

## Supporting Information

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

Jun-ichi Sasaki,<sup>a</sup> Makoto Kobayashi,<sup>a</sup> Yūsuke Ibe,<sup>a</sup> and Hiroshi Nishino<sup>b\*</sup>

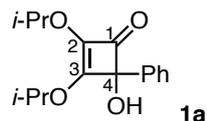
<sup>a</sup> Department of Chemistry, Graduate School of Science and Technology, Kumamoto University,  
Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan

<sup>b</sup> Department of Chemistry, Graduate School of Science, Kumamoto University,  
Kurokami 2-39-1, Chûou-Ku, Kumamoto 860-8555, Japan  
Fax: +81-96-342-3374; E-mail: nishino@kumamoto-u.ac.jp

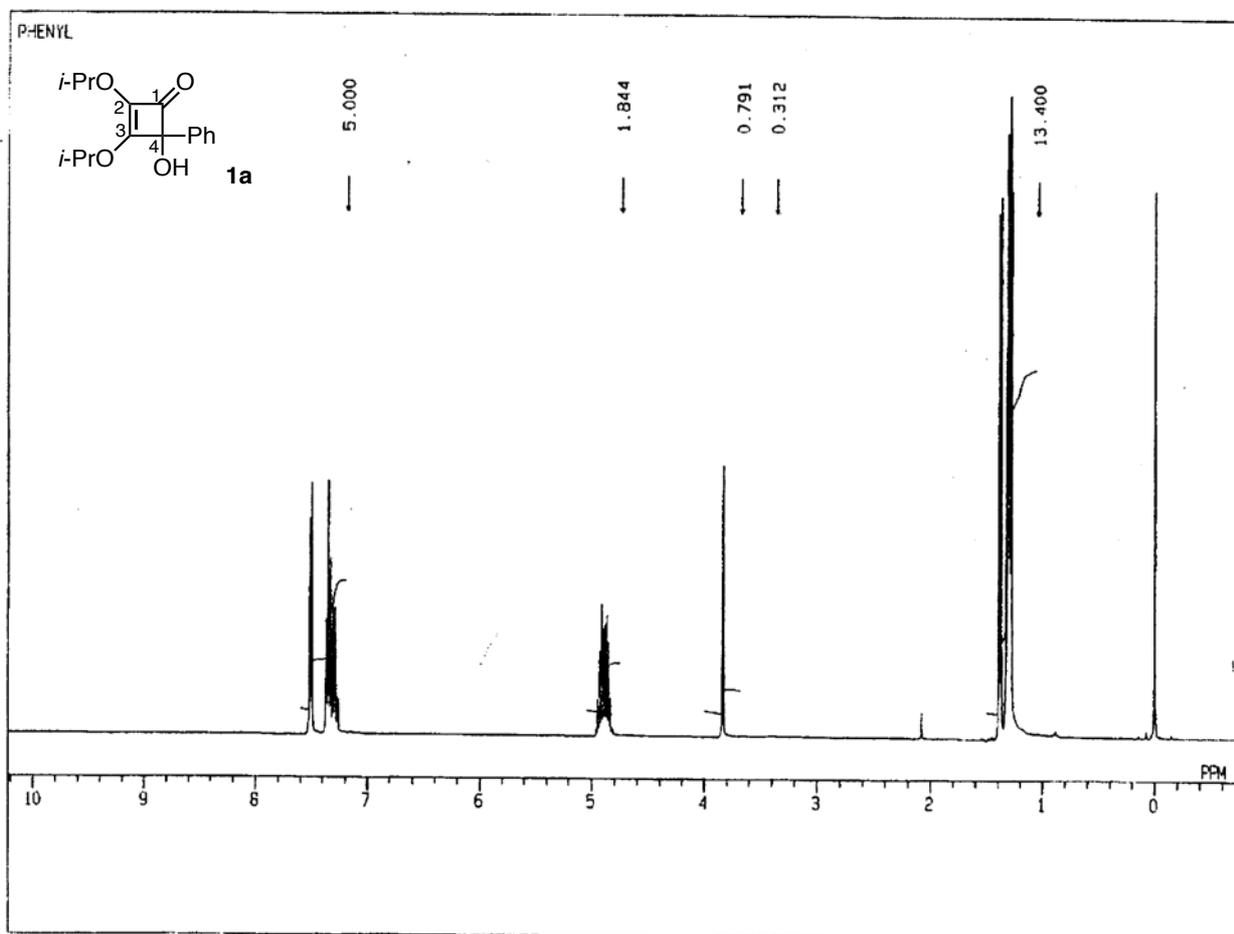
### Table of Contents:

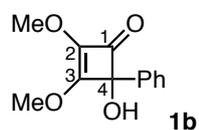
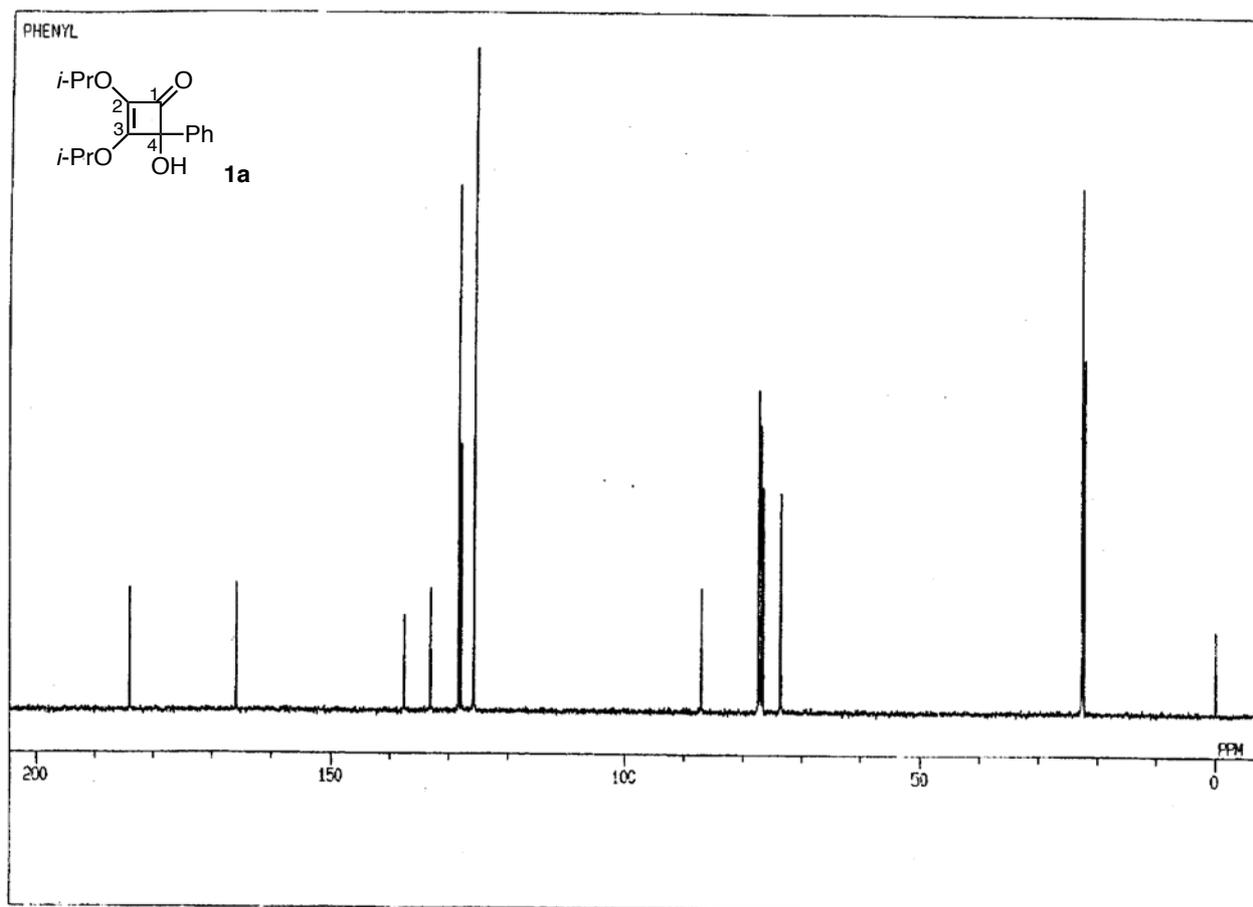
1. Spectral Data, and <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Starting Materials **1a-l**: P.2–P.18.
2. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Bis(butenolide)s **2a-h**: P.19-P.34.
3. COSY Spectrum of *meso*-**2d**: P.25.
4. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Butenolide Monomers **3a, 3a', 3b, 3b', 3c', 3e, 3e', 3f, 3f', 3g and 3g'**: P.35-P. 44.
5. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Products **4i, 5, 6, 4j, 7, 4k, and 4l**: P.45-P.52.
6. HMQC Spectrum of **4j**: P.49.
7. <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Products **8i, 8k, 8l, 9k, 10k, and 11k**: P.53-P.61.
8. HMQC Spectrum of **8k**: P.55.
9. X-ray Crystal Structures of *meso*-**2a**, *rac*-**2a**, *meso*-**2f**, *meso*-**2h**, and **8i**: P.62-68.

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

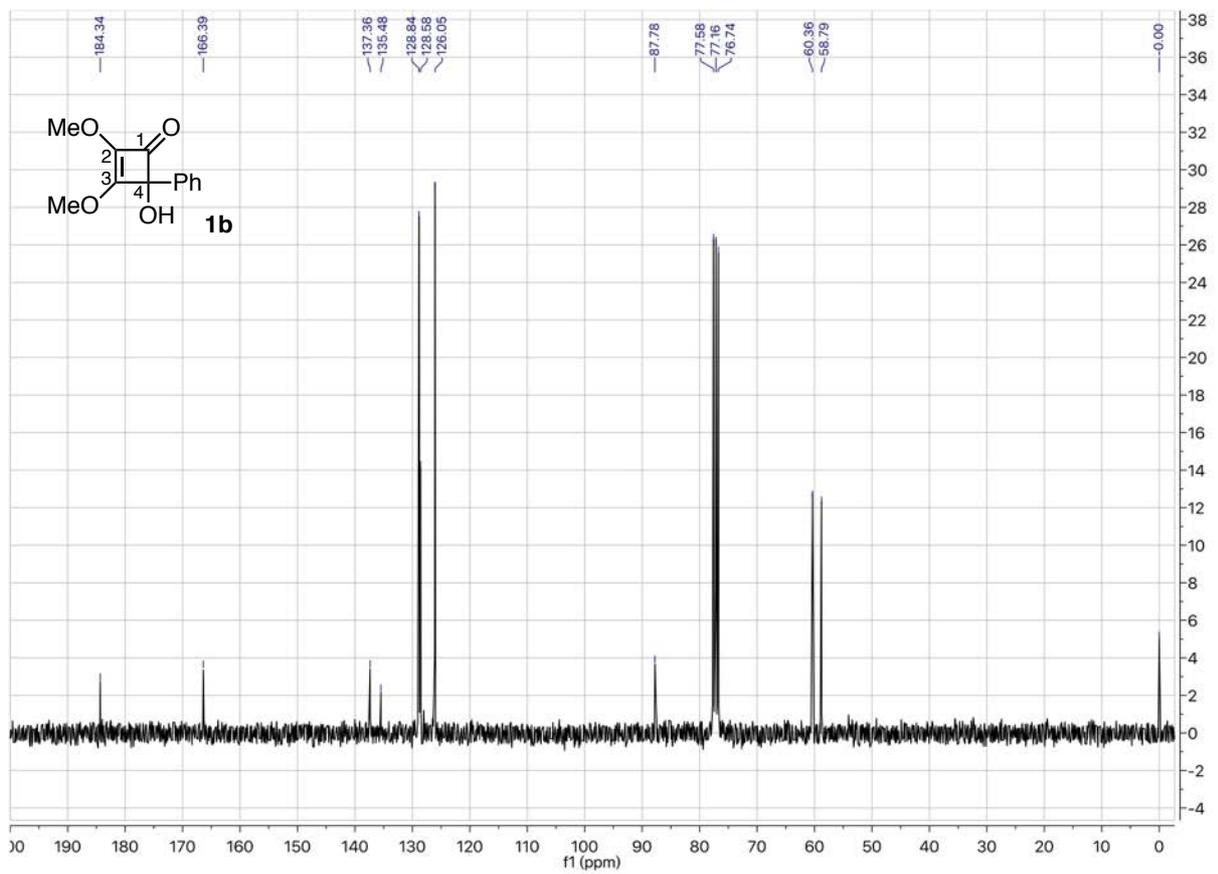
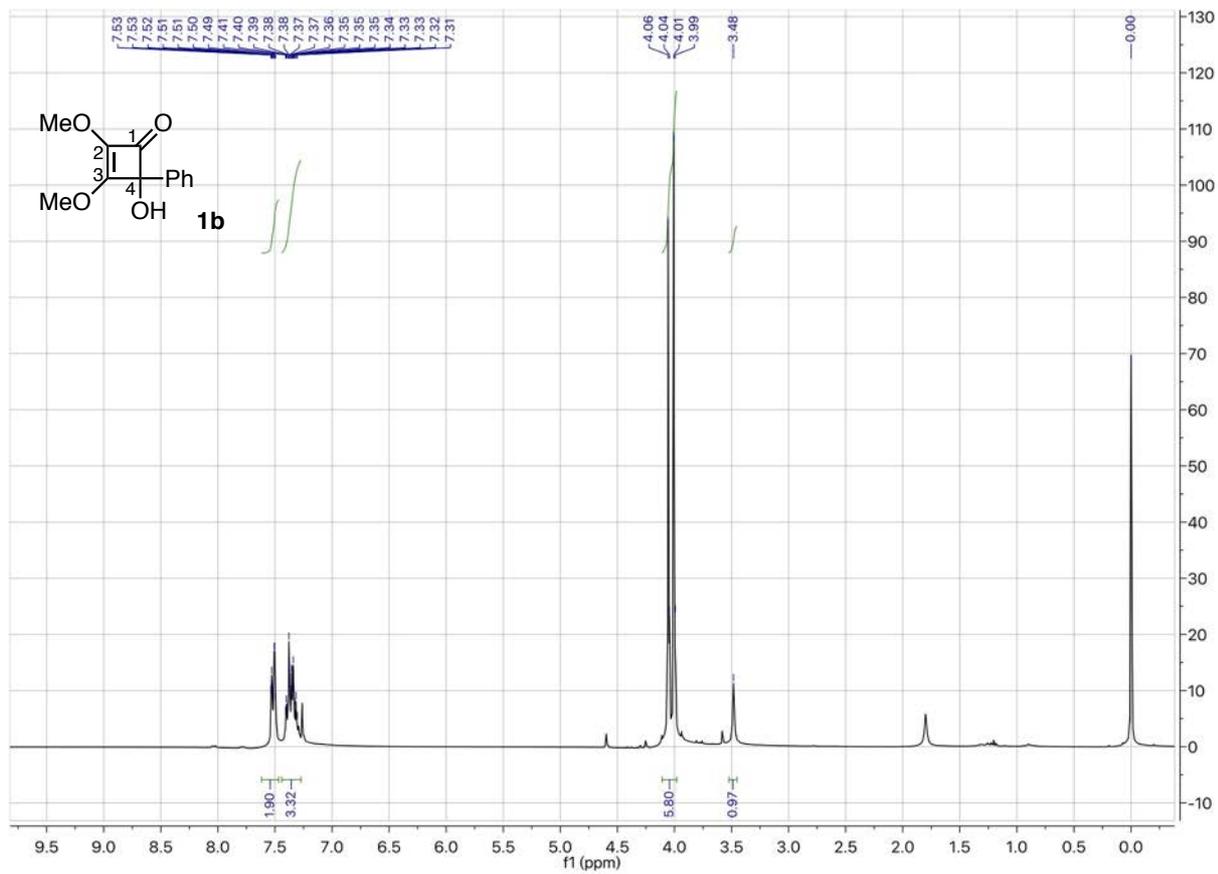


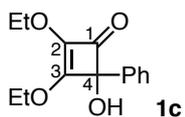
**4-Hydroxy-2,3-diisopropoxy-4-phenylcyclobut-2-en-1-one (1a)<sup>9a</sup>**: yellowish oil; IR ( $\text{CHCl}_3$ )  $\nu$  3400 (OH), 1775 (C=O), 1625 ( $>\text{C}=\text{C}<$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.26 (5H, m, arom H), 4.94 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH-O}$ ), 4.84 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH-O}$ ), 3.83 (1H, s, OH), 1.39 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.28 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.26 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.25 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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 ( $>\text{CH-O}$ ), 22.7 (2C), 22.5, 22.3 ( $\text{CH}_3$ ).



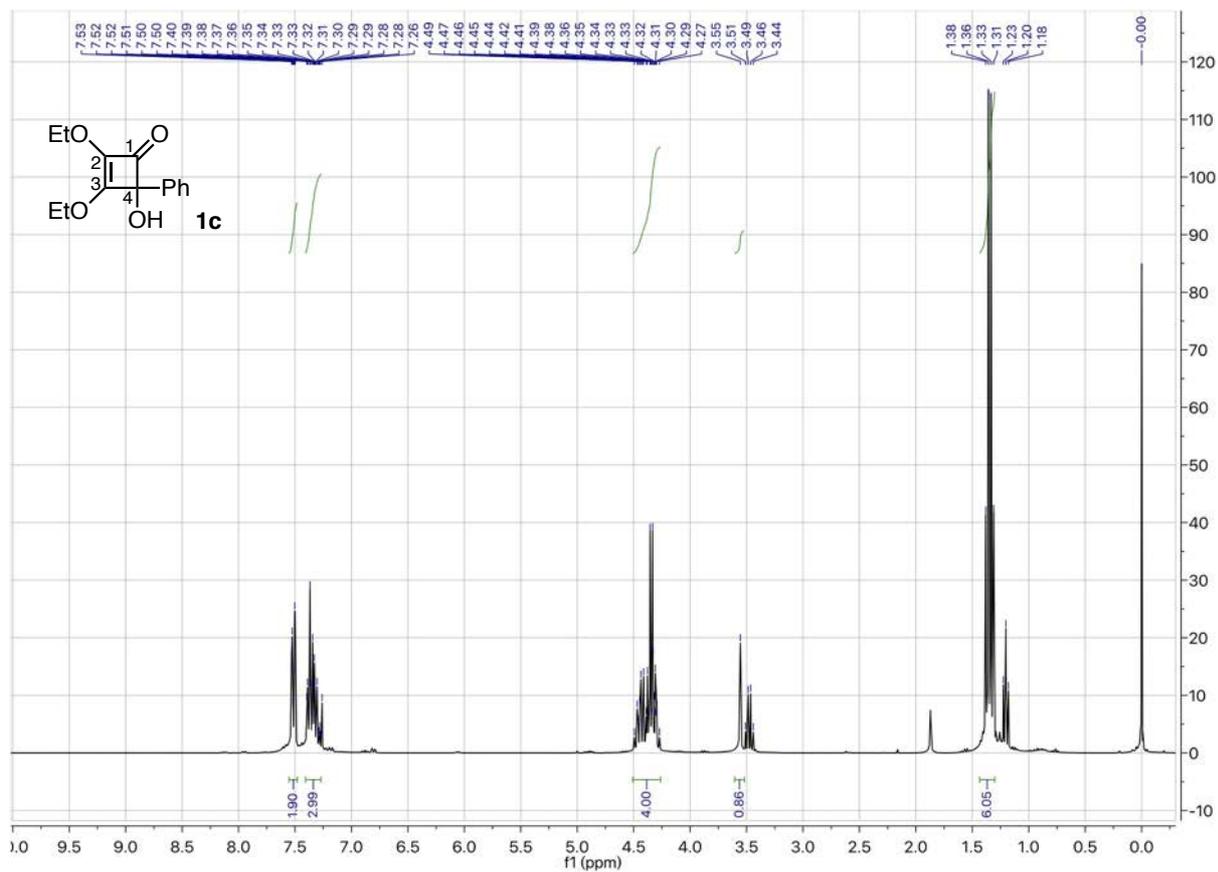


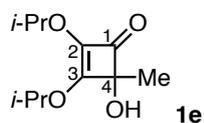
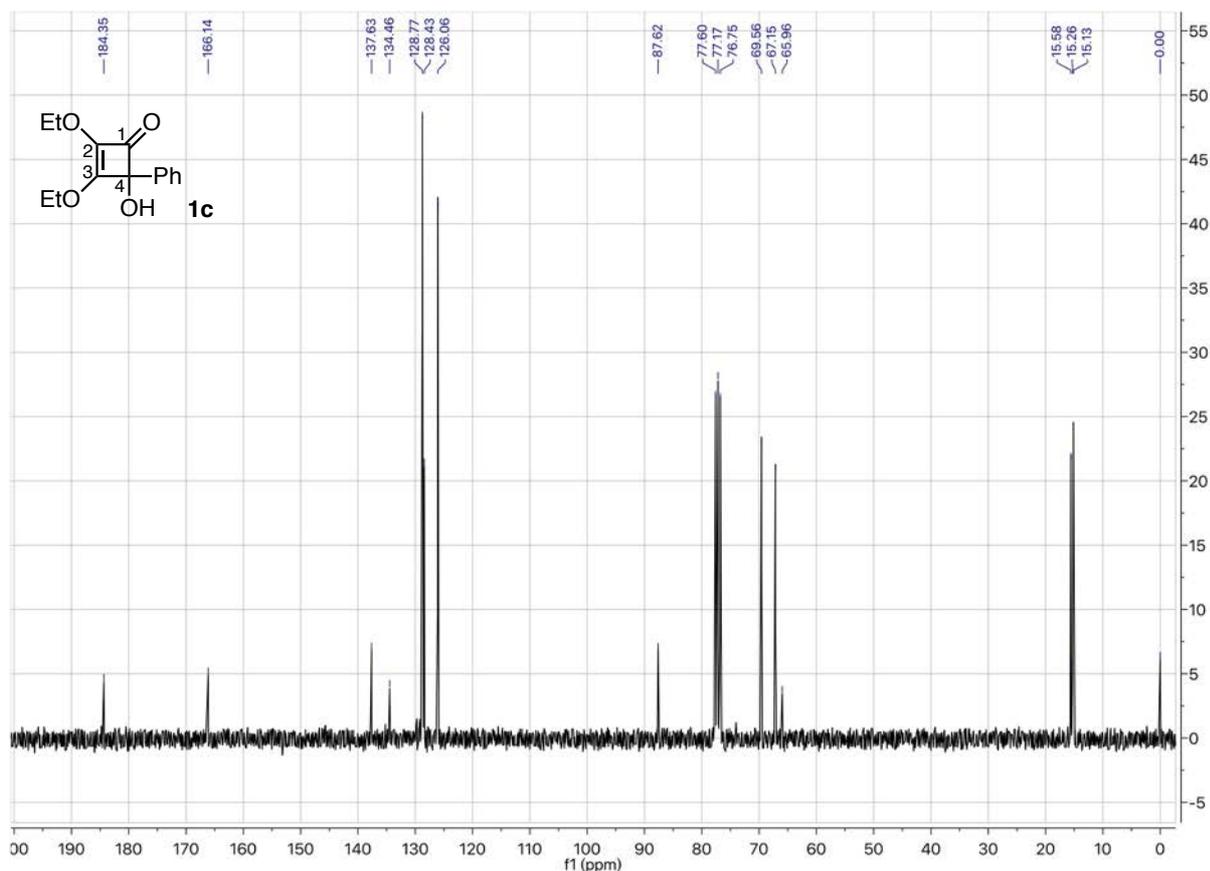
**4-Hydroxy-2,3-dimethoxy-4-phenylcyclobut-2-en-1-one (1b):** colorless microcrystals (from MnOH/jexane); mp 95-98 °C (lit,<sup>22</sup> mp 96-98 °C); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.53-7.50 (2H, m, arom H), 7.40-7.31 (3H, m, arom H), 4.05 (3H, s, CH<sub>3</sub>O), 4.00 (3H, s, CH<sub>3</sub>O), 3.48 (1H, s, OH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 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<sub>3</sub>O).



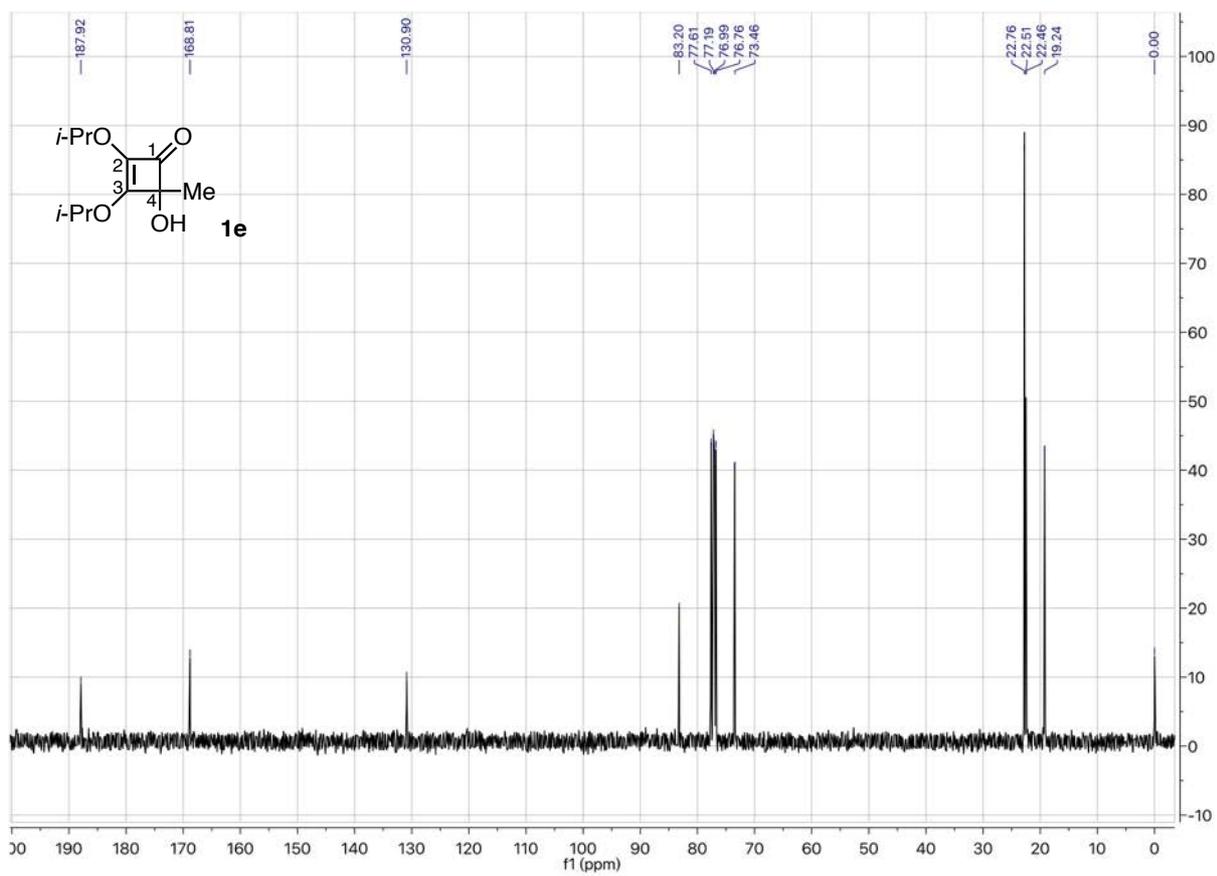
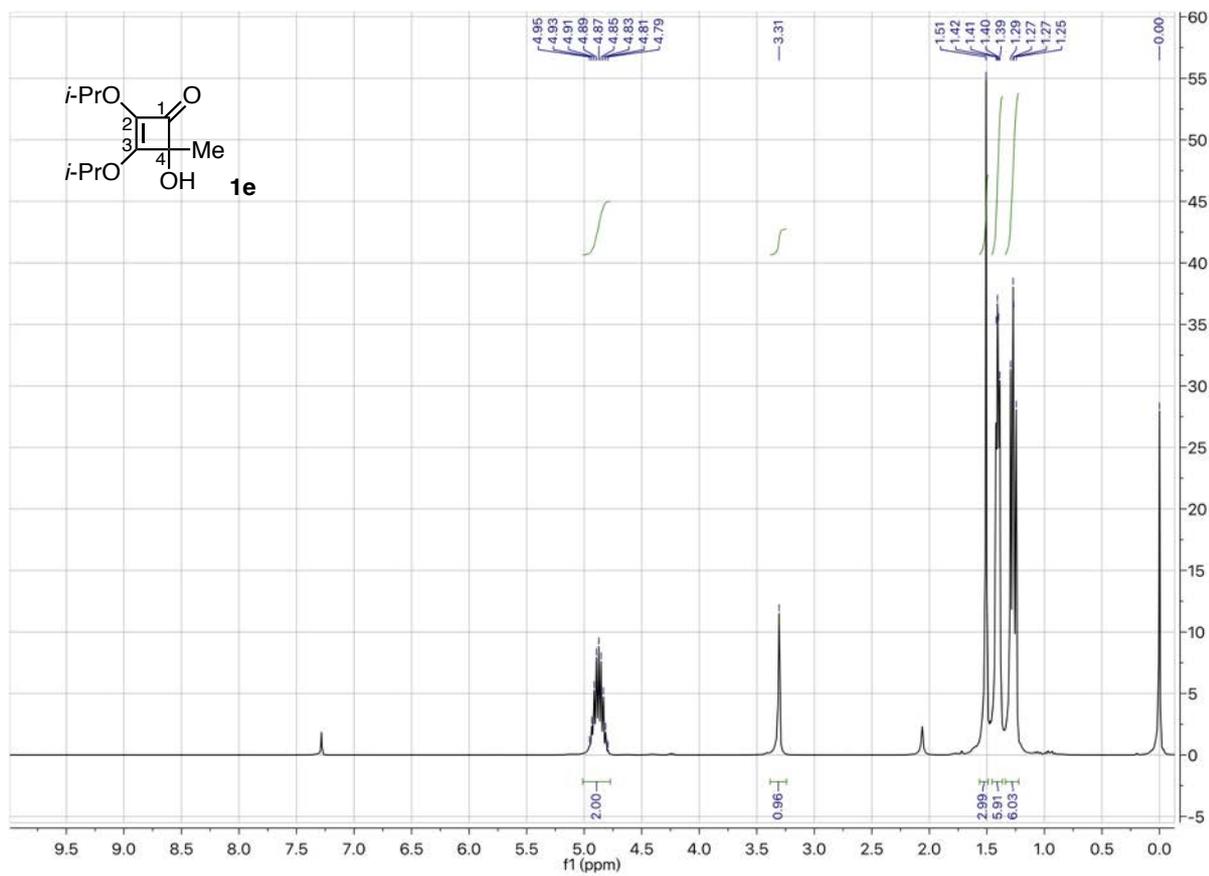


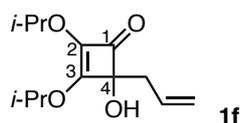
**2,3-Diethoxy-4-hydroxy-4-phenylcyclobut-2-en-1-one (1c)<sup>11a</sup>**: yellowish oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54-7.32 (5H, m, arom H), 4.42 (2H, q, *J* = 6.0 Hz, CH<sub>2</sub>O), 4.35 (2H, q, *J* = 6.0 Hz, CH<sub>2</sub>O), 3.55 (1H, s, OH), 1.36 (3H, t, *J* = 6.0 Hz, CH<sub>3</sub>), 1.33 (3H, t, *J* = 6.0 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 (CH<sub>2</sub>-O), 15.6, 15.1 (CH<sub>3</sub>).



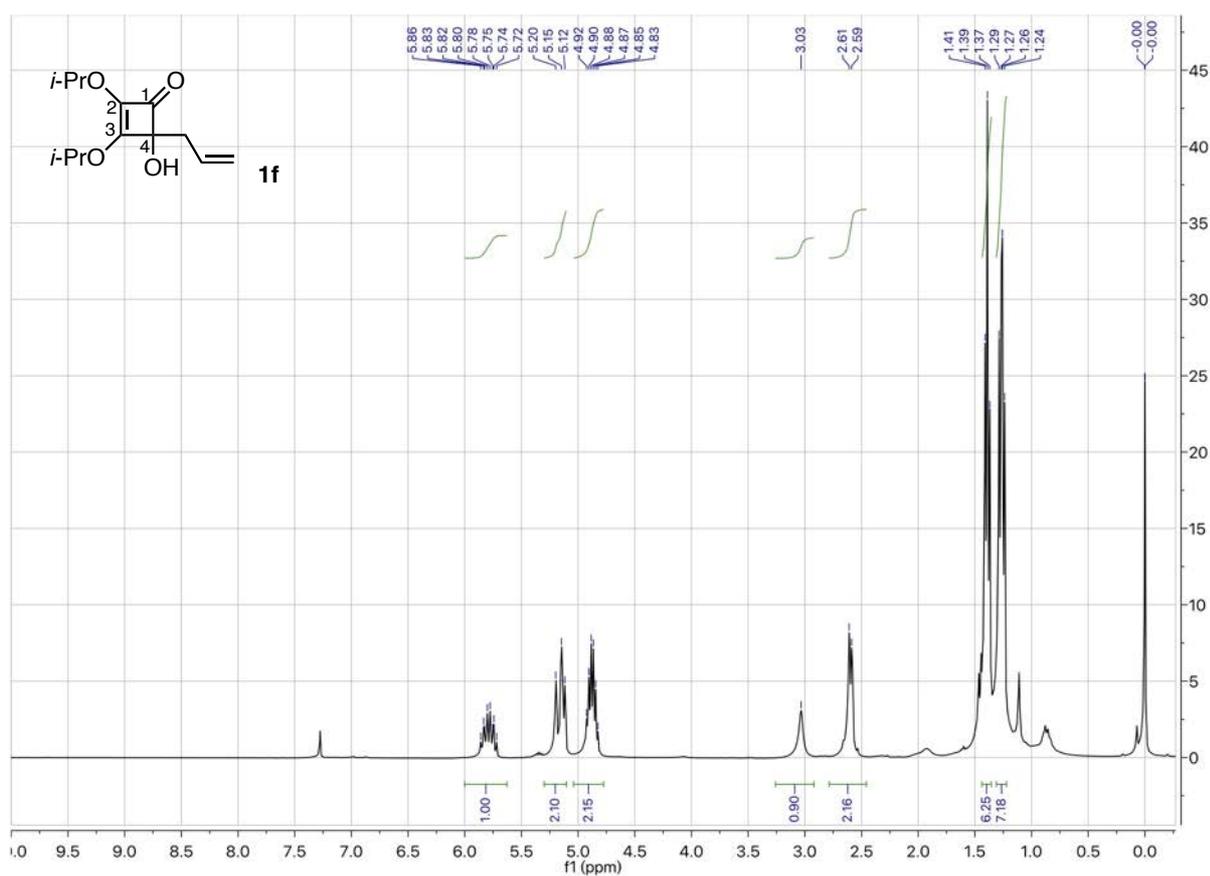


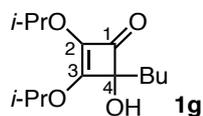
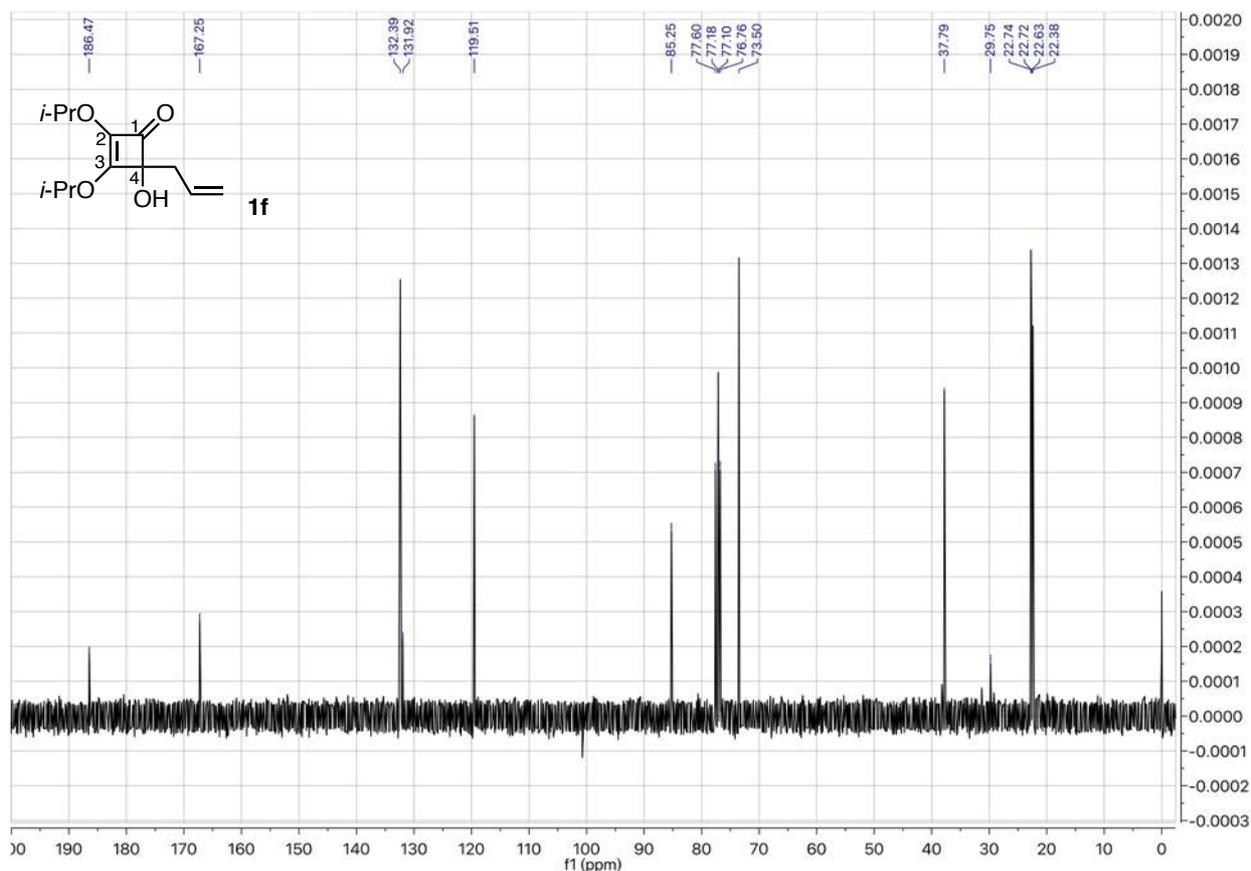
**4-Hydroxy-2,3-diisopropoxy-4-methylcyclobut-2-en-1-one (1e)<sup>9a</sup>:**  $R_f = 0.35$  (7:3 Et<sub>2</sub>O/hexane v/v); yield 72%; colorless solid; mp 35-36 °C; IR (CHCl<sub>3</sub>)  $\nu$  3370 (OH), 1766 (C=O), 1620 (>C=C<); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.88 (2H, sept,  $J = 6.1$  Hz, >CH-O  $\times$ 2), 3.31 (1H, s, OH), 1.51 (3H, s, CH<sub>3</sub>), 1.41 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.40 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.28 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.26 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>).



