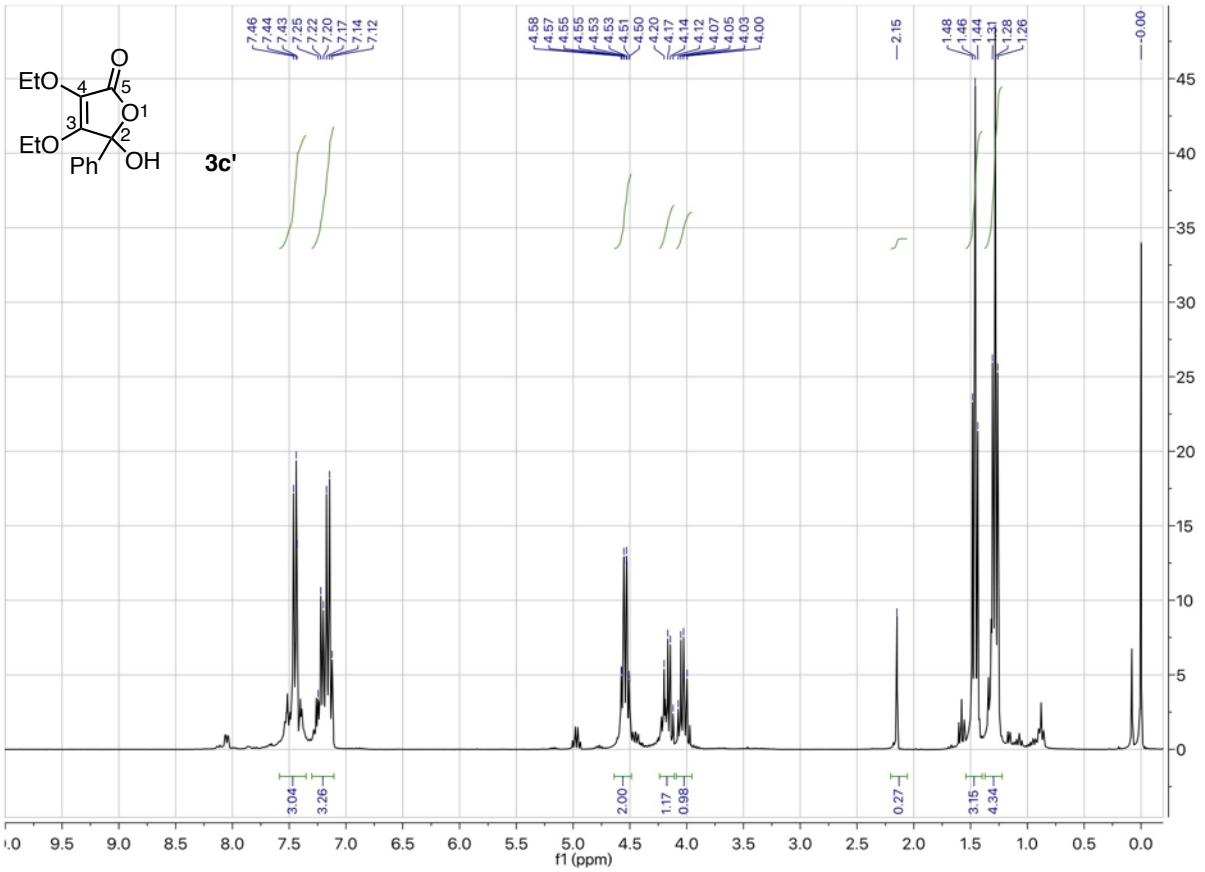


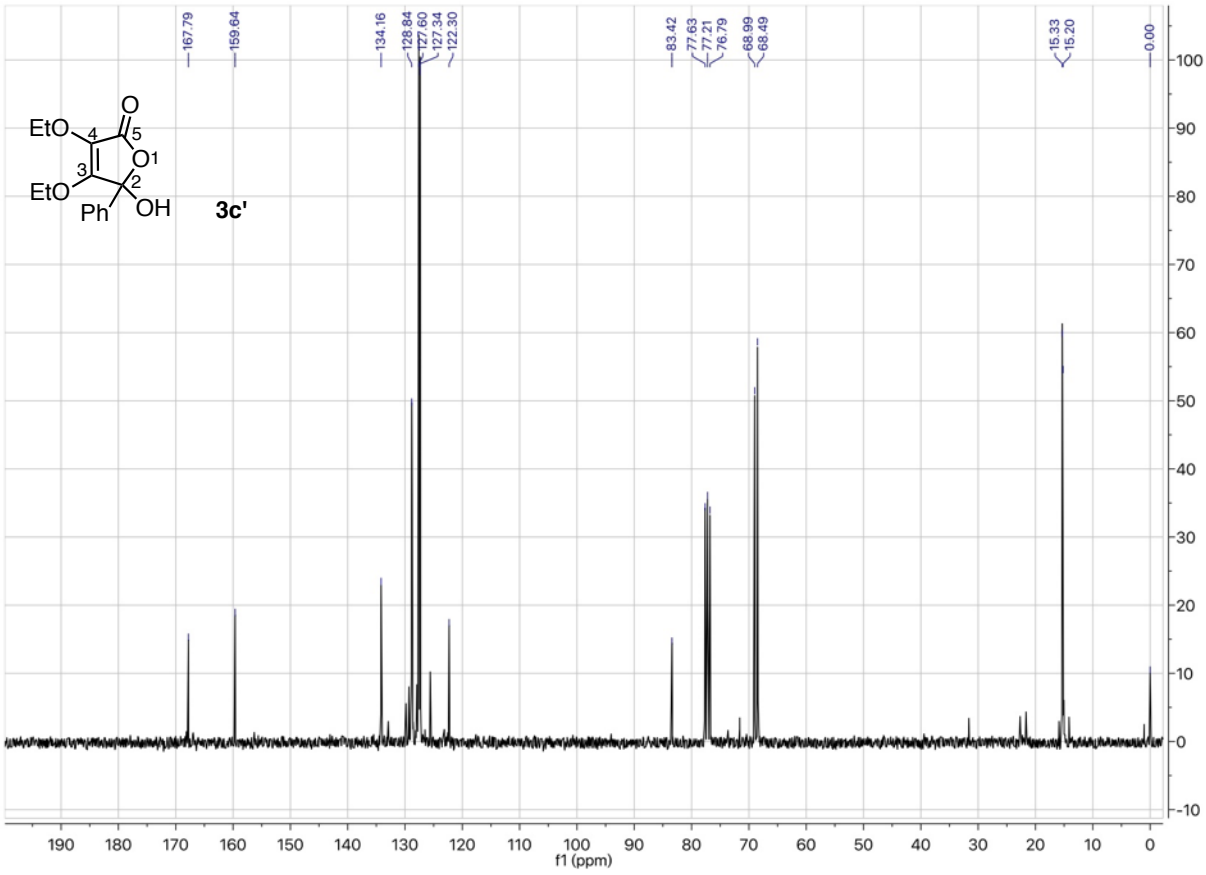
A Mixture of 3,4-Dimethoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3b) and 5-Hydroxy-3,4-dimethoxy-5-phenylfuran-2(5*H*)-one (3b') [11a,11c,22]:



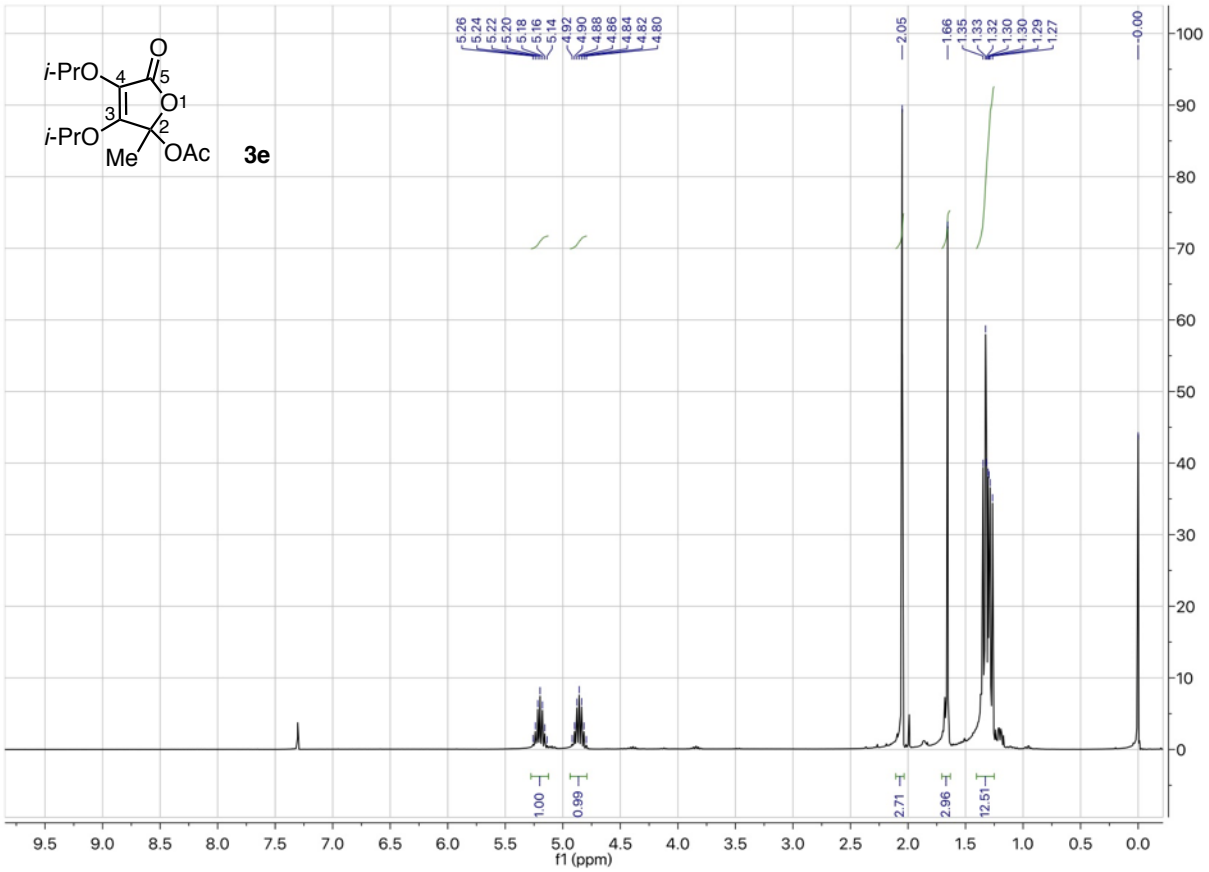


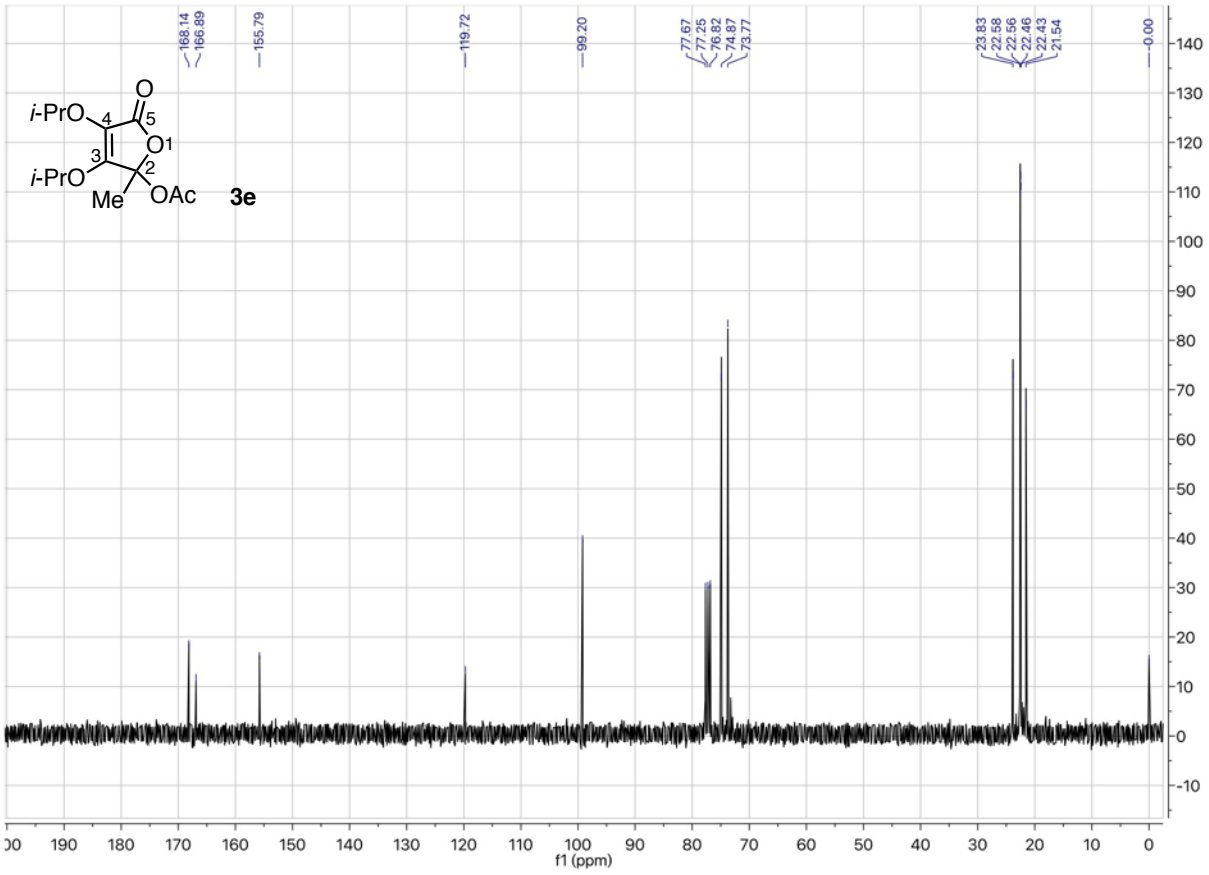
3,4-Diethoxy-5-hydroxy-5-phenylfuran-2(5*H*)-one (3c') [11a,11c]:



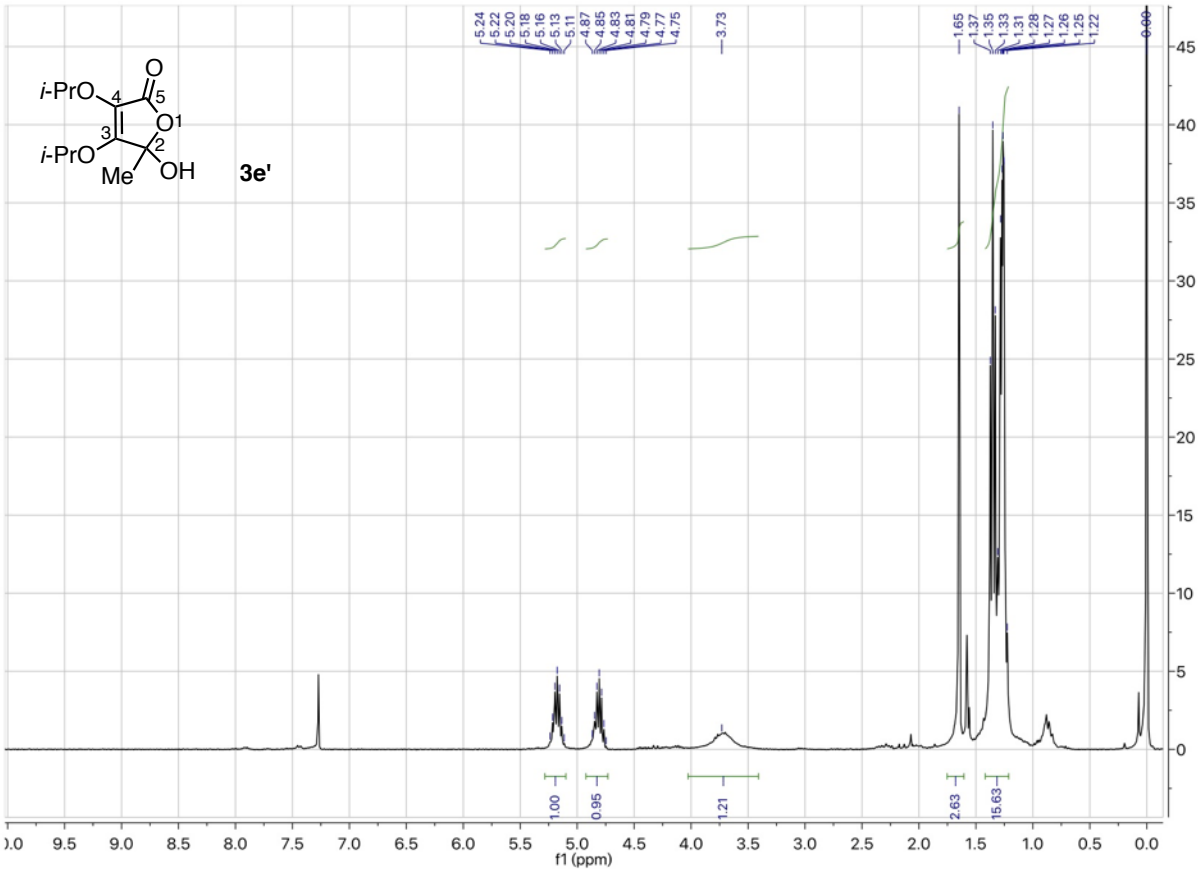


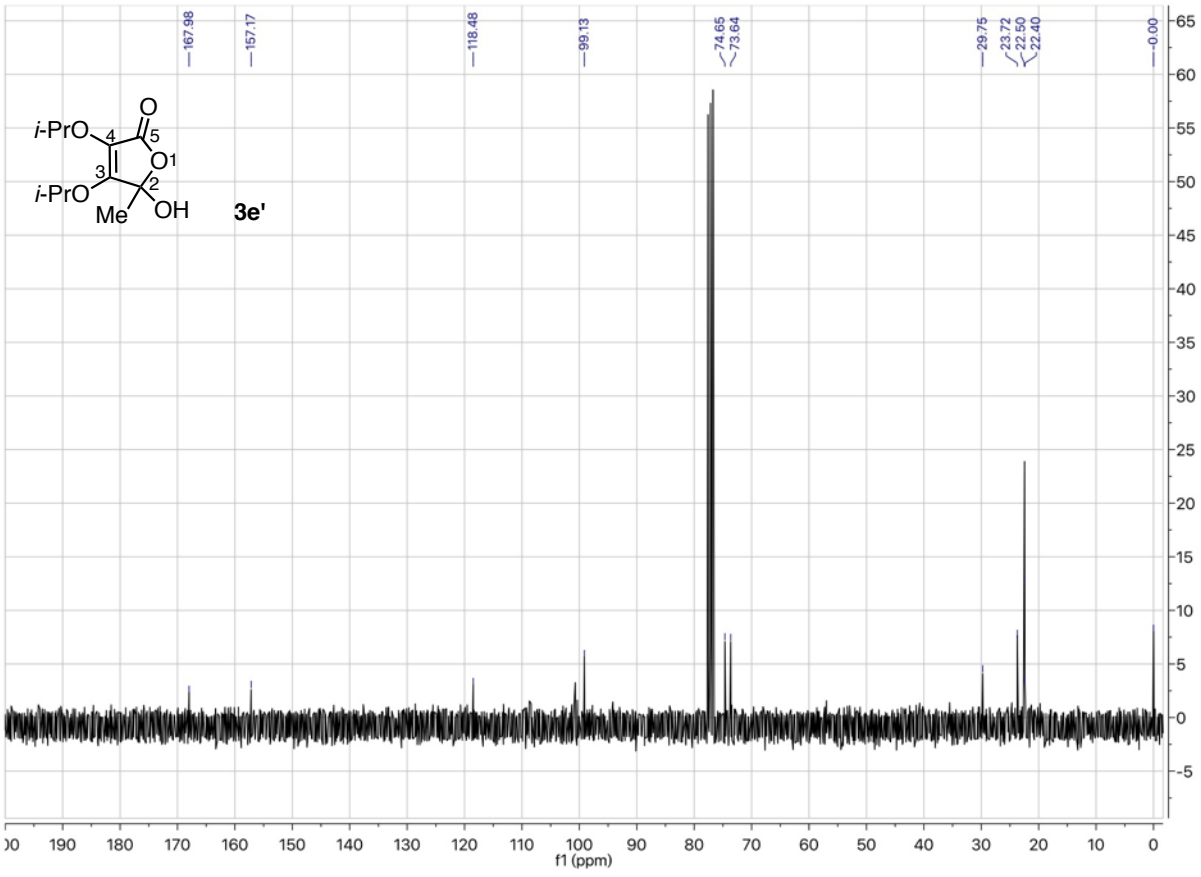
3,4-Diisopropoxy-2-methyl-5-oxo-2,5-dihydrofuran-2-yl acetate (3e):