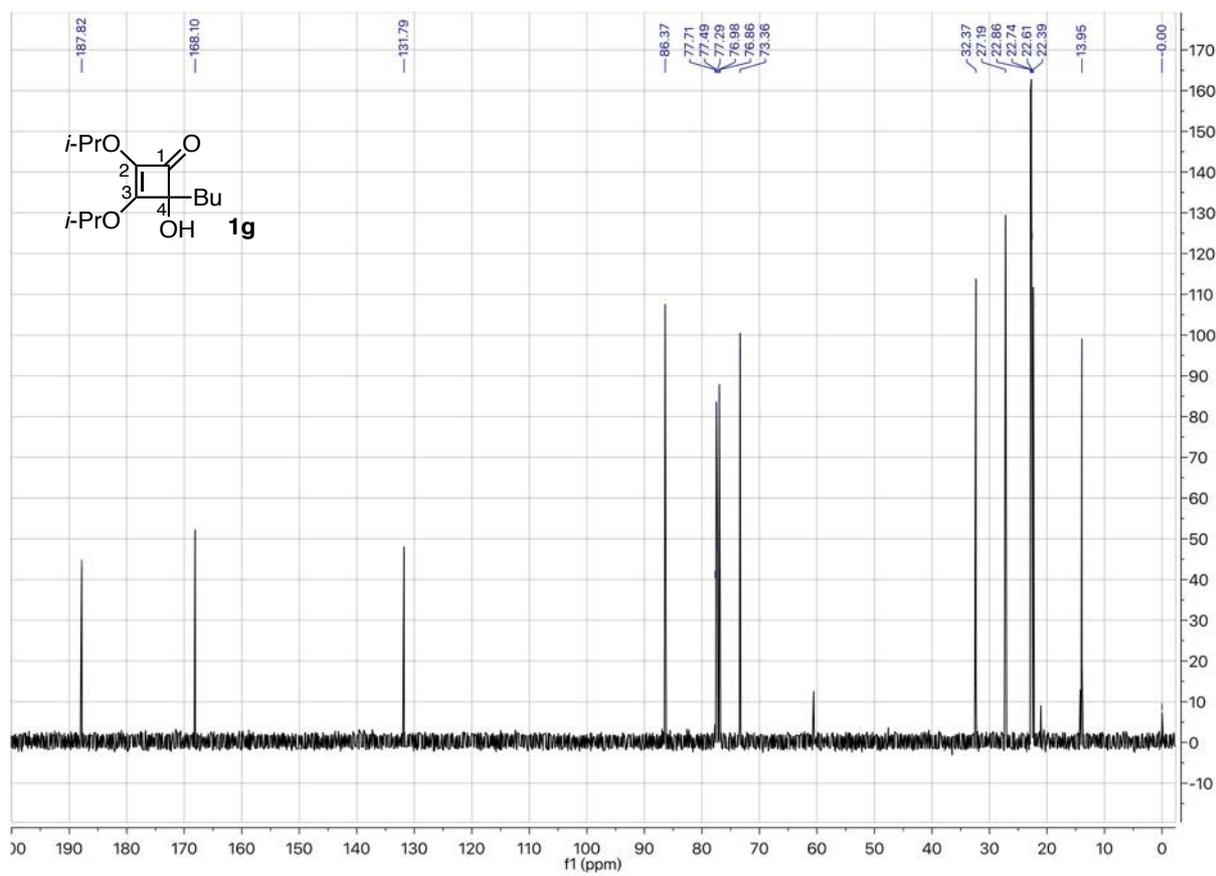
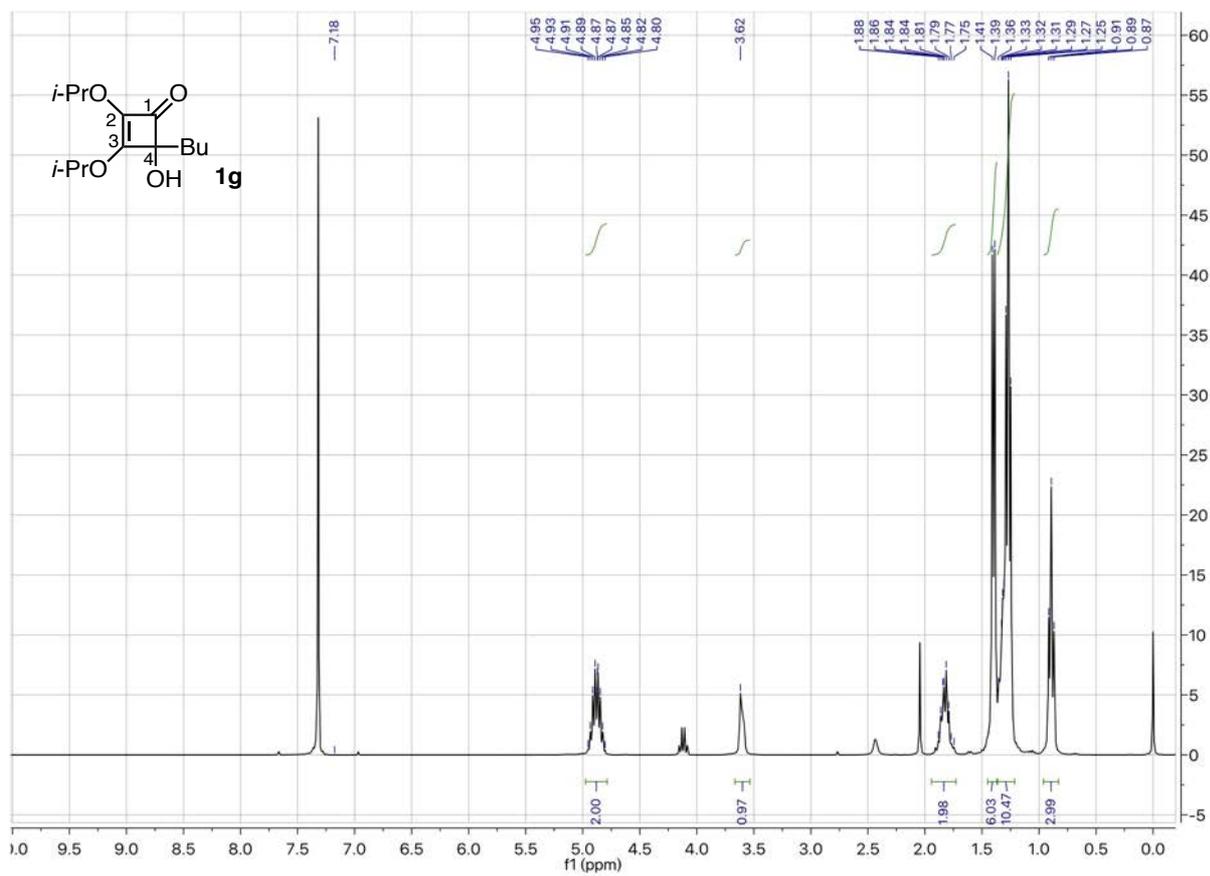


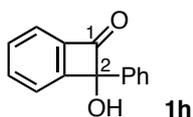
**4-Allyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1f):**  $R_f = 0.29$  (7:3 Et<sub>2</sub>O/hexane v/v); yellow solid; mp 37-38 °C; IR (CHCl<sub>3</sub>)  $\nu$  3373 (OH), 1767 (C=O), 1620 (>C=C<); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.86-5.72 (1H, m, -CH=), 5.17 (1H, d,  $J = 17.1$  Hz, =CH<sub>trans</sub>H<sub>cis</sub>), 5.13 (1H, d,  $J = 10.7$  Hz, =CH<sub>trans</sub>H<sub>cis</sub>), 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<sub>2</sub>-), 1.40 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.38 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.28 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.25 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  186.5 (C-1), 167.3 (C-3), 132.4 (-CH=), 131.9 (C-2), 119.5 (=CH<sub>2</sub>), 85.3 (C-4), 77.1, 73.5 (>CH-O), 37.8 (-CH<sub>2</sub>-), 22.74, 22.72, 22.6, 22.4 (CH<sub>3</sub>).



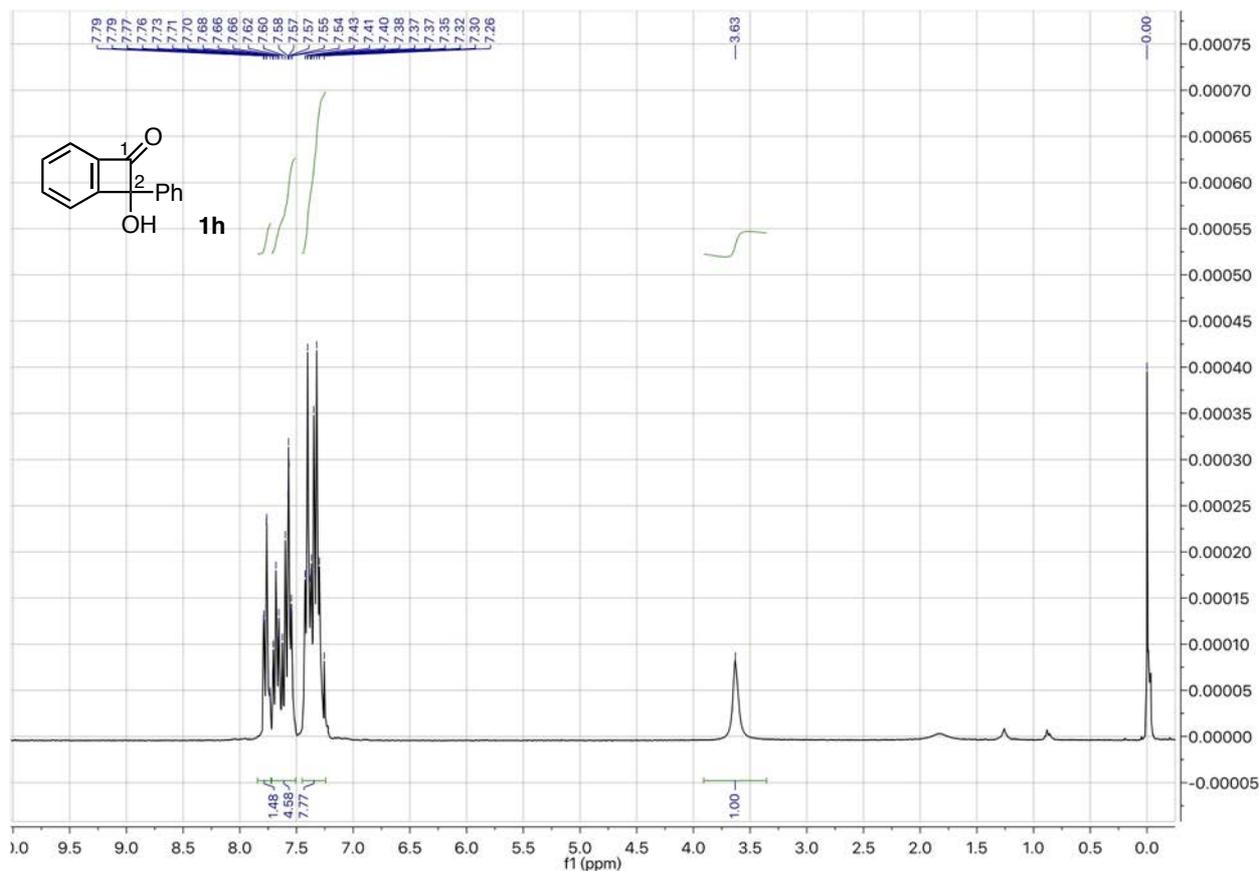


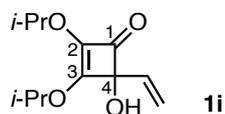
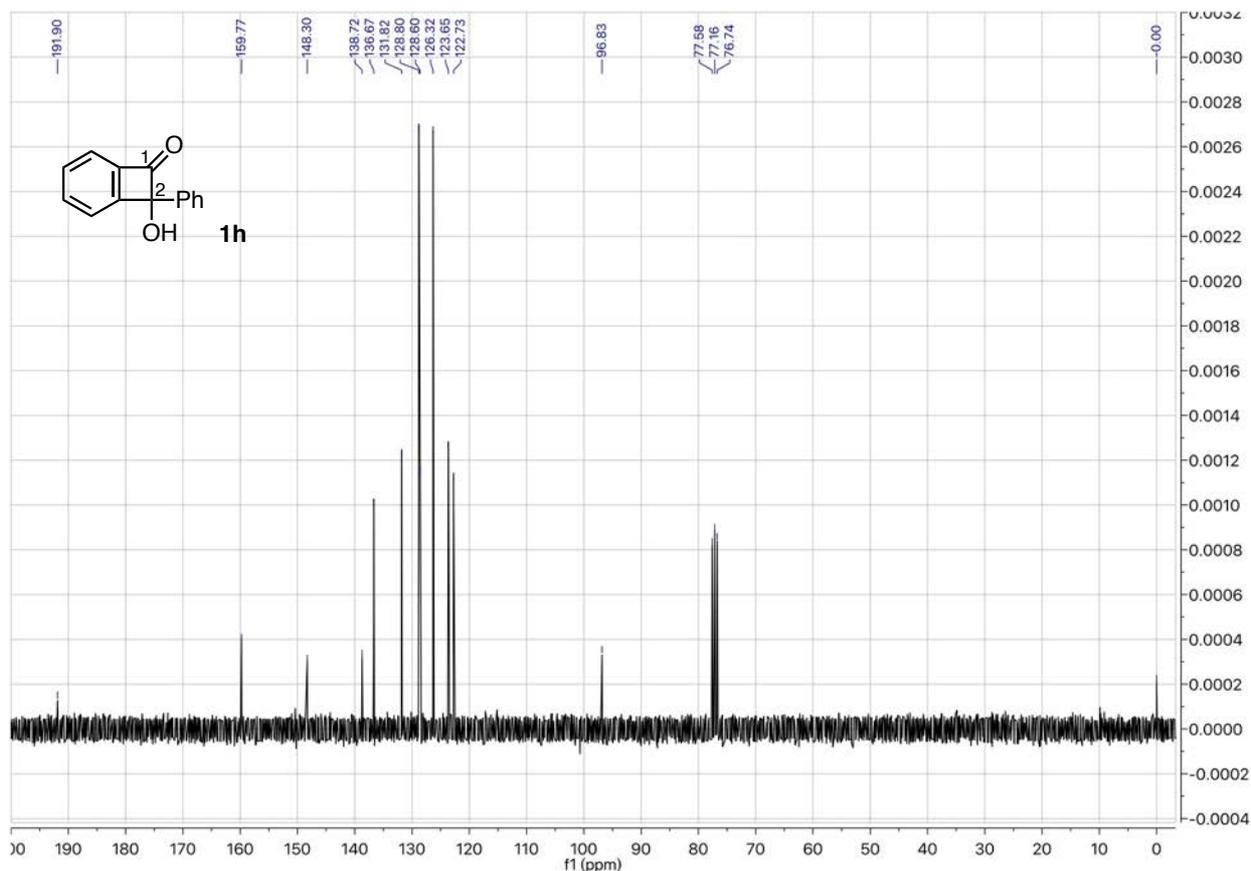
**4-Butyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1g)<sup>9a</sup>:**  $R_f = 0.15$  ( $\text{CHCl}_3$ ); yield 83%; yellow oil; IR ( $\text{CHCl}_3$ )  $\nu$  3370 (OH), 1765 (C=O), 1616 ( $>\text{C}=\text{C}<$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.89 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH}-\text{O}$ ), 4.86 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH}-\text{O}$ ), 3.62 (1H, s, OH), 1.88-1.75 (2H, m,  $-\text{CH}_2-$ ), 1.41 (6H, d,  $J = 6.1$  Hz,  $\text{CH}_3 \times 2$ ), 1.27 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.26 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.39-1.28 (4H, m,  $-\text{CH}_2- \times 2$ ), 0.89 (3H, t,  $J = 6.9$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  187.8 (C-1), 168.1 (C-3), 131.8 (C-2), 86.4 (C-4), 76.99, 73.4 ( $>\text{CH}-\text{O}$ ), 32.4, 27.2, 22.9 ( $-\text{CH}_2-$ ), 22.7 (2C), 22.6, 22.4, 13.95 ( $\text{CH}_3$ ).



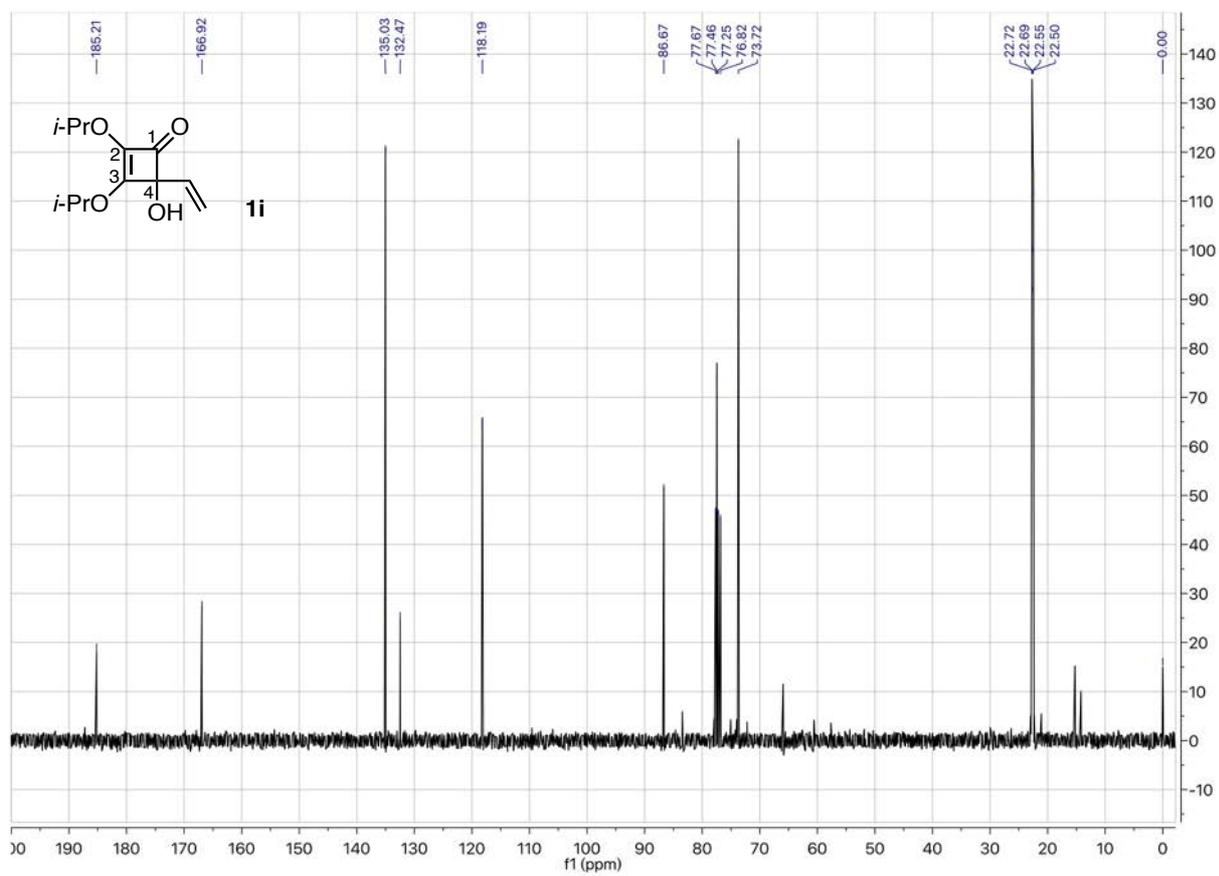
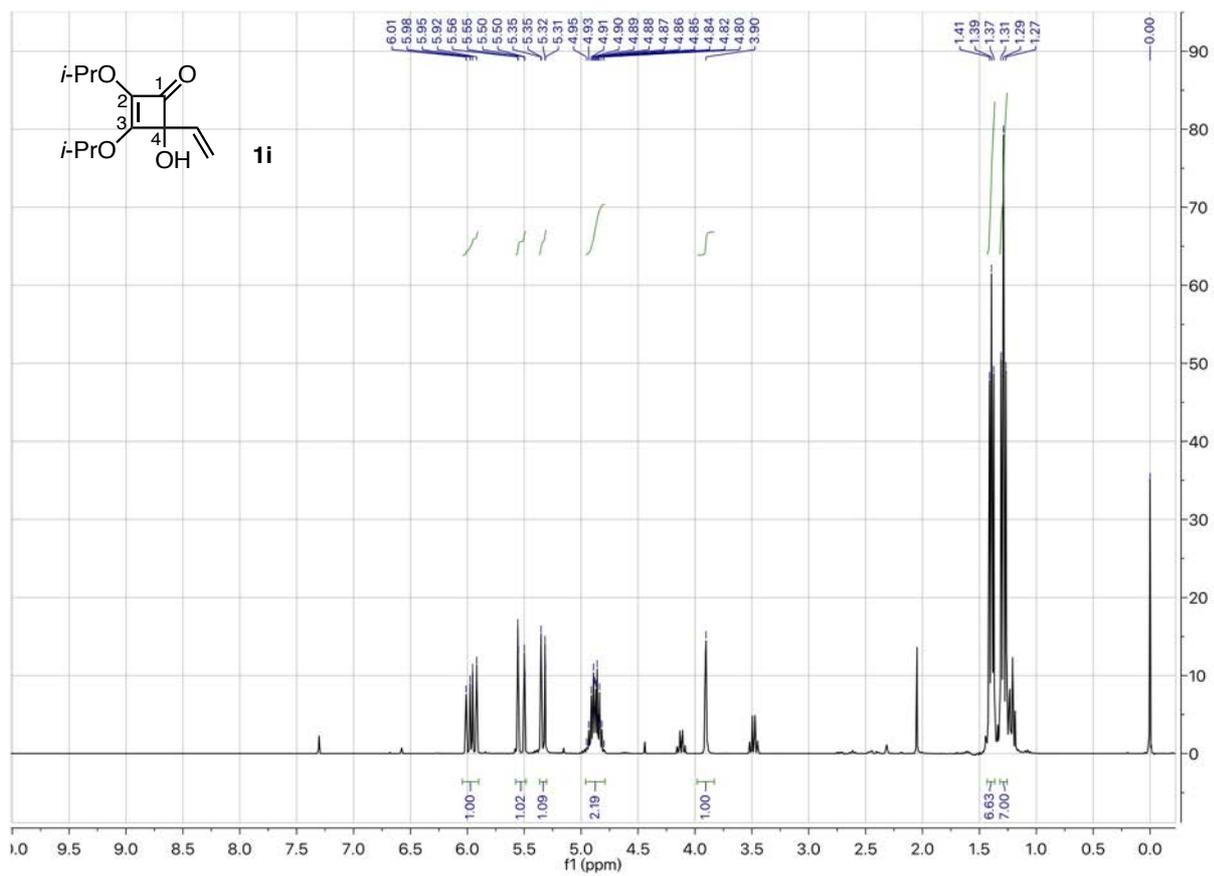


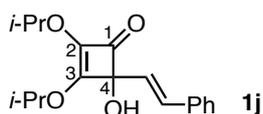
**2-Hydroxy-2-phenylbenzocyclobuten-1(2H)-one (1h)**<sup>18</sup>:  $R_f = 0.09$  ( $\text{CHCl}_3$ ); colorless microcrystals (from  $\text{CHCl}_3$ /hexane); mp 102-103 °C; IR (KBr)  $\nu$  3400-3200 (OH), 1760 ( $>\text{C}=\text{O}$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.73 (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);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9 ( $>\text{C}=\text{O}$ ), 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 ( $\text{C}-\text{OH}$ ).



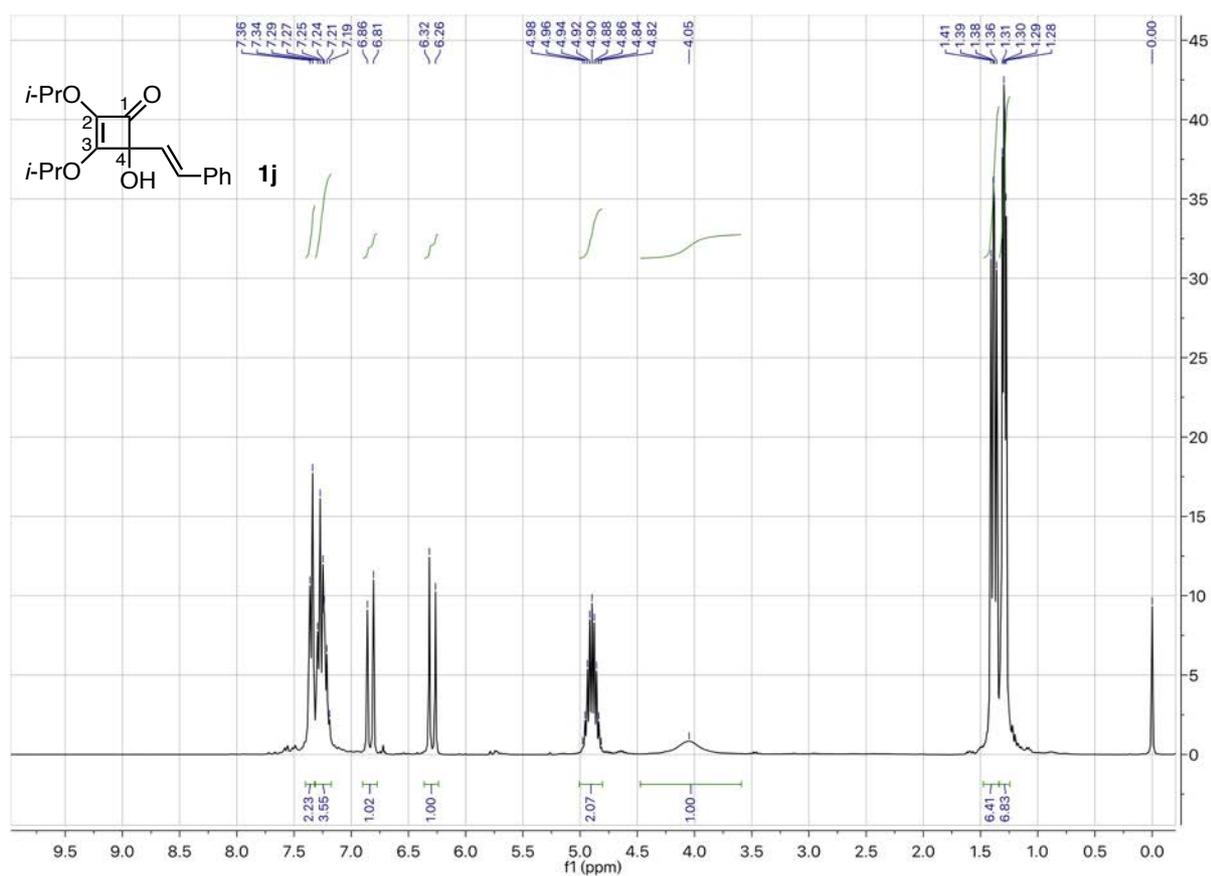


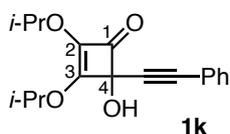
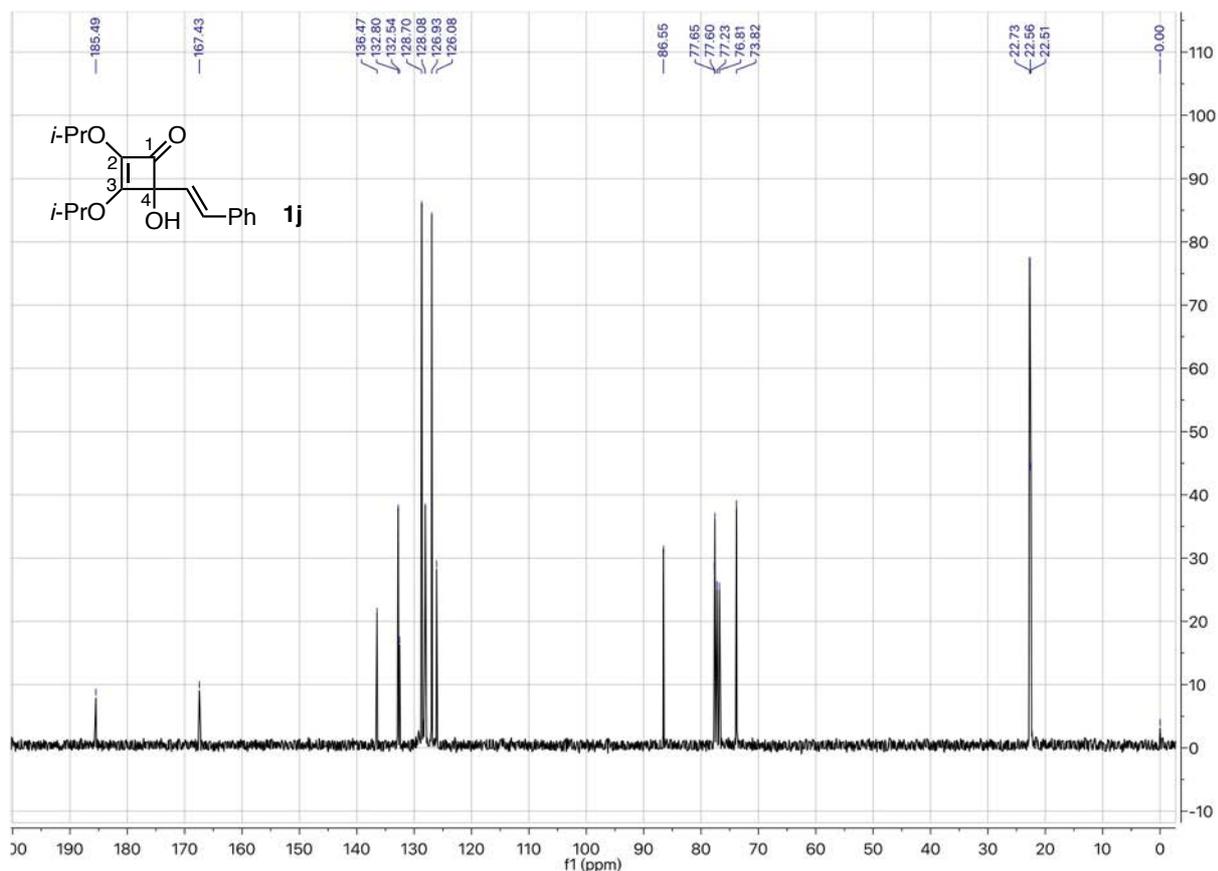
**4-Hydroxy-2,3-diisopropoxy-4-vinylcyclobut-2-en-1-one (1i)**<sup>25</sup>:  $R_f = 0.47$  (7:3 Et<sub>2</sub>O/hexane v/v); yield 60%; yellow oil; IR (CHCl<sub>3</sub>)  $\nu$  3375 (OH), 1768 (C=O), 1619 (>C=C<); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  5.97 (1H, dd,  $J = 17.3, 10.7$  Hz, -CH=), 5.53 (1H, dd,  $J = 17.3, 0.9$  Hz, =CH<sub>trans</sub>H<sub>cis</sub>), 5.34 (1H, dd,  $J = 10.7, 0.9$  Hz, =CH<sub>trans</sub>H<sub>cis</sub>), 4.95-4.80 (2H, m, >CH-O), 3.90 (1H, s, OH), 1.40 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.38 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.30 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.28 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  185.2 (C-1), 166.9 (C-3), 135.0 (-CH=), 132.5 (C-2), 118.2 (=CH<sub>2</sub>), 86.7 (C-4), 77.5, 73.7 (>CH-O), 22.7, 22.69, 22.55, 22.5 (CH<sub>3</sub>).



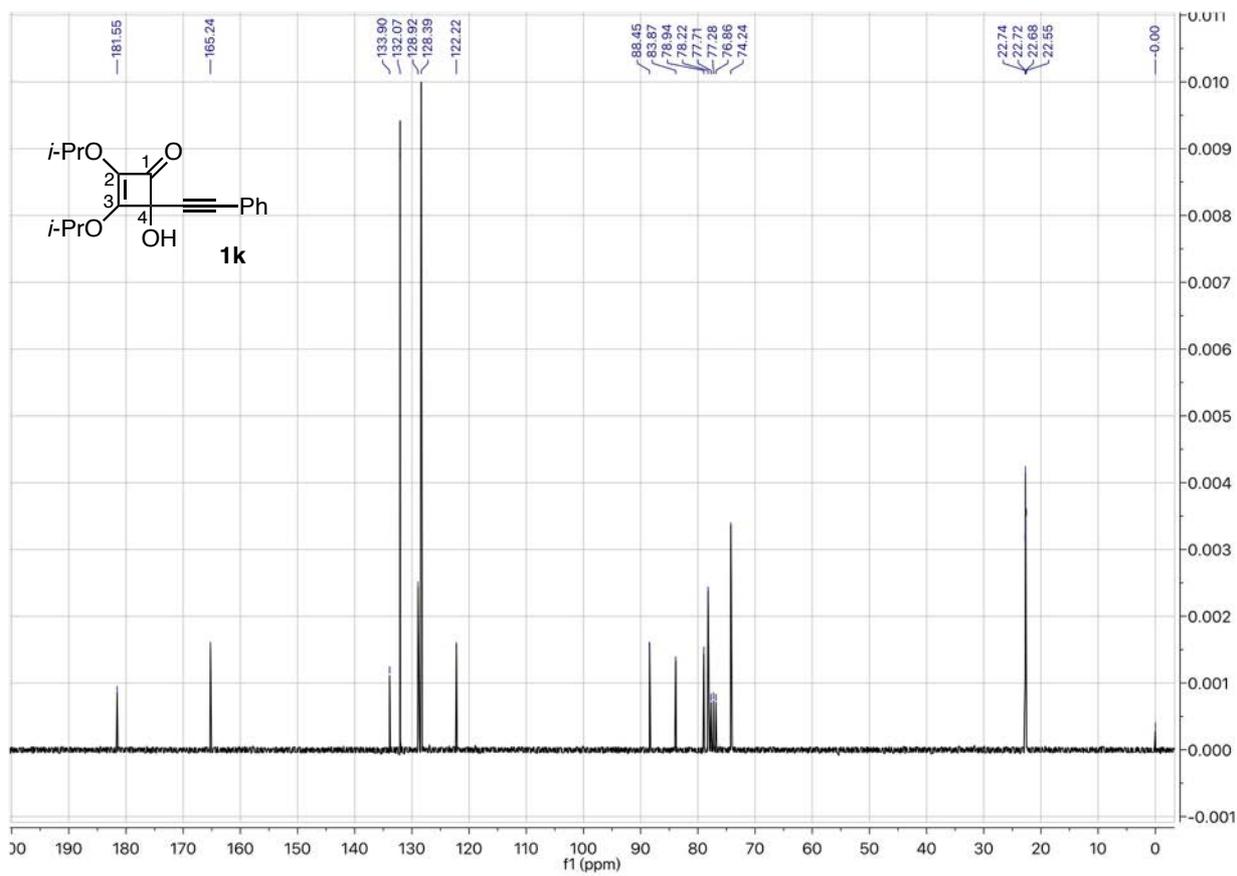
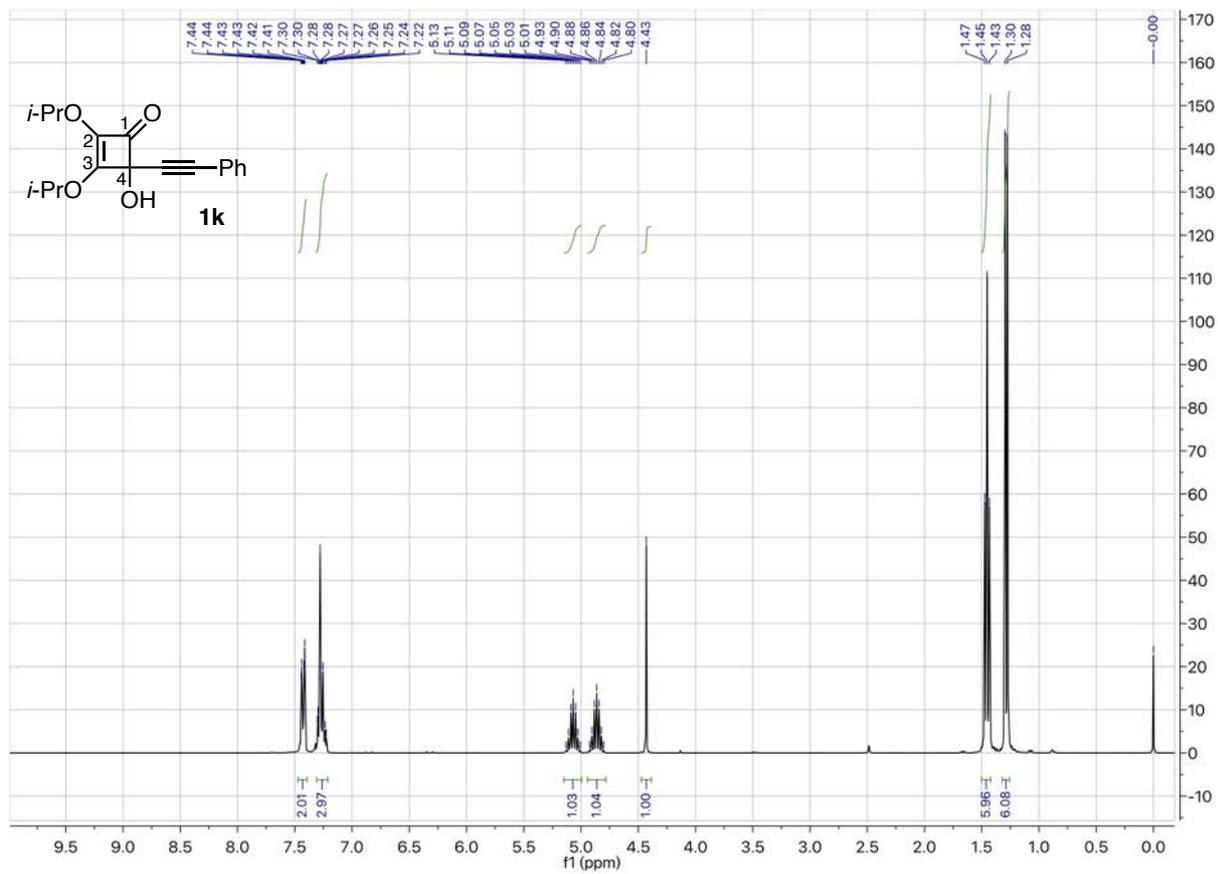


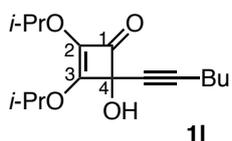
**(*E*)-4-Hydroxy-2,3-diisopropoxy-4-styrylcyclobut-2-en-1-one (1j):**  $R_f = 0.55$  (7:3 Et<sub>2</sub>O/hexane v/v); yellow solid; mp 83-85 °C; IR (CHCl<sub>3</sub>)  $\nu$  3362 (OH), 1767 (C=O), 1618 (>C=C<); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.33 (2H, m, arom H), 7.29-7.21 (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  $\times 2$ ), 4.05 (1H, s, OH), 1.40 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.37 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.30 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.29 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>).



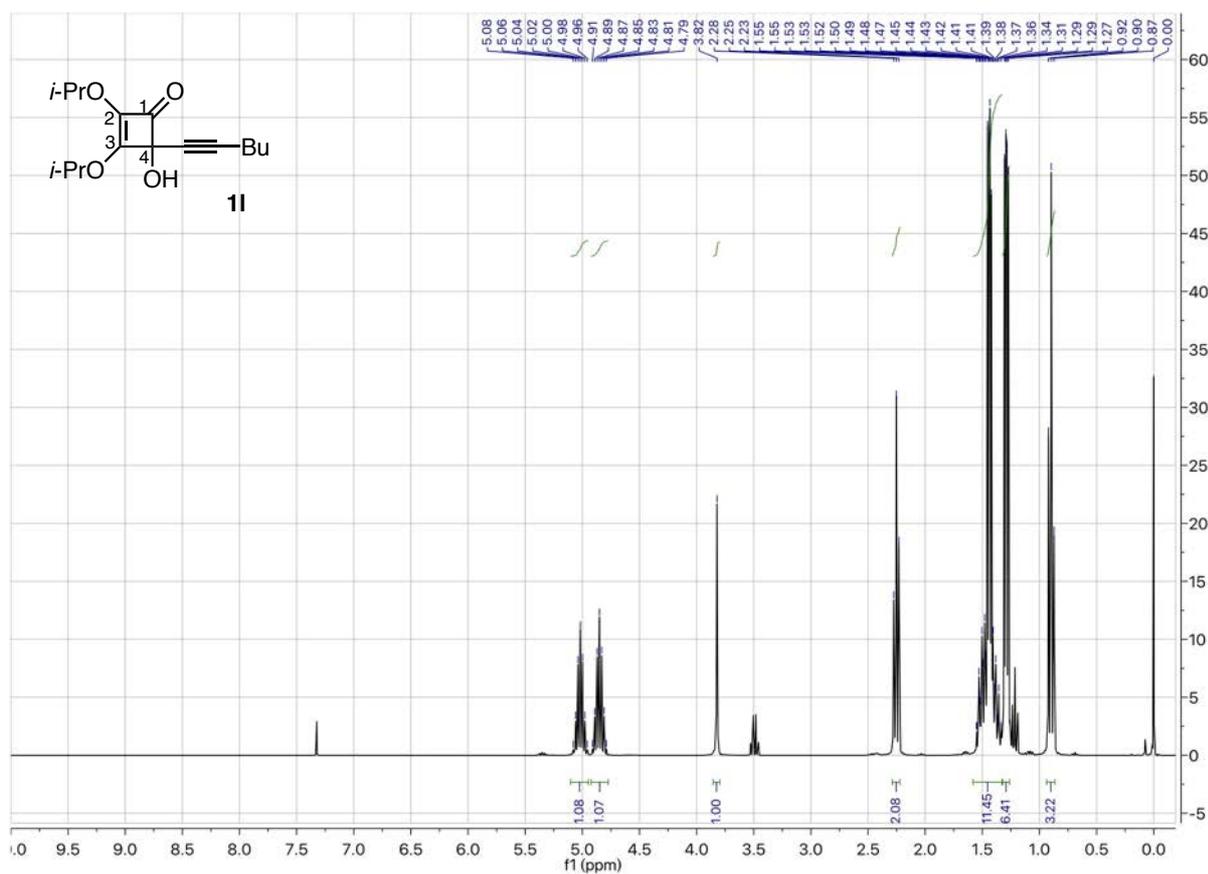


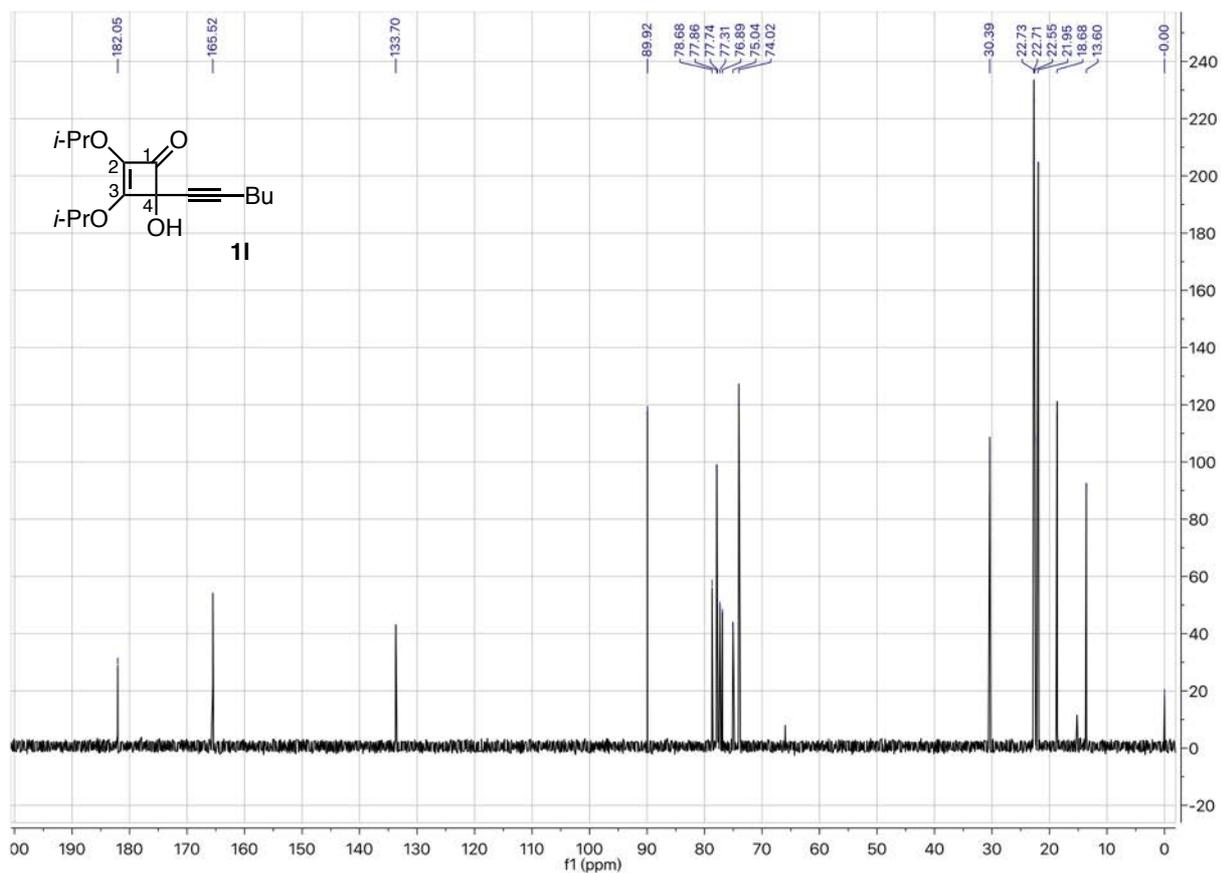
4-Hydroxy-2,3-diisopropoxy-4-(phenylethynyl)cyclobut-2-en-1-one (**1k**)<sup>9a</sup>:  $R_f = 0.49$  (7:3 Et<sub>2</sub>O/hexane v/v); yellow microcrystals (from Et<sub>2</sub>O-hexane); mp 104-105 °C (lit,<sup>5b</sup> mp 73-7 °C from CH<sub>2</sub>Cl<sub>2</sub>-hexane); IR (CHCl<sub>3</sub>)  $\nu$  3306 (OH), 2226 (C≡C), 1774 (C=O), 1626 (>C=C<); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>), 1.44 (3H, d,  $J = 6.1$  Hz, CH<sub>3</sub>), 1.28 (6H, d,  $J = 6.1$  Hz, CH<sub>3</sub> ×2); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>3</sub>).



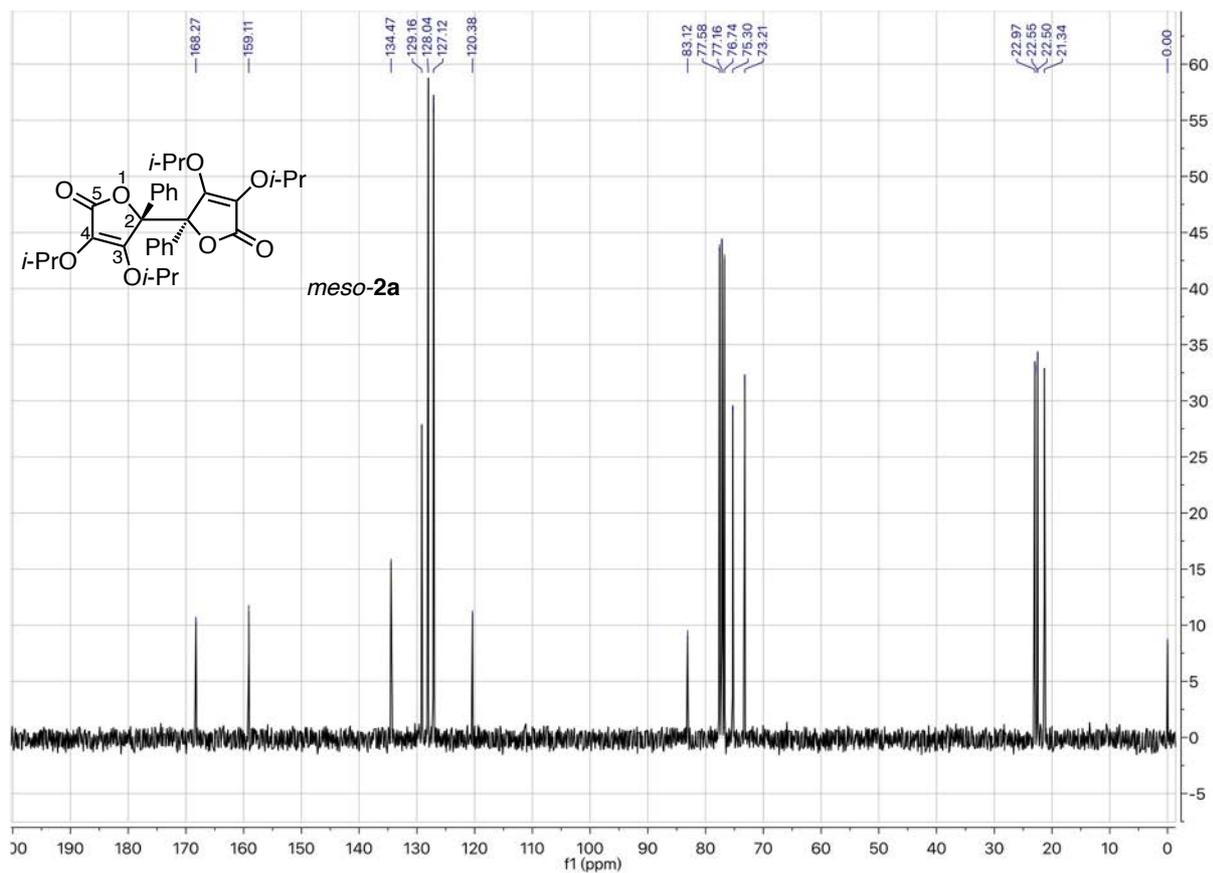
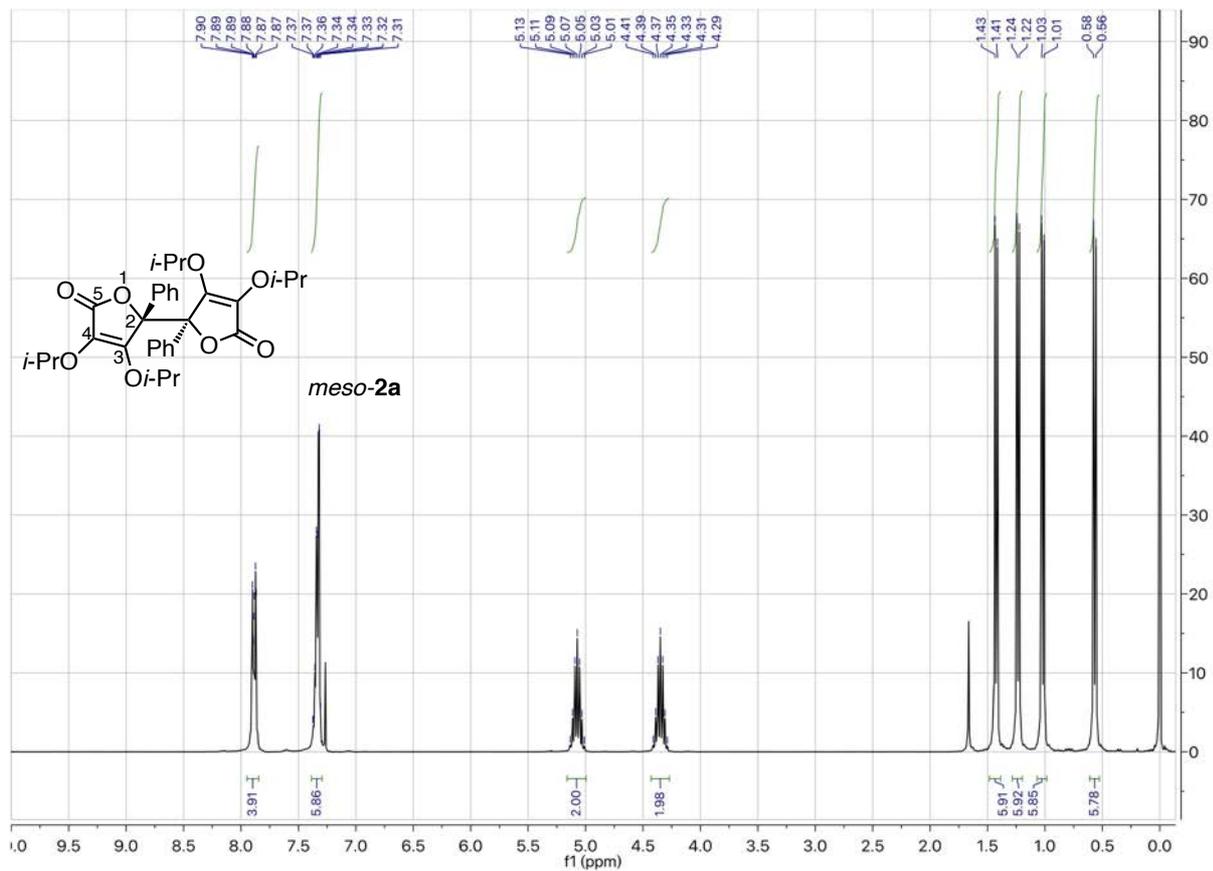


**4-(Hex-1-yn-1-yl)-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (11)<sup>9a</sup>:**  $R_f = 0.20$  ( $\text{CHCl}_3$ ); yield 98%; colorless oil; IR ( $\text{CHCl}_3$ )  $\nu$  3342 (OH), 2233 ( $\text{C}\equiv\text{C}$ ), 1774 ( $\text{C}=\text{O}$ ), 1614 ( $>\text{C}=\text{C}<$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.02 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH}-\text{O}$ ), 4.85 (1H, sept,  $J = 6.1$  Hz,  $>\text{CH}-\text{O}$ ), 3.82 (1H, s, OH), 2.25 (2H, t,  $J = 7.0$  Hz,  $-\text{CH}_2-$ ), 1.55-1.33 (4H, m,  $-\text{CH}_2-$   $\times 2$ ), 1.44 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.43 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.30 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 1.28 (3H, d,  $J = 6.1$  Hz,  $\text{CH}_3$ ), 0.90 (3H, t,  $J = 7.0$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  182.1 (C-1), 165.5 (C-3), 133.7 (C-2), 89.9 (C-4), 78.7 ( $\text{C}\equiv\text{C}$ ), 77.9 ( $>\text{CH}-\text{O}$ ), 75.0 ( $\text{C}\equiv\text{C}$ ), 74.0 ( $>\text{CH}-\text{O}$ ), 30.4 ( $-\text{CH}_2-$ ), 22.73 (2C), 22.71, 22.6 ( $\text{CH}_3$ ), 22.0, 18.7 ( $-\text{CH}_2-$ ), 13.6 ( $\text{CH}_3$ ).

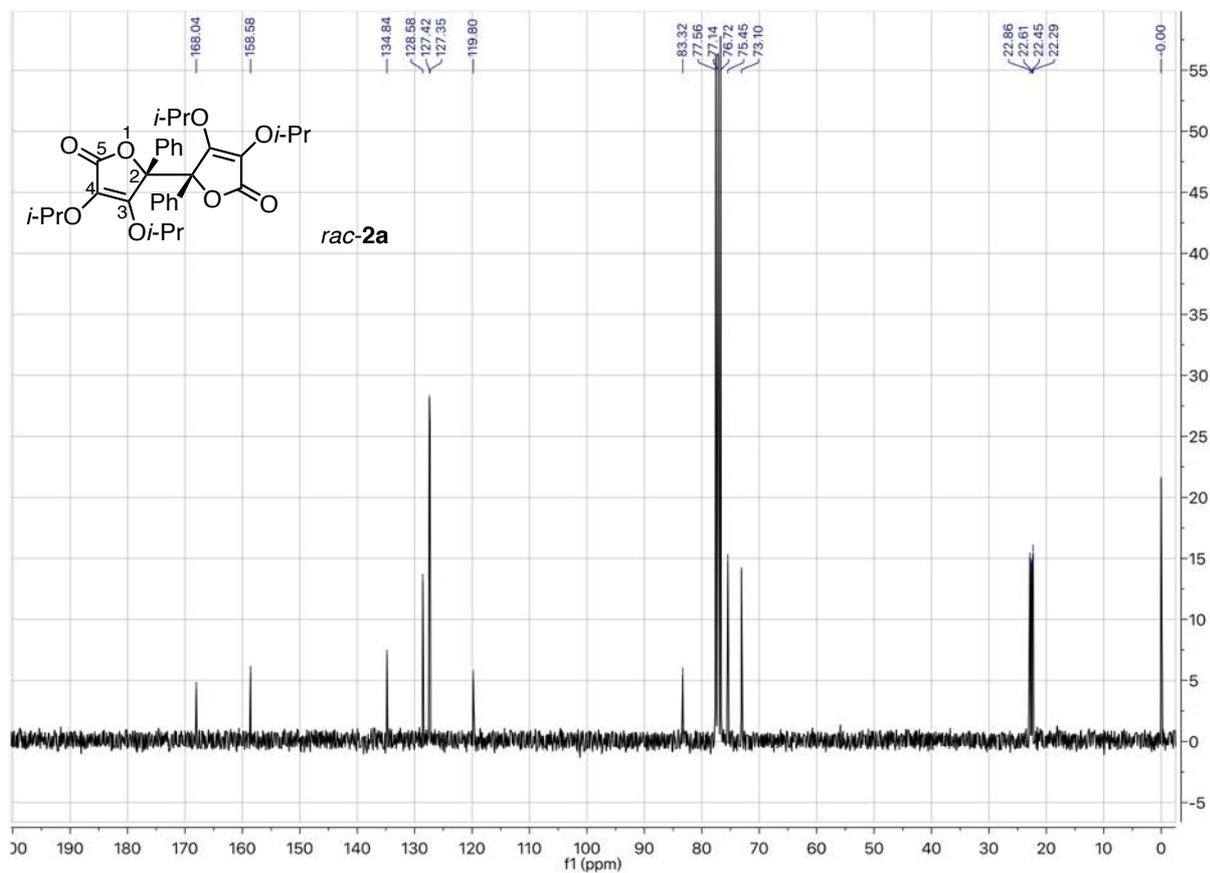
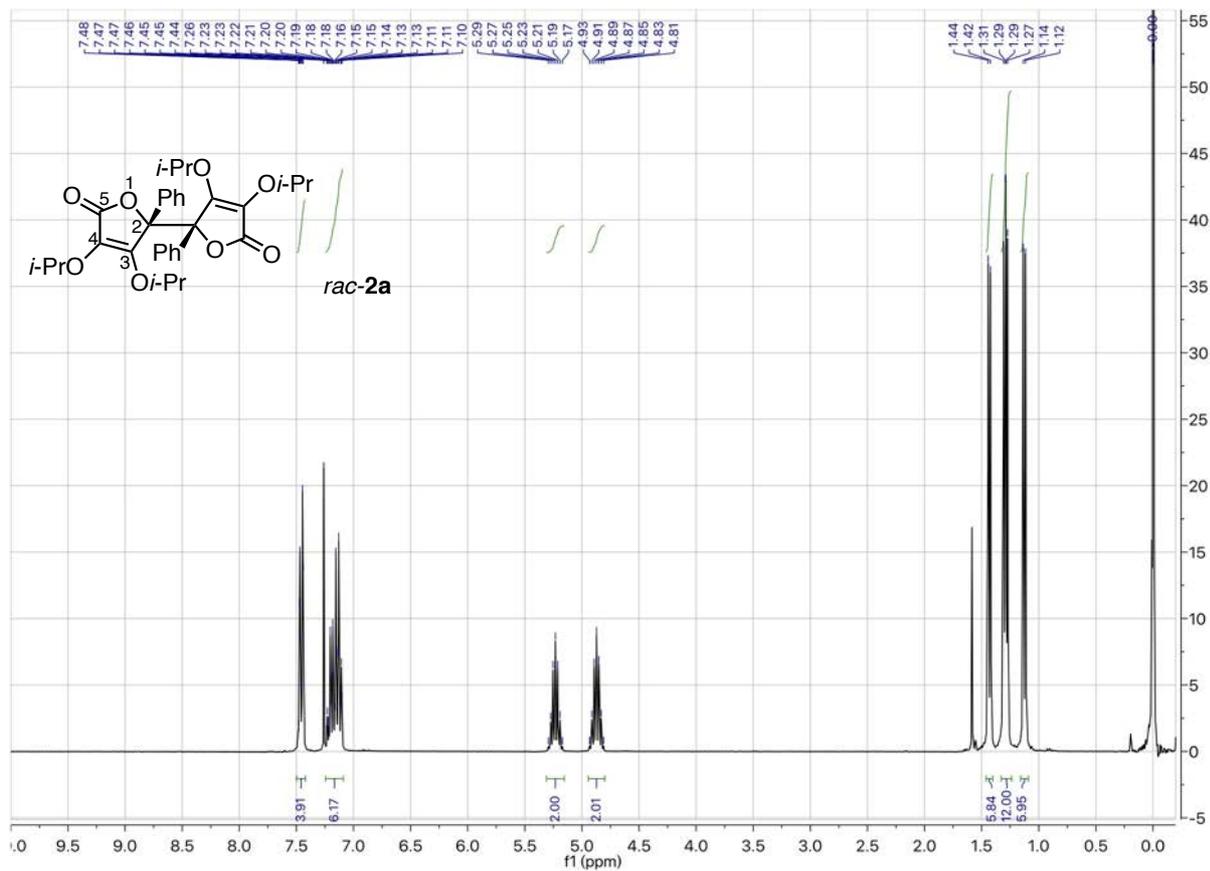




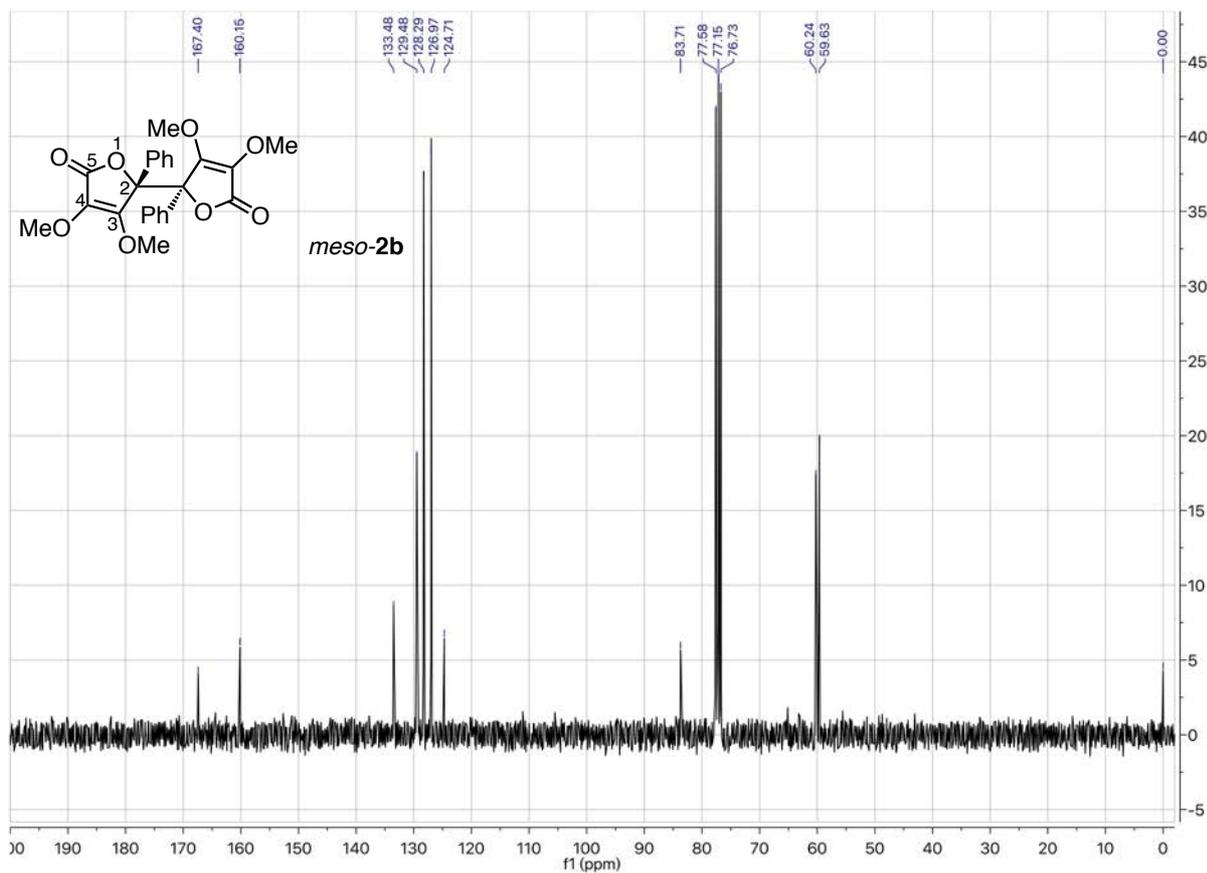
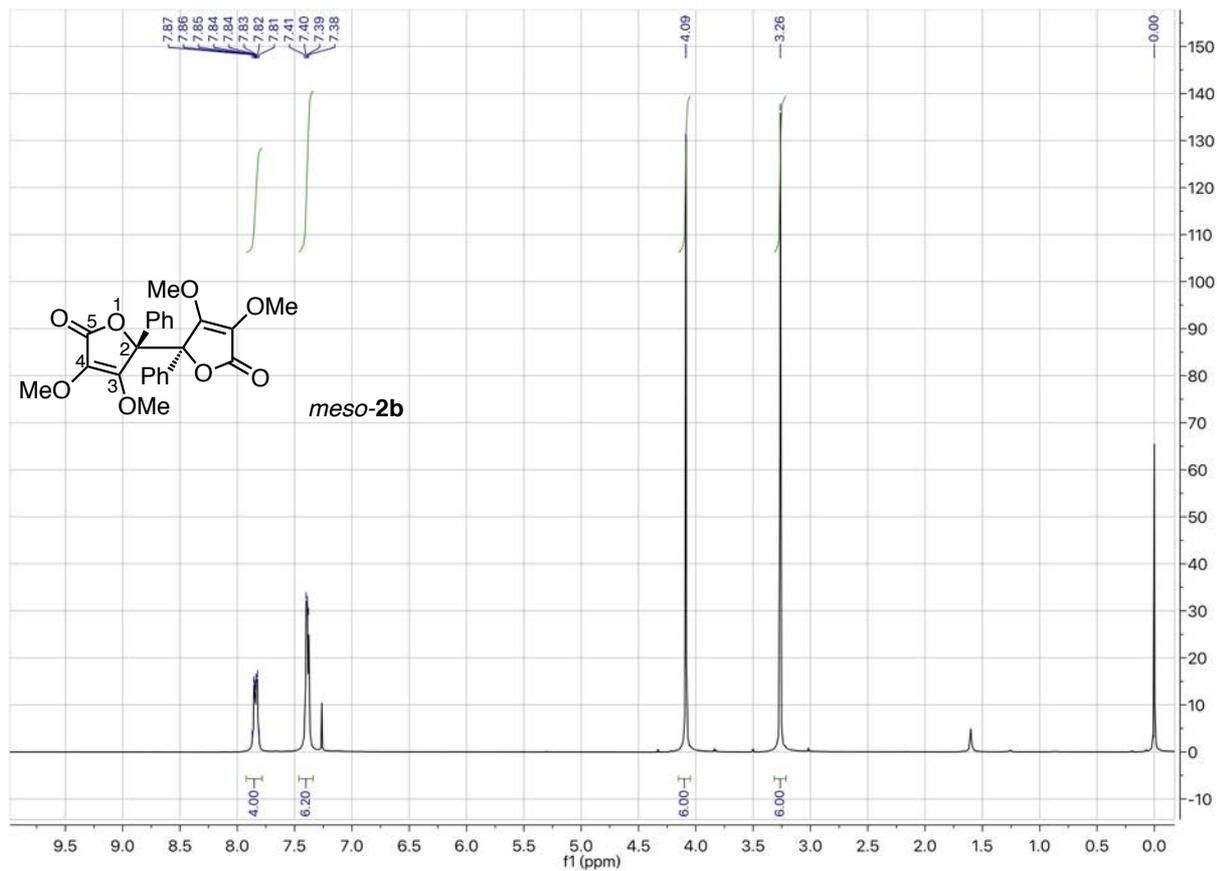
***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2a):**