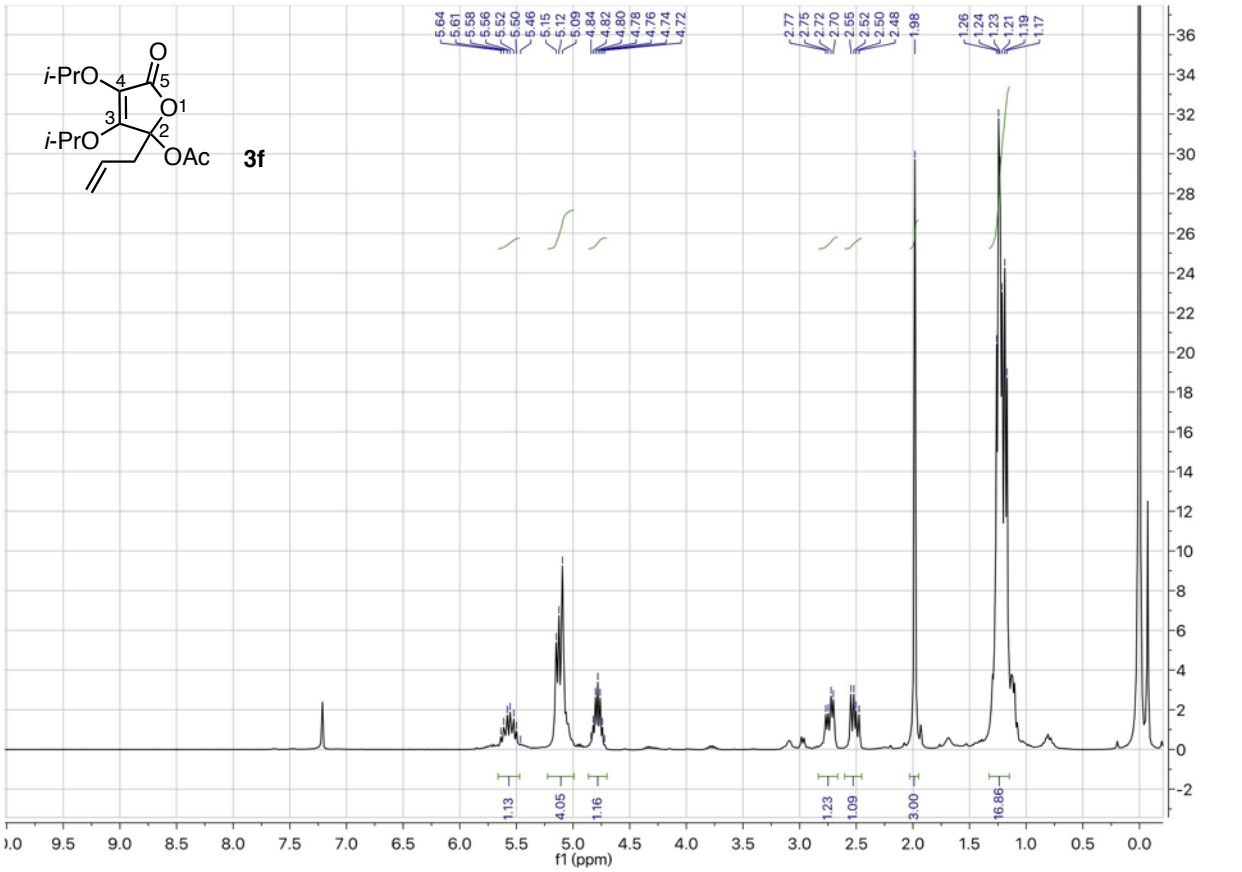


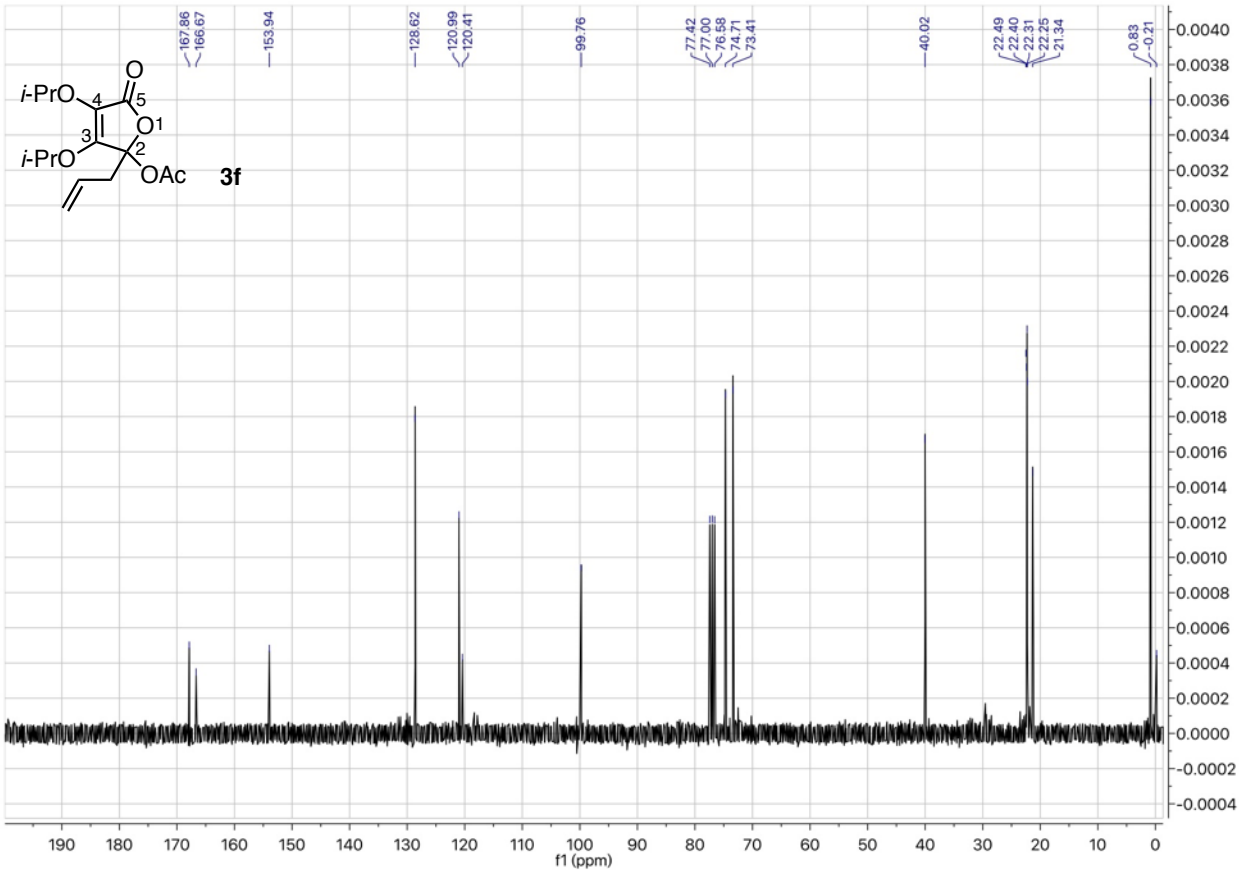
5-Hydroxy-3,4-diisopropoxy-5-methylfuran-2(5H)-one (3e'):



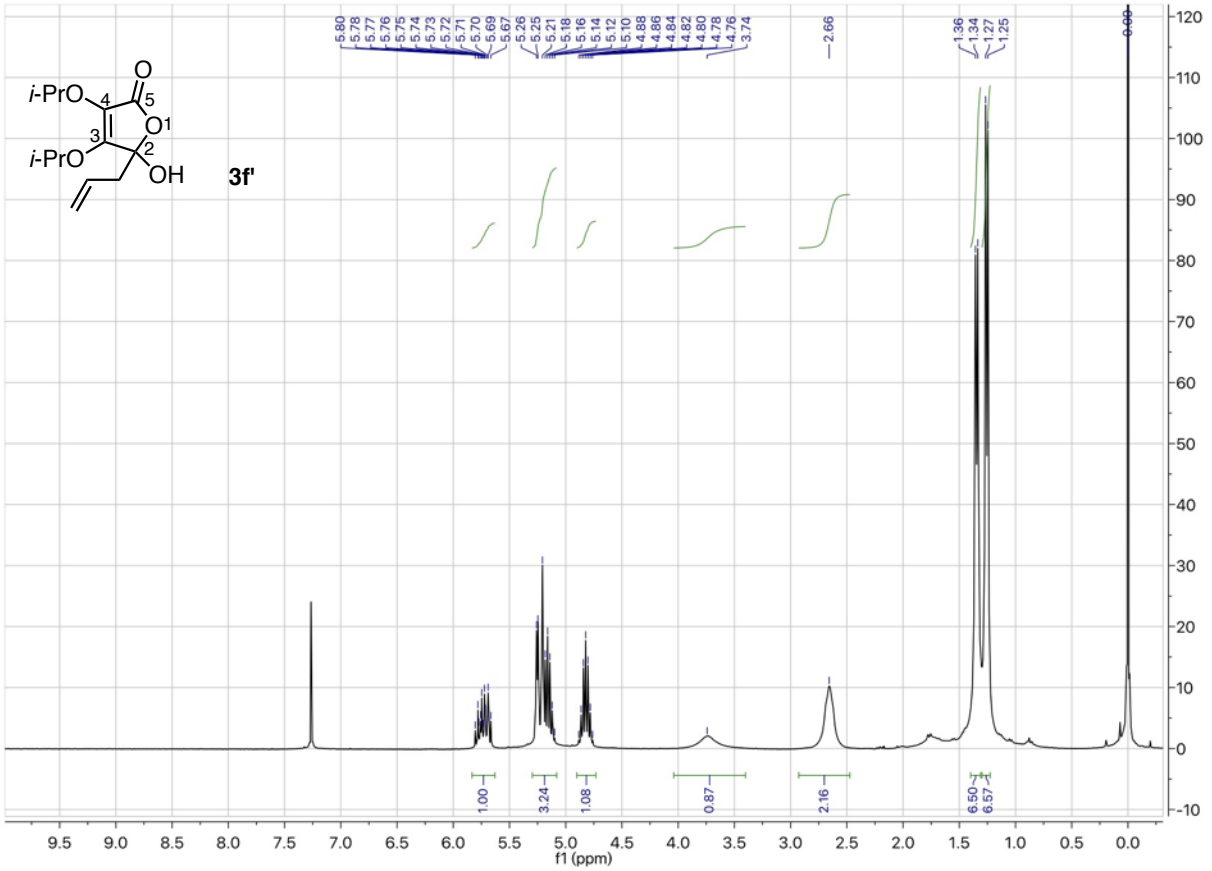


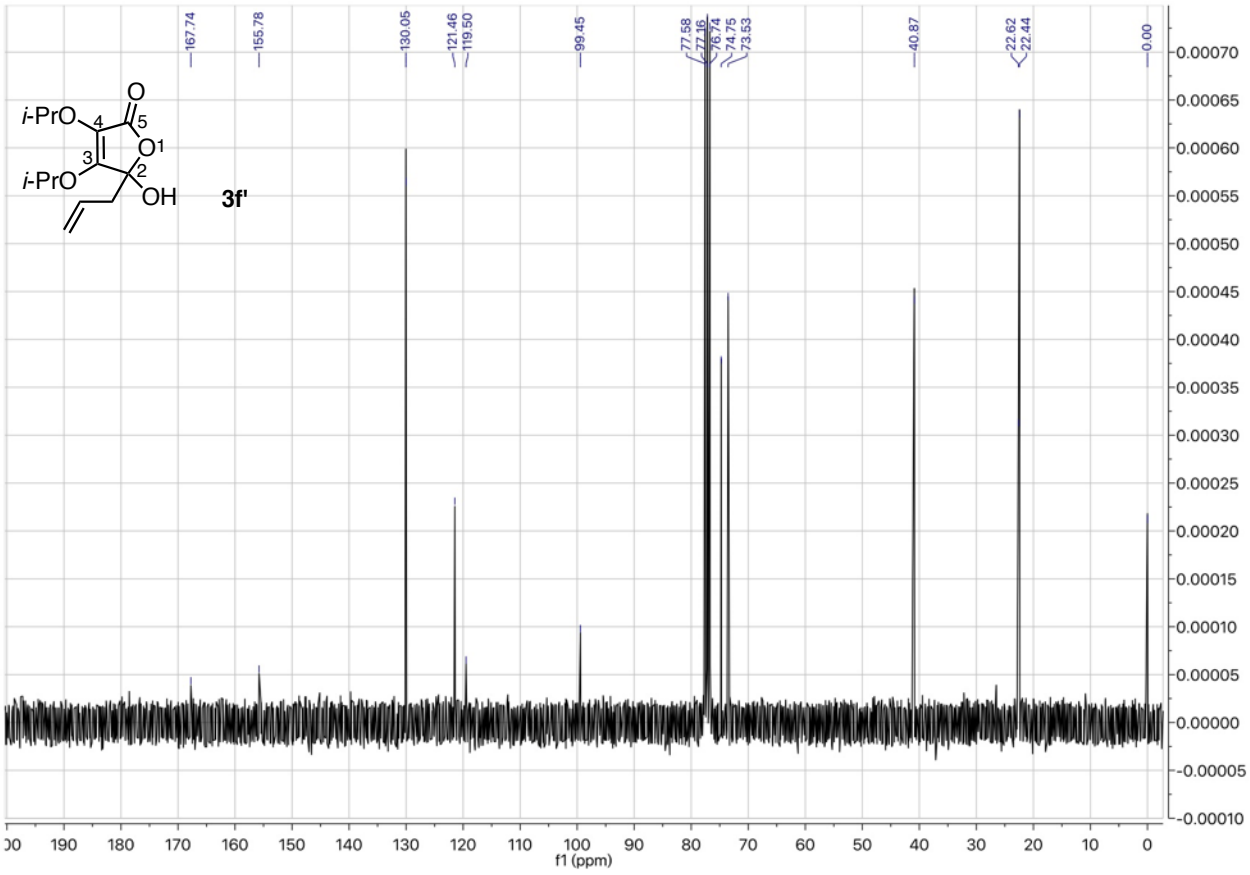
2-Allyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3f):



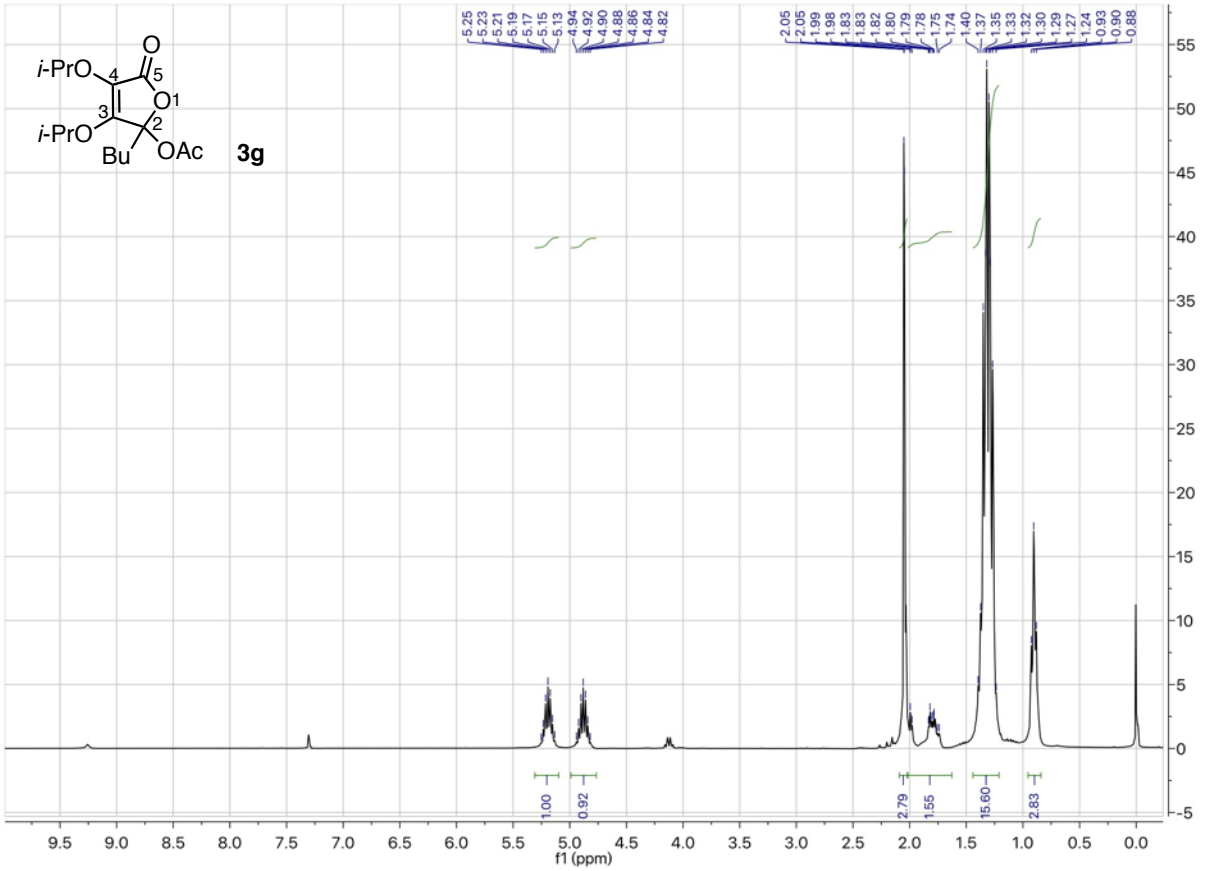


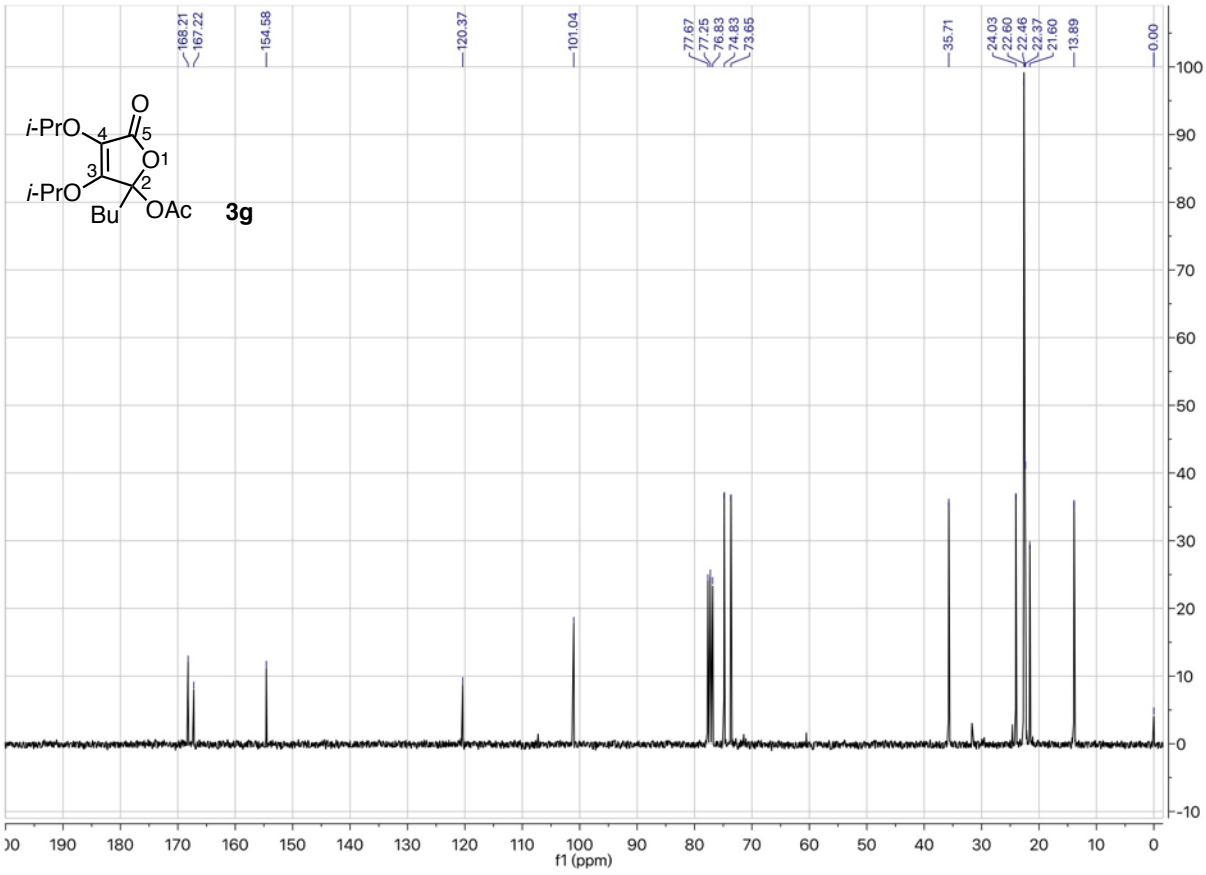
5-Allyl-5-hydroxy-3,4-diisopropoxyfuran-2(5*H*)-one (3f'):



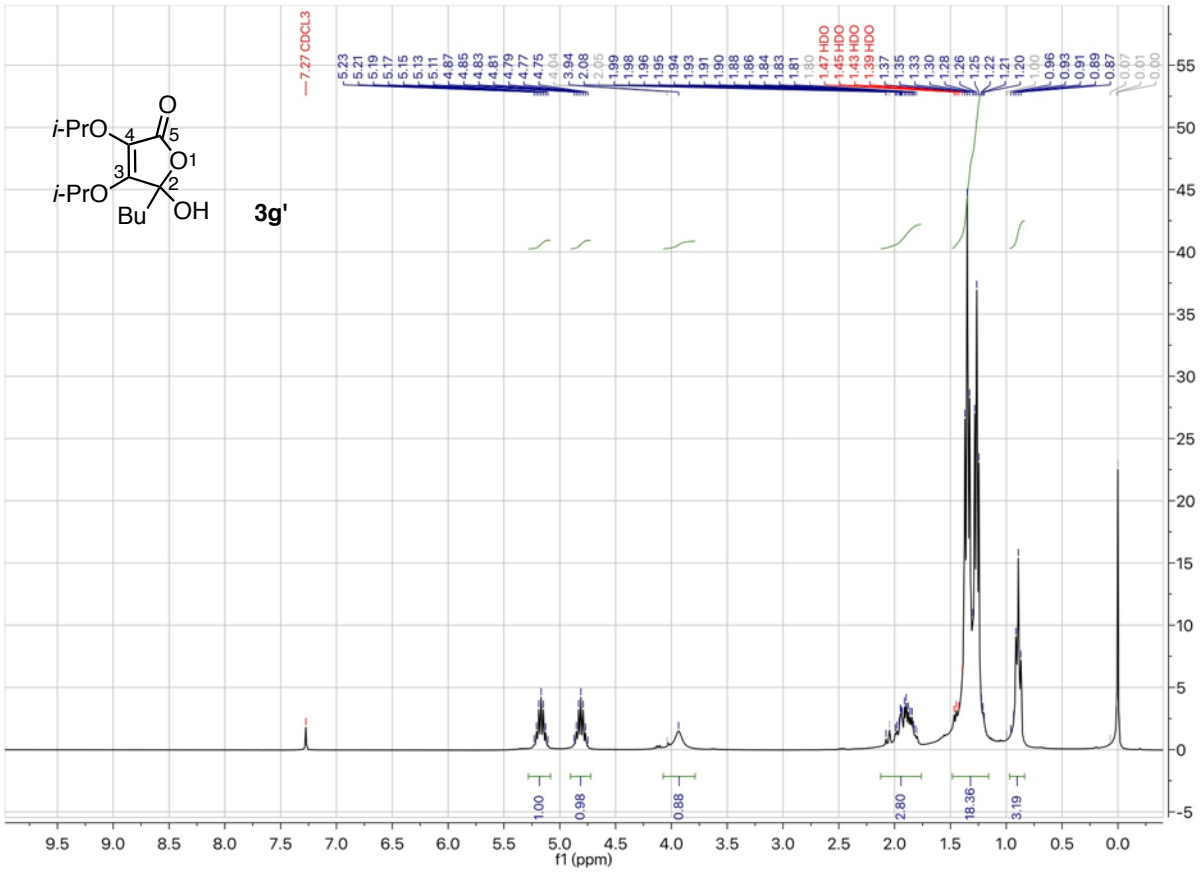


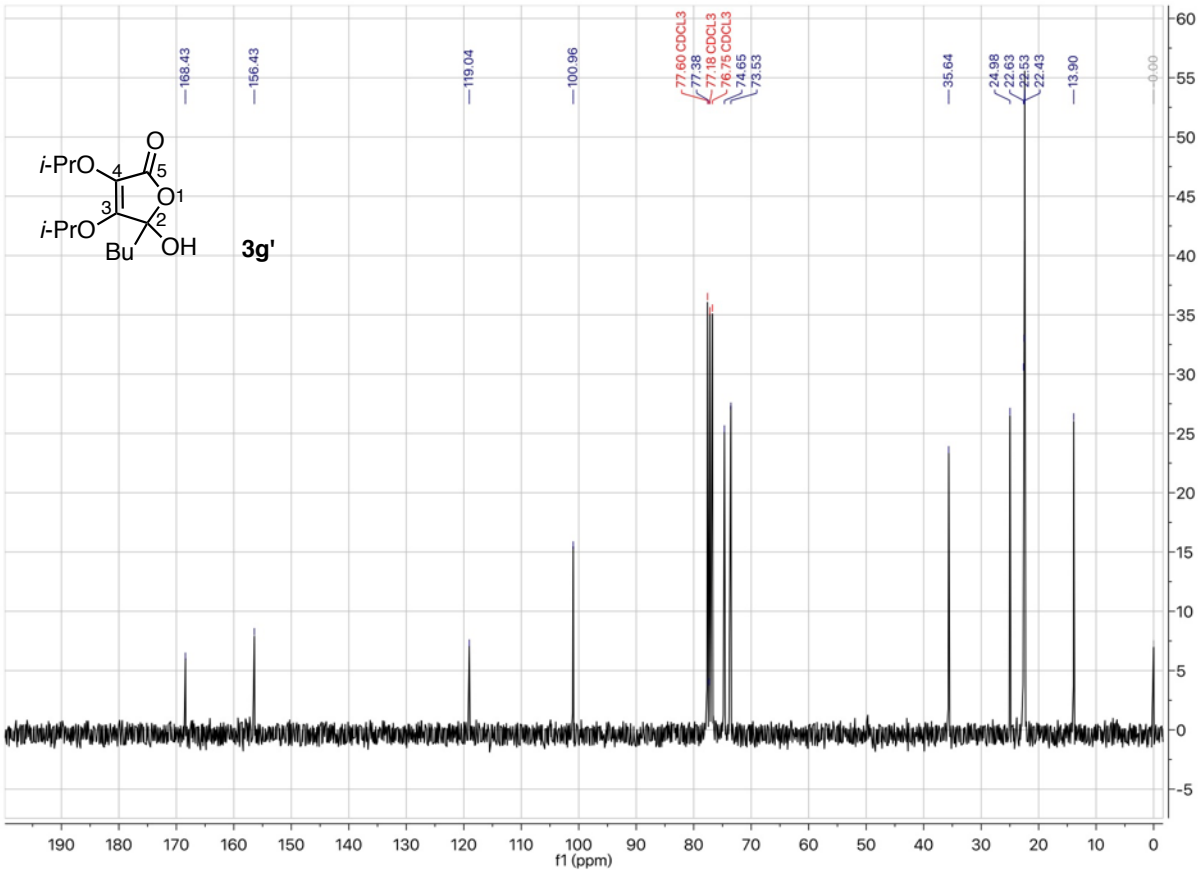
2-Butyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3g):