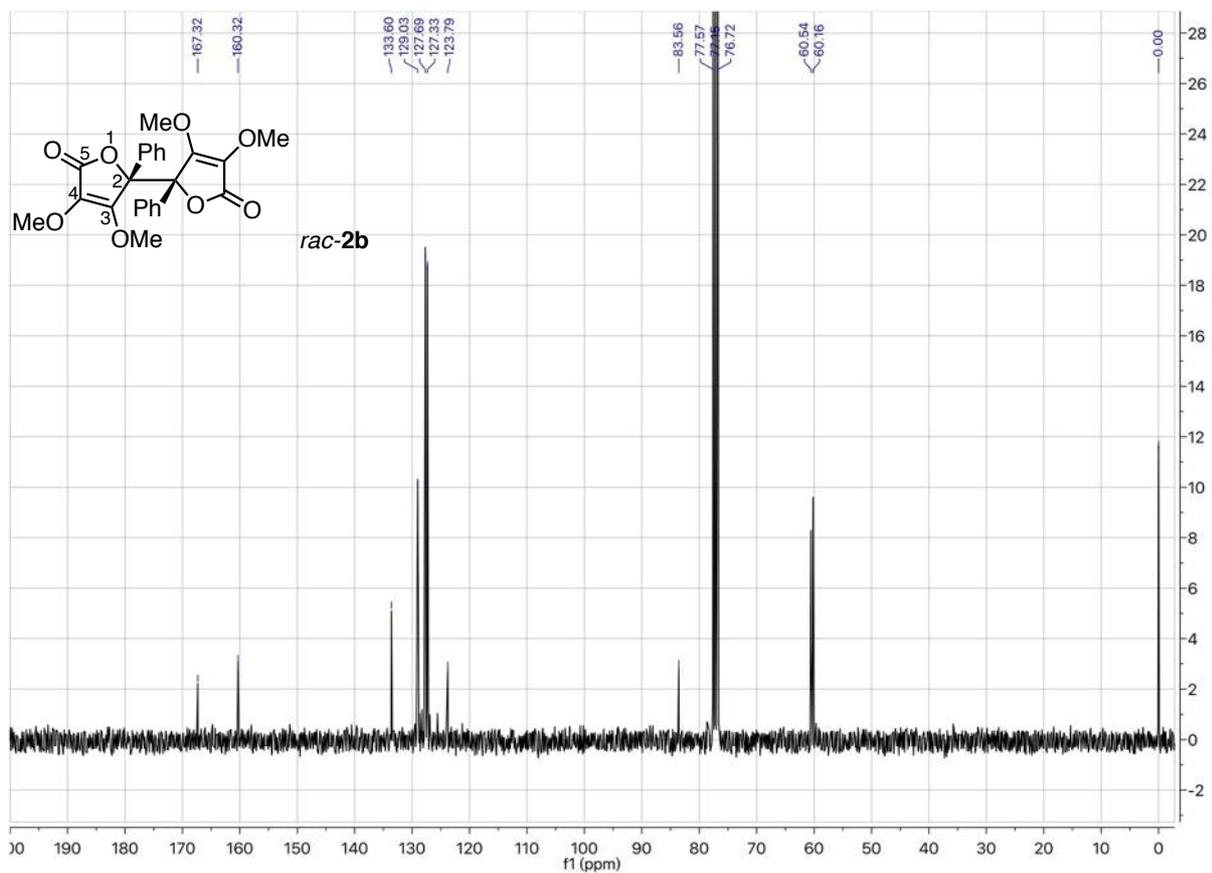
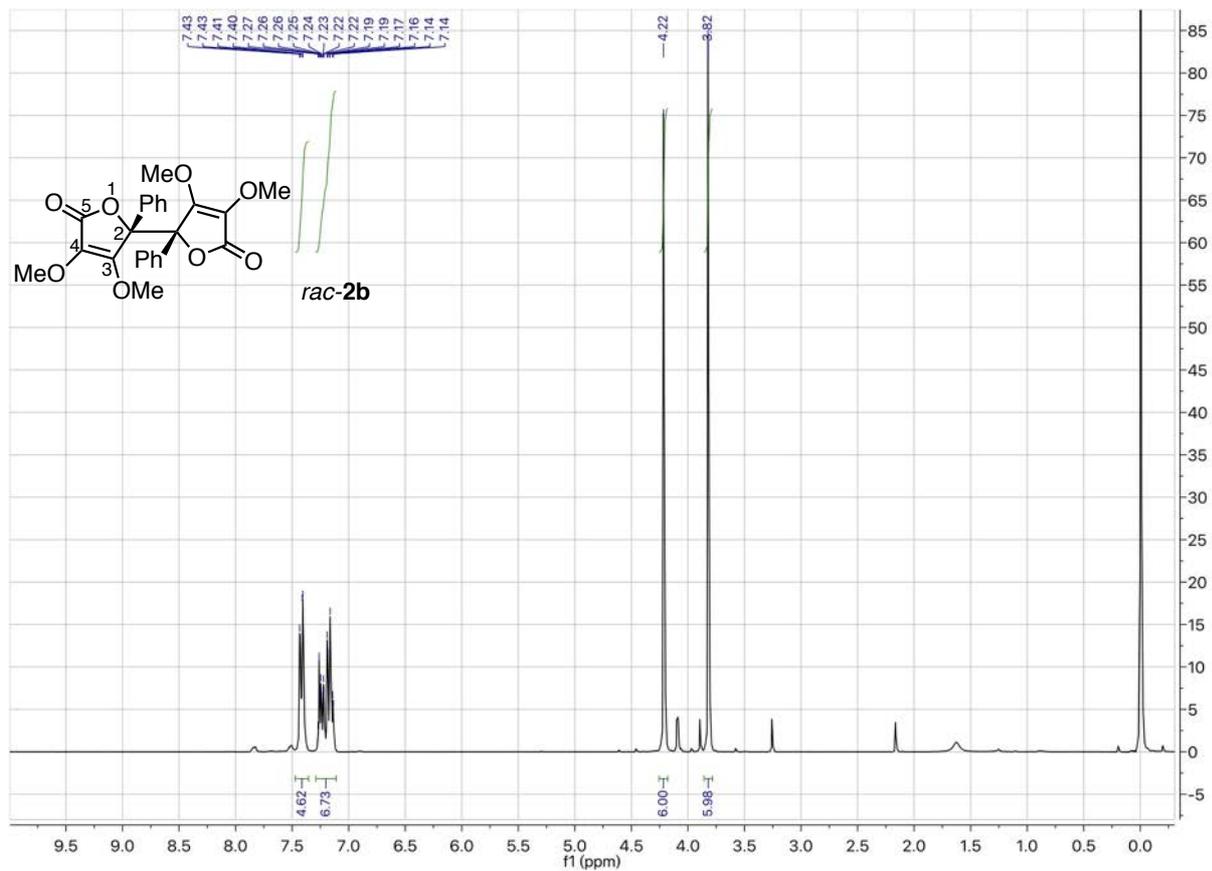
*rac*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2a):



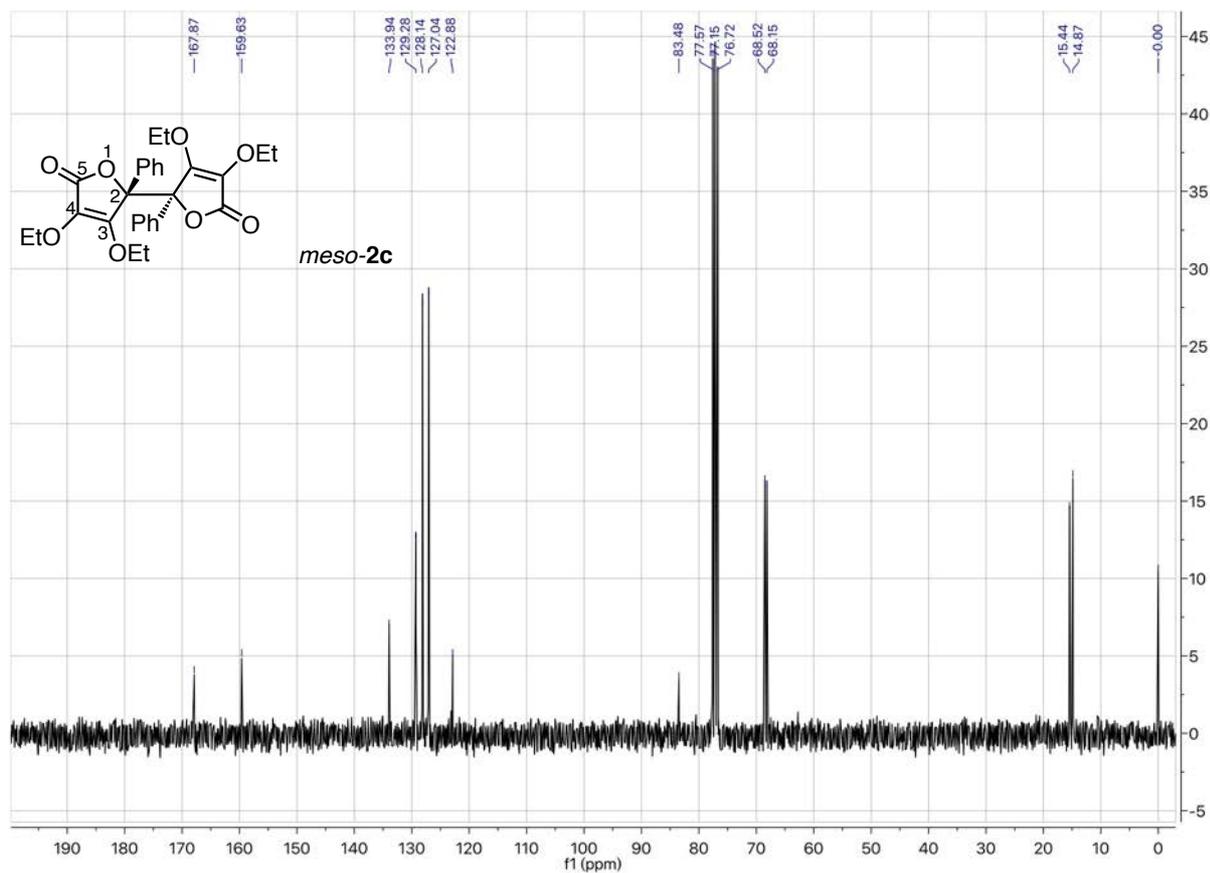
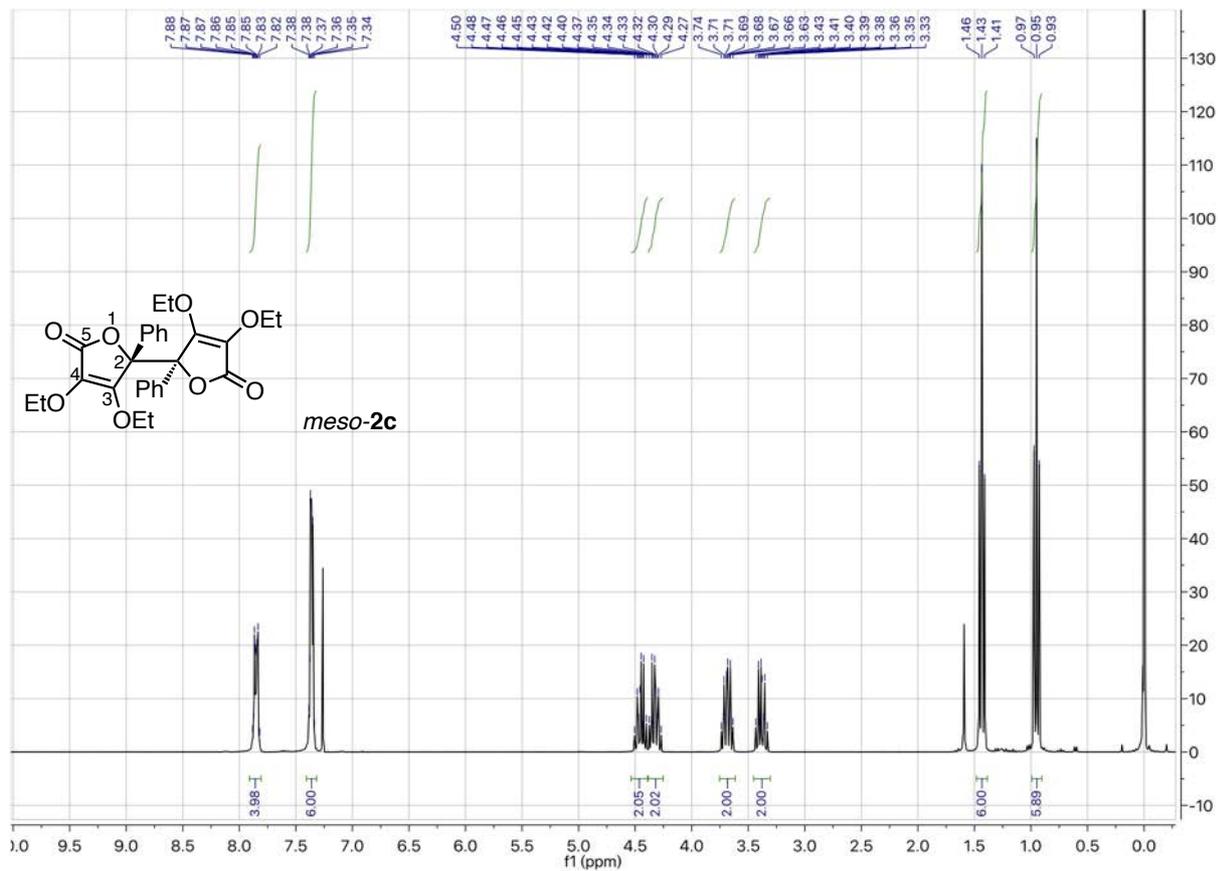
*meso*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2b):



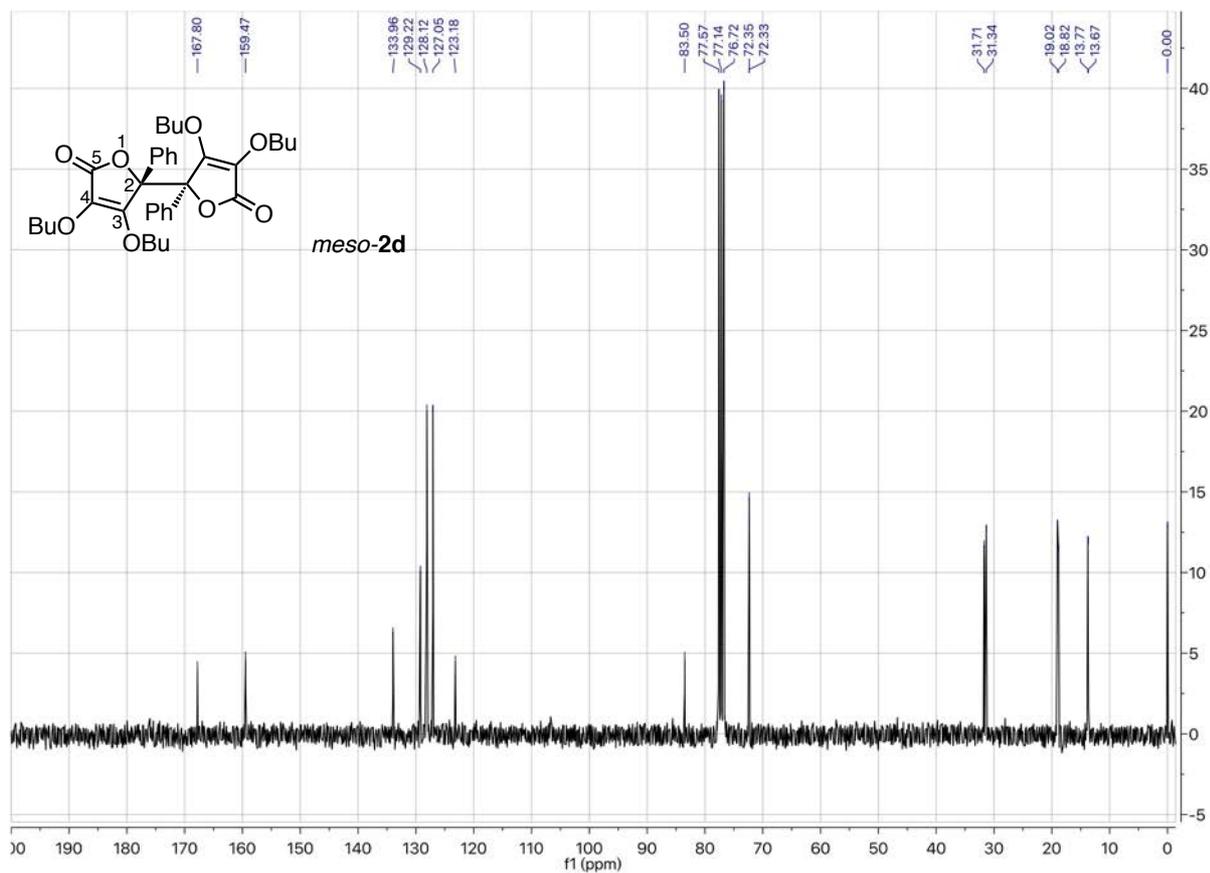
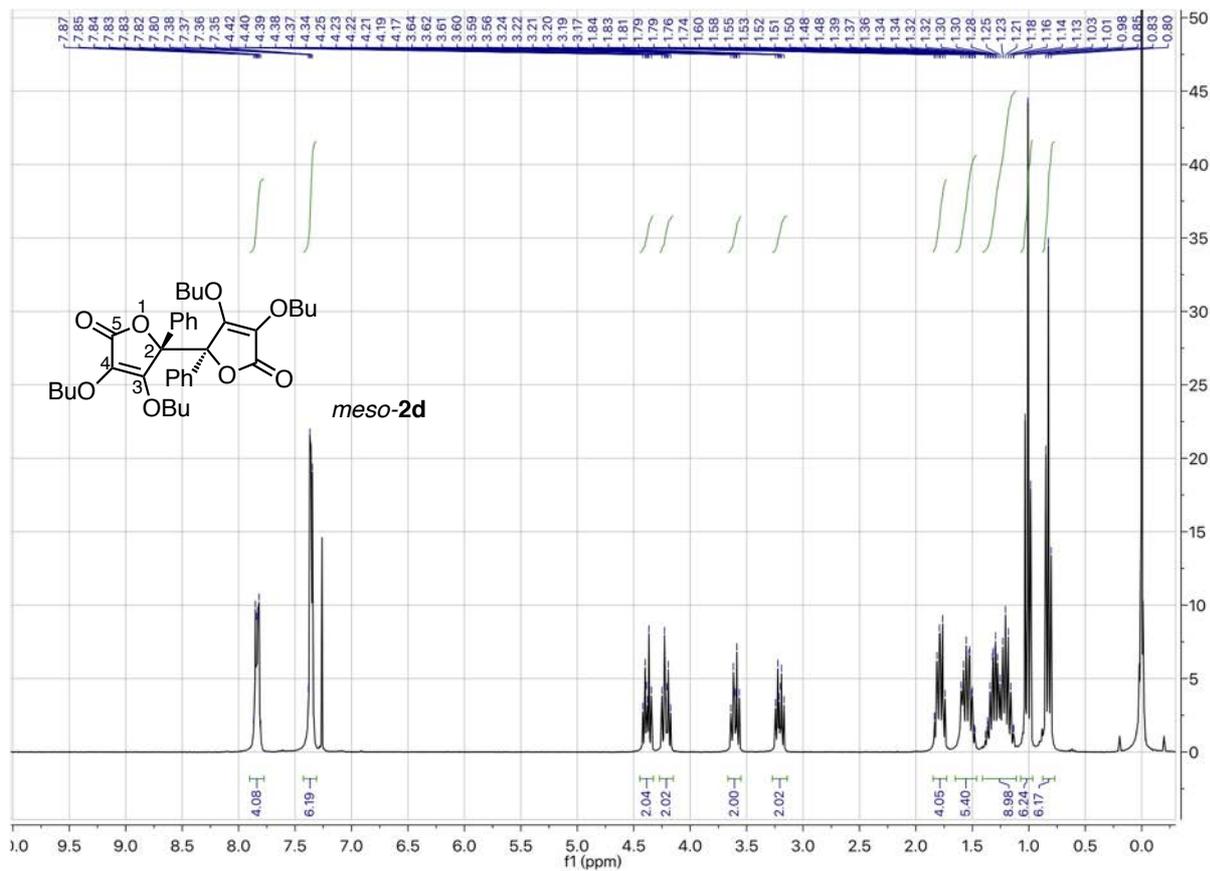
*rac*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2b):

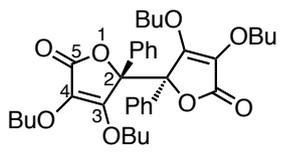


*meso*-3,3',4,4'-Tetraethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2c):

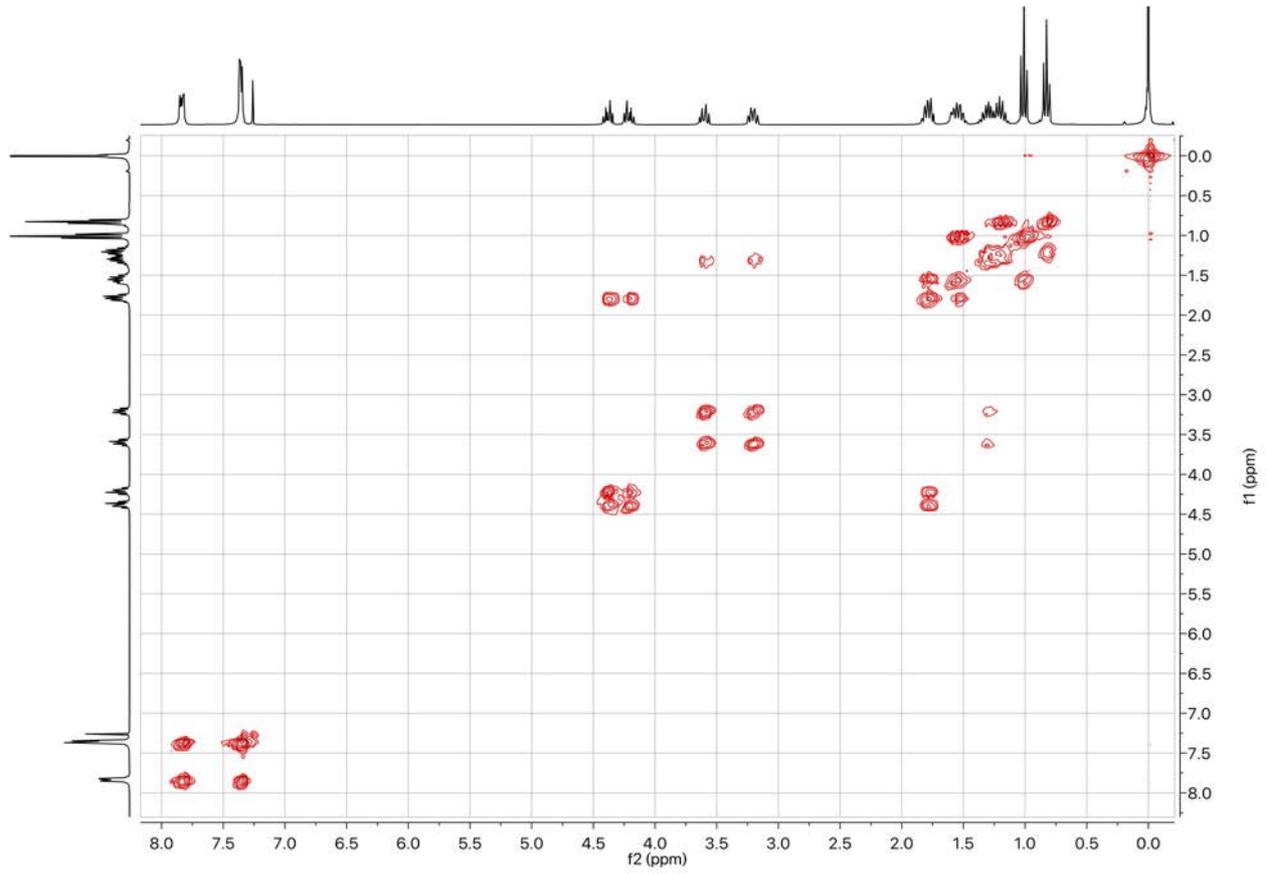


*meso*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2d):

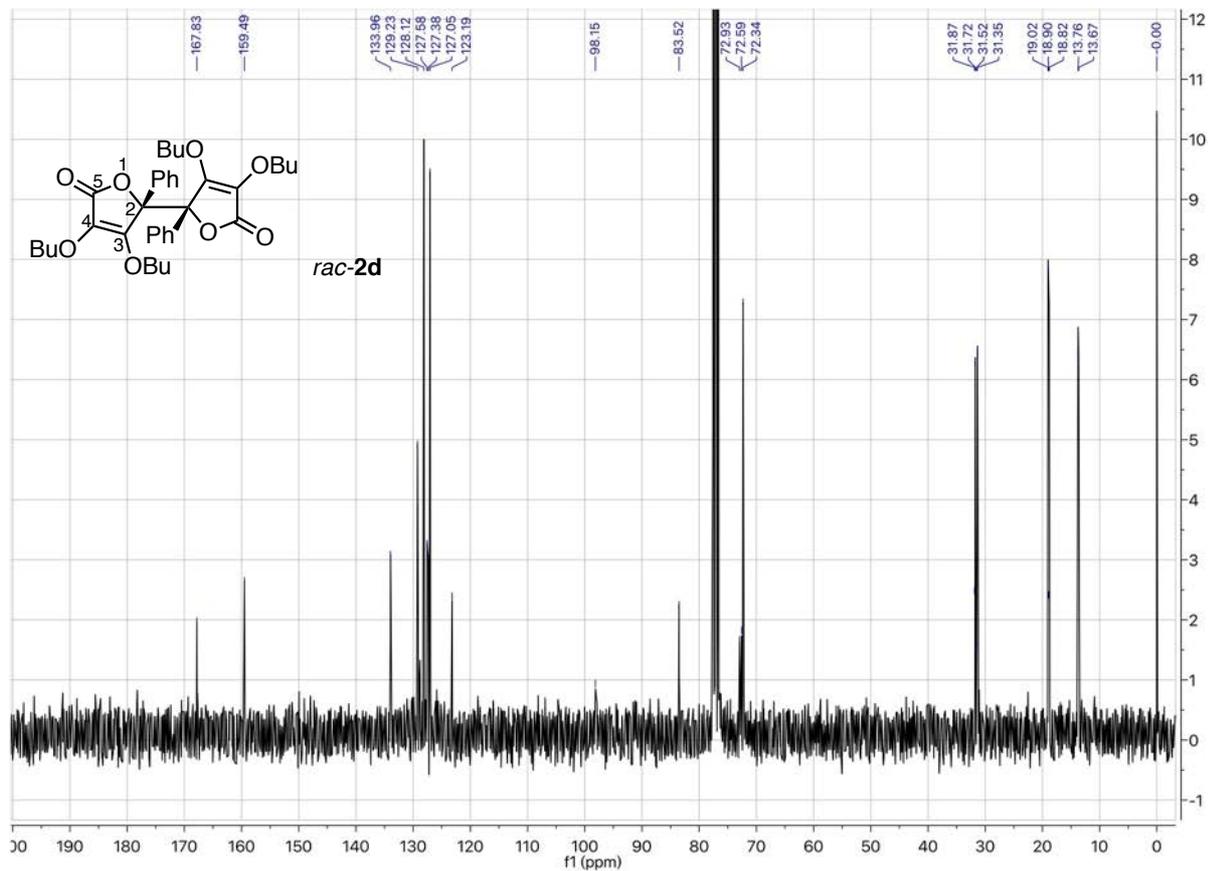
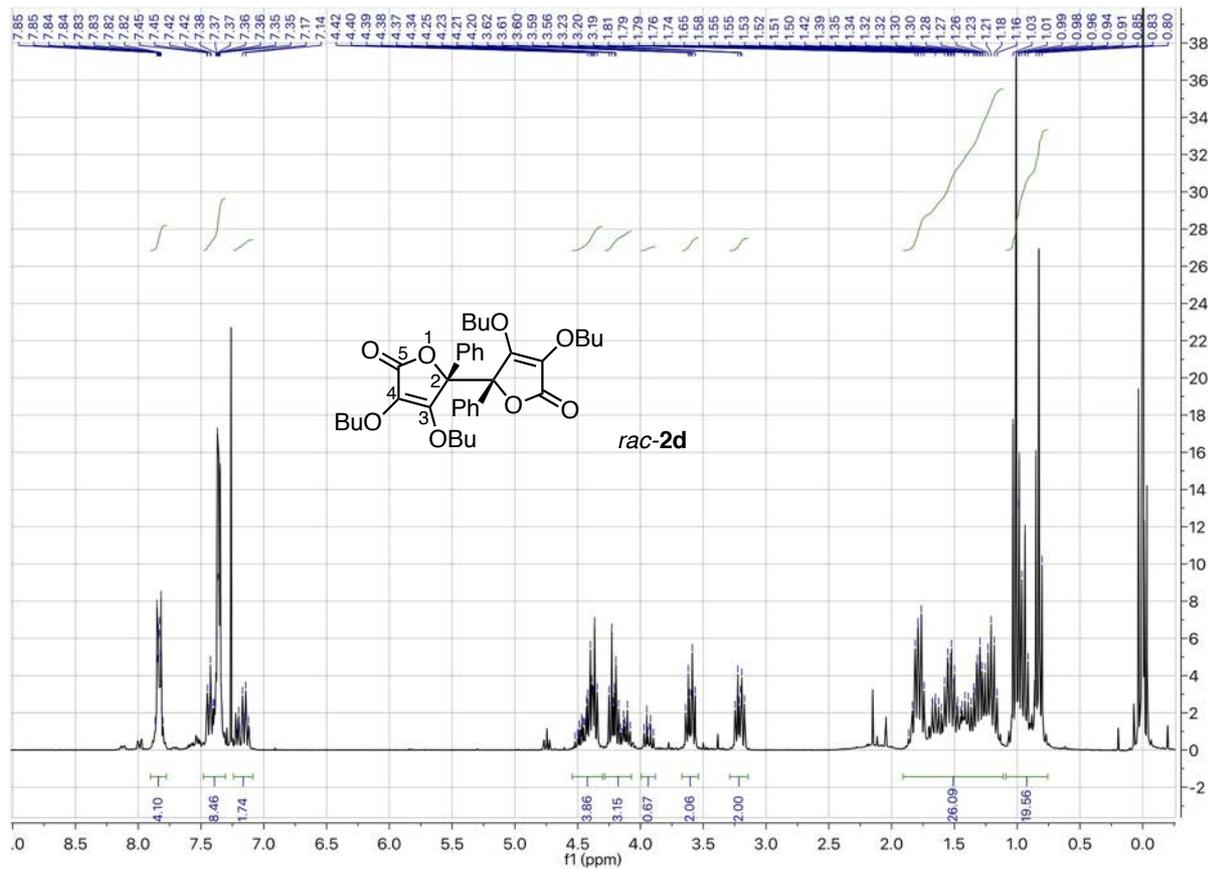




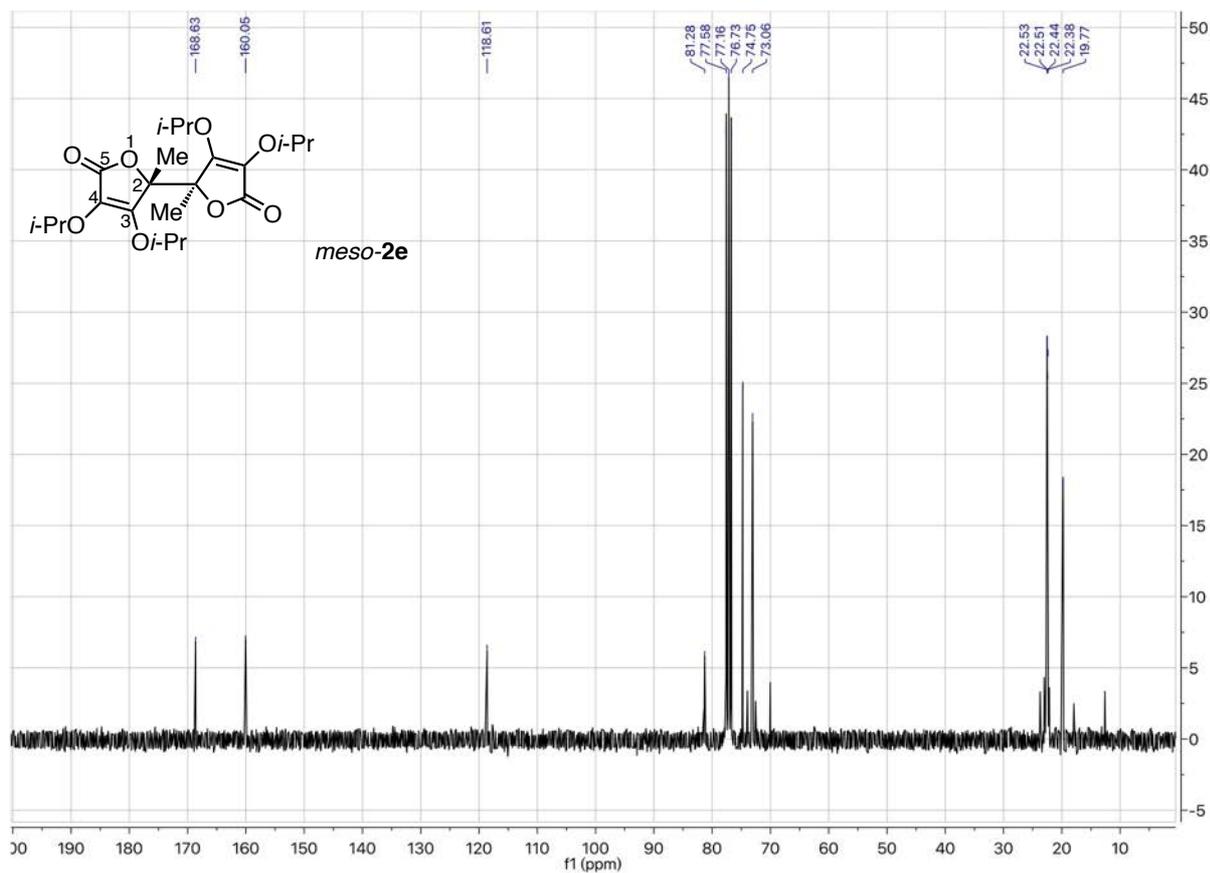
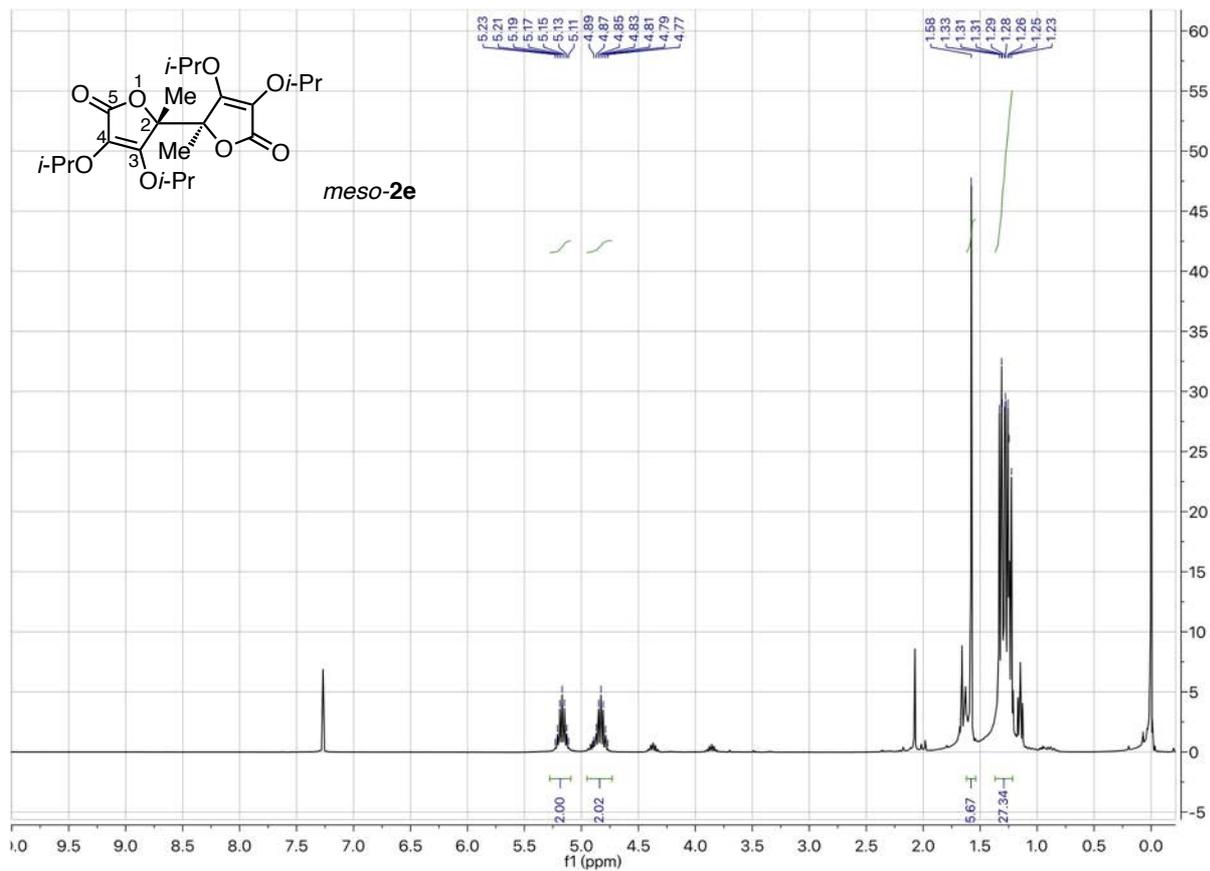
*meso*-2d



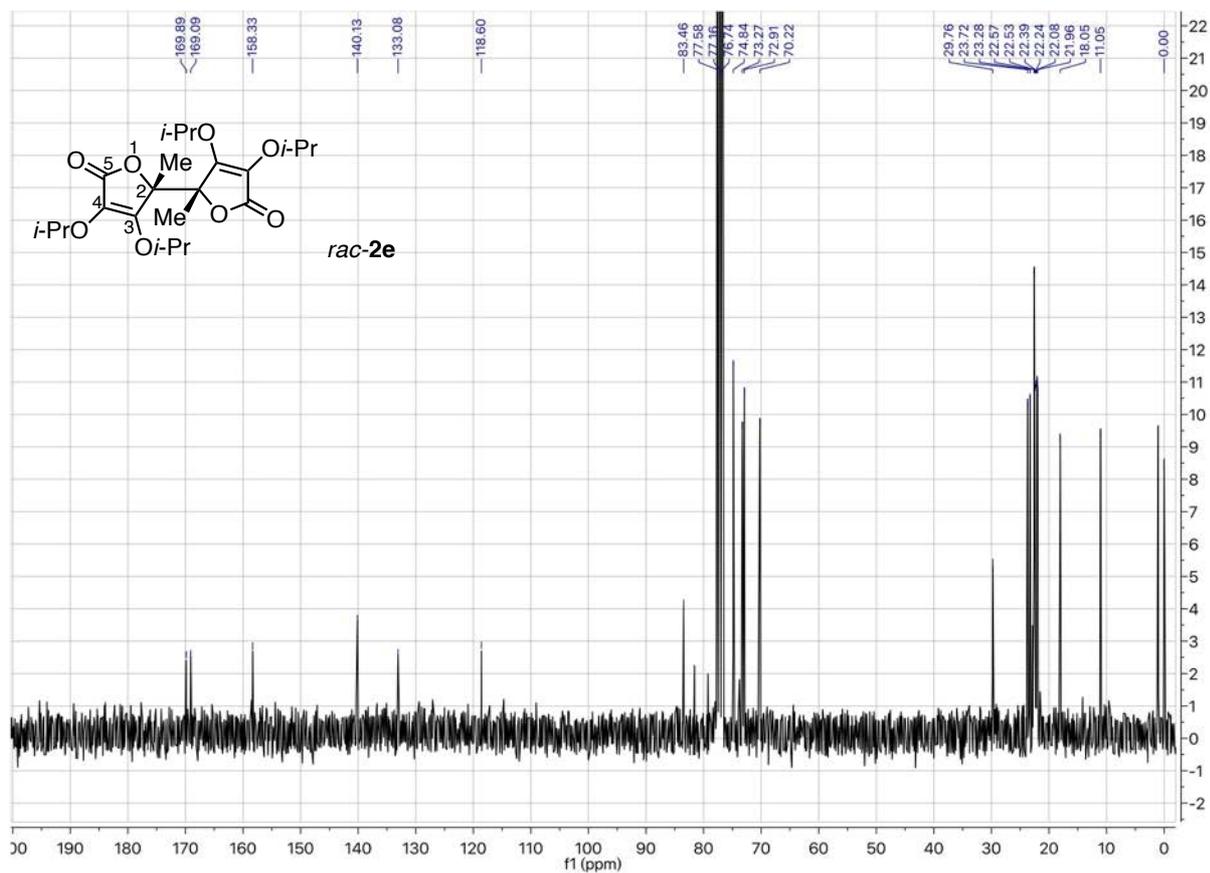
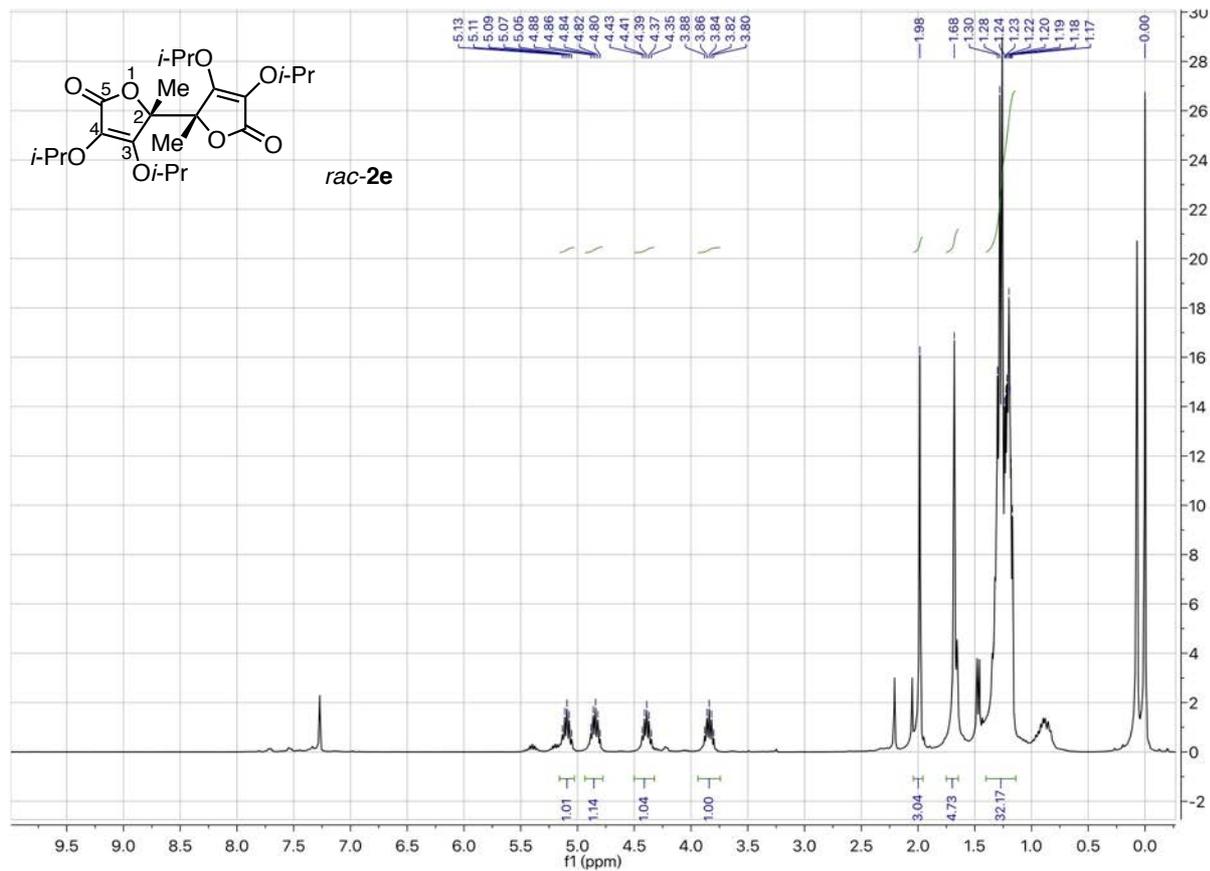
***rac*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2d):**



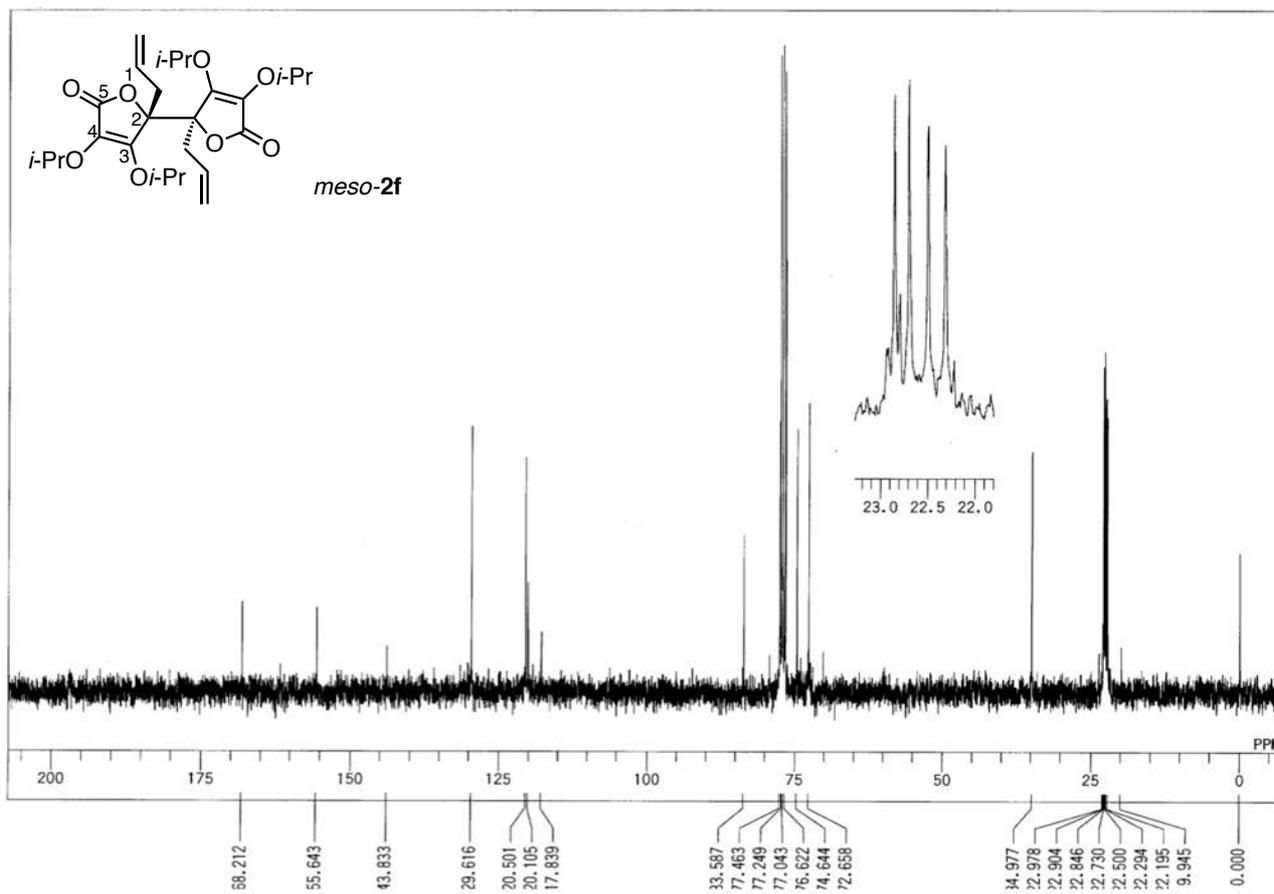
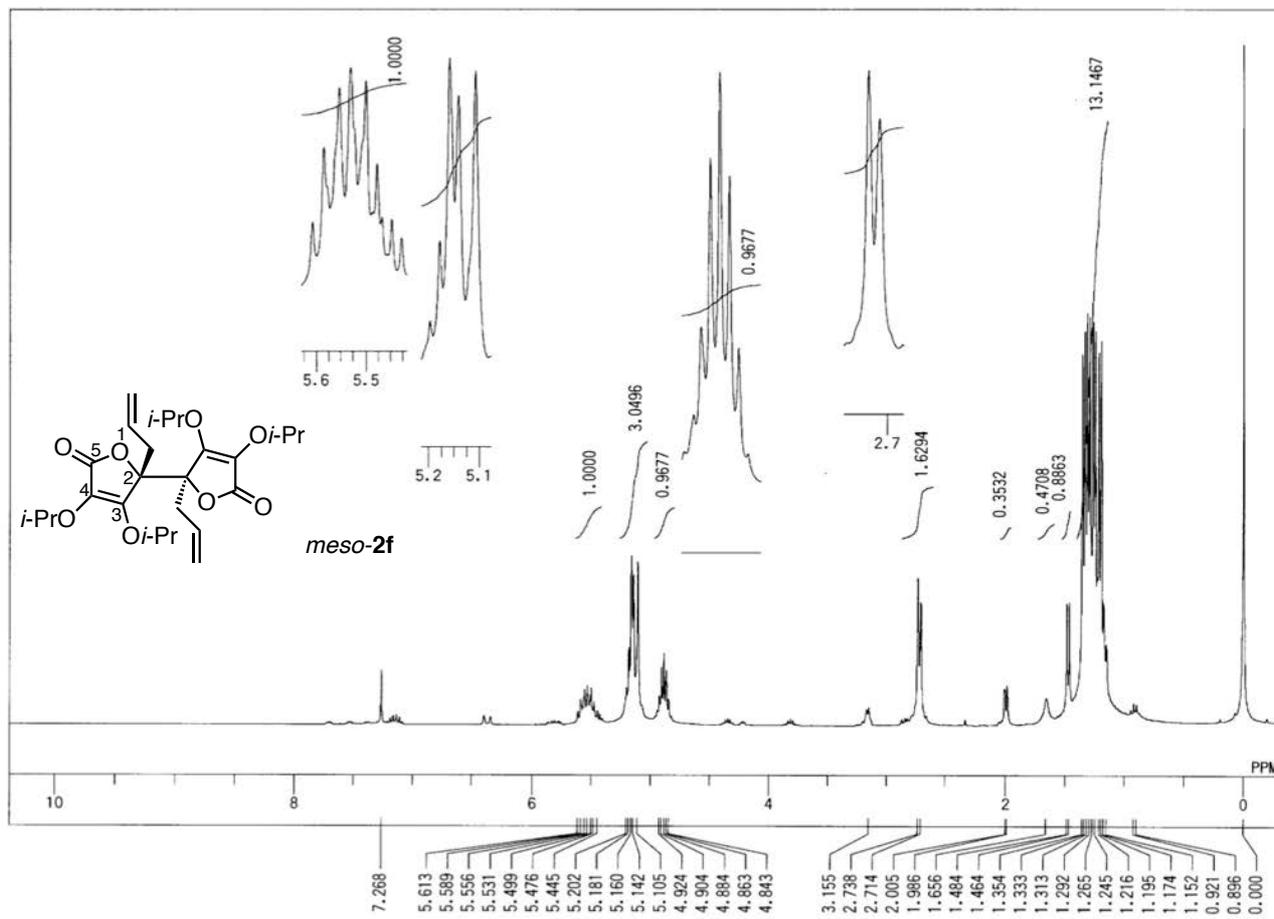
***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2e):**



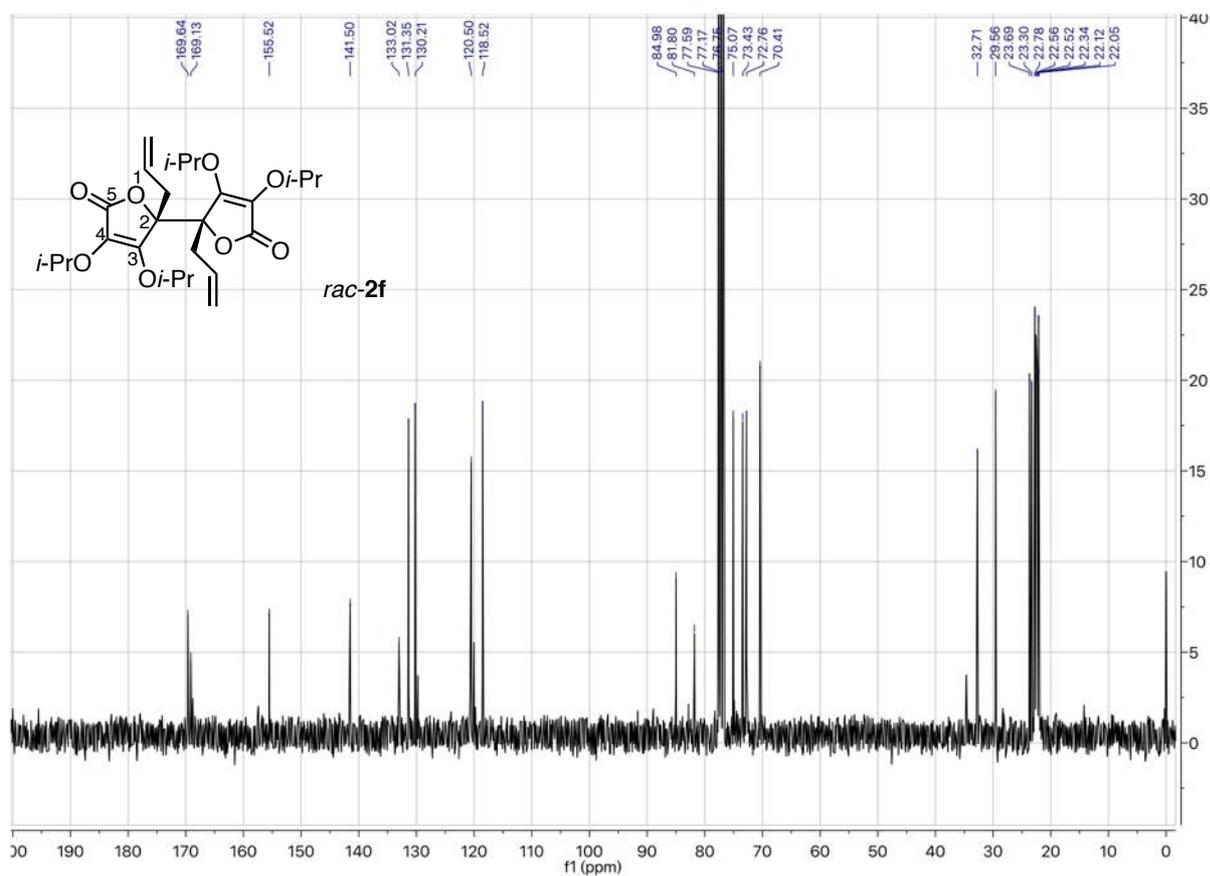
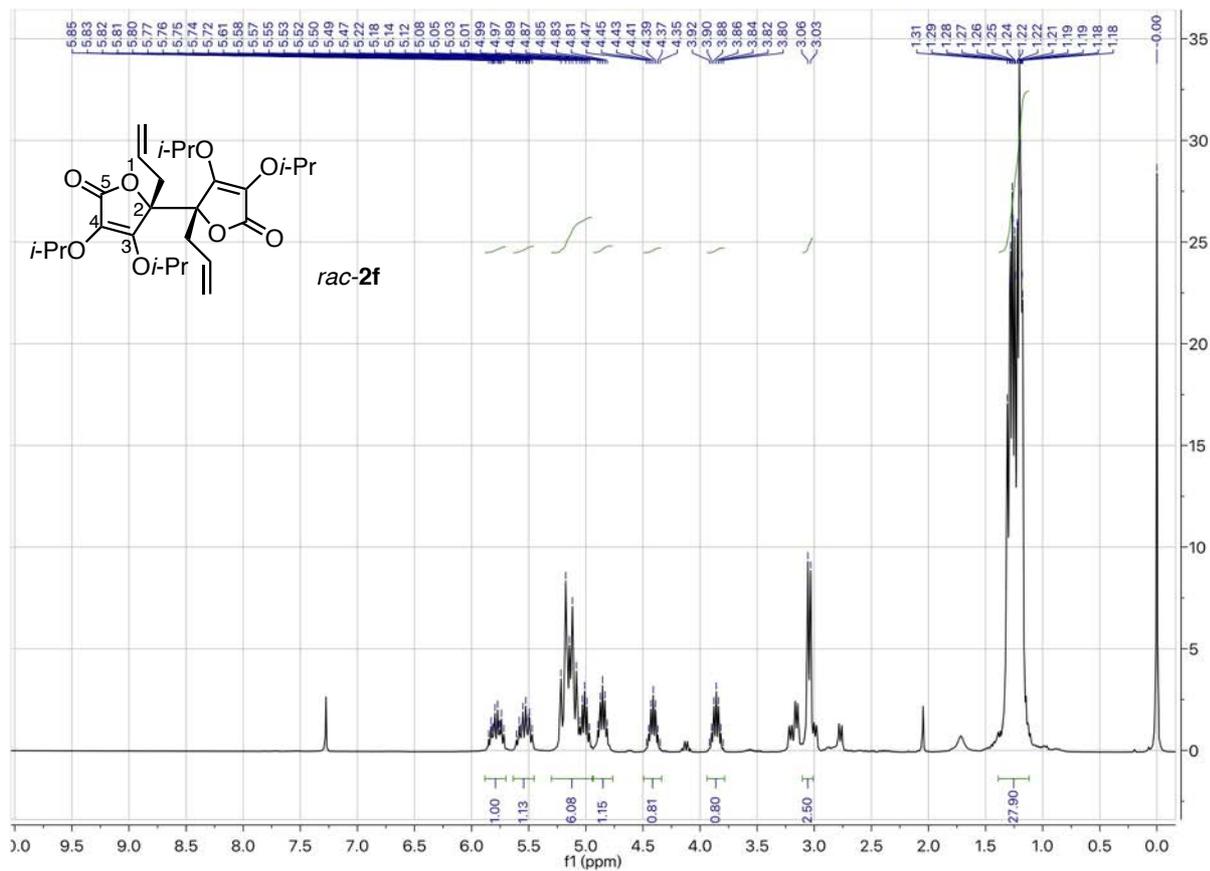
*rac*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2*e*):



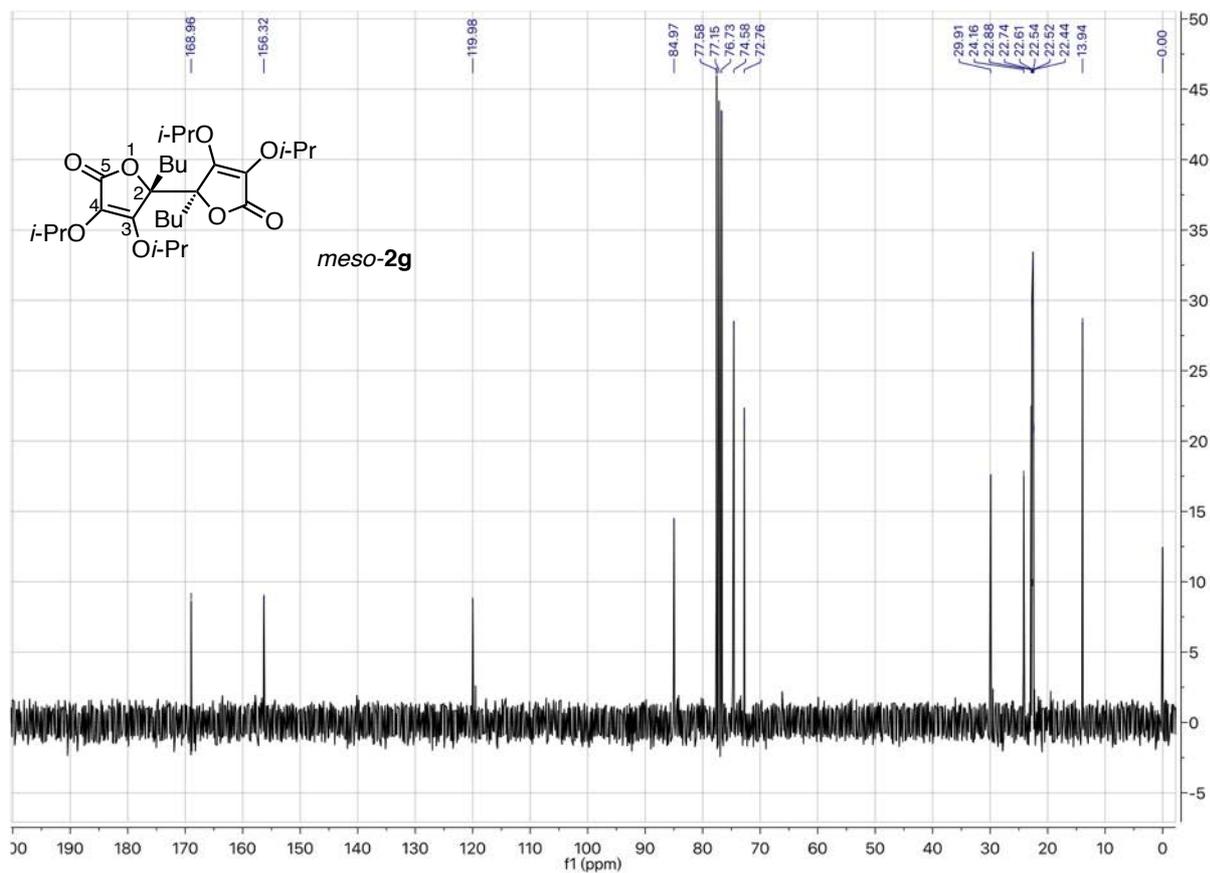
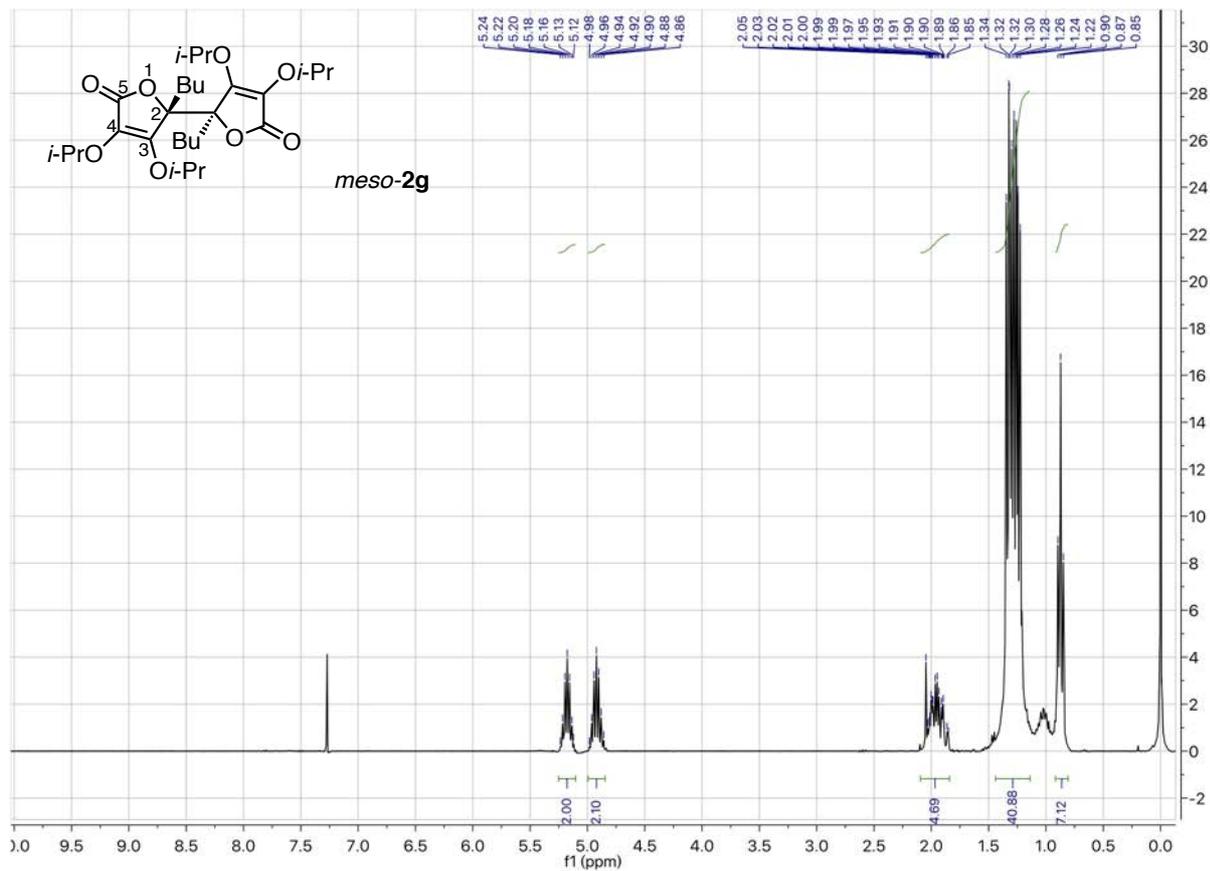
*meso*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2f):



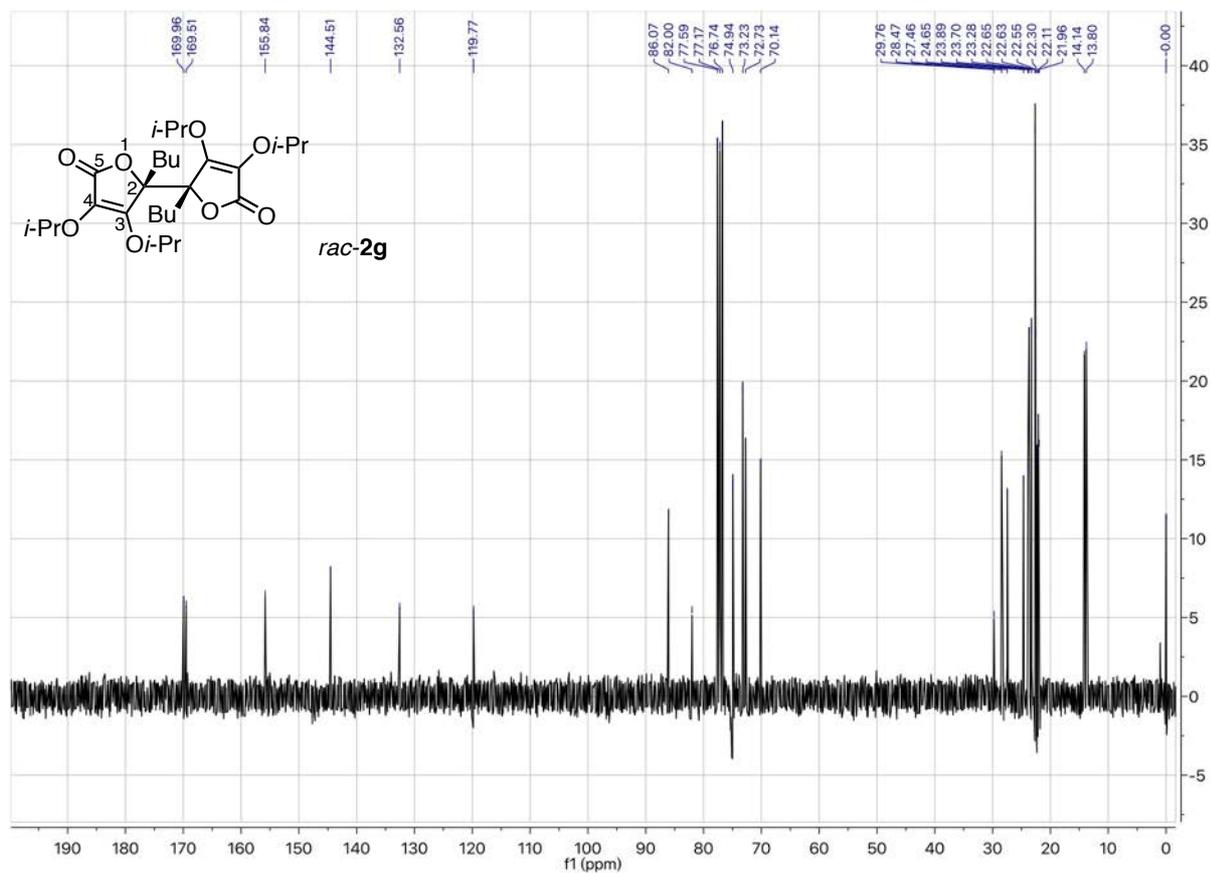
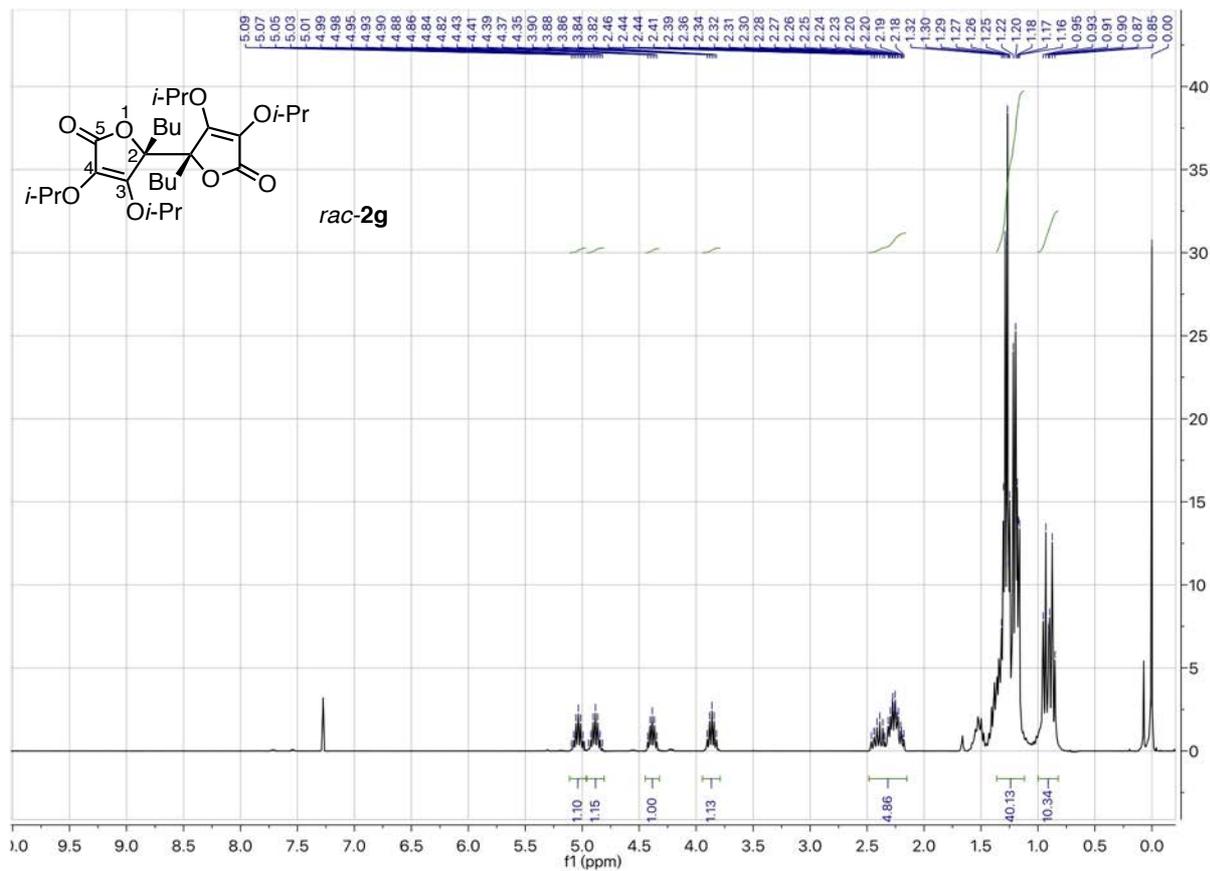
***rac*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(*2H,2'H*)-dione (*rac*-2f):**