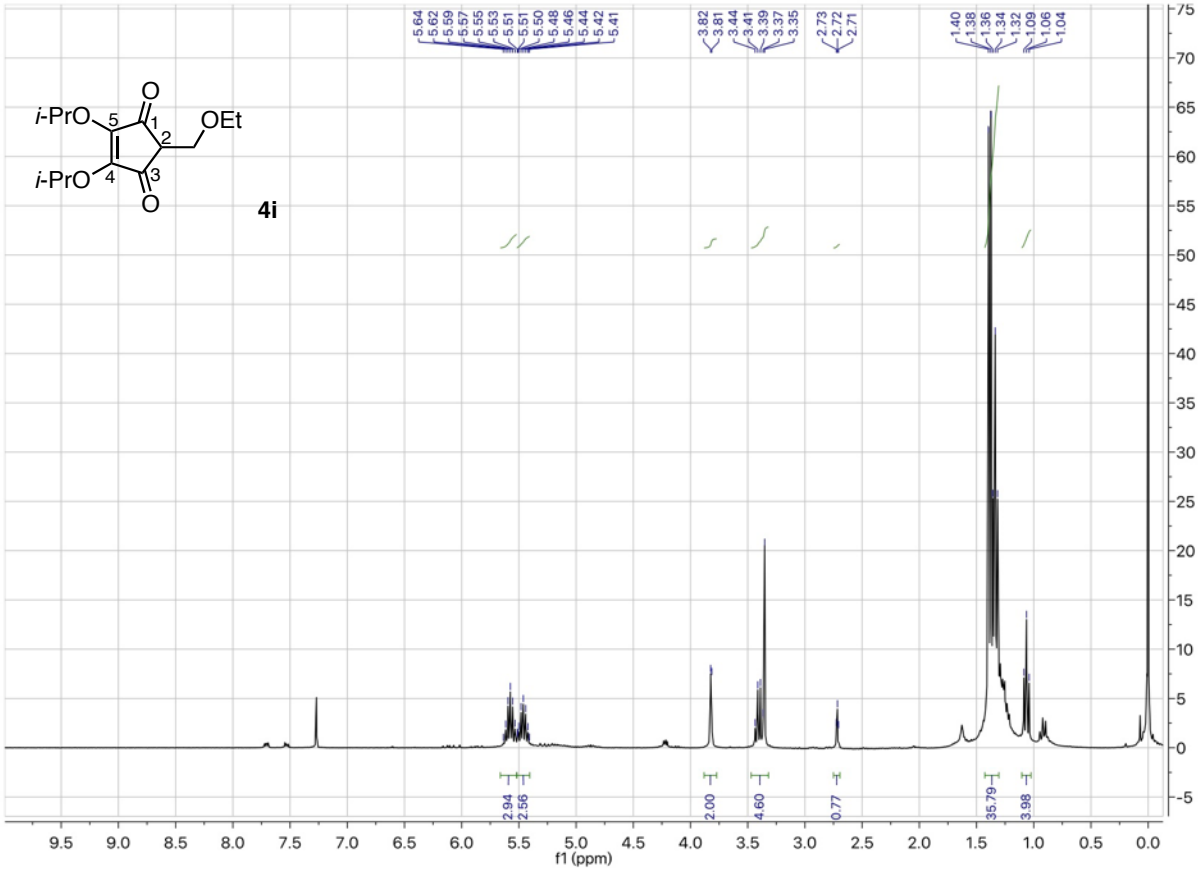


5-Butyl-5-hydroxy-3,4-diisopropoxyfuran-2(5*H*)-one (3g'):

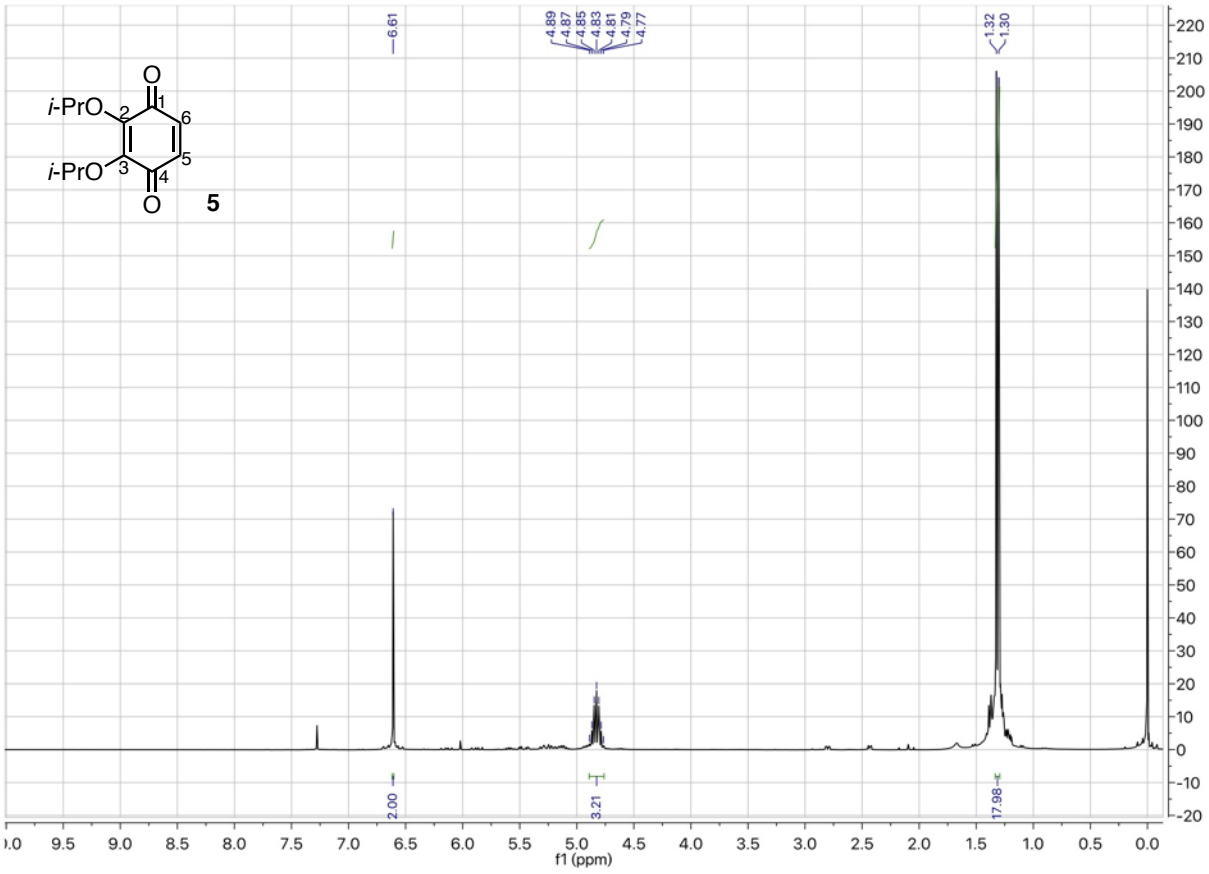


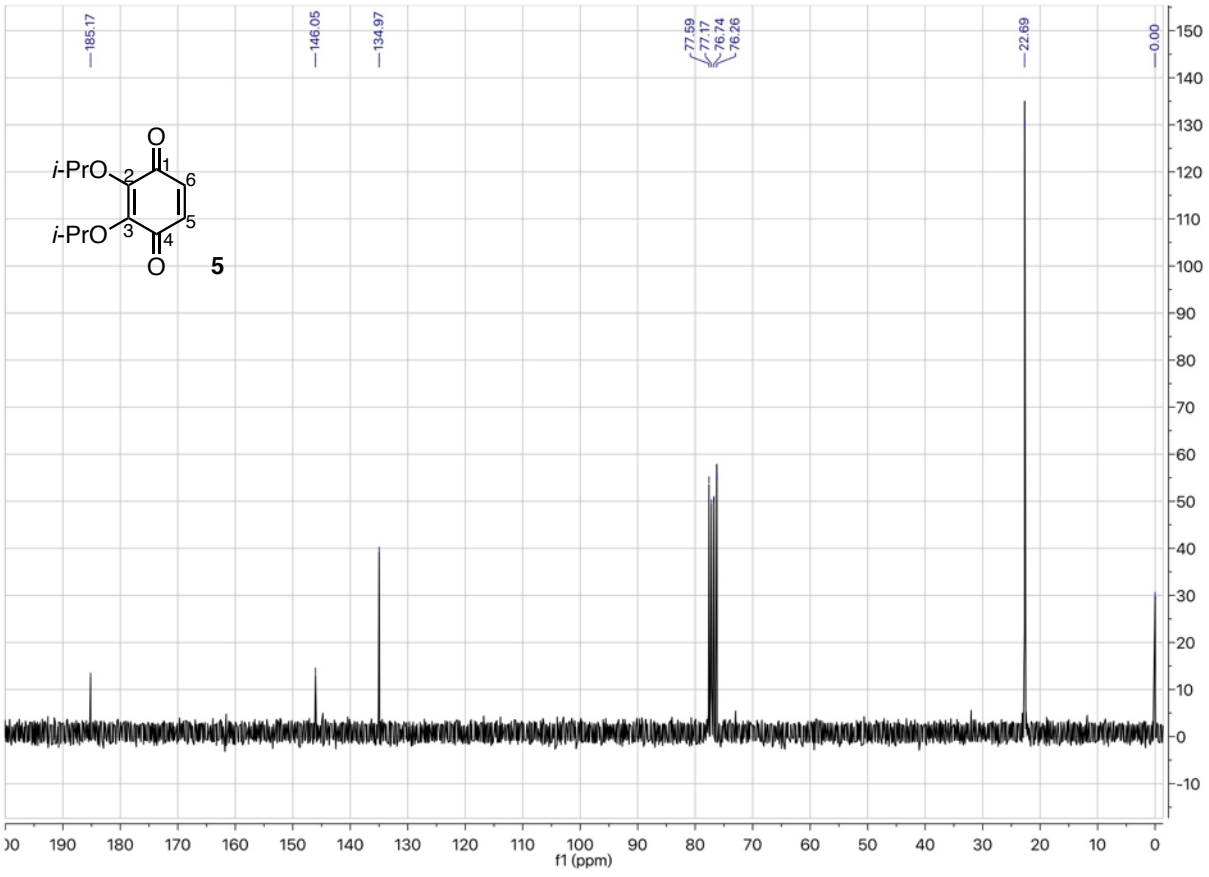


2-(Ethoxymethyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4i):

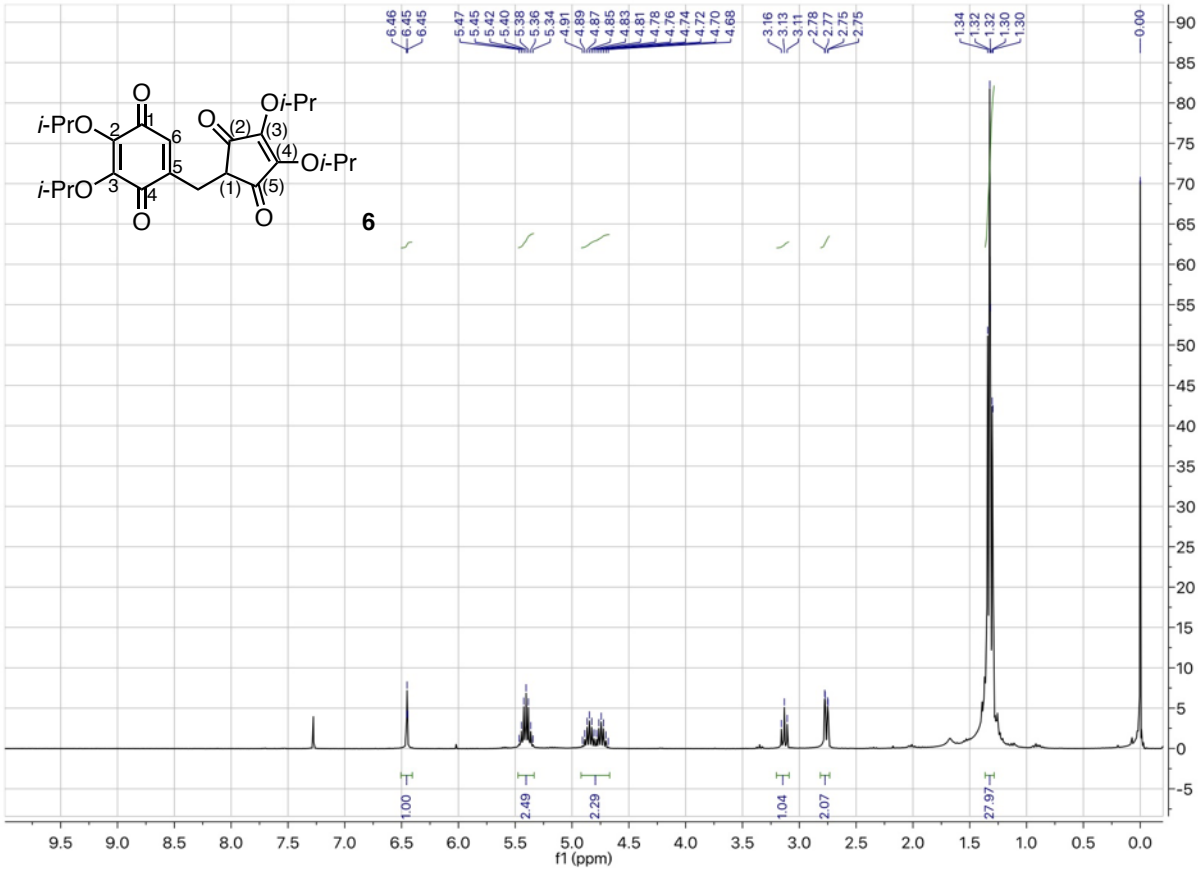


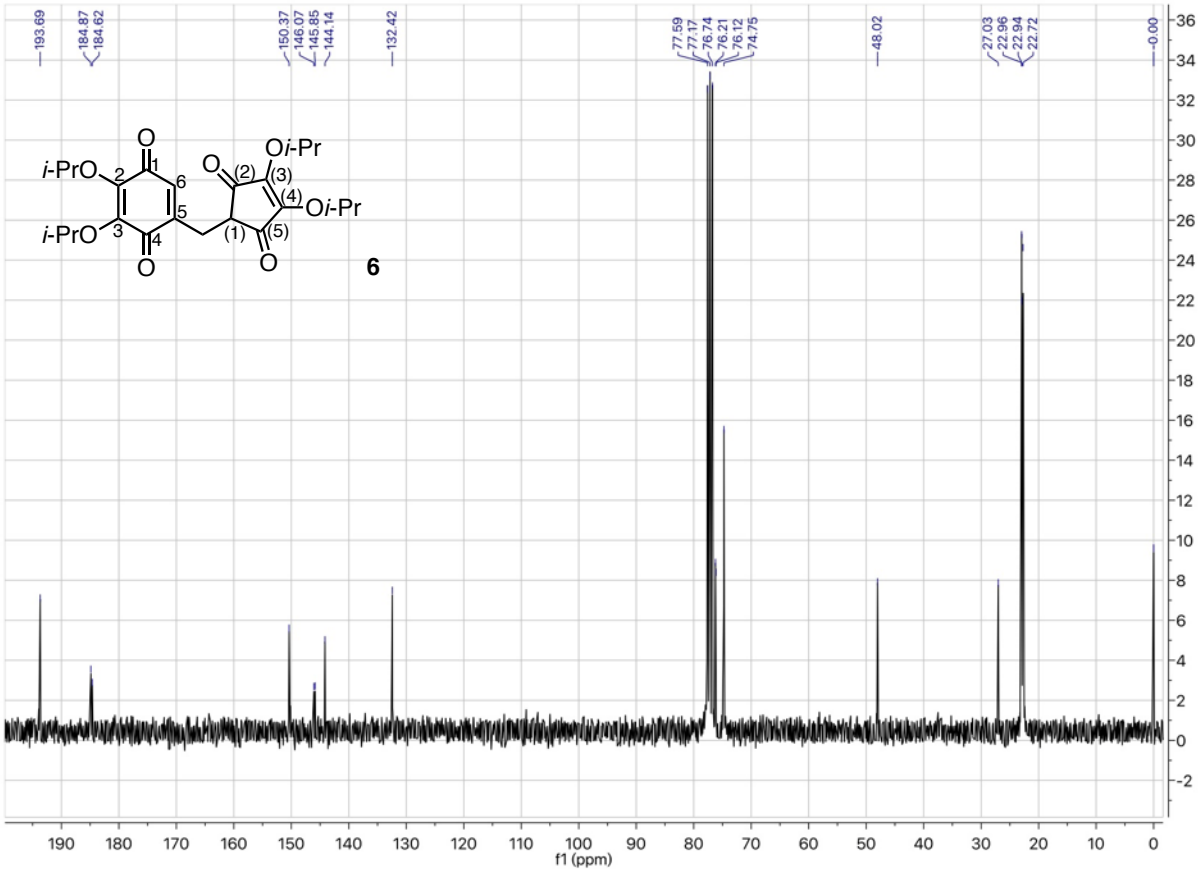
2,3-Diisopropoxycyclohexa-2,5-diene-1,4-dione (5)[30]:



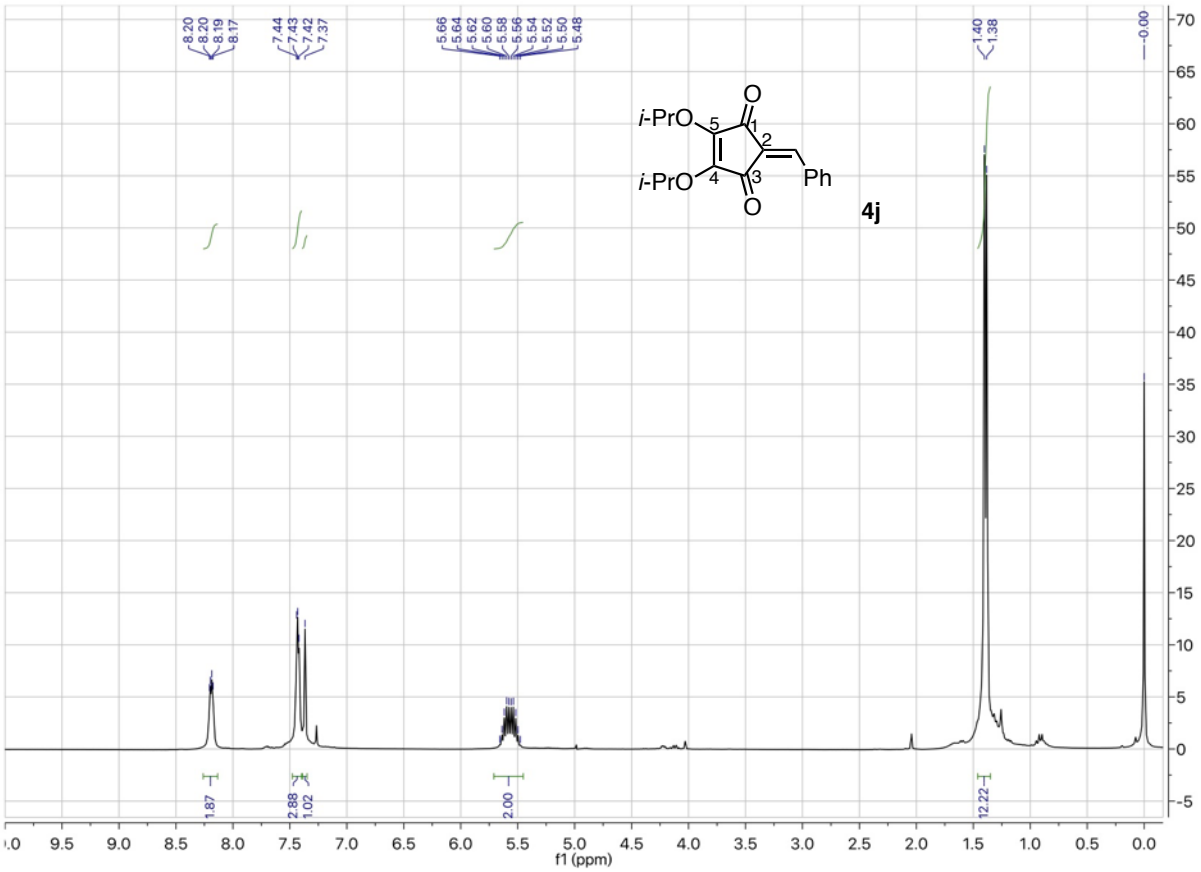


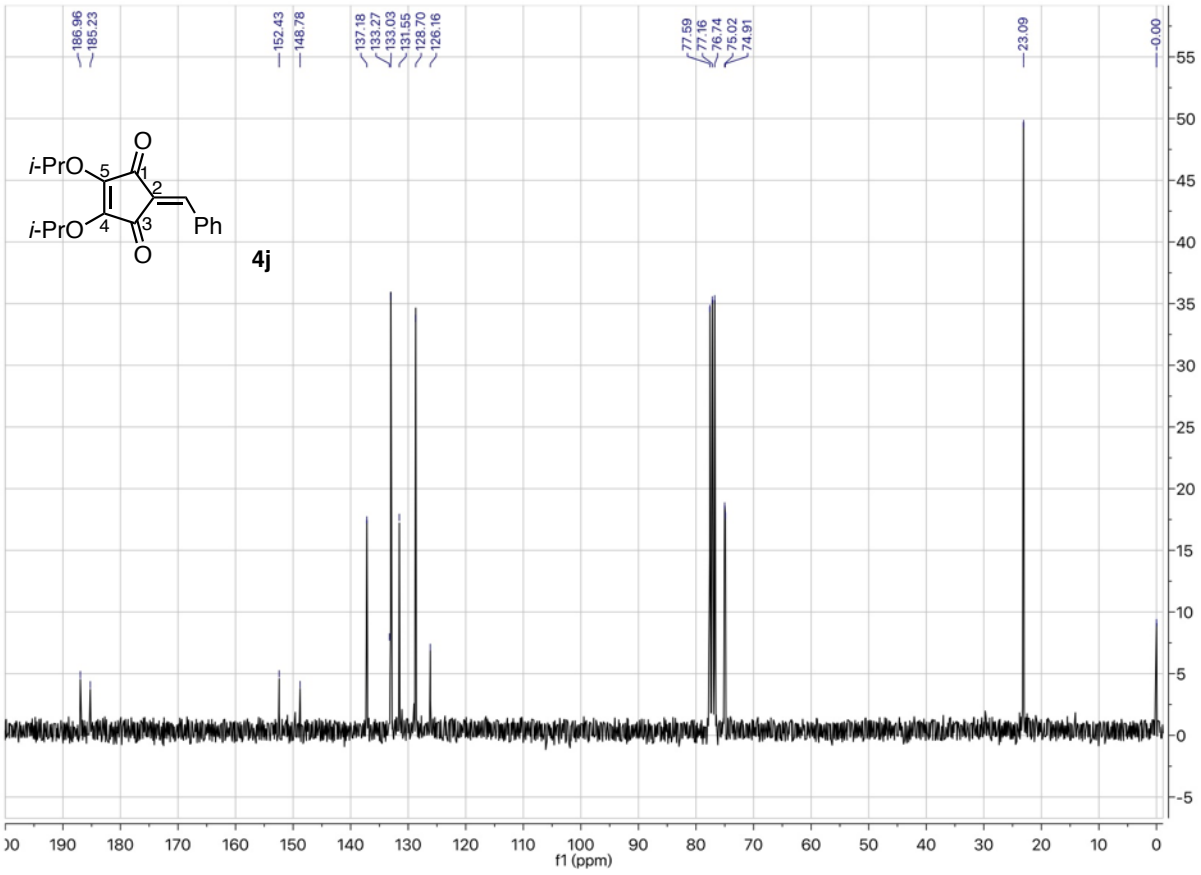
5-((3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-yl)methyl)-2,3-diisopropoxycyclohexa-2,5-diene-1,4-dione (6):

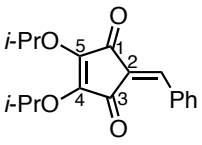




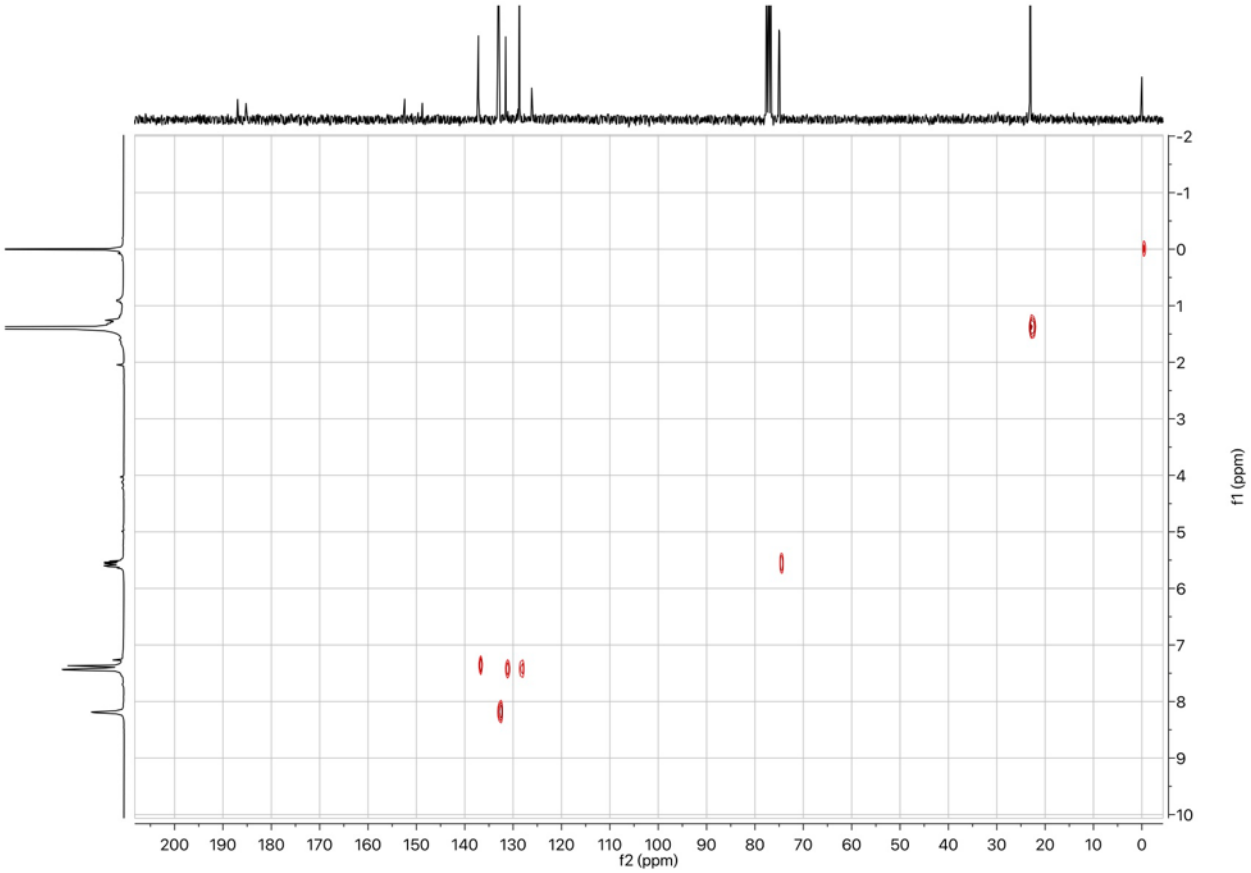
2-Benzylidene-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4j):



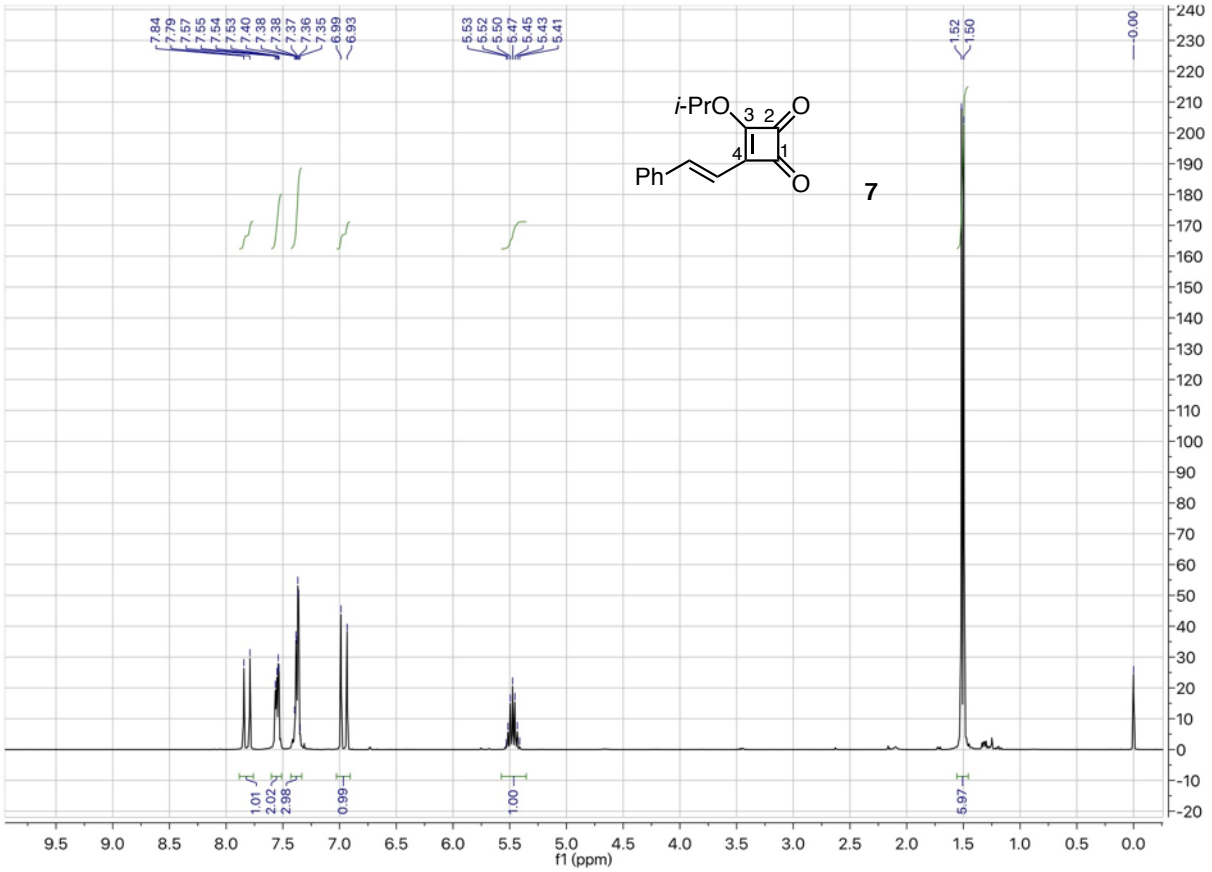


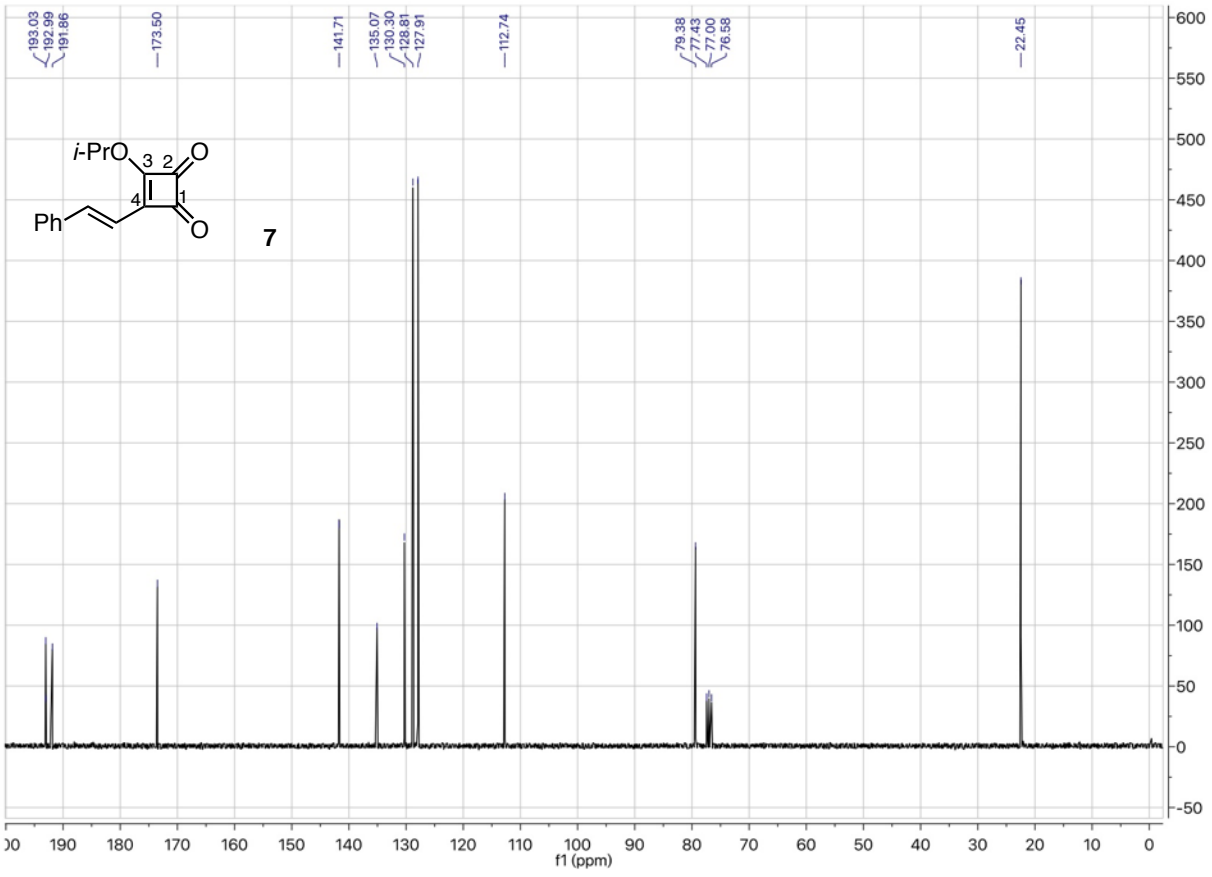


4j

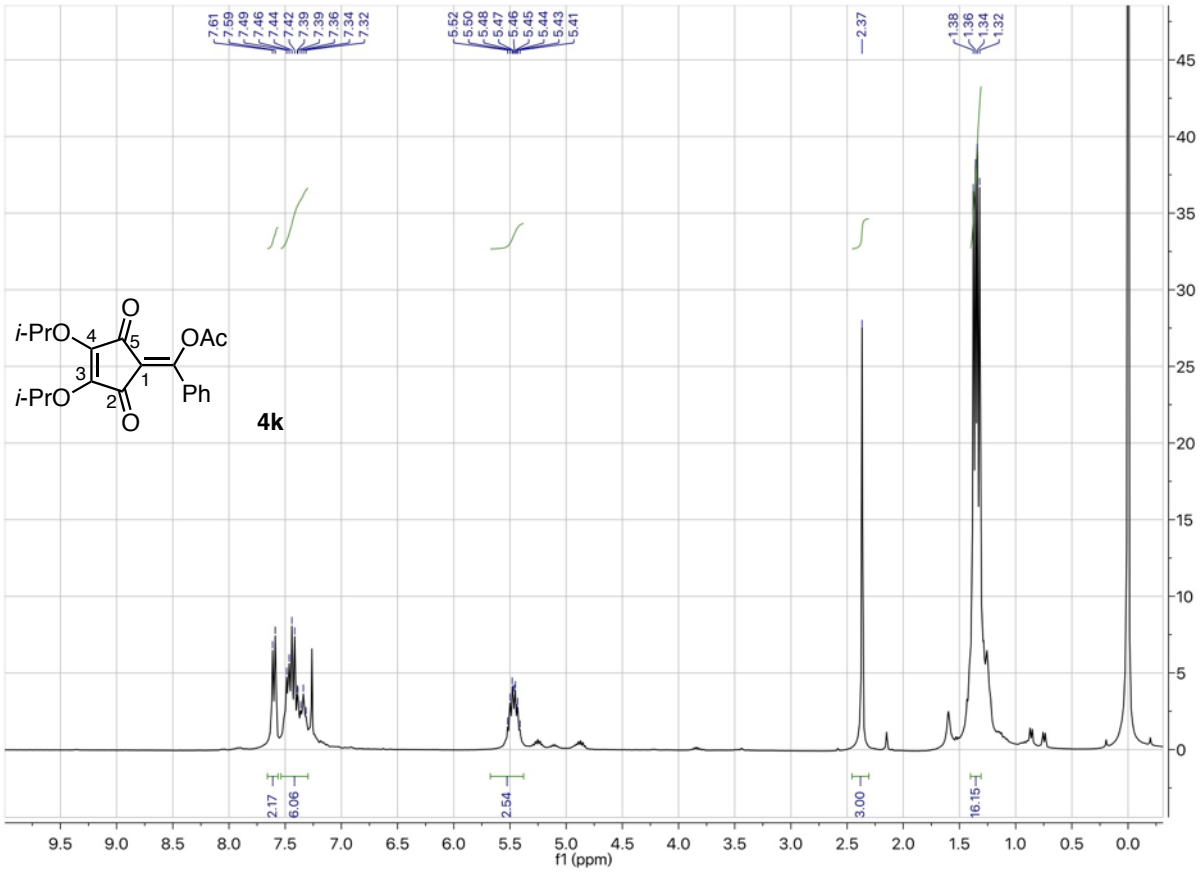


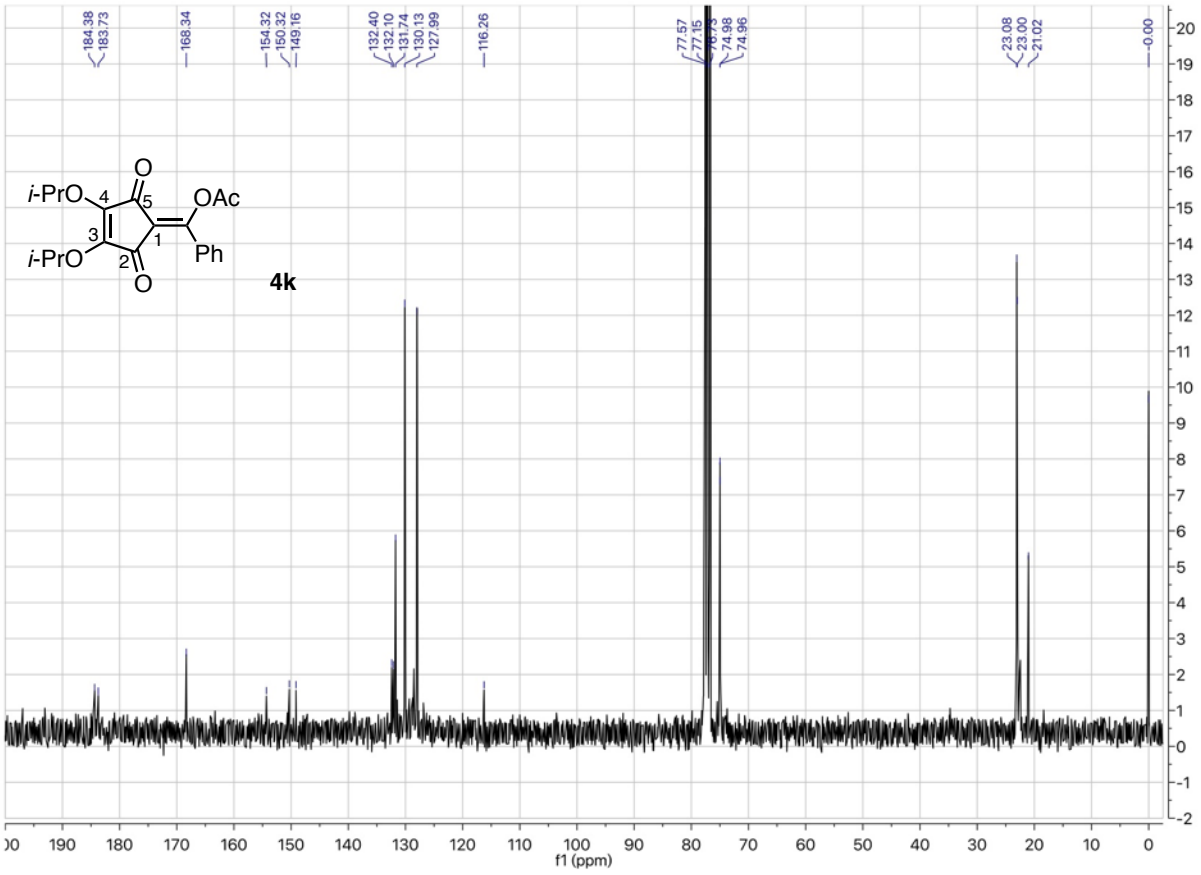
(*E*)-3-Isopropoxy-4-styrylcyclobut-3-ene-1,2-dione (7)[31]:



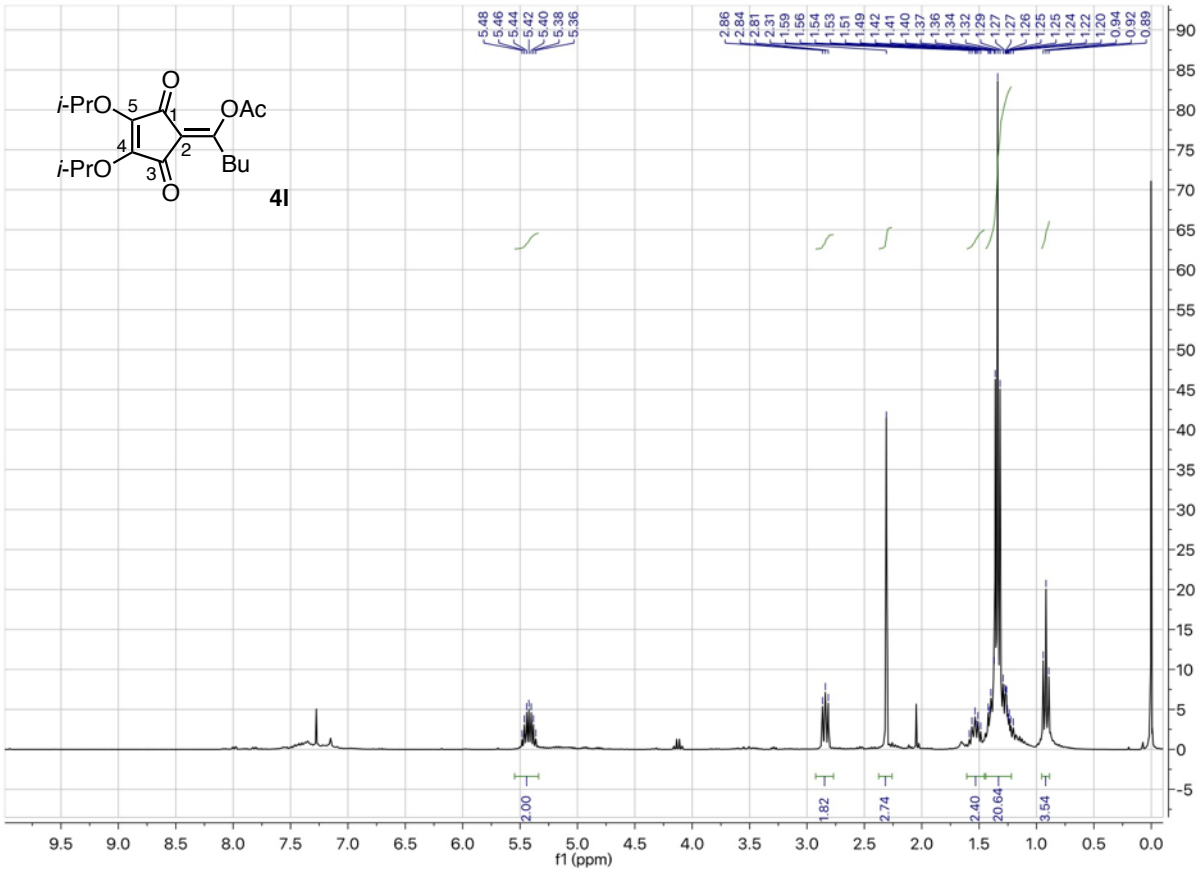


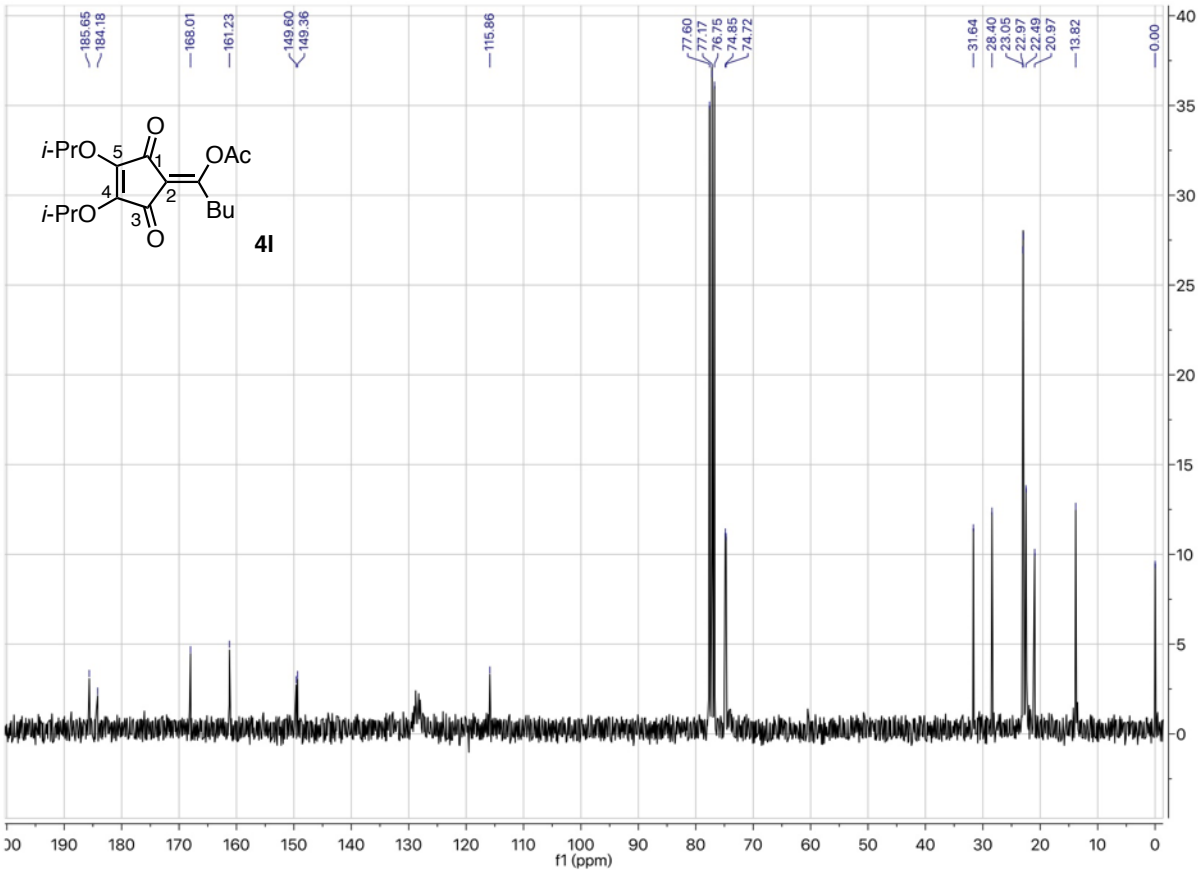
(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)(phenyl)methyl acetate (4k):



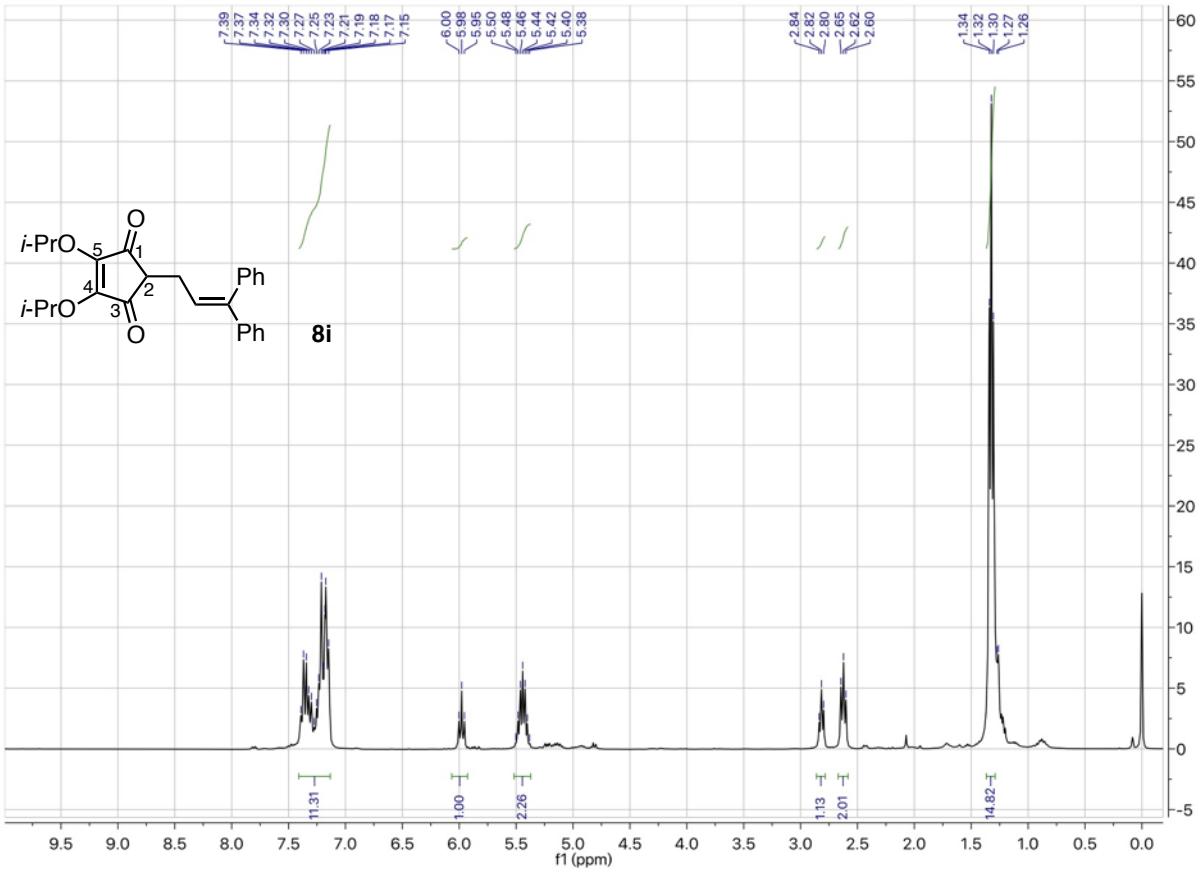


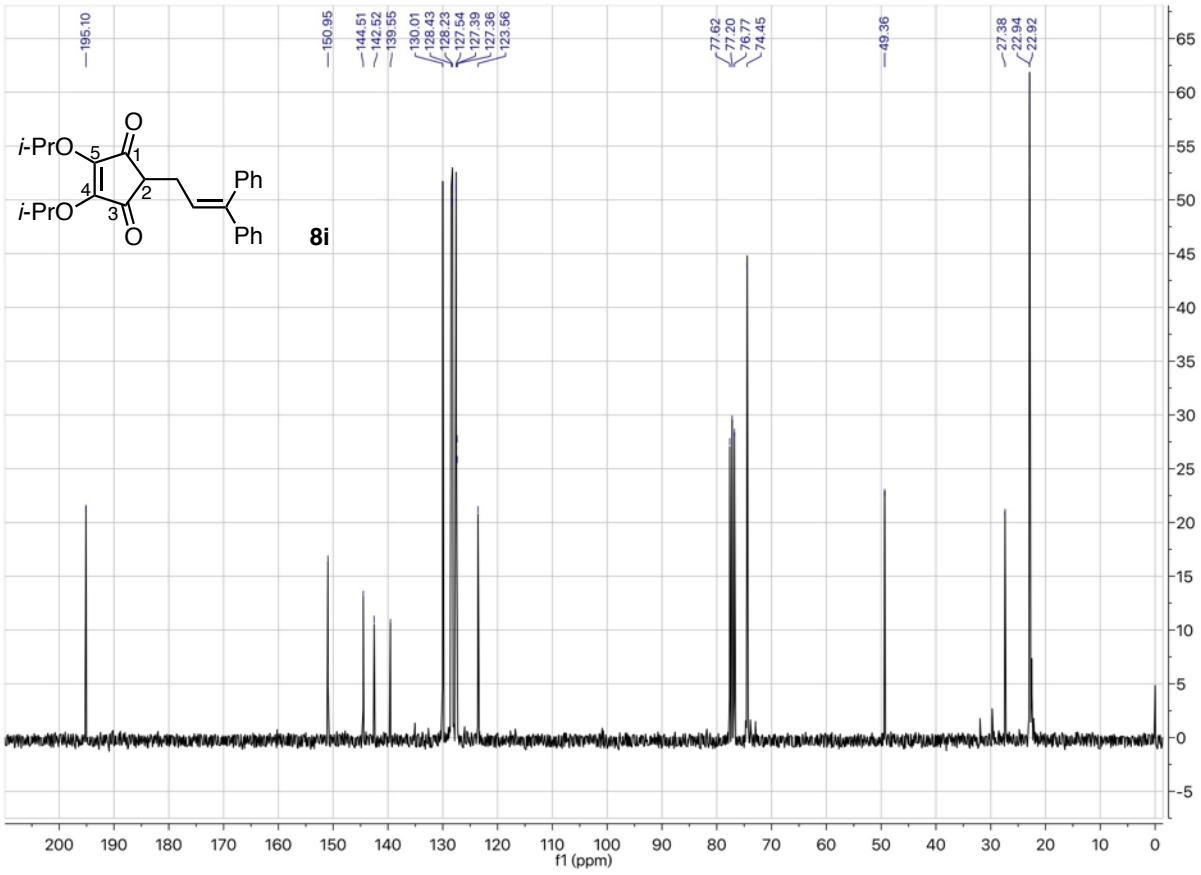
1-(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)pentyl acetate (4l):



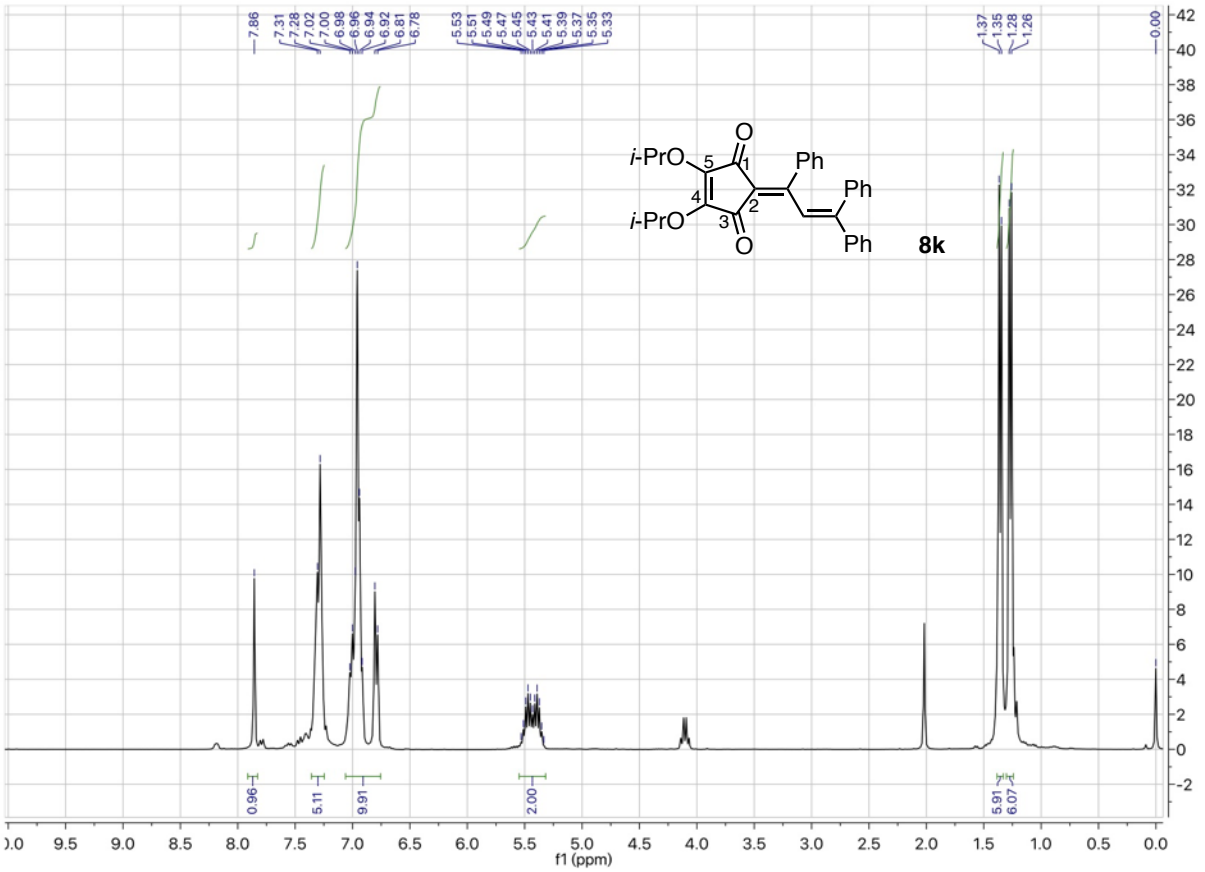


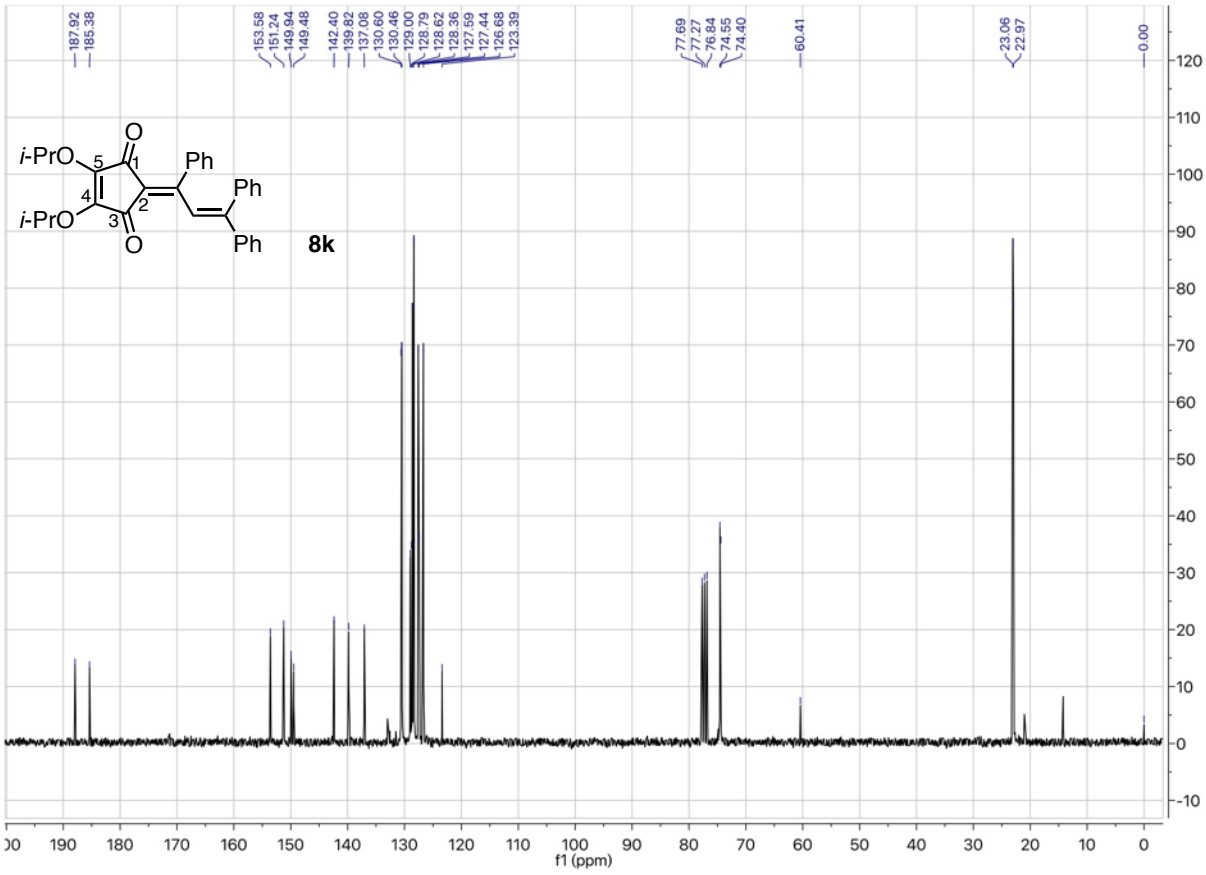
2-(3,3-diphenylallyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8i):