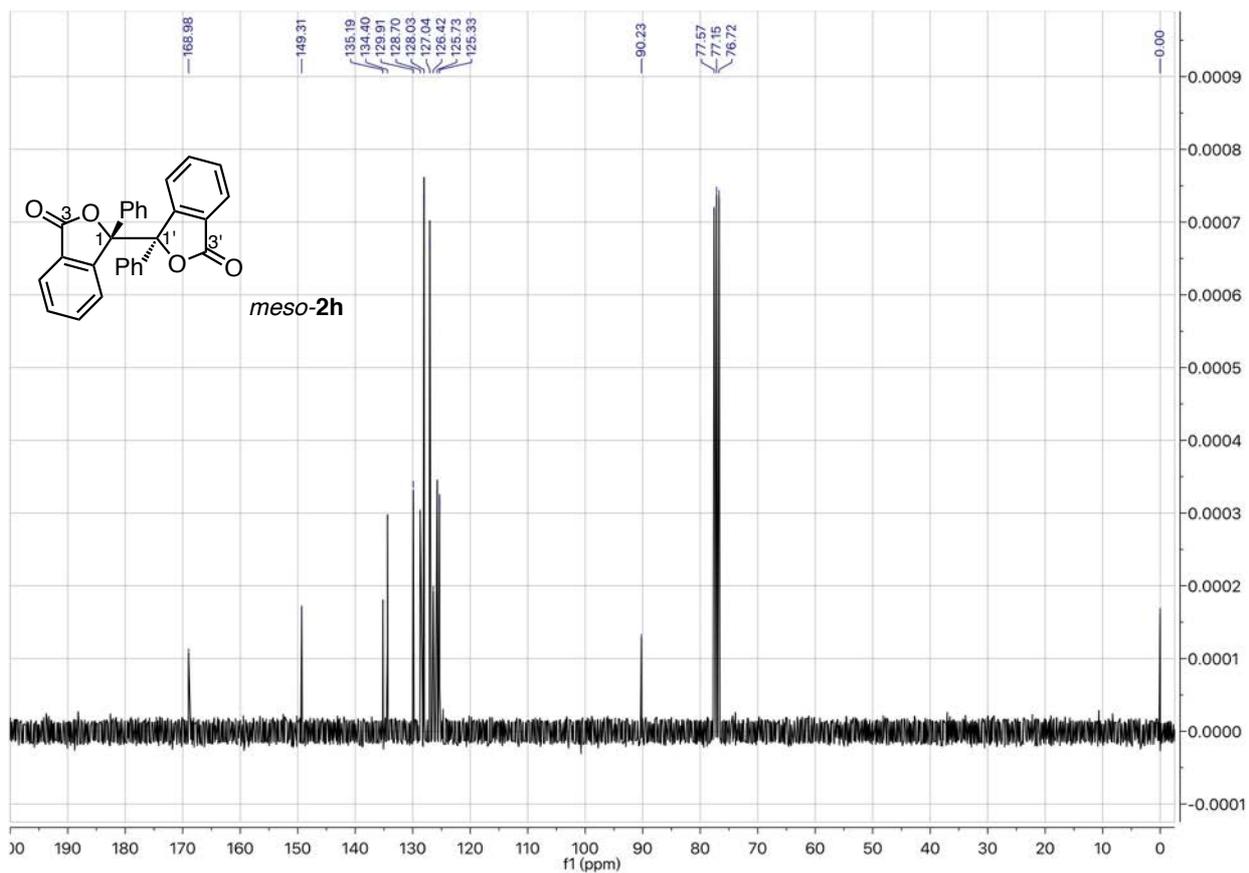
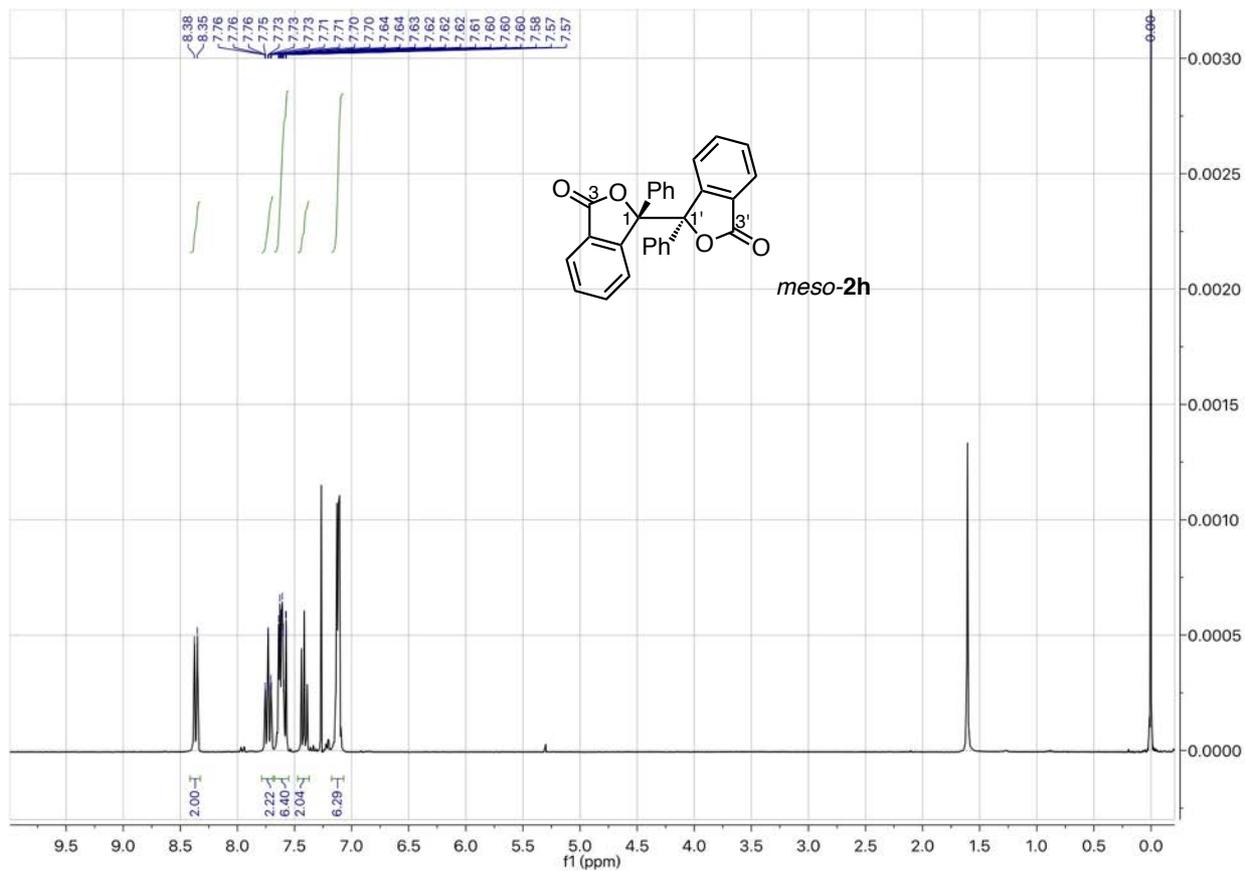
*meso*-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2*g*):



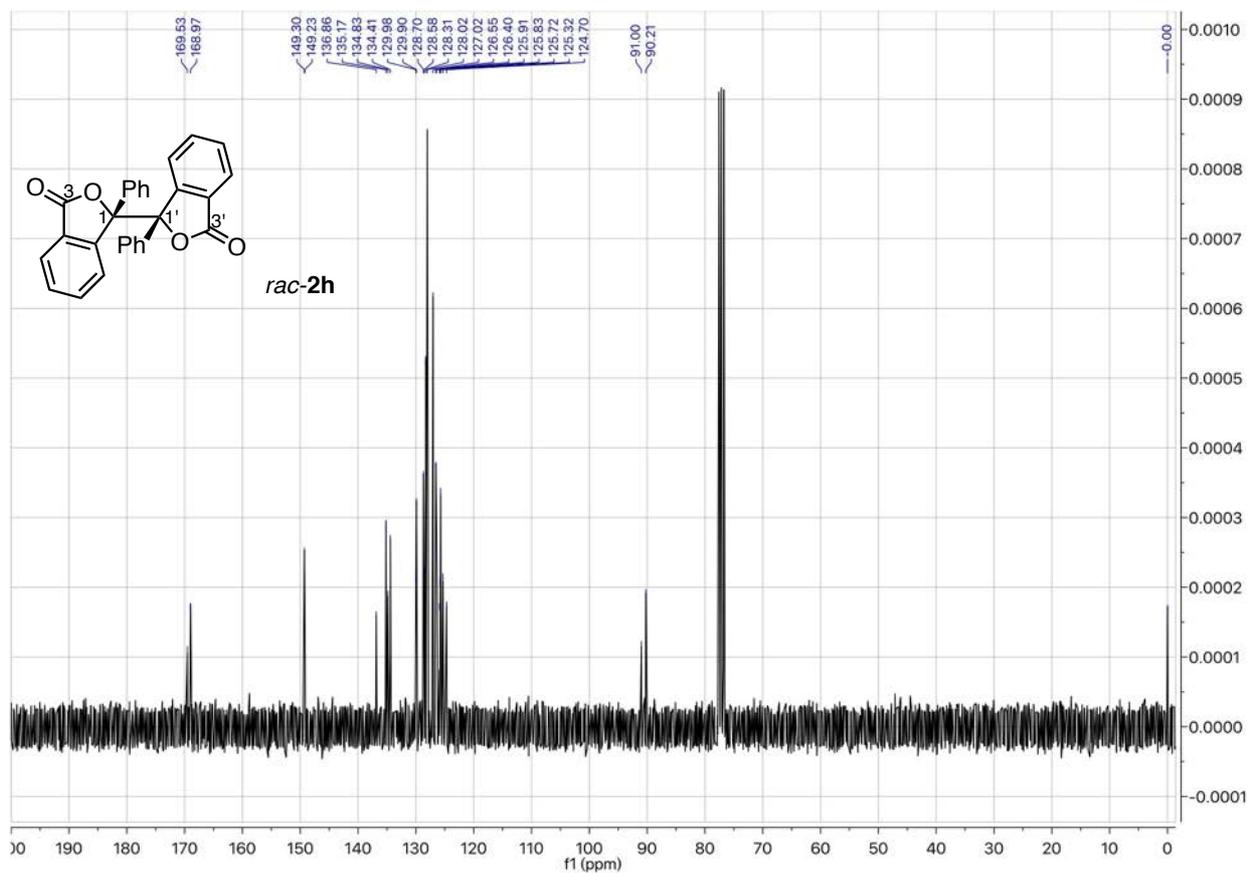
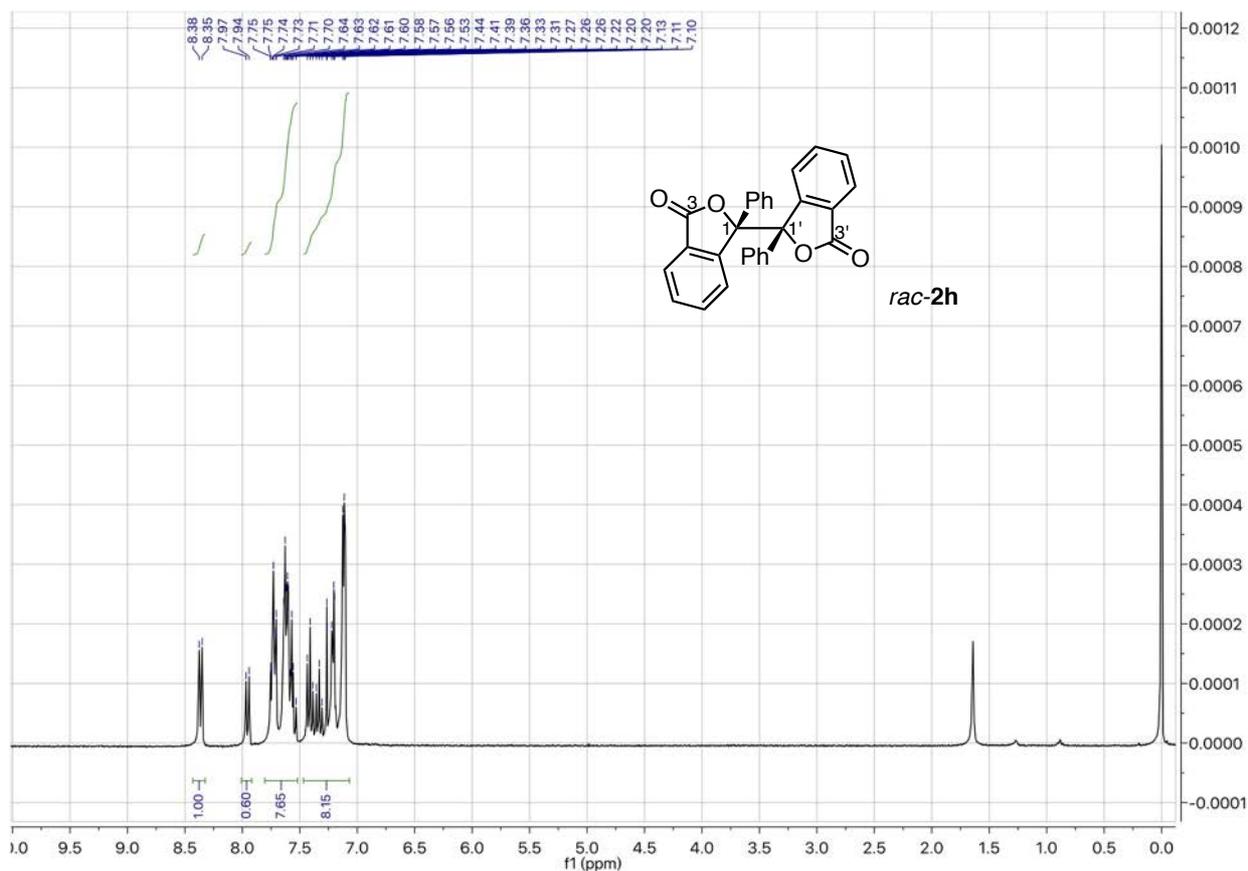
*rac*-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2*g*):



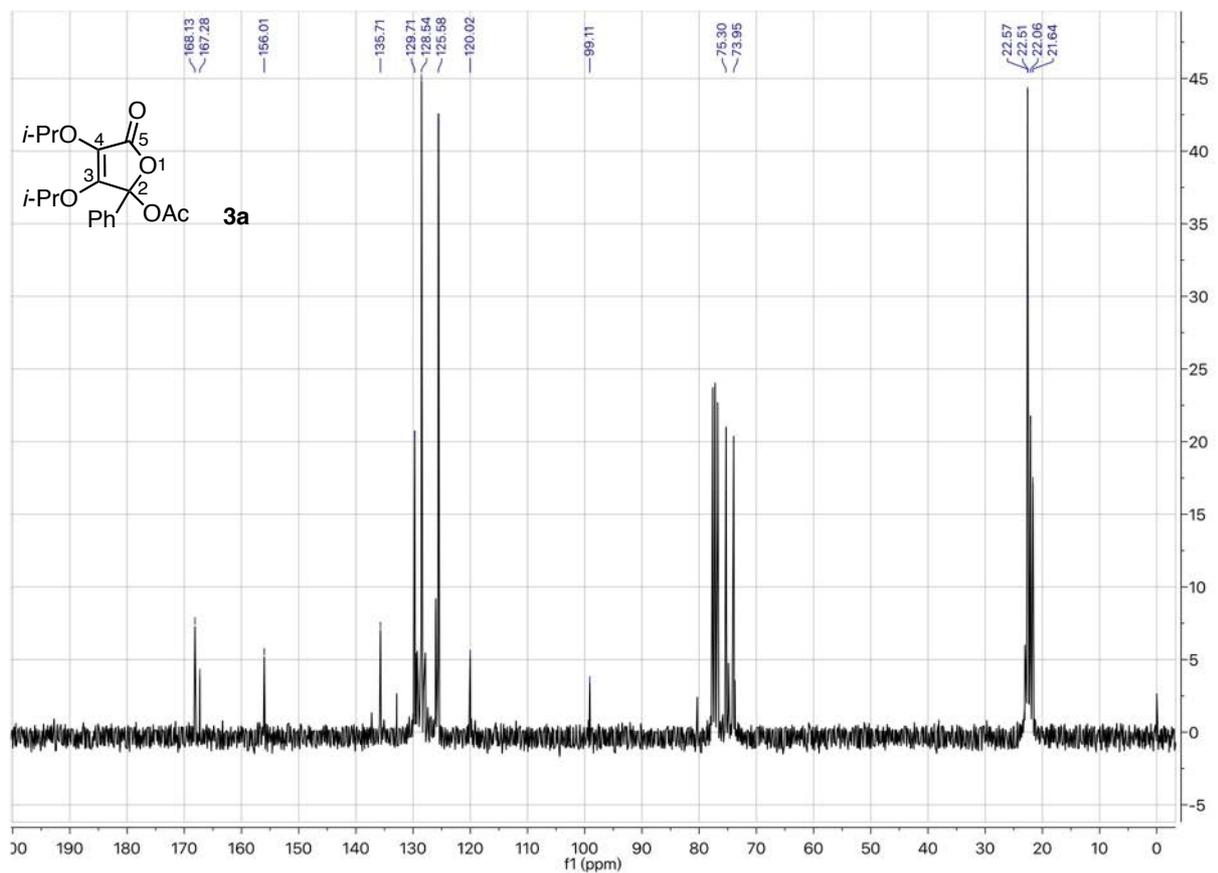
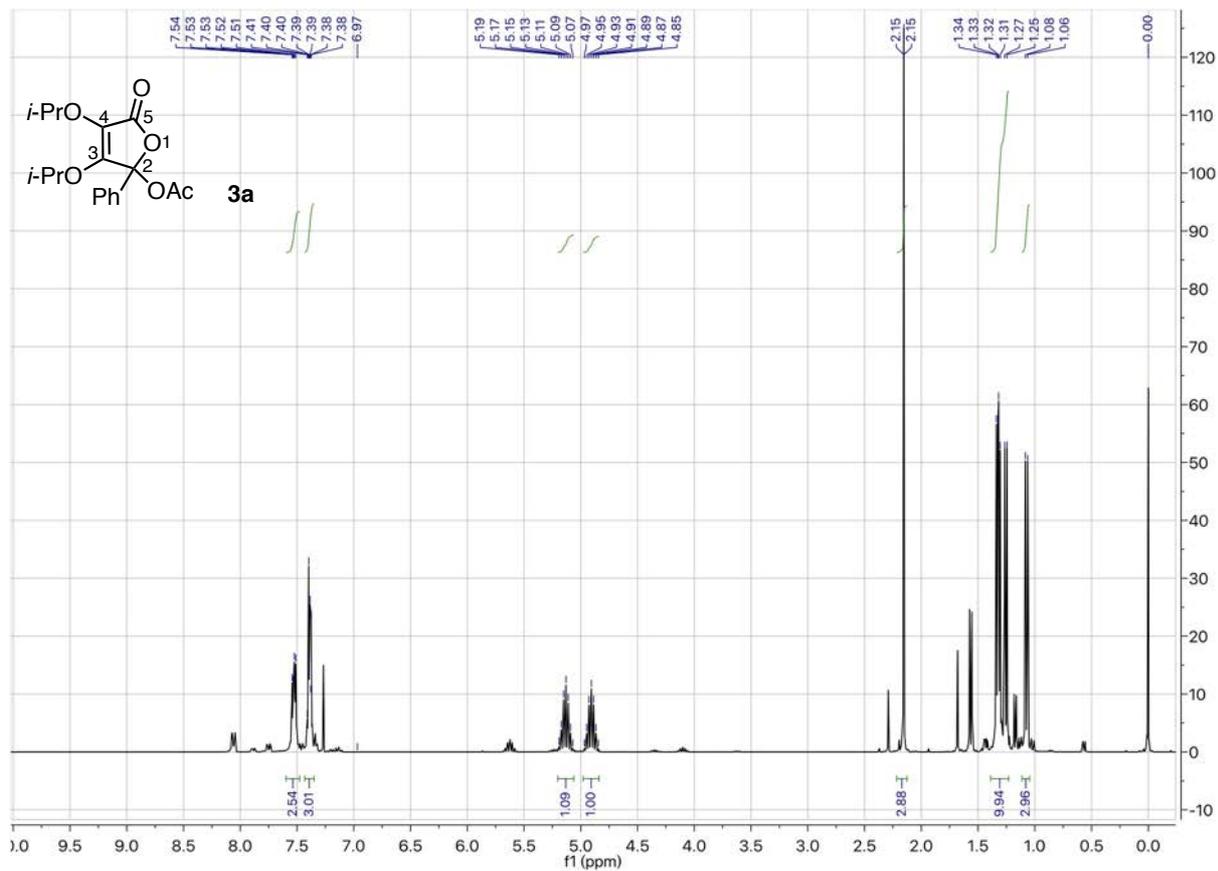
**meso-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1H,1'H)-dione (meso-2h):**



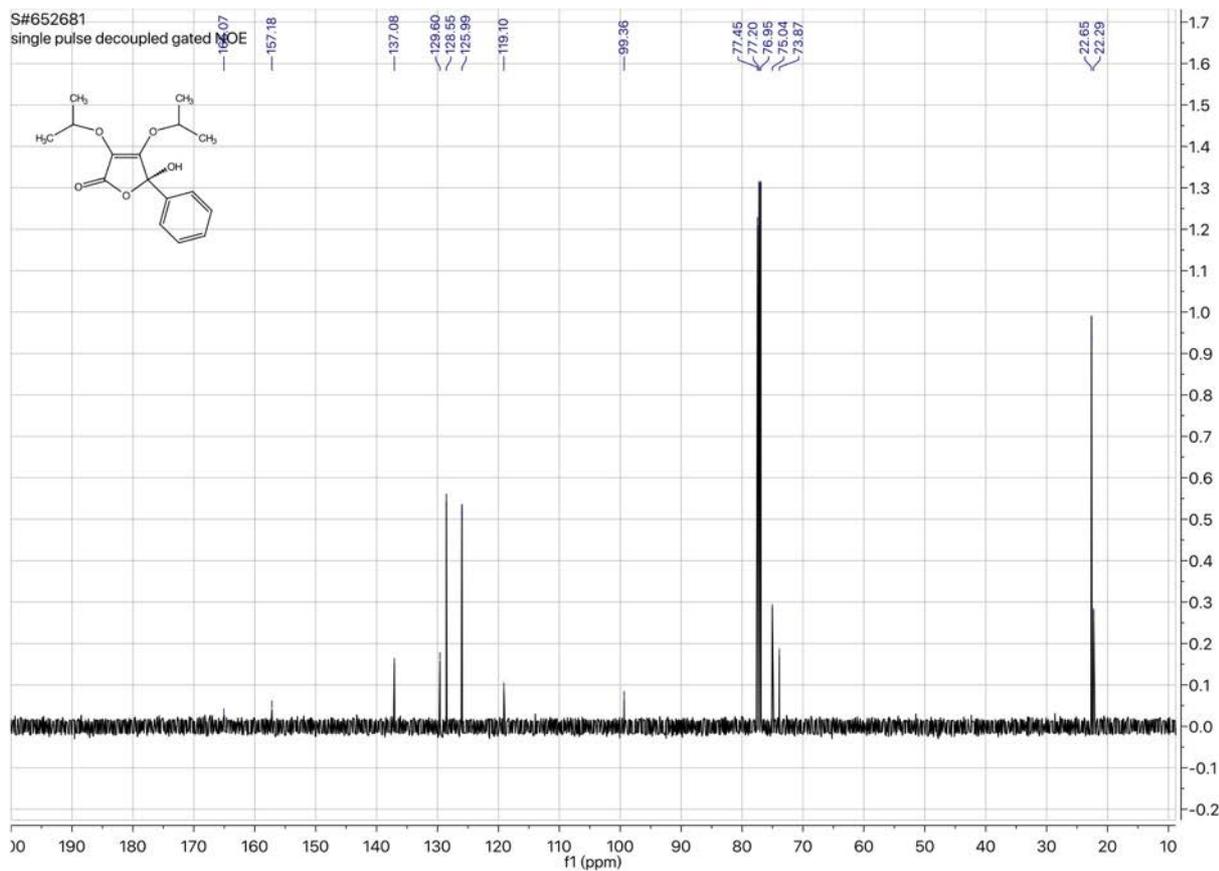
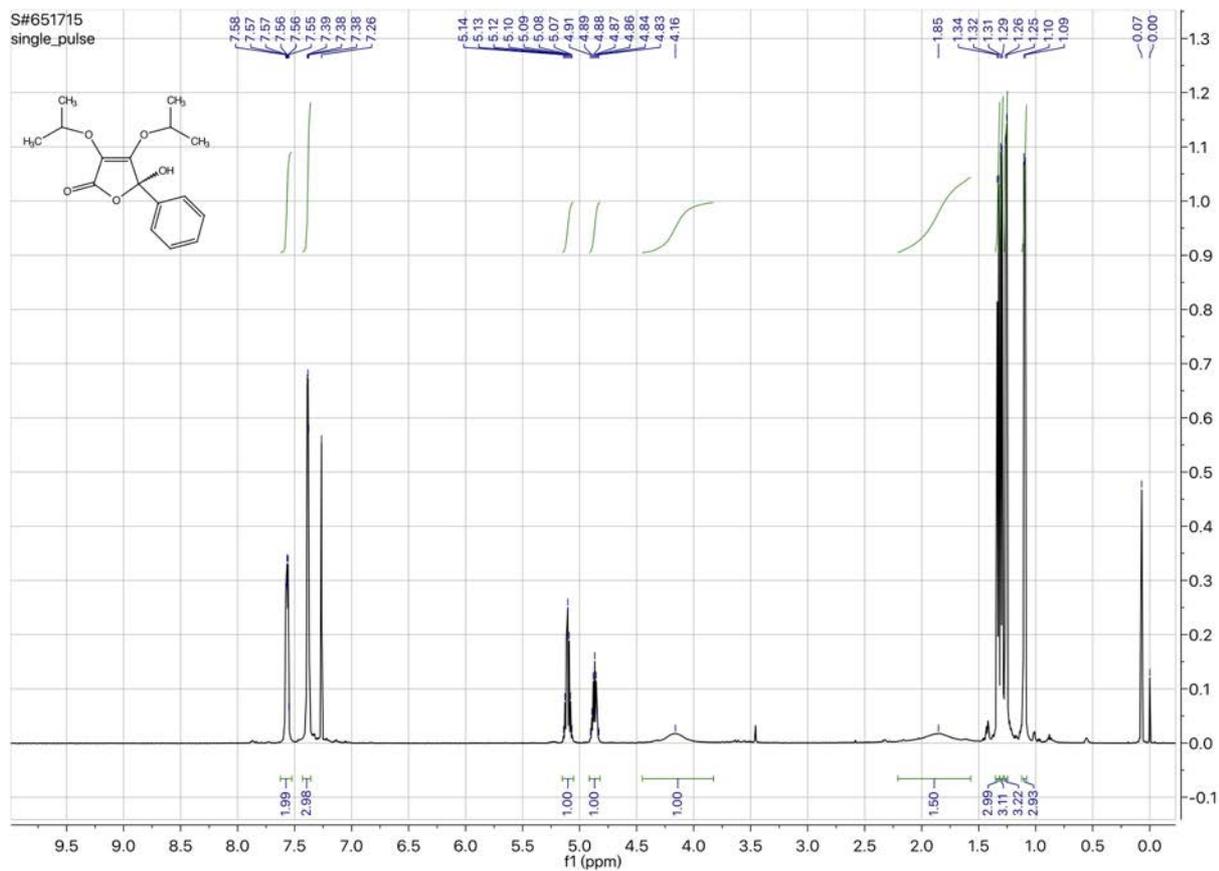
*rac*-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*rac*-2h)<sup>19</sup>:



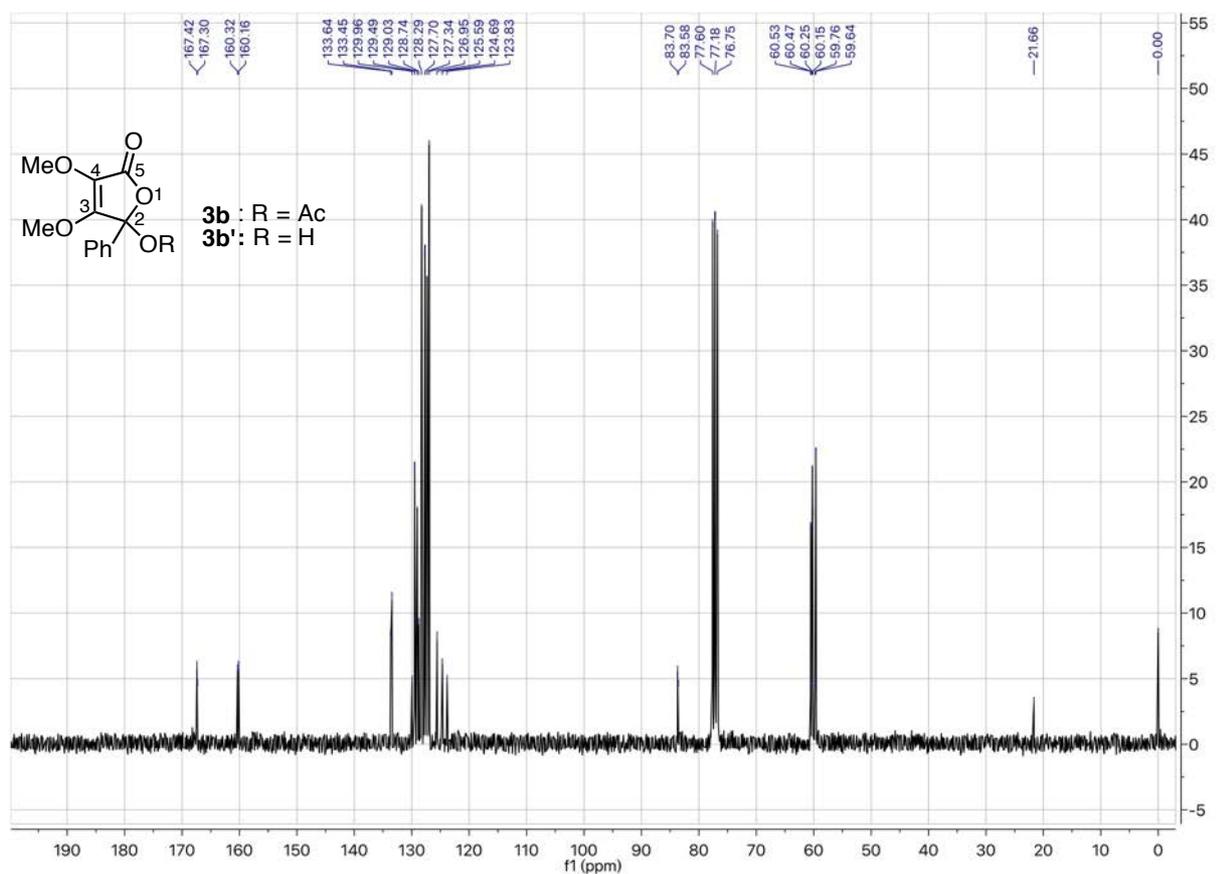
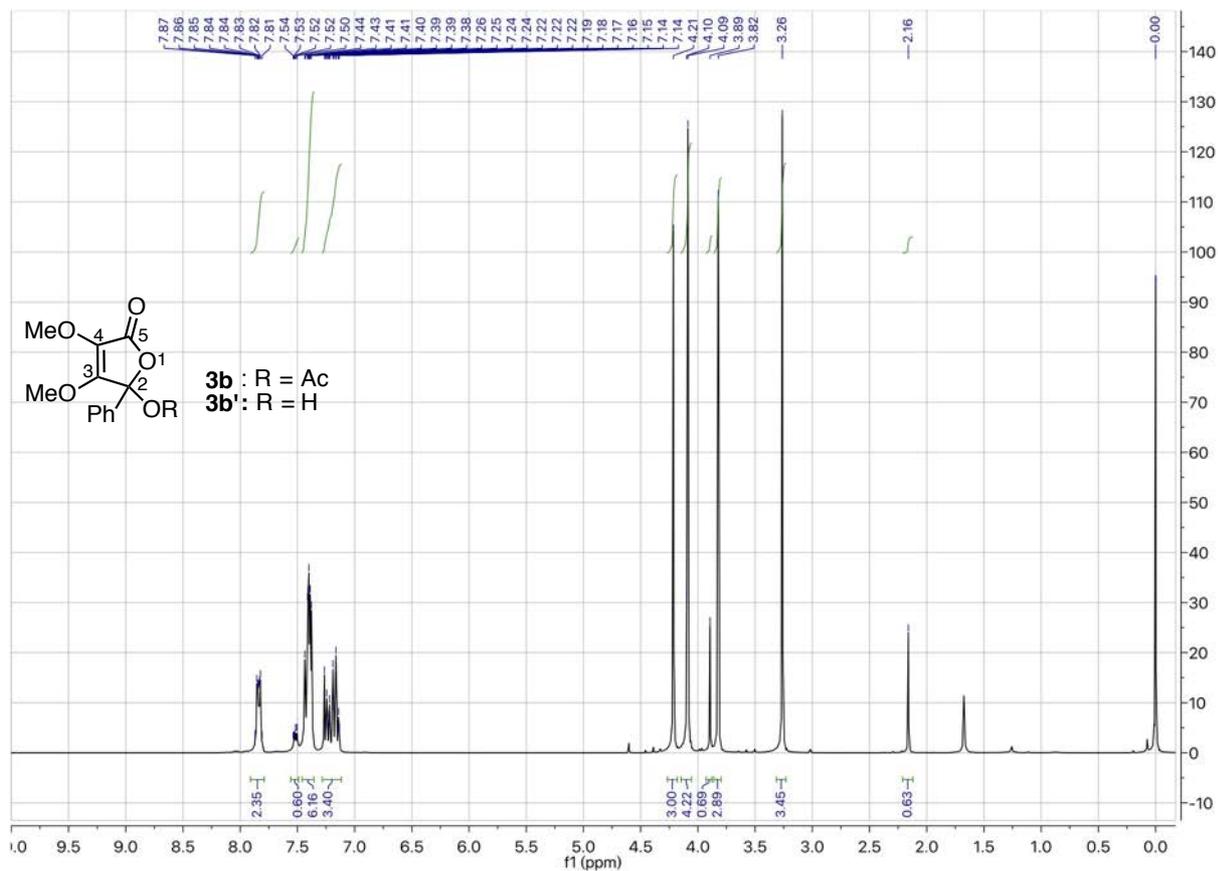
**3,4-Diisopropoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3a):**



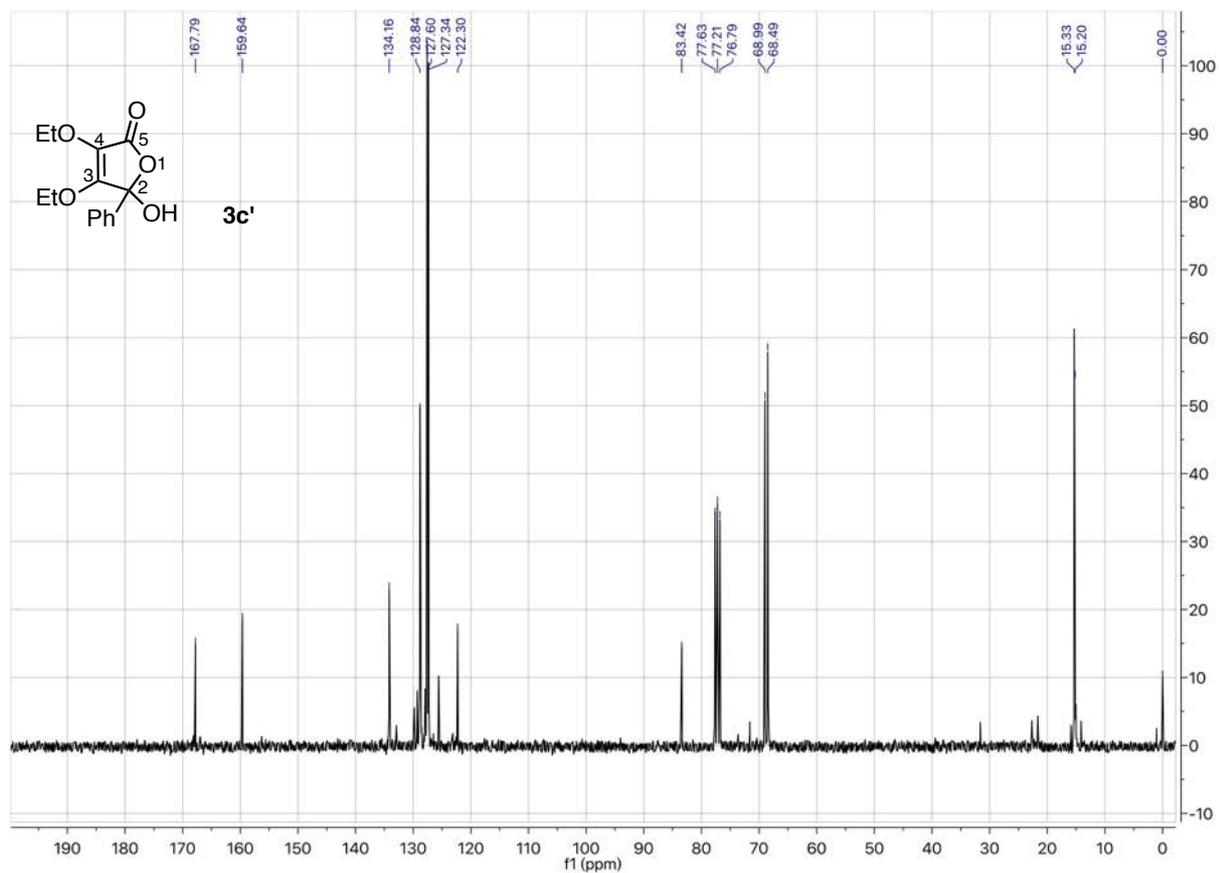
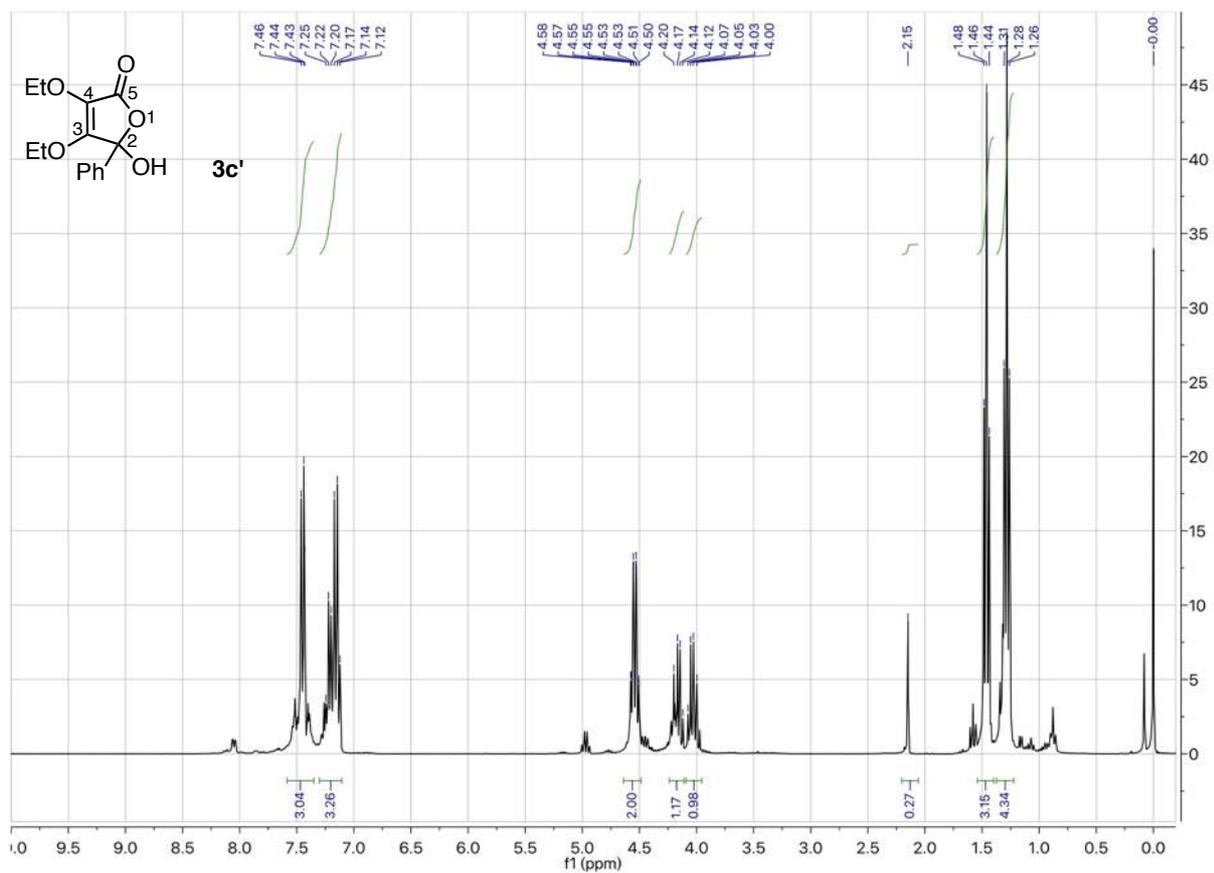
**5-Hydroxy-3,4-diisopropoxy-5-phenylfuran-2(5H)-one (3a')**



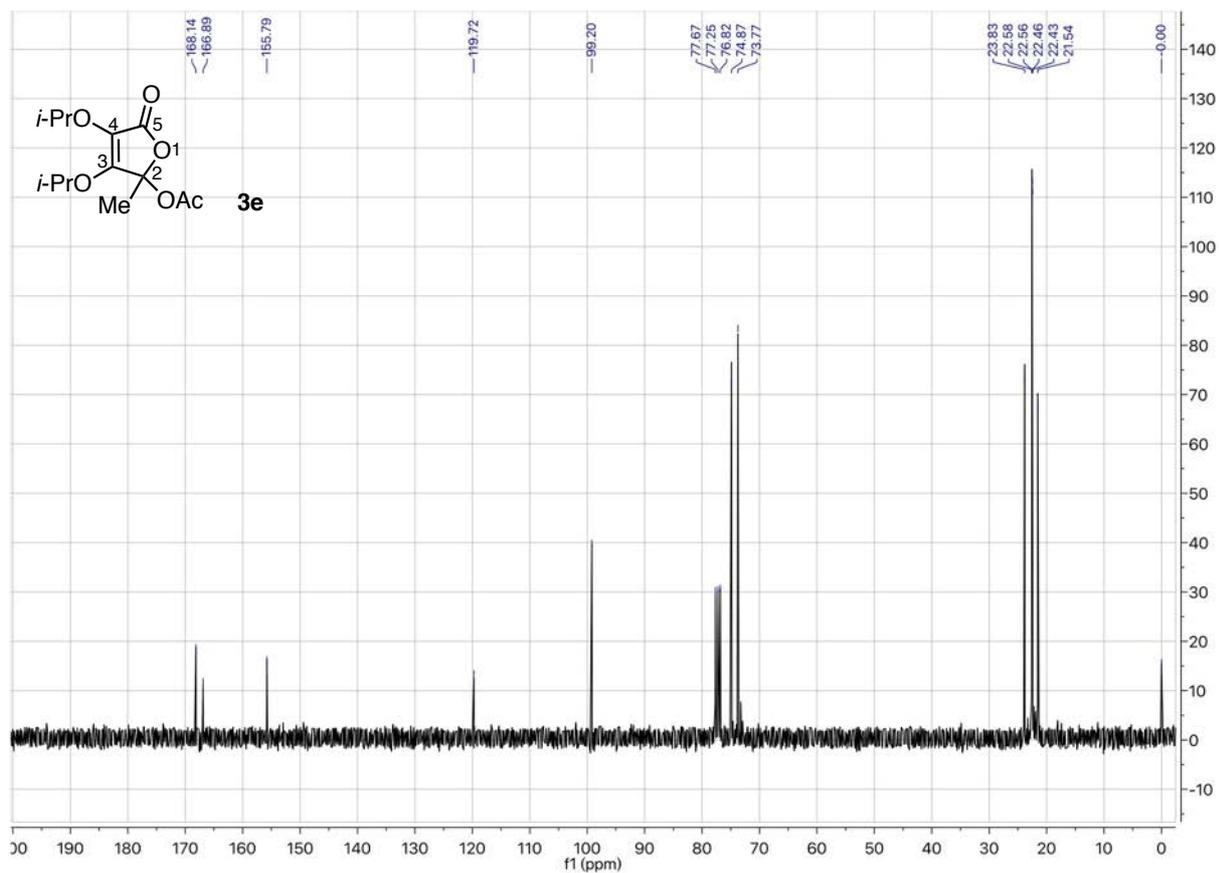
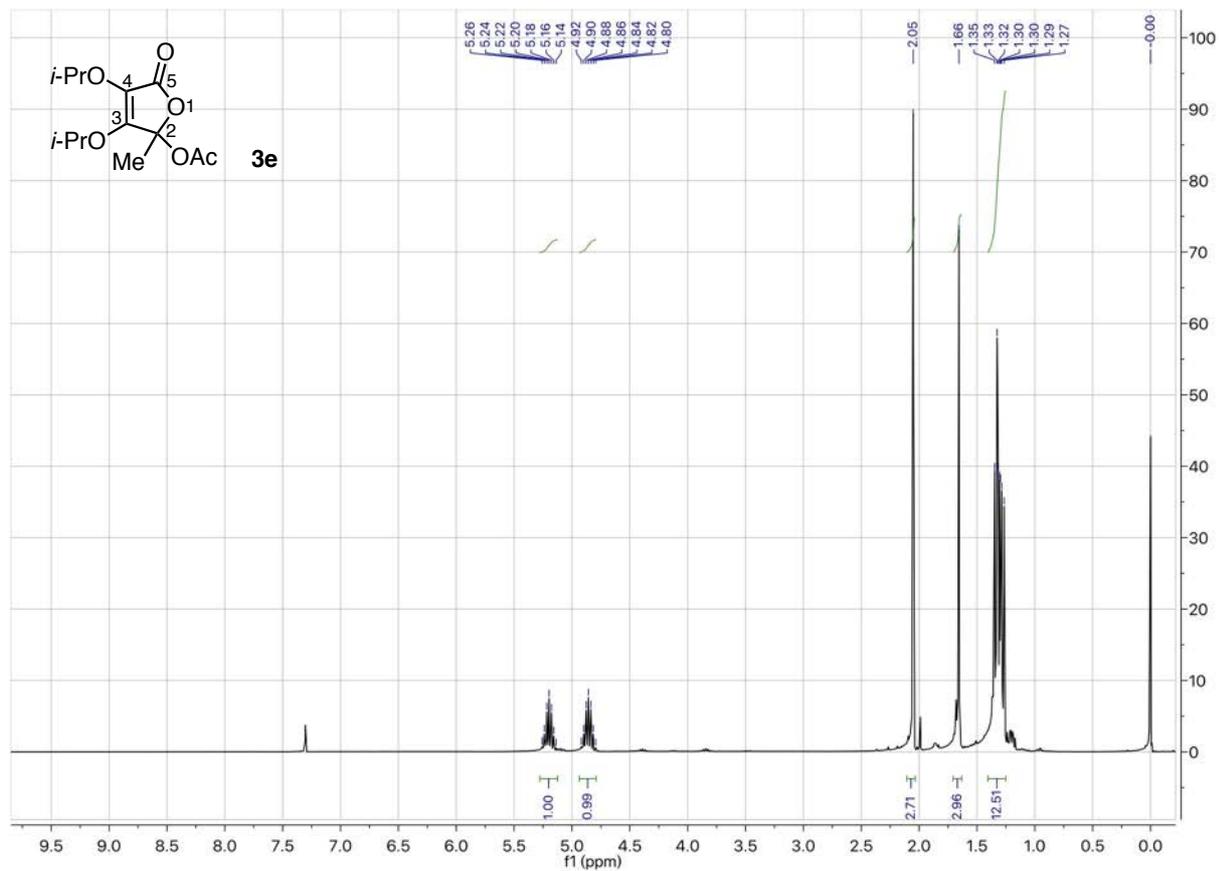
A Mixture of 3,4-Dimethoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (**3b**) and 5-Hydroxy-3,4-dimethoxy-5-phenylfuran-2(*5H*)-one (**3b'**)<sup>11a,11c,22</sup>:



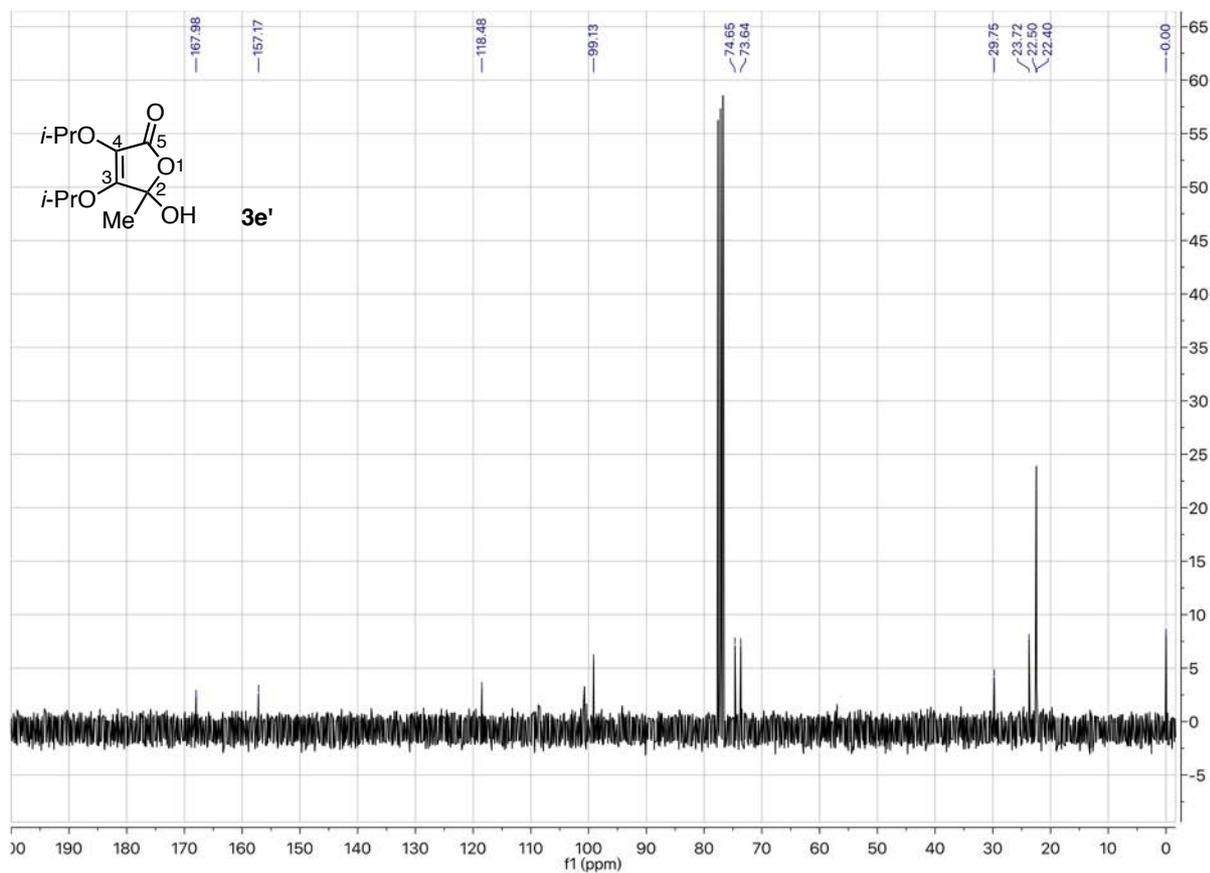
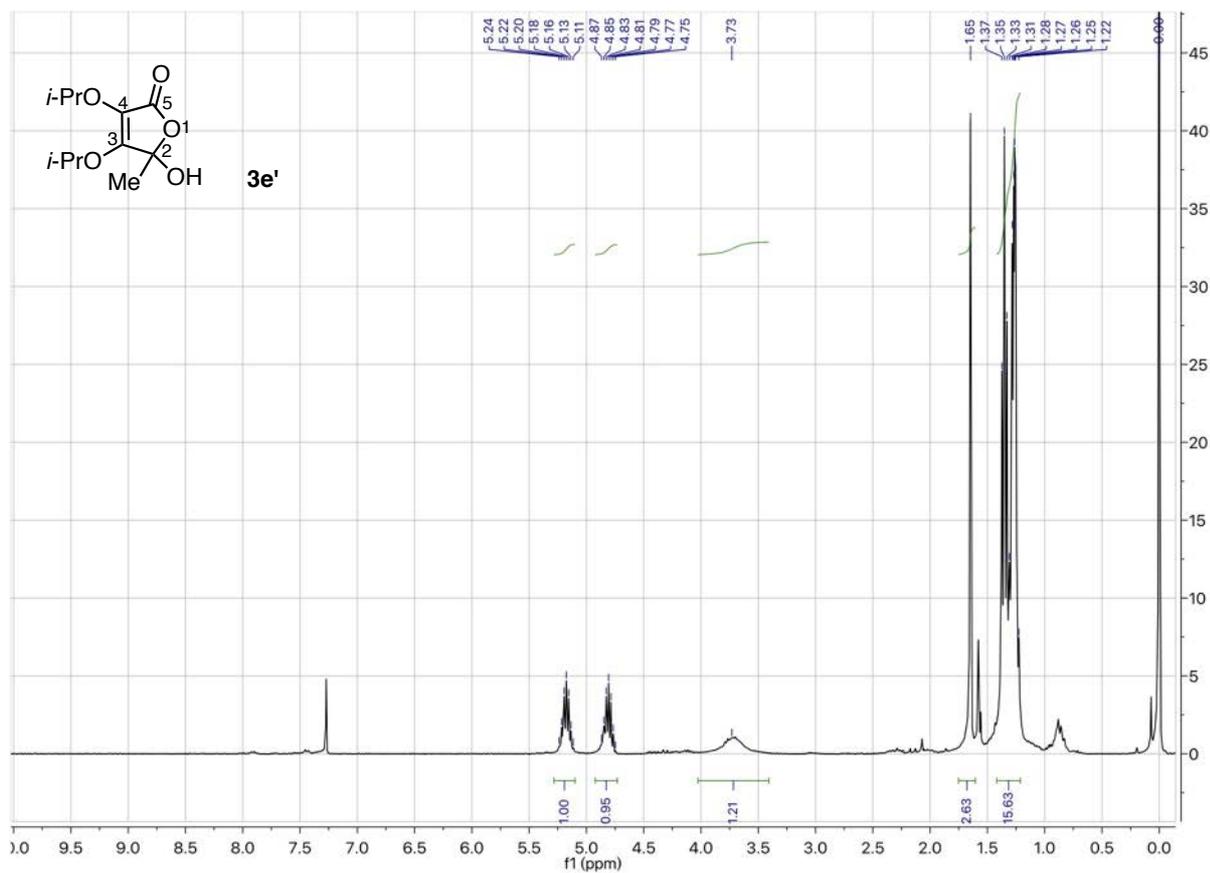
3,4-Diethoxy-5-hydroxy-5-phenylfuran-2(5H)-one (3c')<sup>11a,11c</sup>:



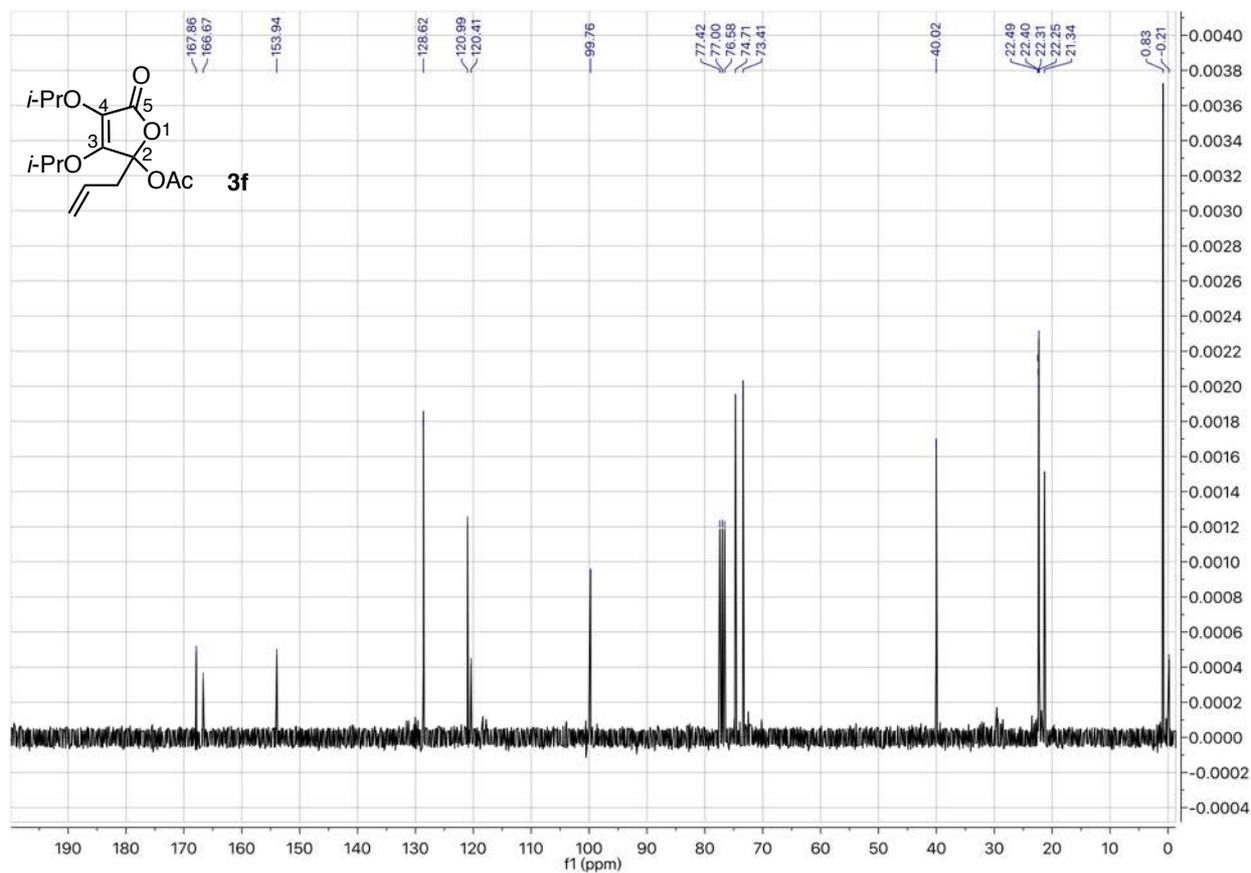
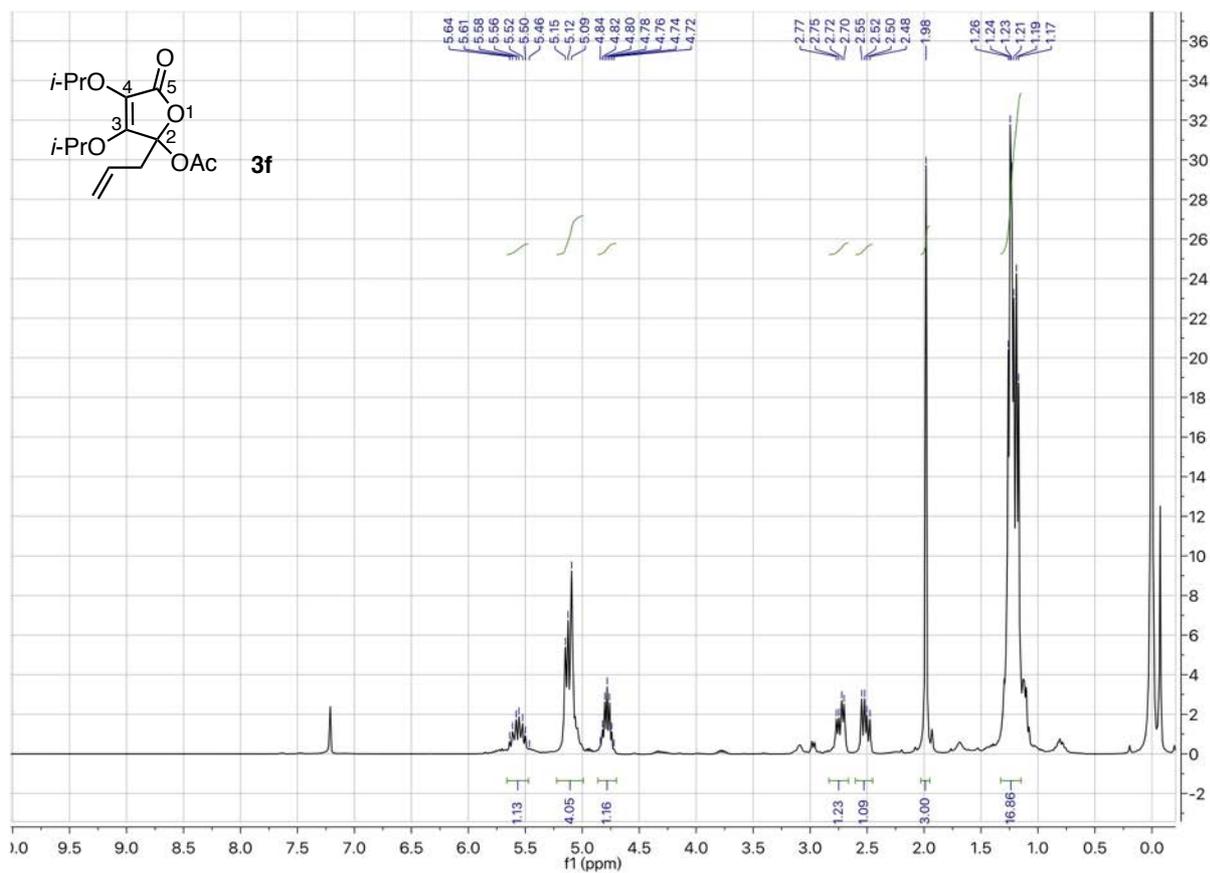
**3,4-Diisopropoxy-2-methyl-5-oxo-2,5-dihydrofuran-2-yl acetate (3e):**



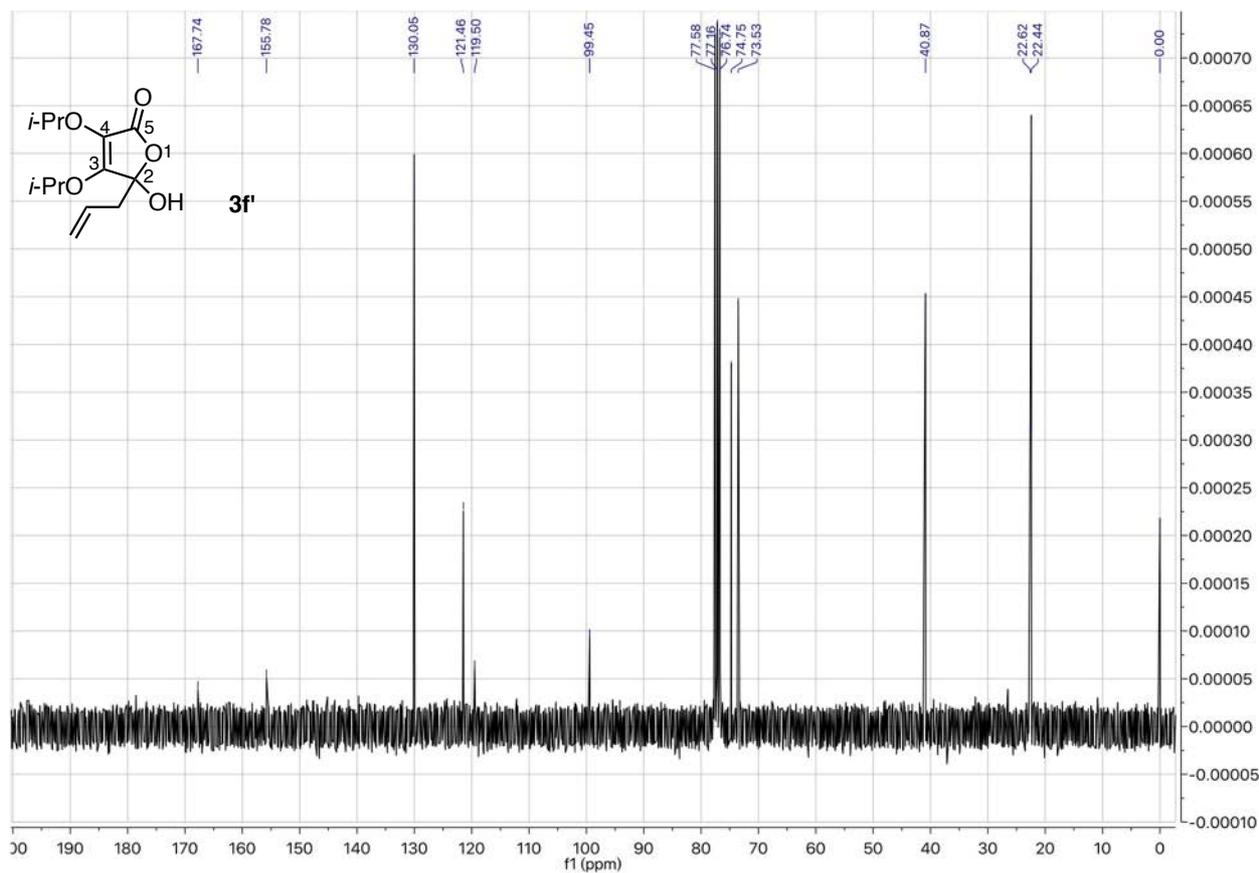
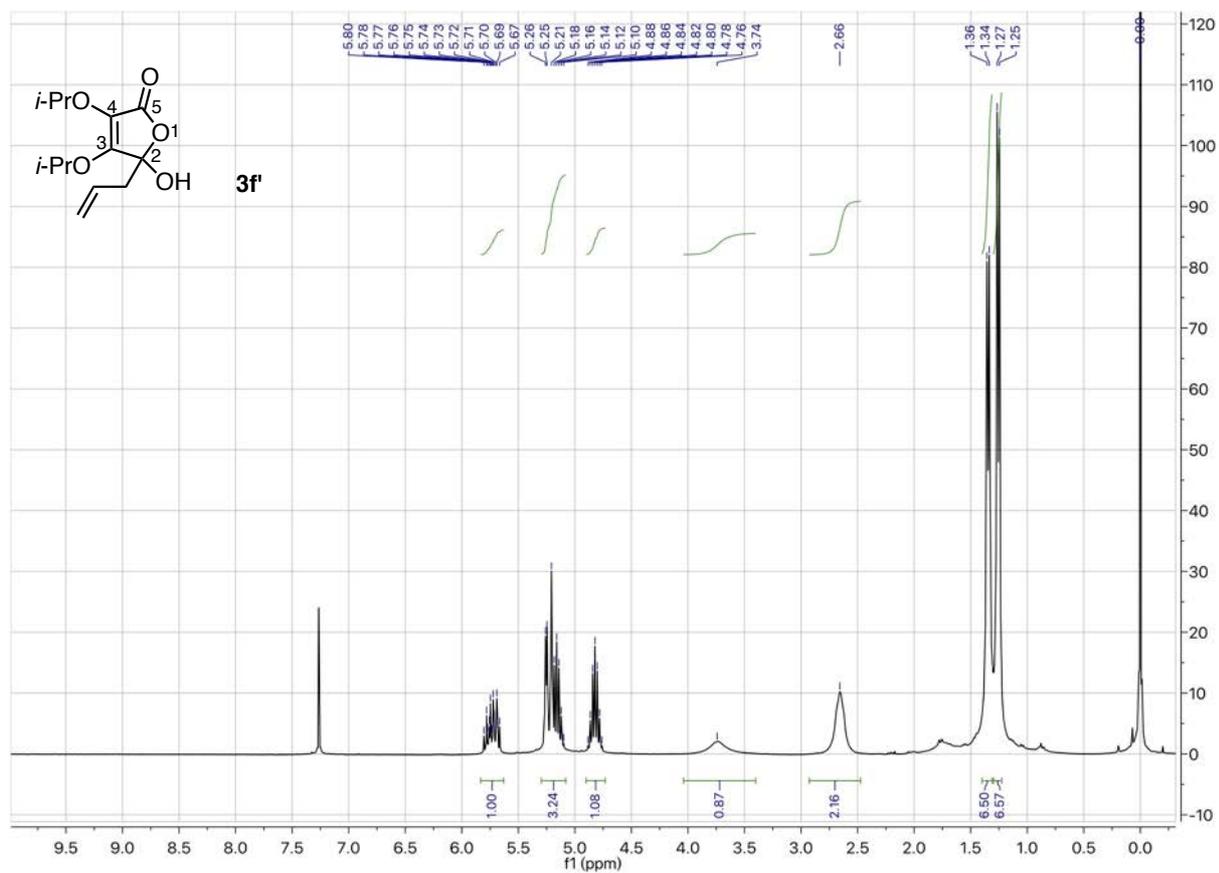
5-Hydroxy-3,4-diisopropoxy-5-methylfuran-2(5H)-one (3e')