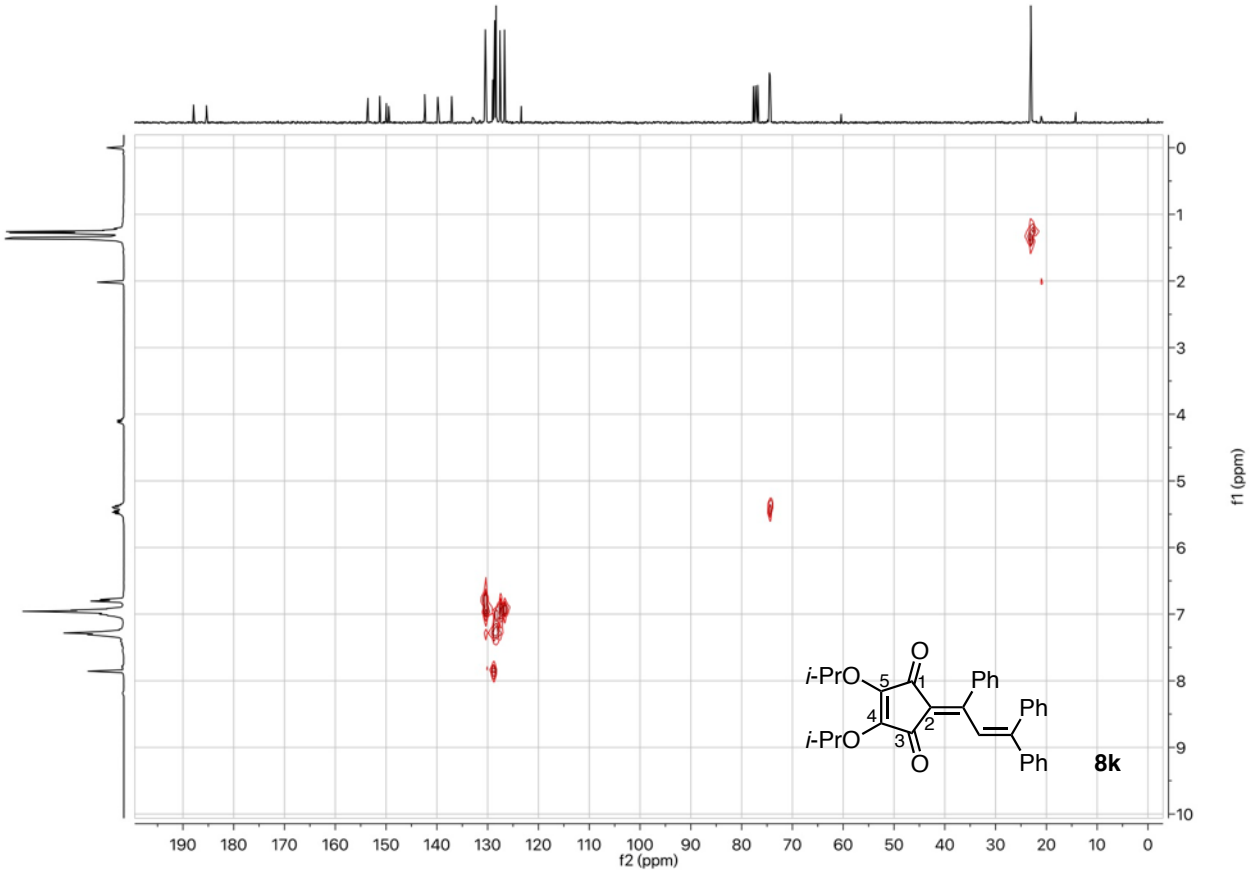


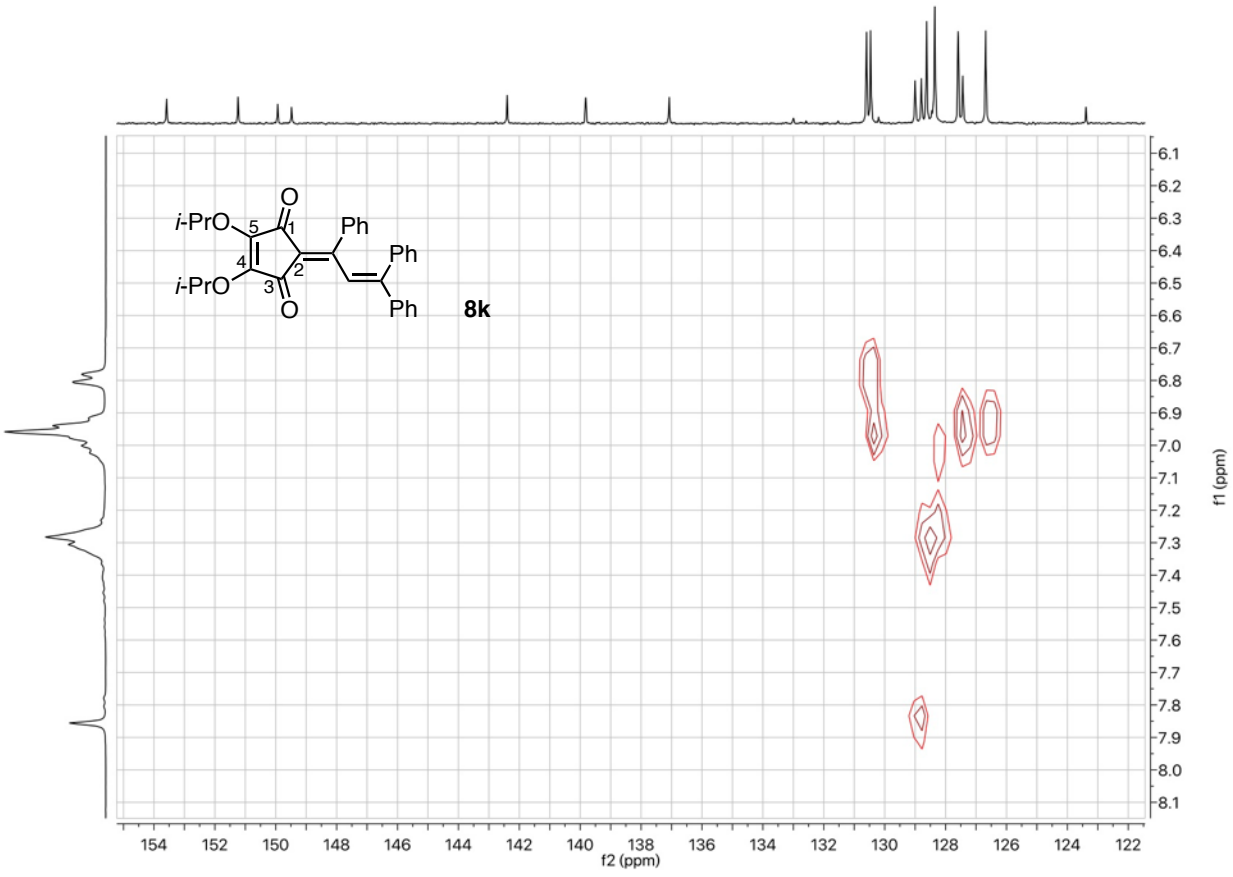


4,5-Diisopropoxy-2-(1,3,3-triphenylallylidene)cyclopent-4-ene-1,3-dione (8k):

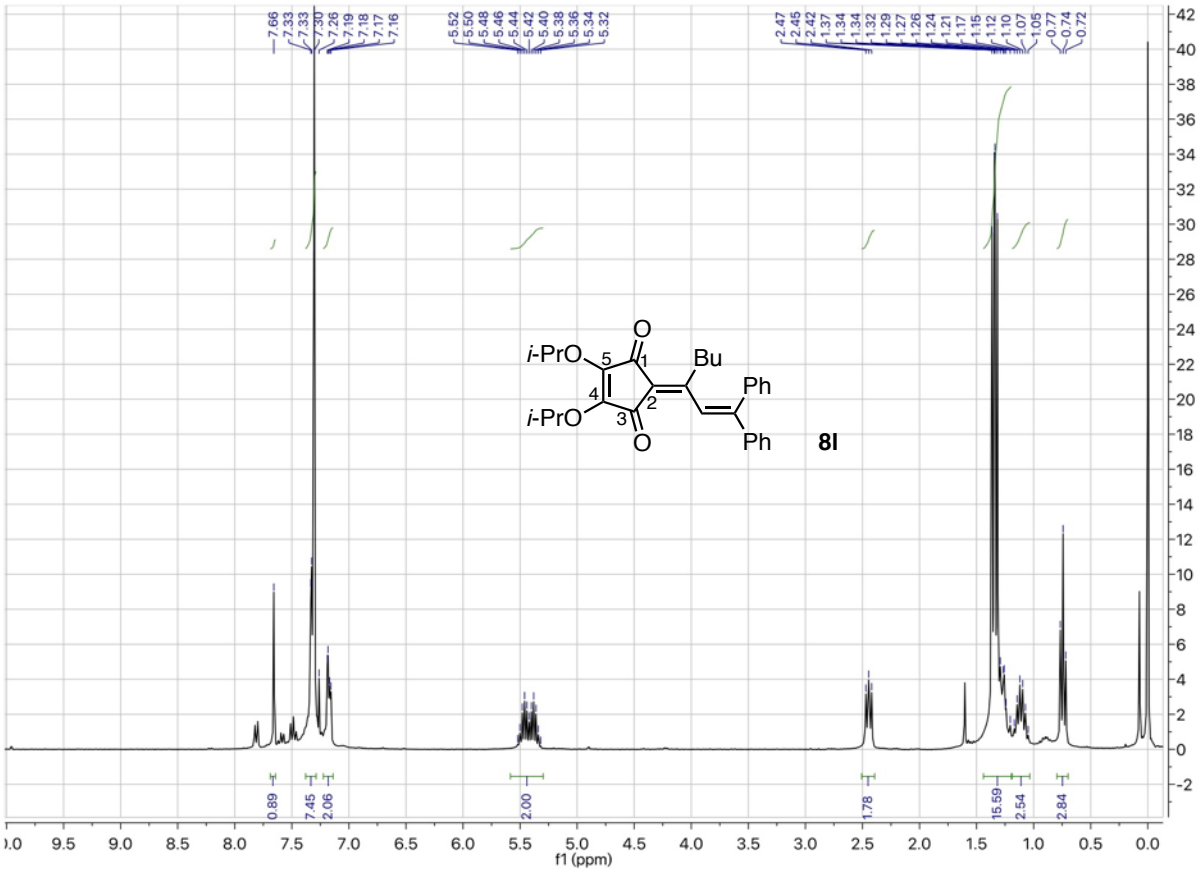


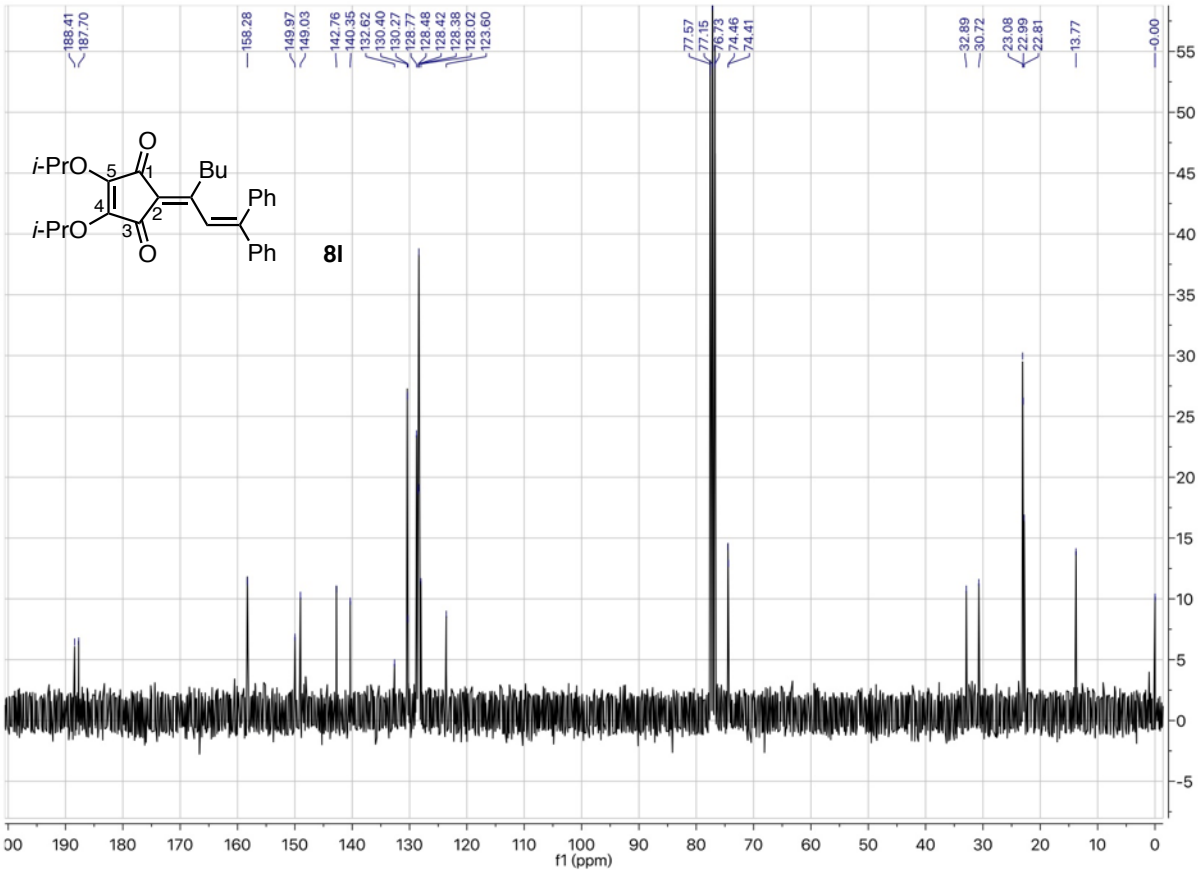



f2 (ppm)
f1 (ppm)
i-PrO
i-PrO
Ph
Ph
Ph
O
O
O
8k

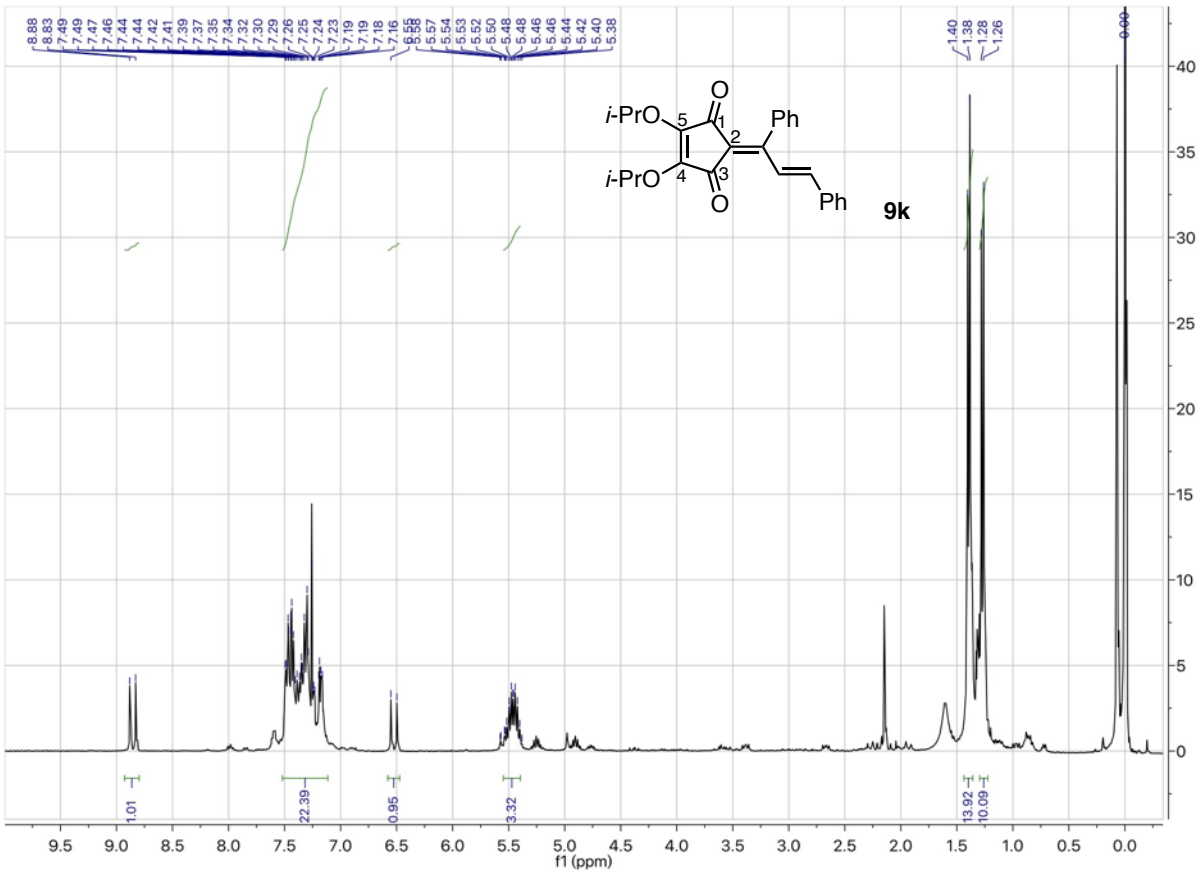

f2 (ppm)
f1 (ppm)
i-PrO
i-PrO
Ph
Ph
Ph
O
O
O
8k

2-(1,1-Diphenylhept-1-en-3-ylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8l):

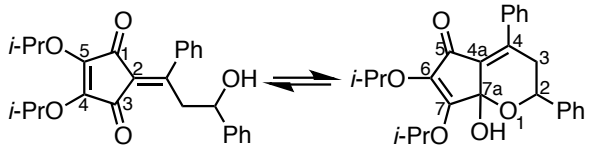




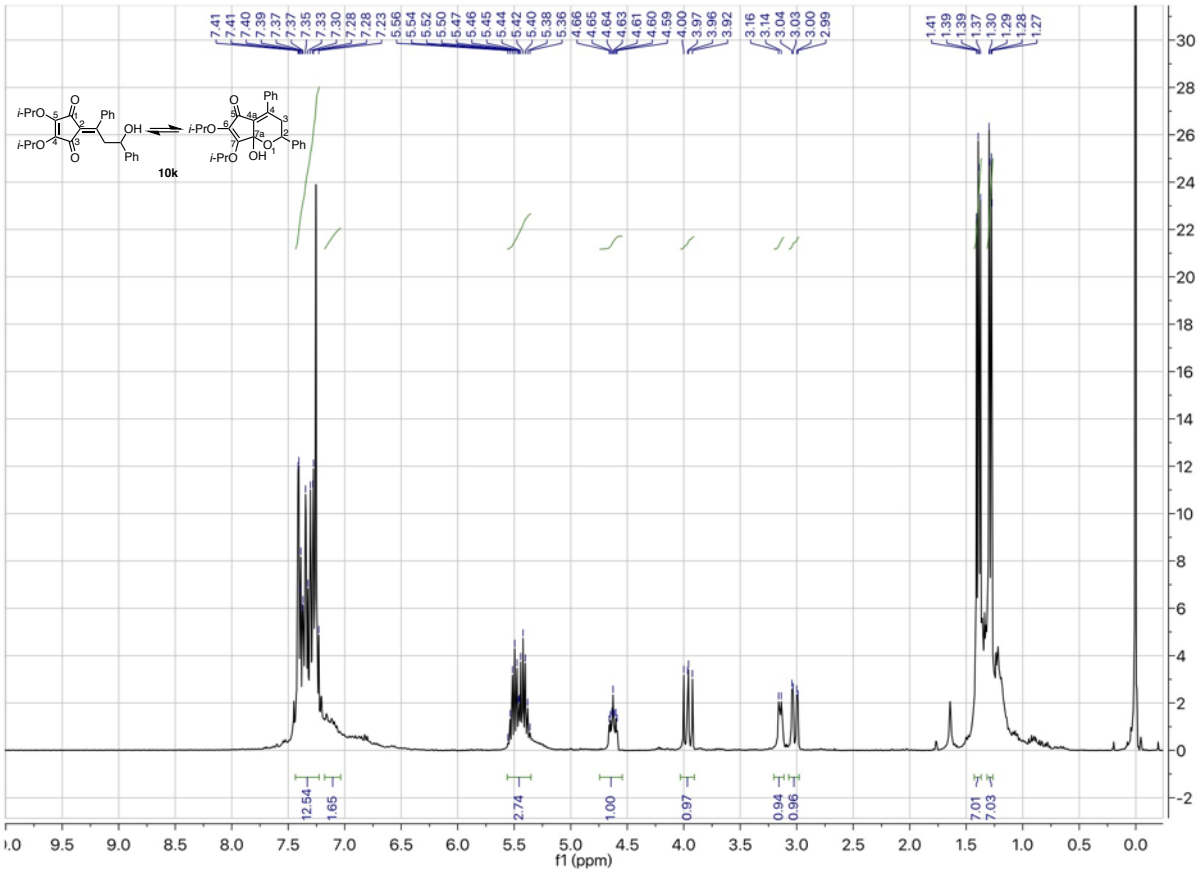
(*E*)-2-(1,3-Diphenylallylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (9k):



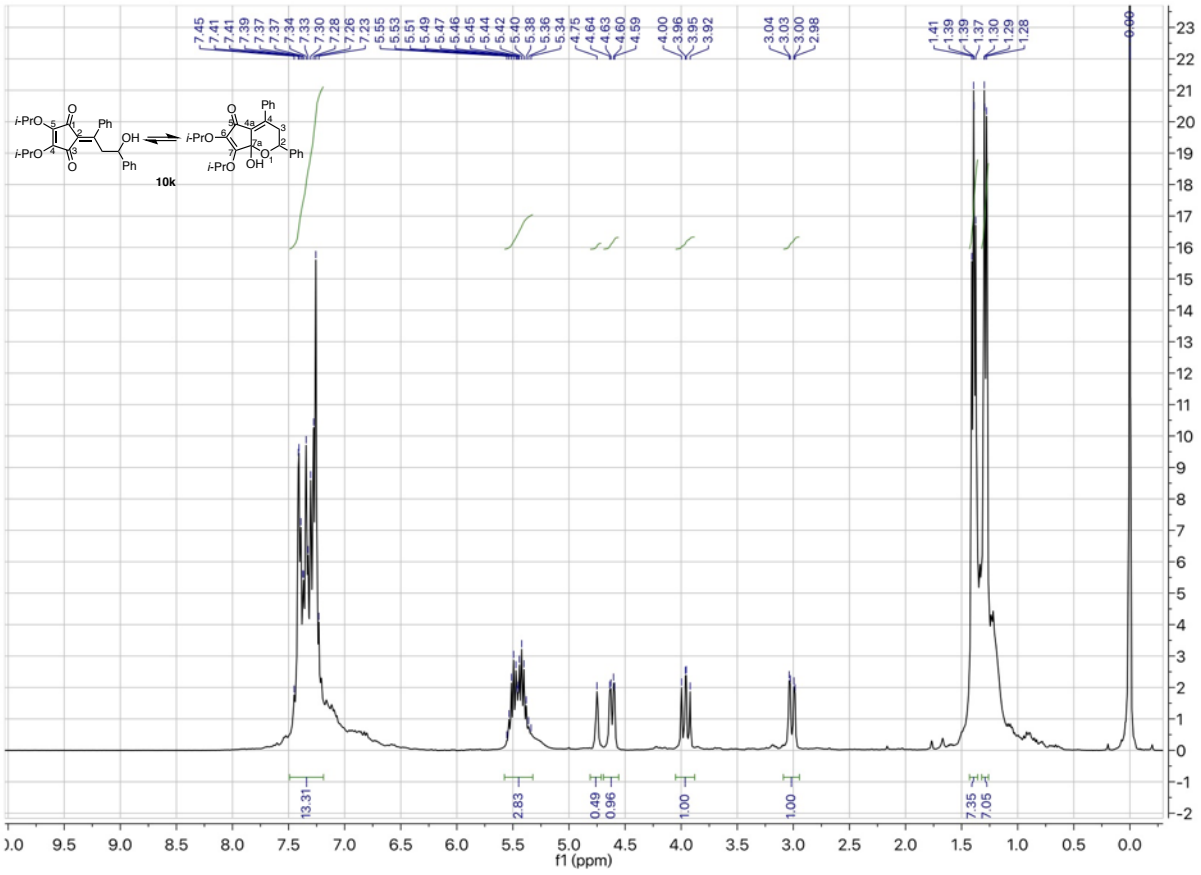
An equilibrium mixture of 2-(3-hydroxy-1,3-diphenylpropylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione and 7a-hydroxy-6,7-diisopropoxy-2,4-diphenyl-3,7a-dihydrocyclopenta[*b*]pyran-5(2*H*)-one (10k):

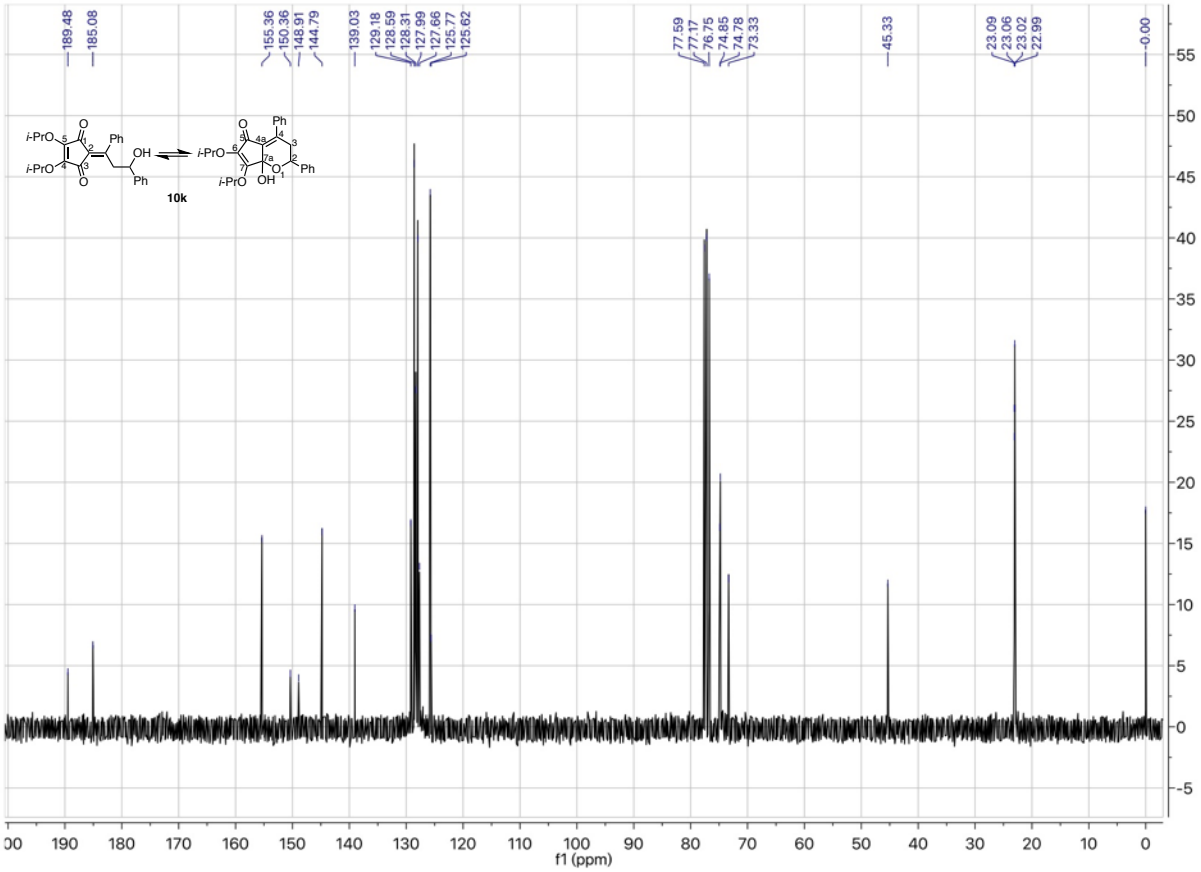


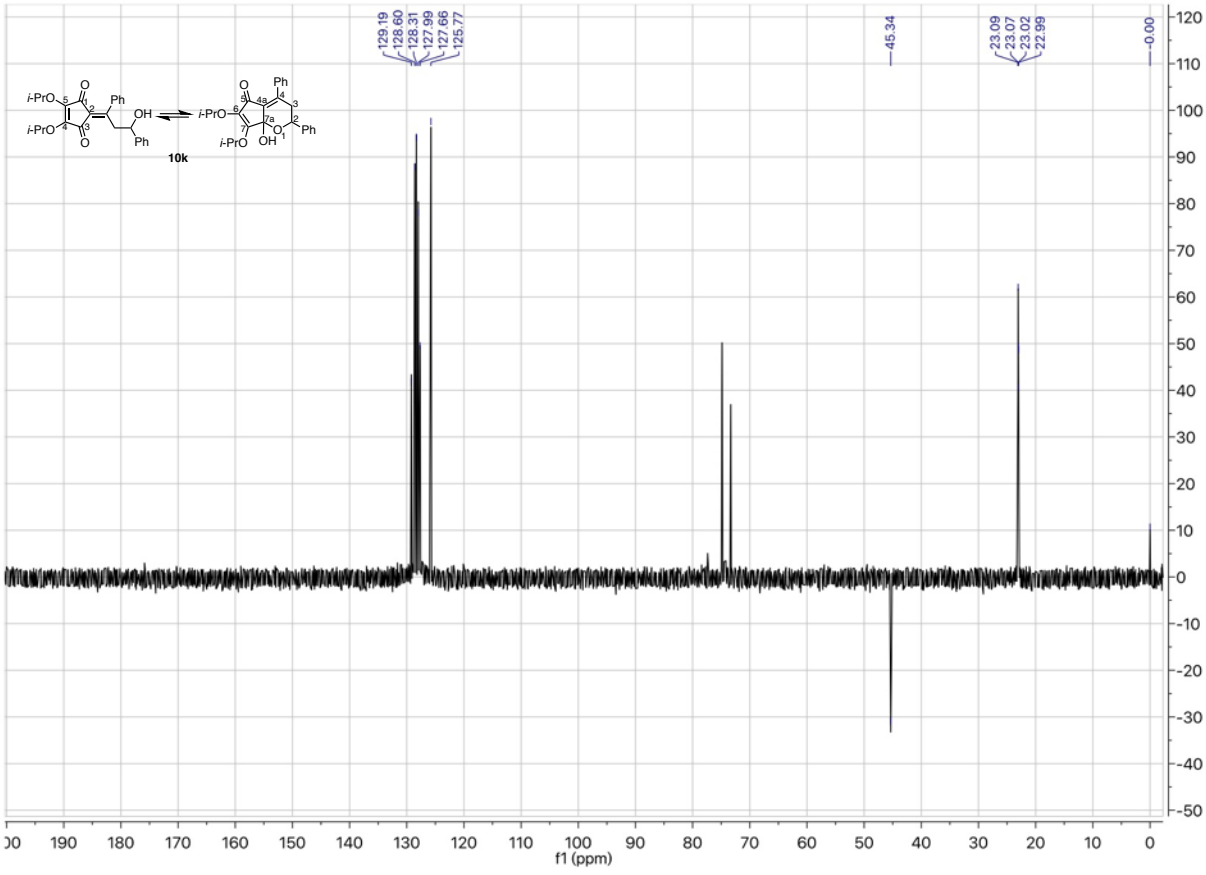
10k



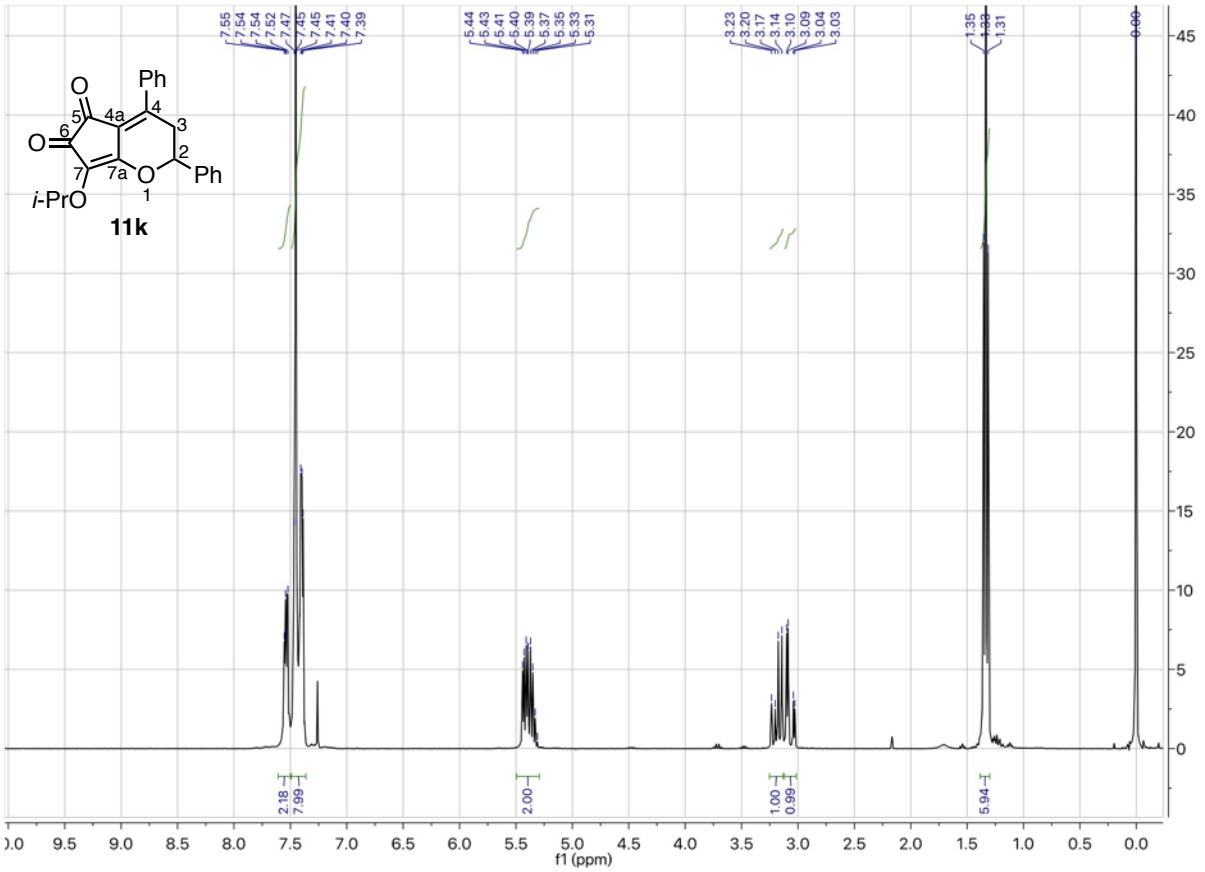
D_2O Exchange Experiment of 10k:

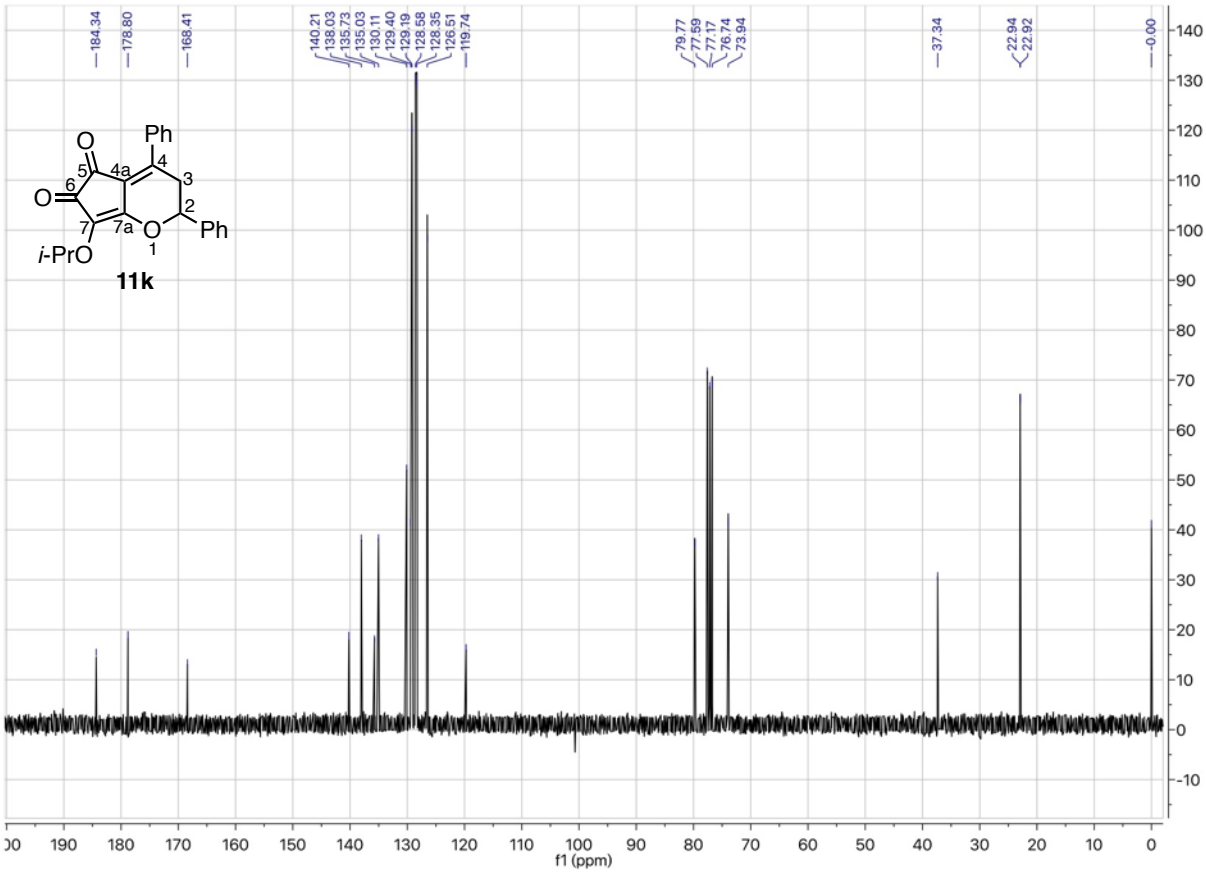


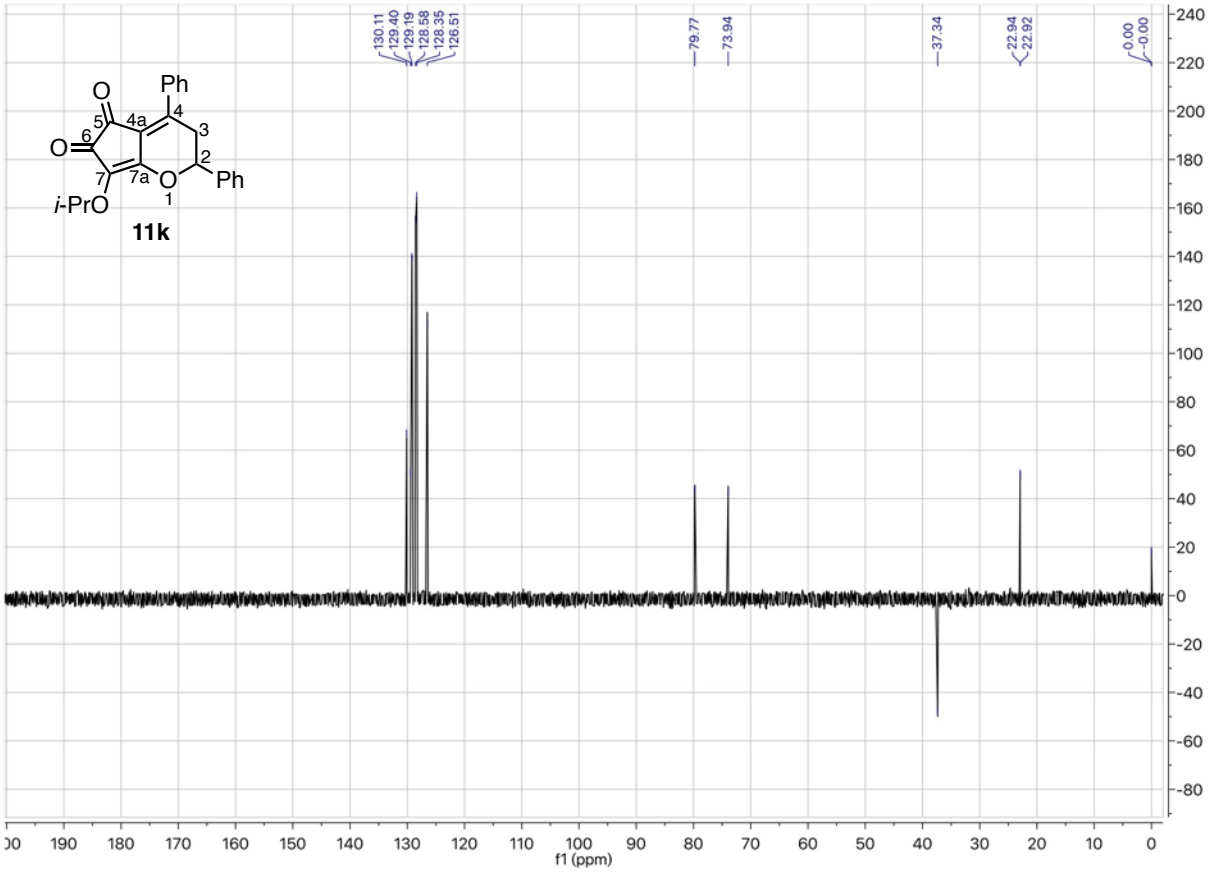

189.48
185.08
155.36
150.36
148.91
144.79
139.03
129.18
128.59
128.31
127.99
127.66
125.77
125.62
77.59
77.17
76.75
74.85
74.78
73.33
45.33
23.09
23.06
23.02
22.99
0.00
10k
f1 (ppm)


129.19
128.60
128.31
127.99
127.66
125.77
45.34
23.09
23.07
23.02
22.99
0.00
10k
f1 (ppm)

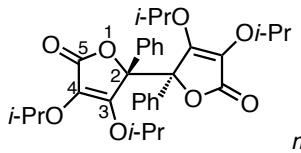
7-Isopropoxy-2,4-diphenyl-2,3-dihydrocyclopenta[*b*]pyran-5,6-dione (11k):



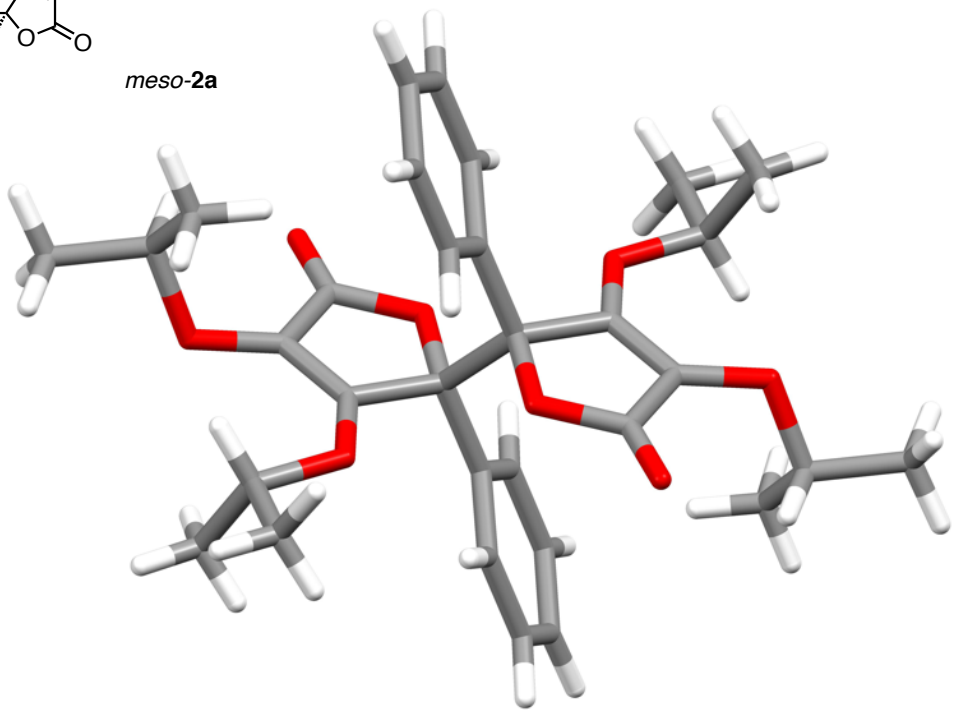


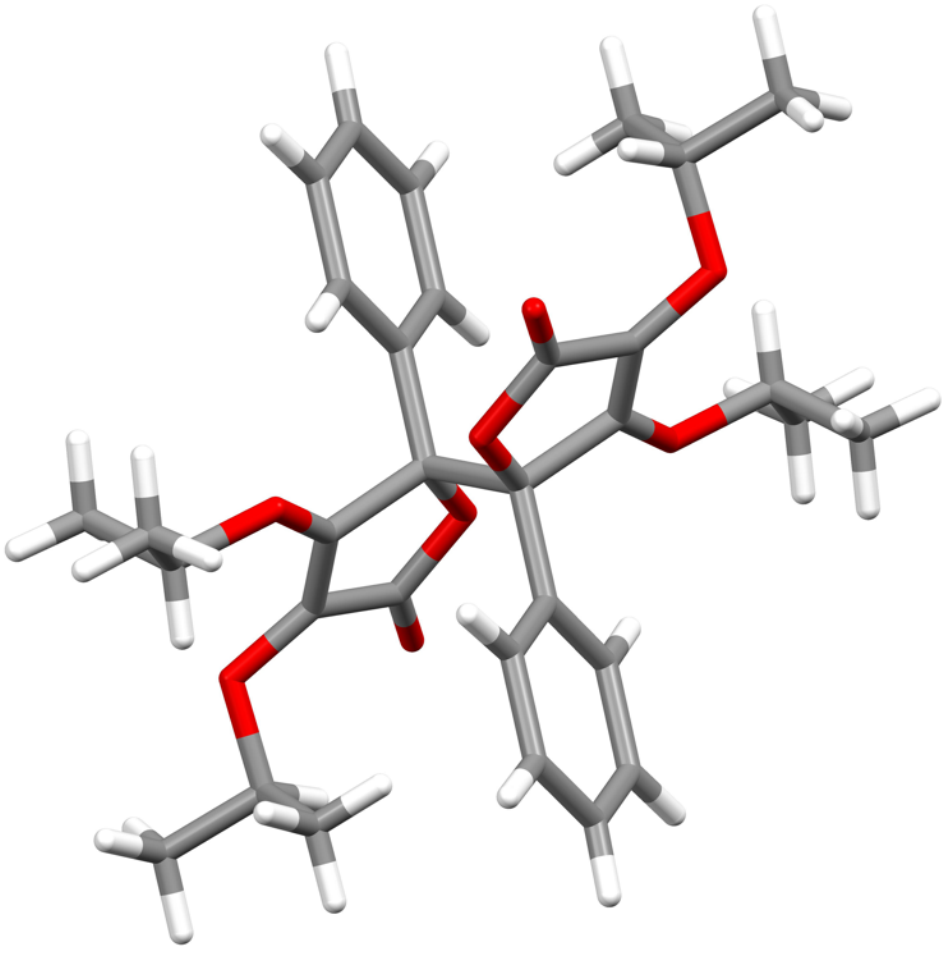

130.11
129.40
129.19
128.58
128.35
126.51
79.77
73.94
37.34
22.94
22.92
0.00
-0.00
O
Ph
5
4a
4
3
6
O
2
7
7a
O
Ph
1
i-PrO
11k
f1 (ppm)

X-ray Crystal Structure of *meso*-2a:

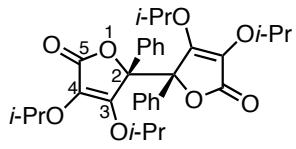


meso-**2a**

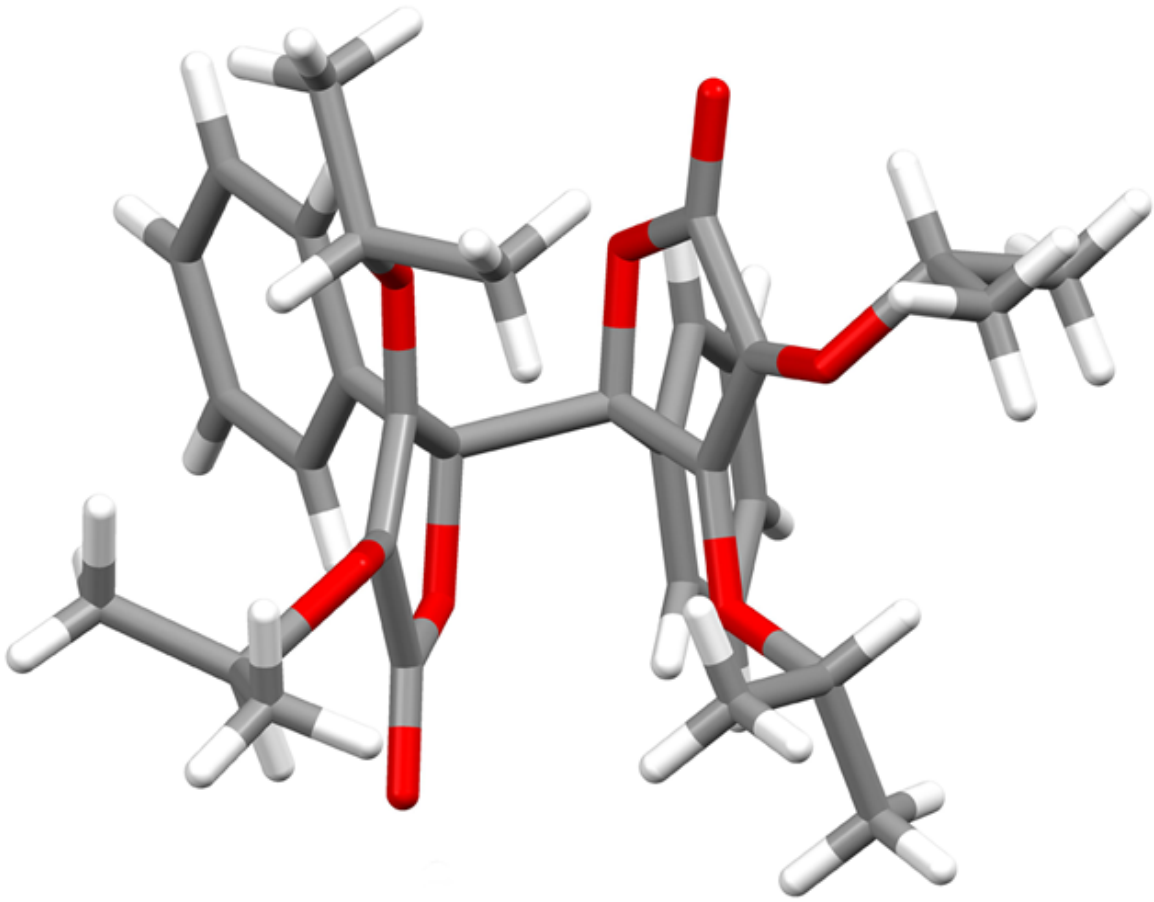


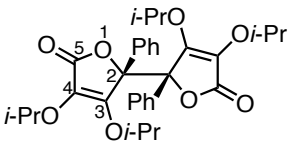


X-ray Crystal Structure of *rac*-2a:

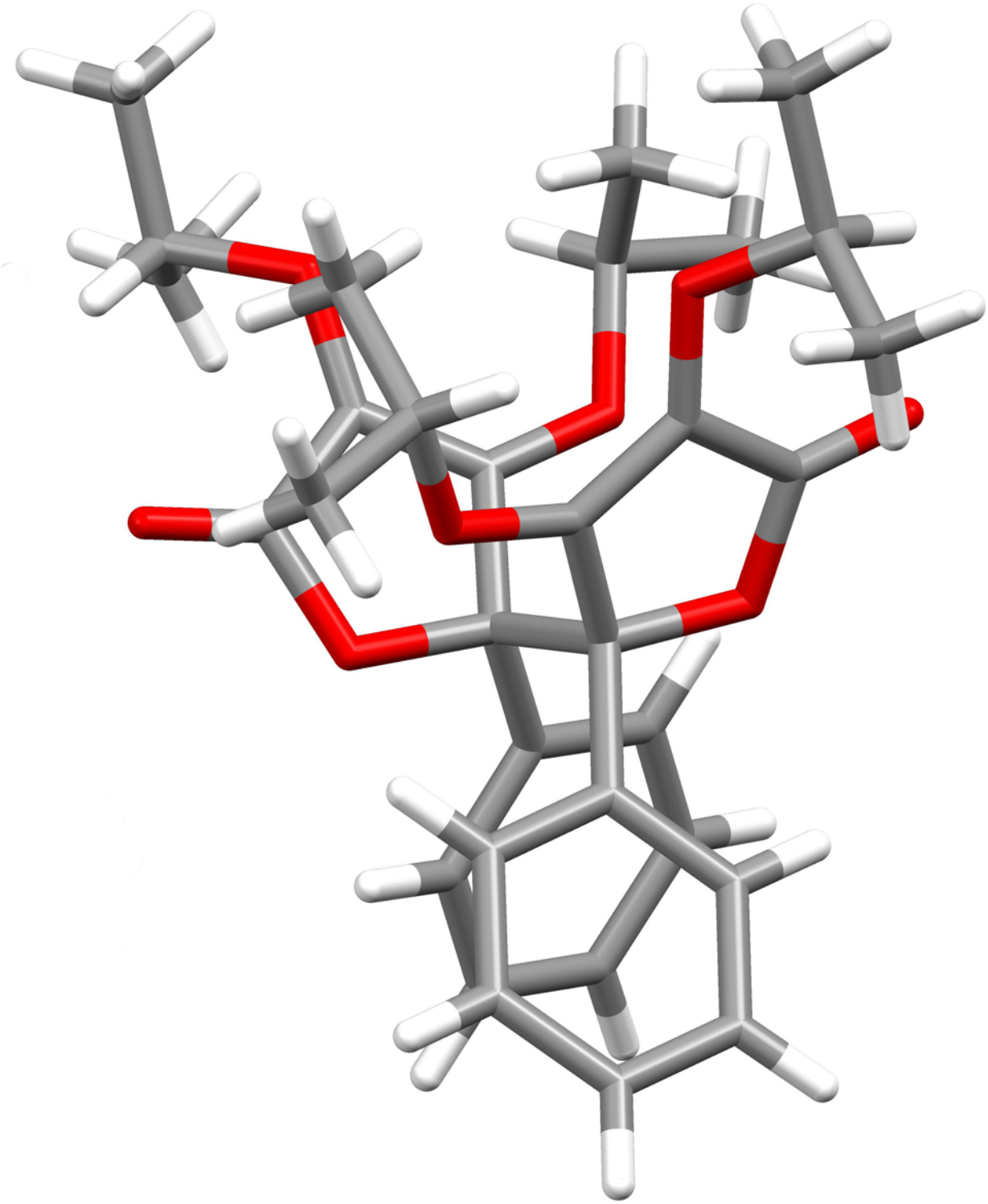


rac-**2a**

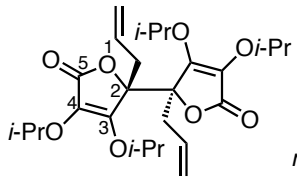




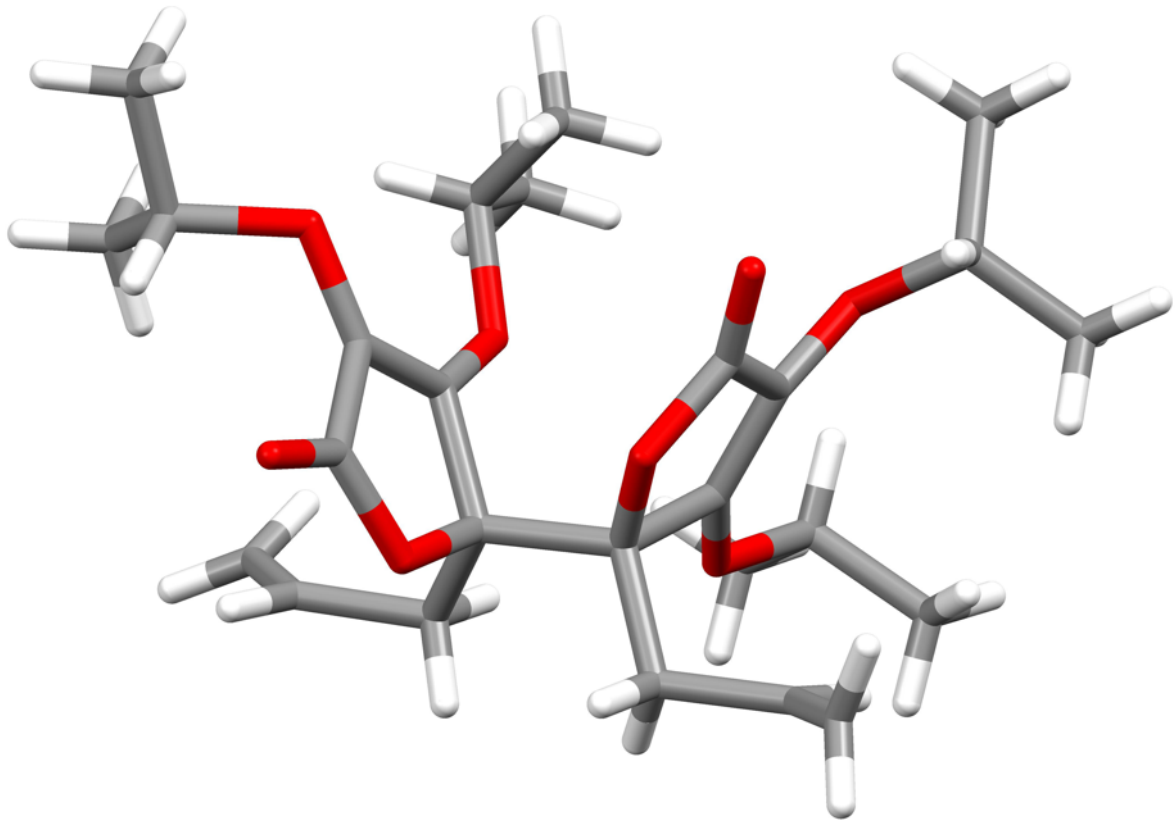
rac-**2a**



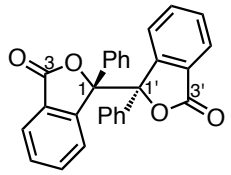
X-ray Crystal Structure of *meso*-2f:



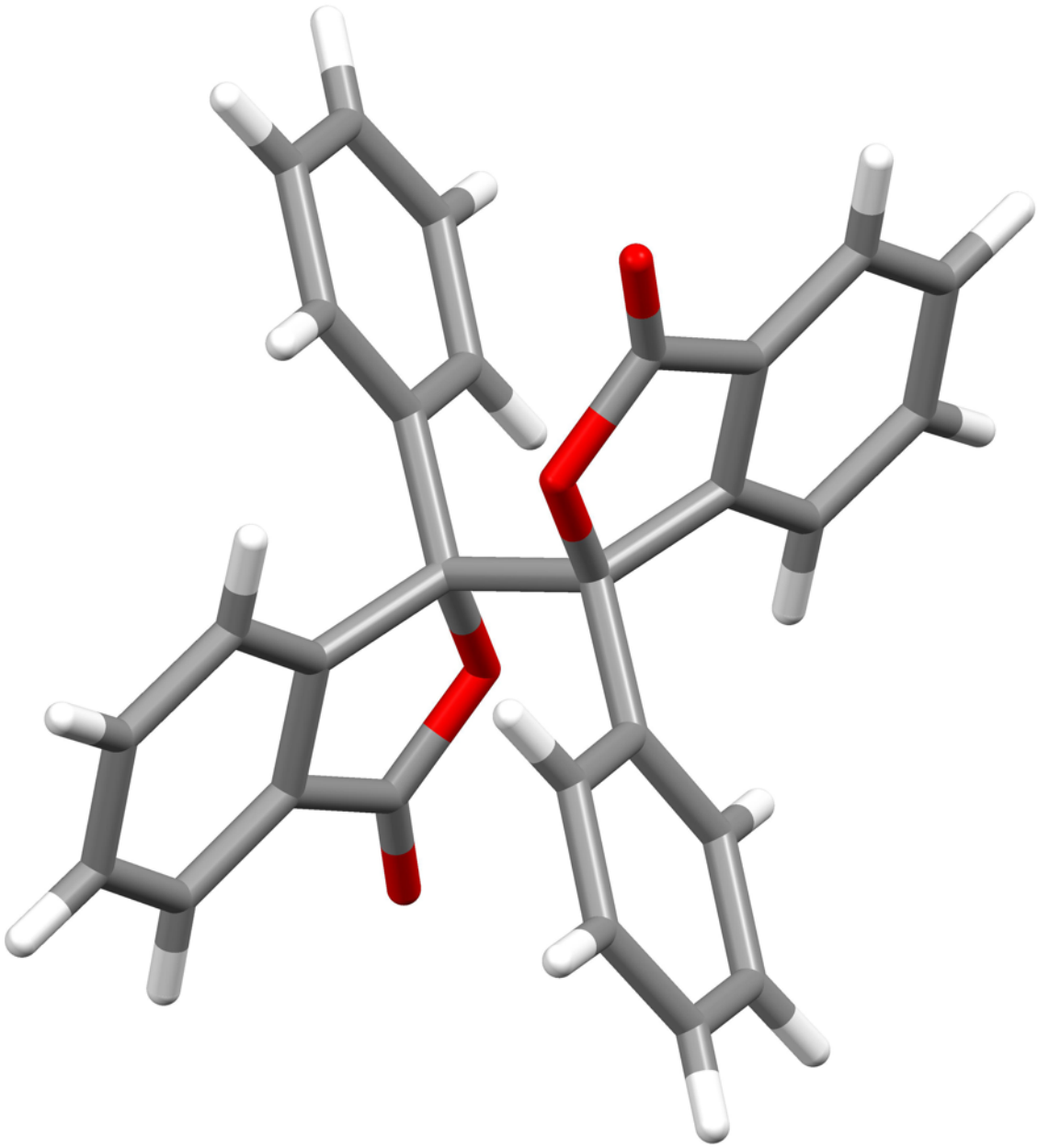
meso-**2f**



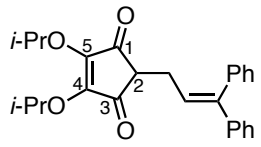
X-ray Crystal Structure of *meso*-2h:



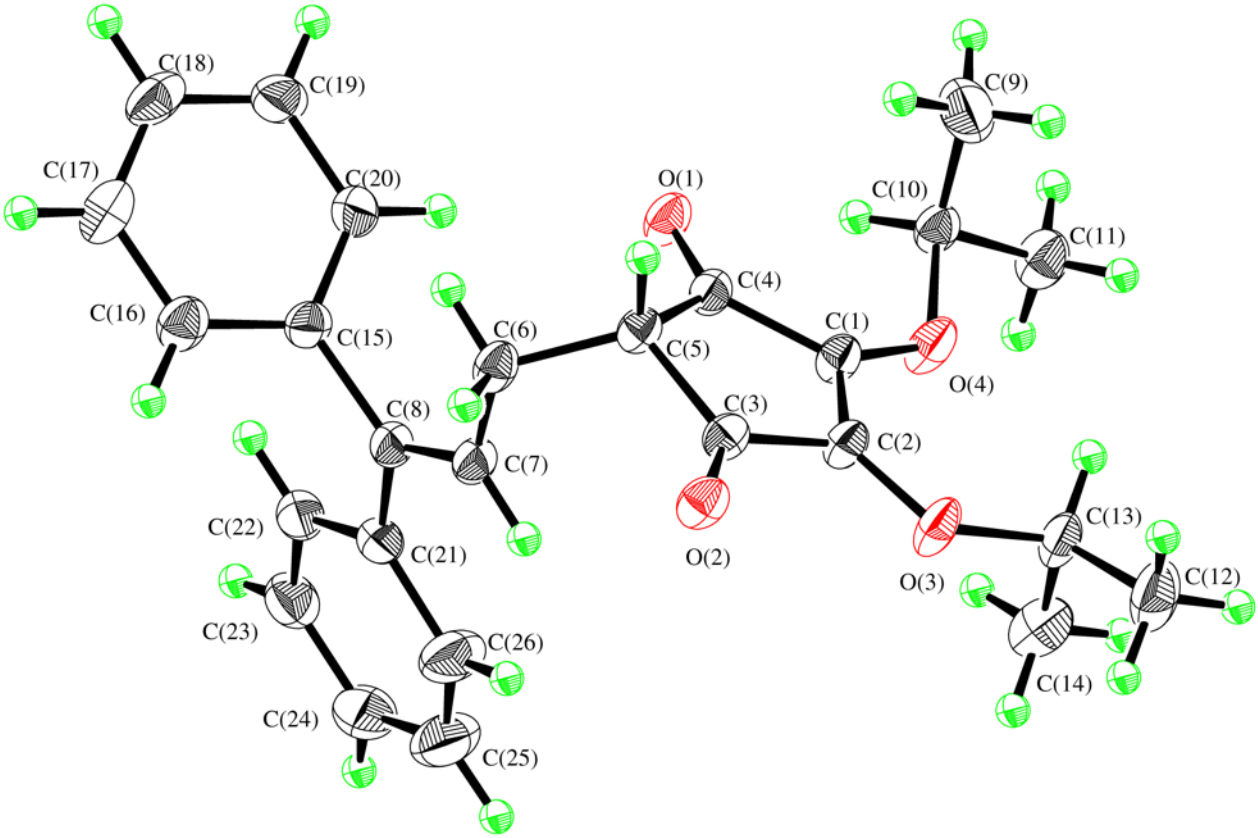
meso-**2h**

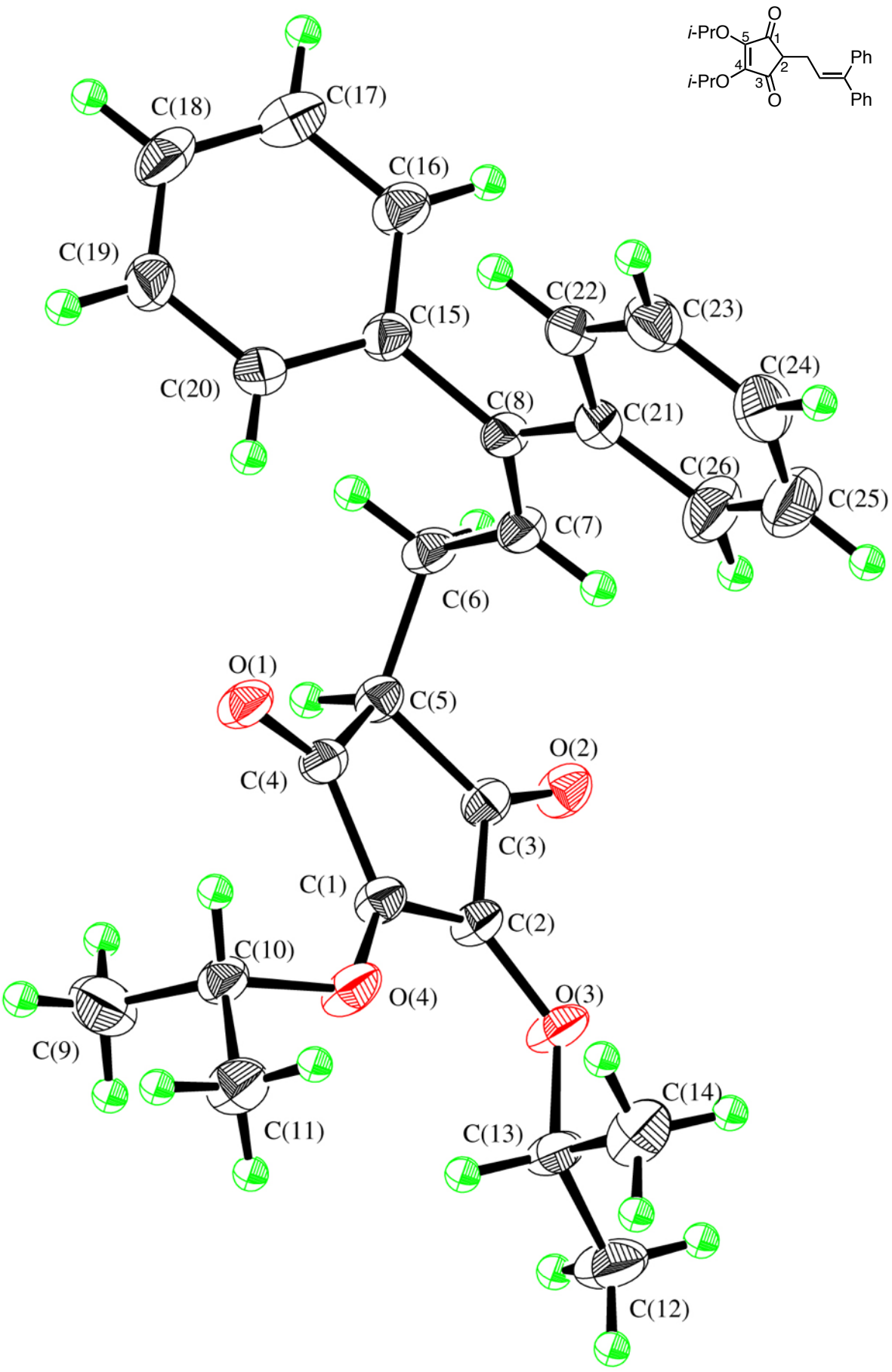


X-ray Crystal Structure of 8i:



8i




C(18)
C(17)
C(16)
C(19)
C(22)
C(23)
C(15)
C(24)
C(20)
C(8)
C(21)
C(26)
C(25)
C(7)
C(6)
O(1)
C(5)
O(2)
C(4)
C(3)
C(1)
C(2)
C(10)
O(4)
O(3)
C(9)
C(14)
C(11)
C(13)
C(12)

i-PrO
i-PrO
O
O
Ph
Ph
1
2
3
4
5

8i