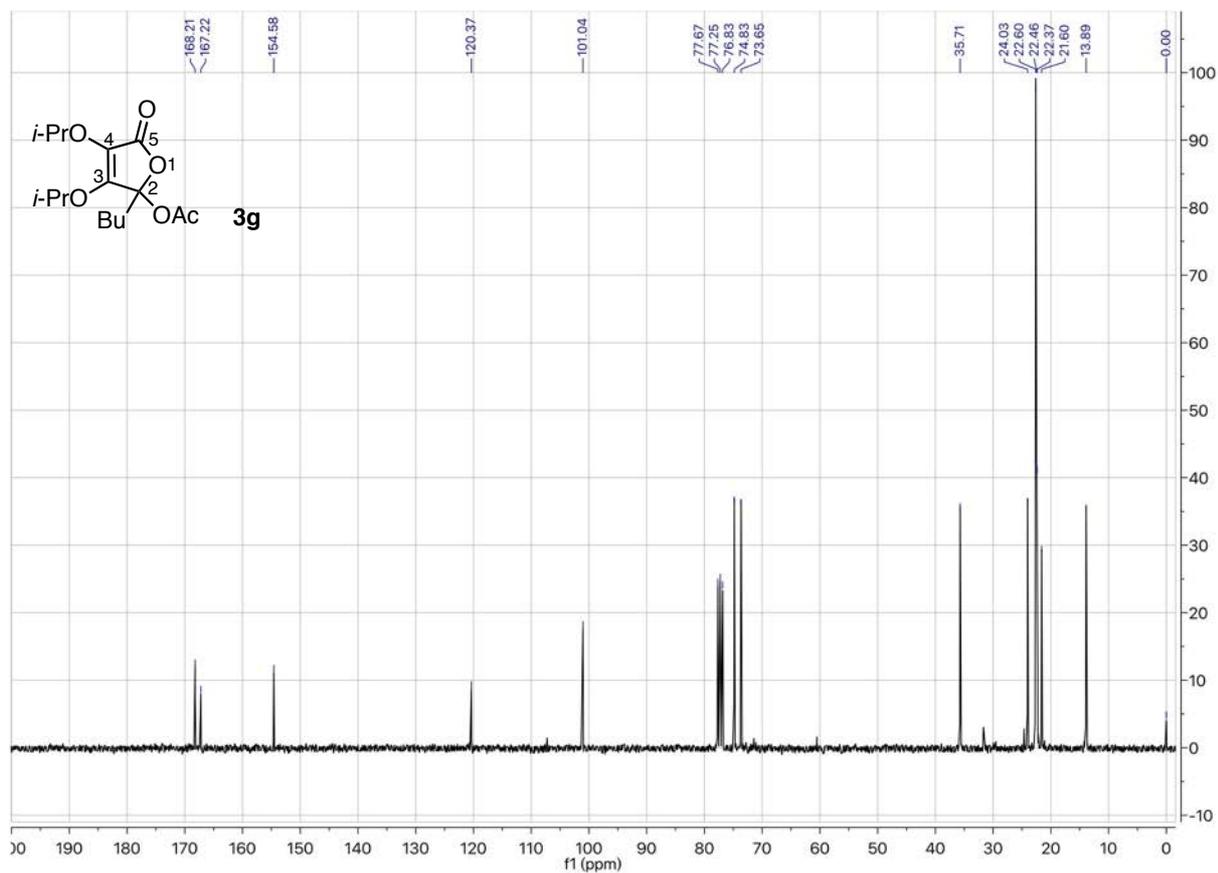
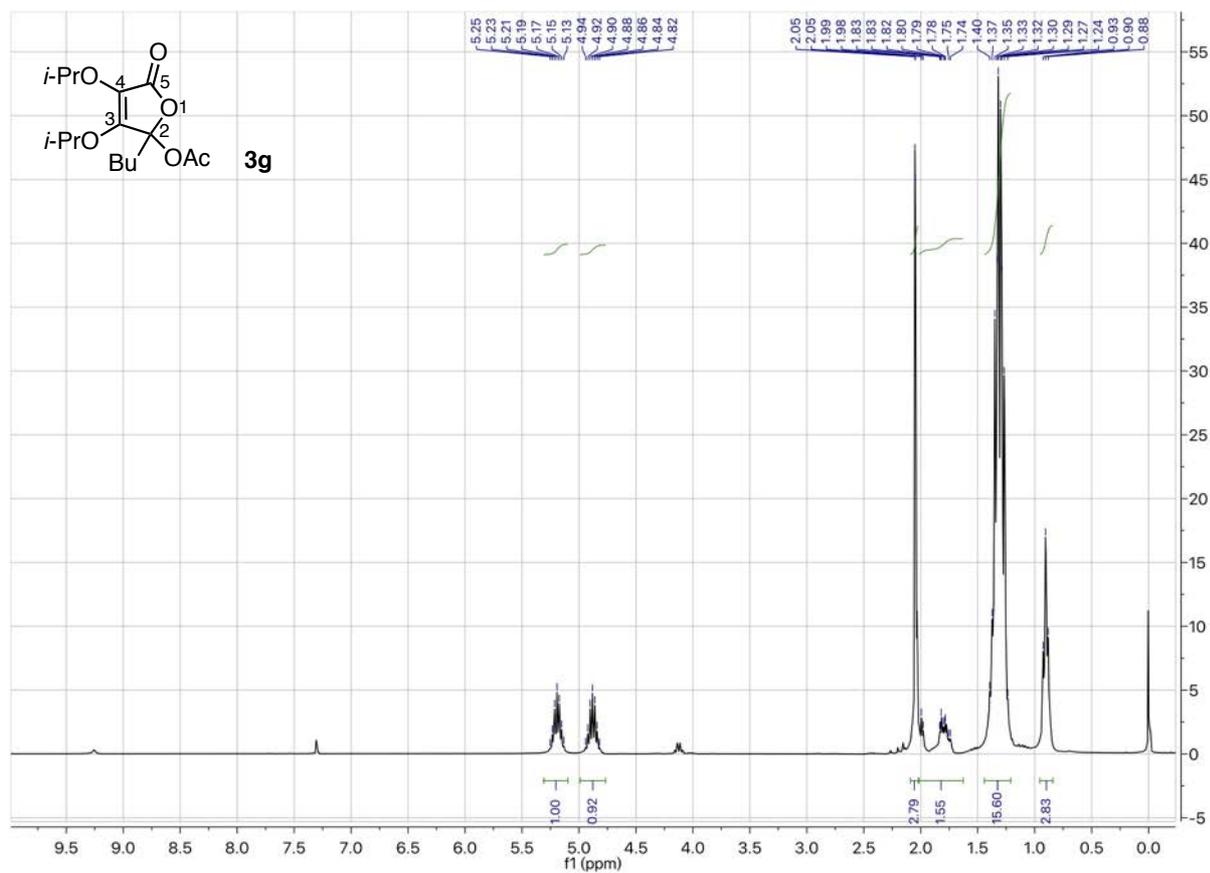
2-Allyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3f):



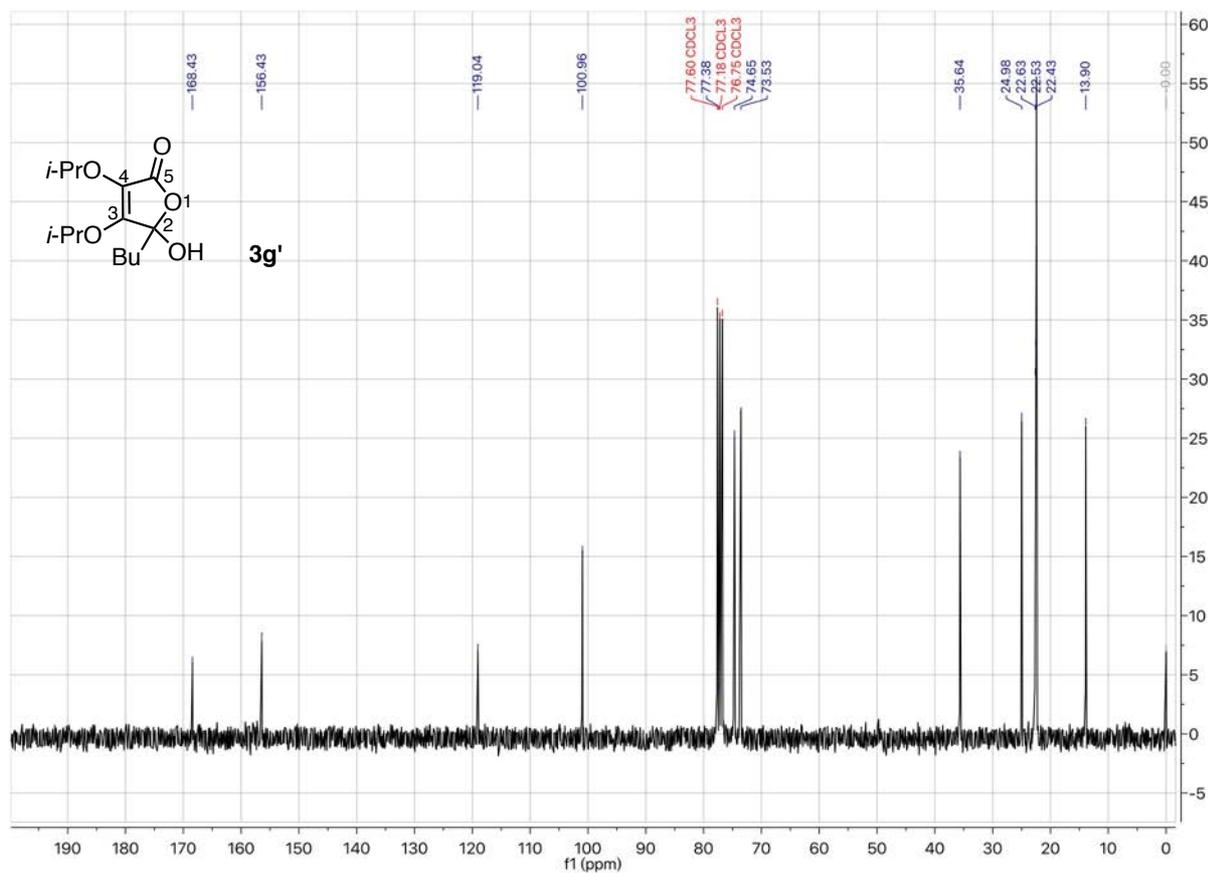
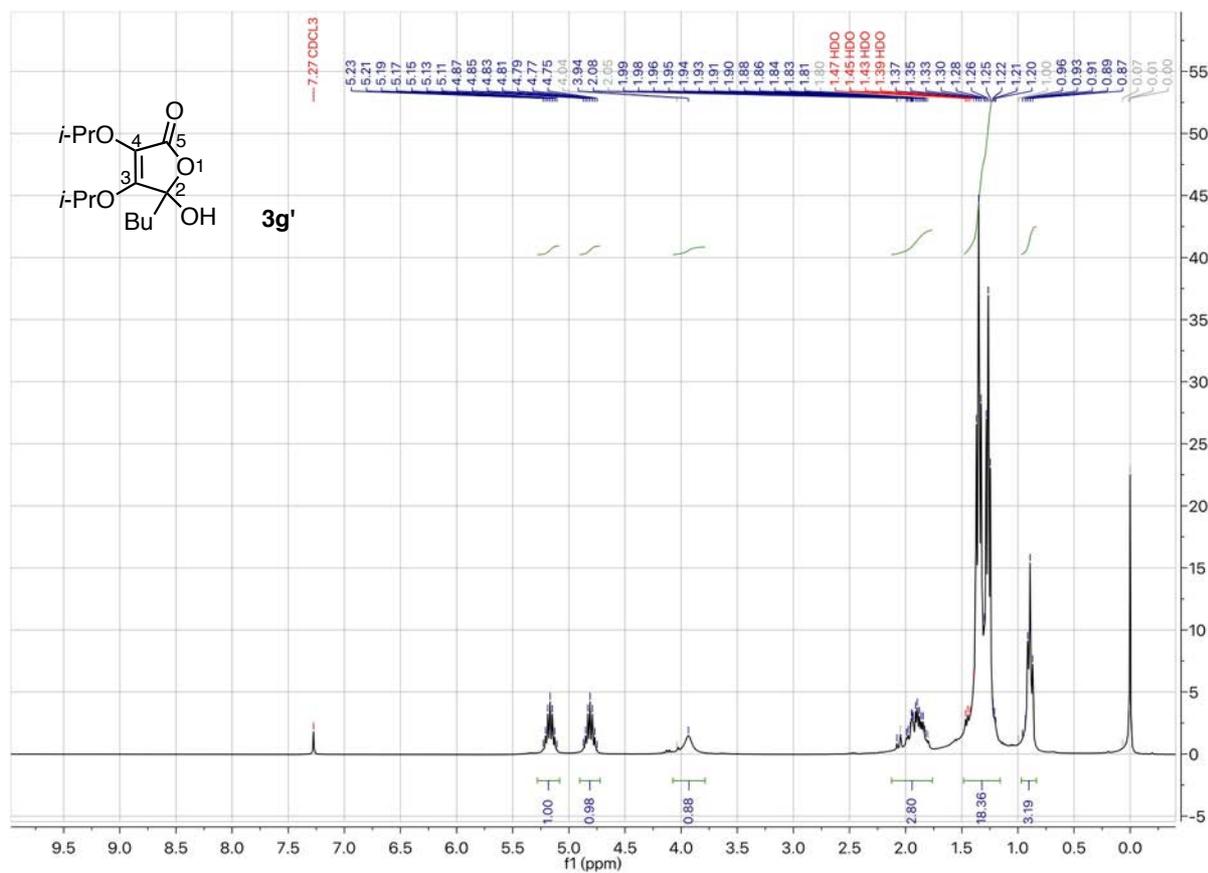
5-Allyl-5-hydroxy-3,4-diisopropoxyfuran-2(5H)-one (3f')



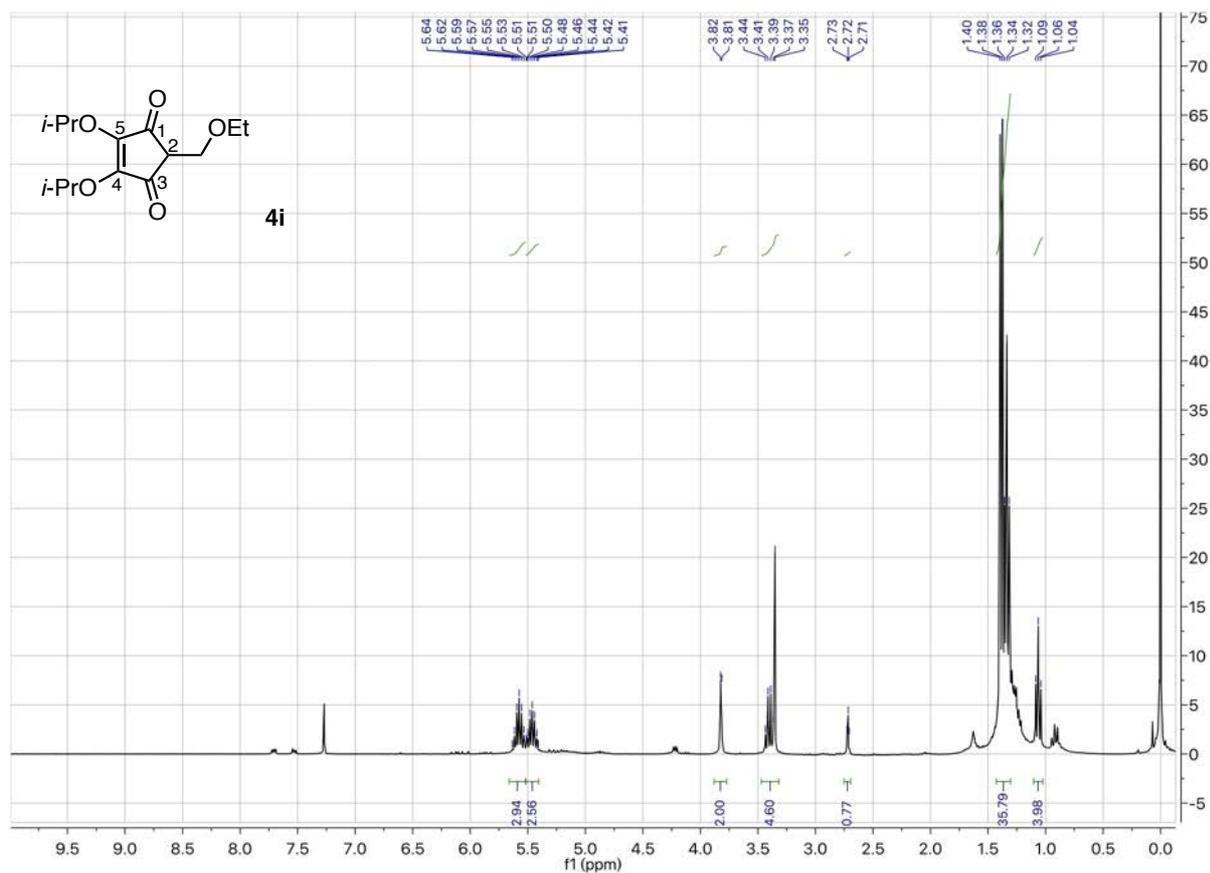
2-Butyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (**3g**):



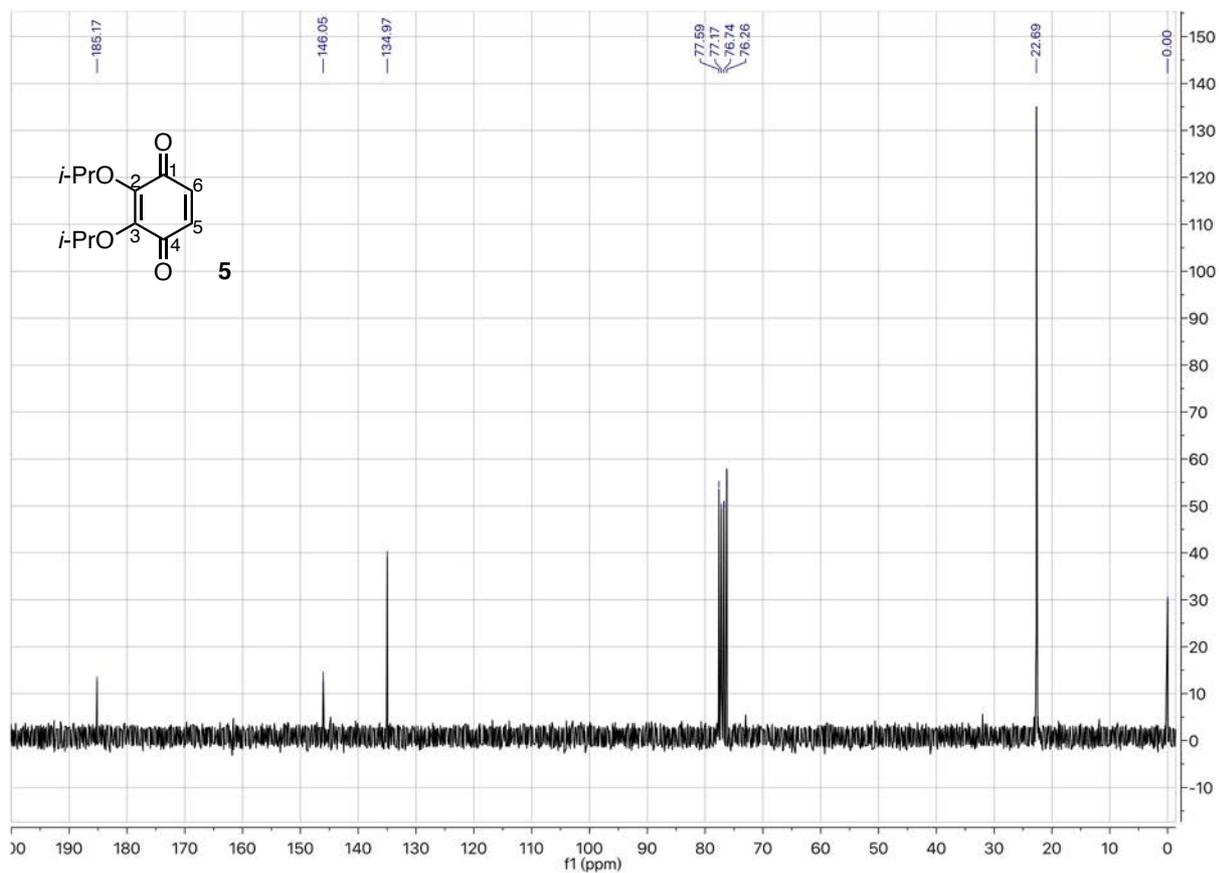
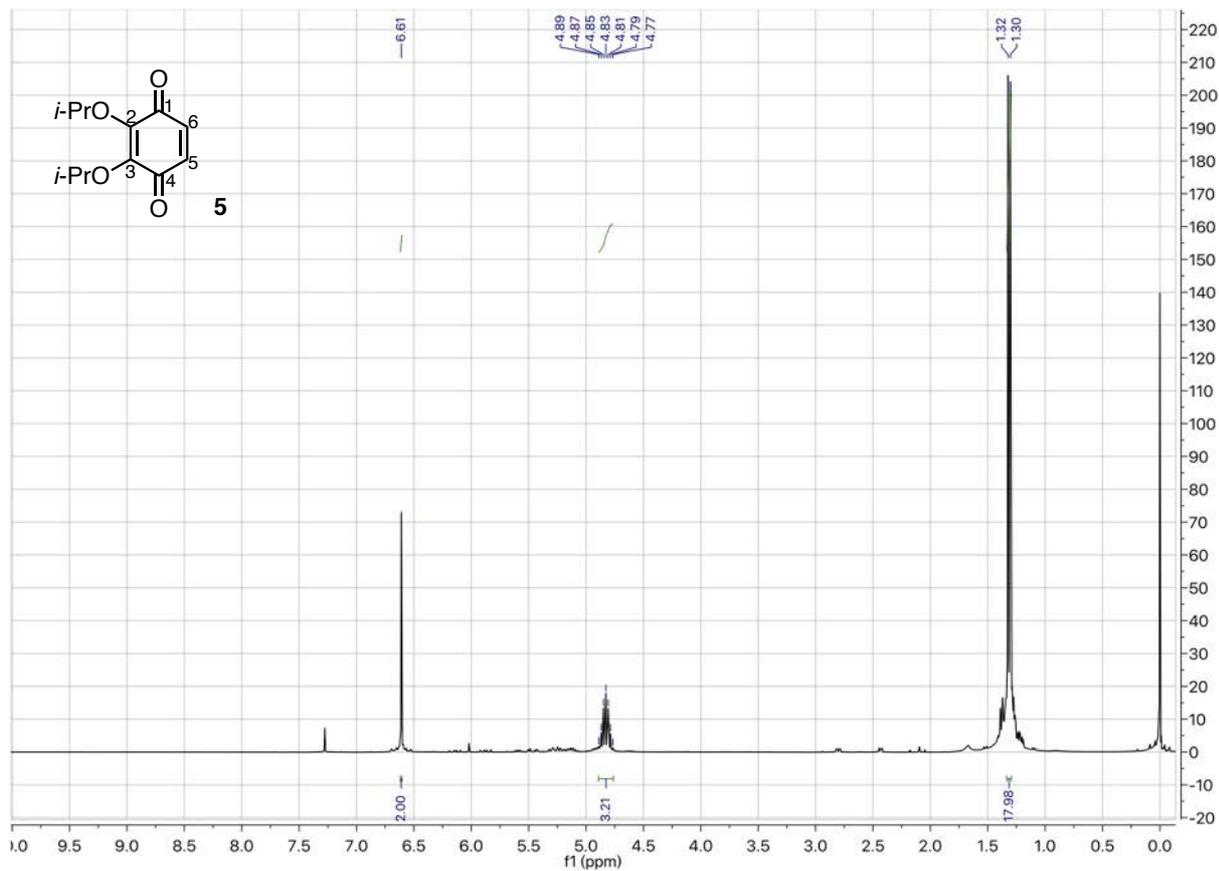
5-Butyl-5-hydroxy-3,4-diisopropoxyfuran-2(5H)-one (3g')



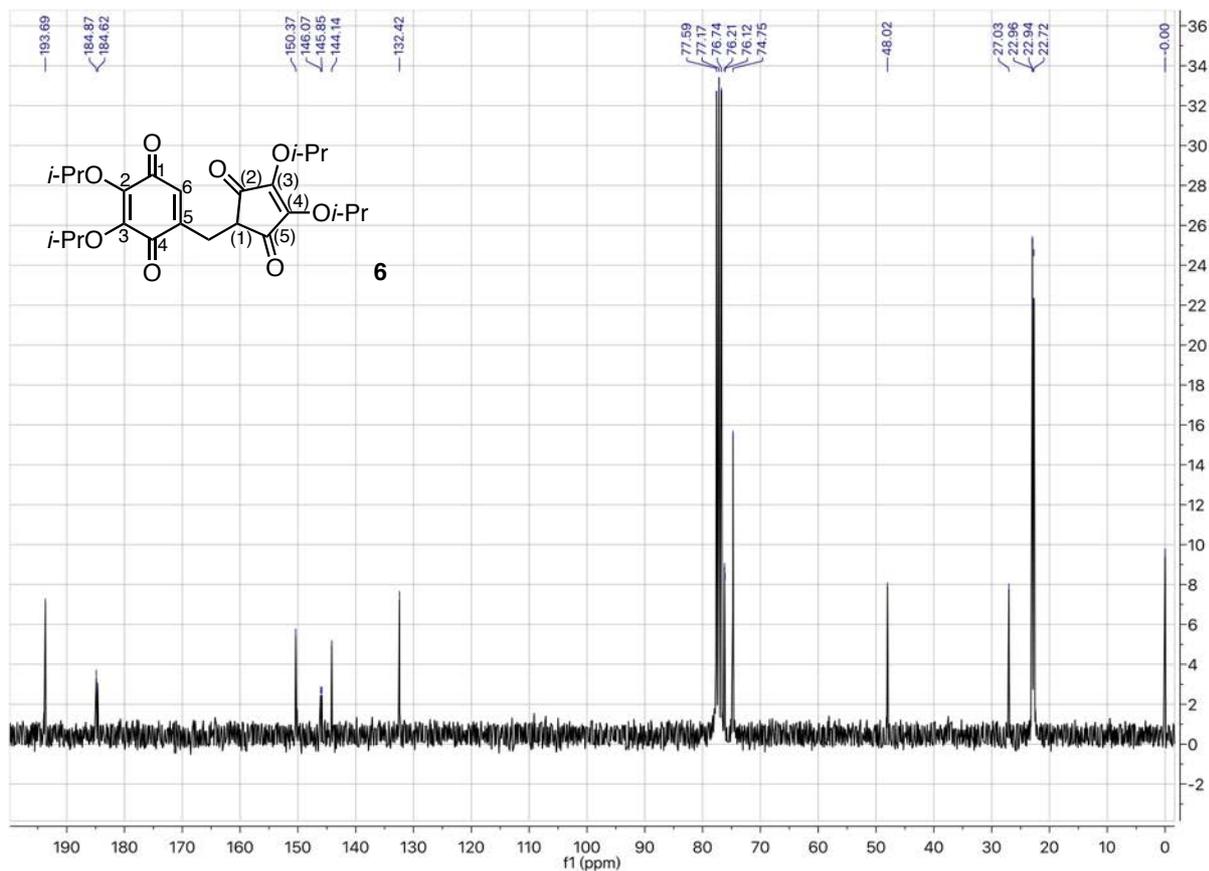
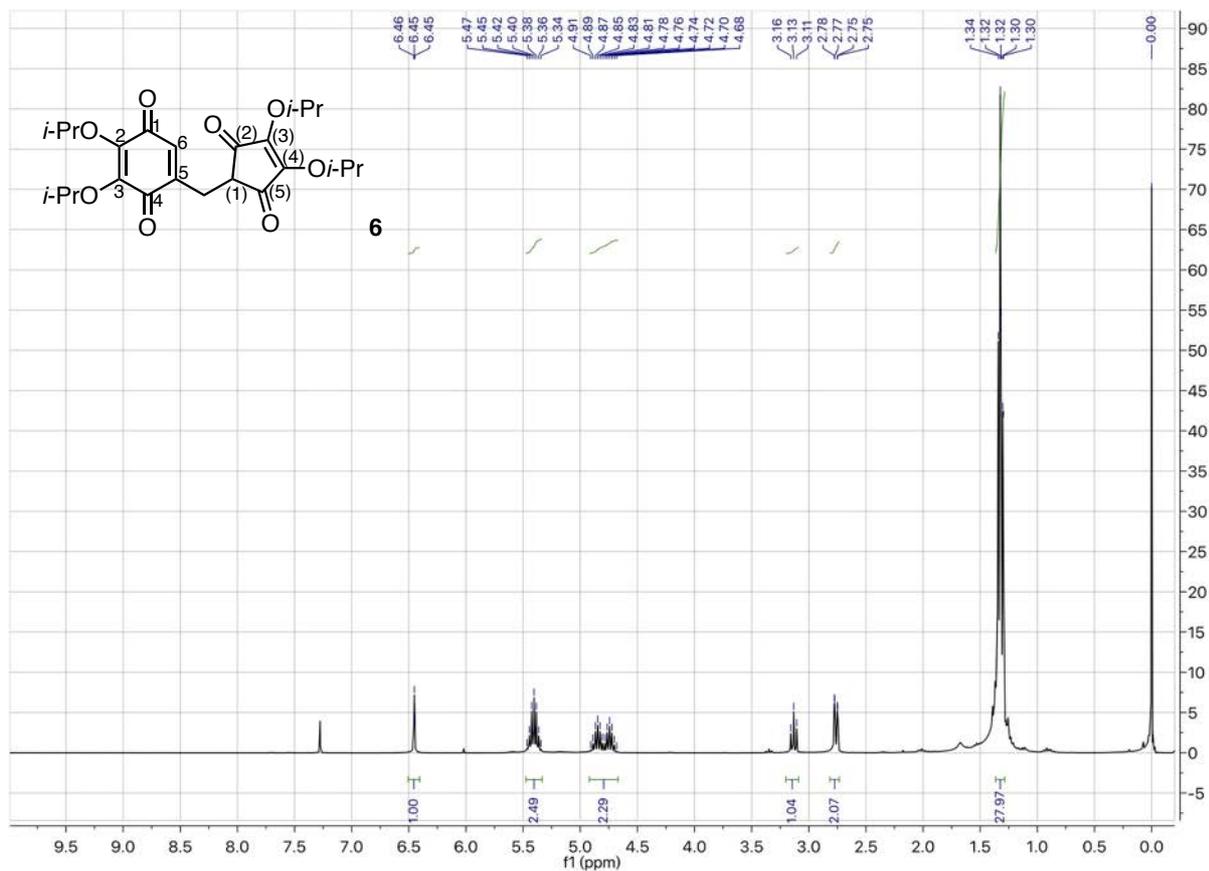
2-(Ethoxymethyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4i):



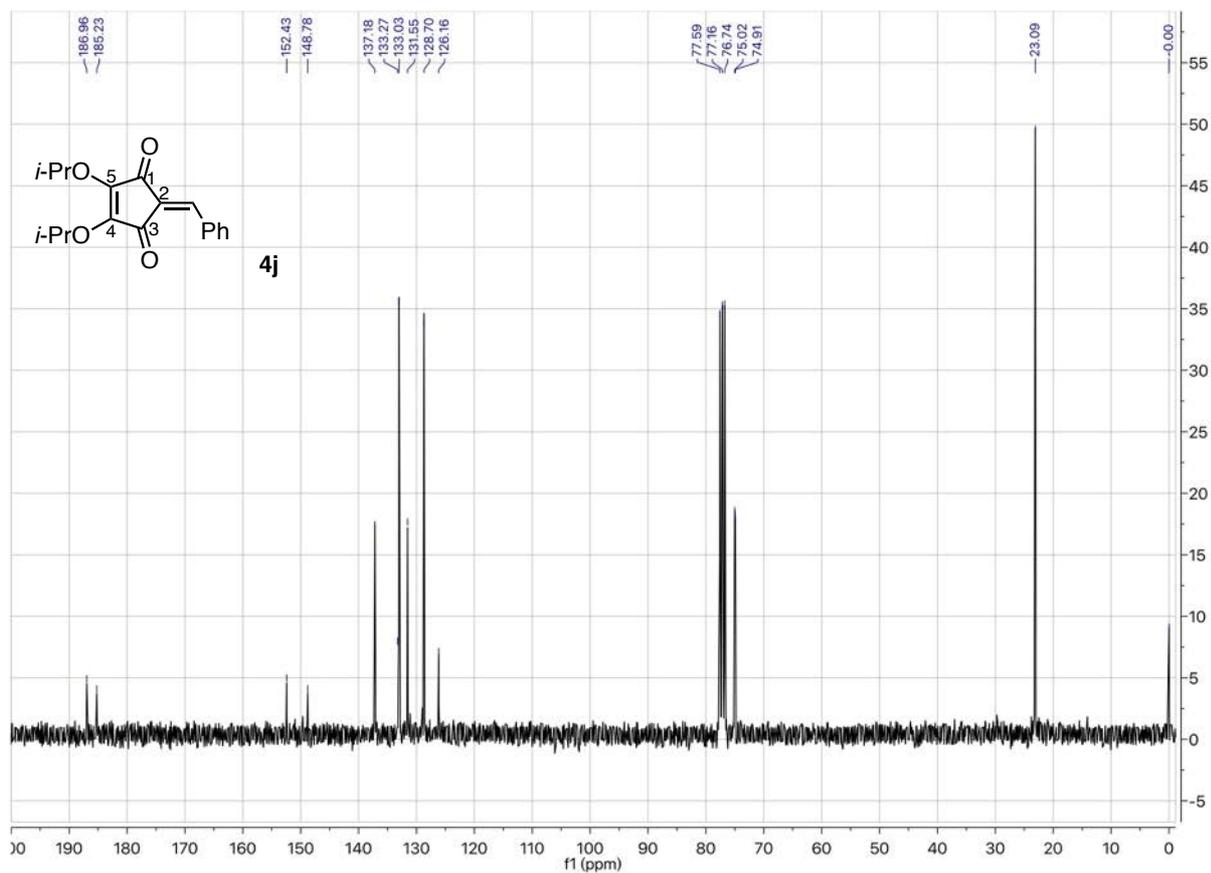
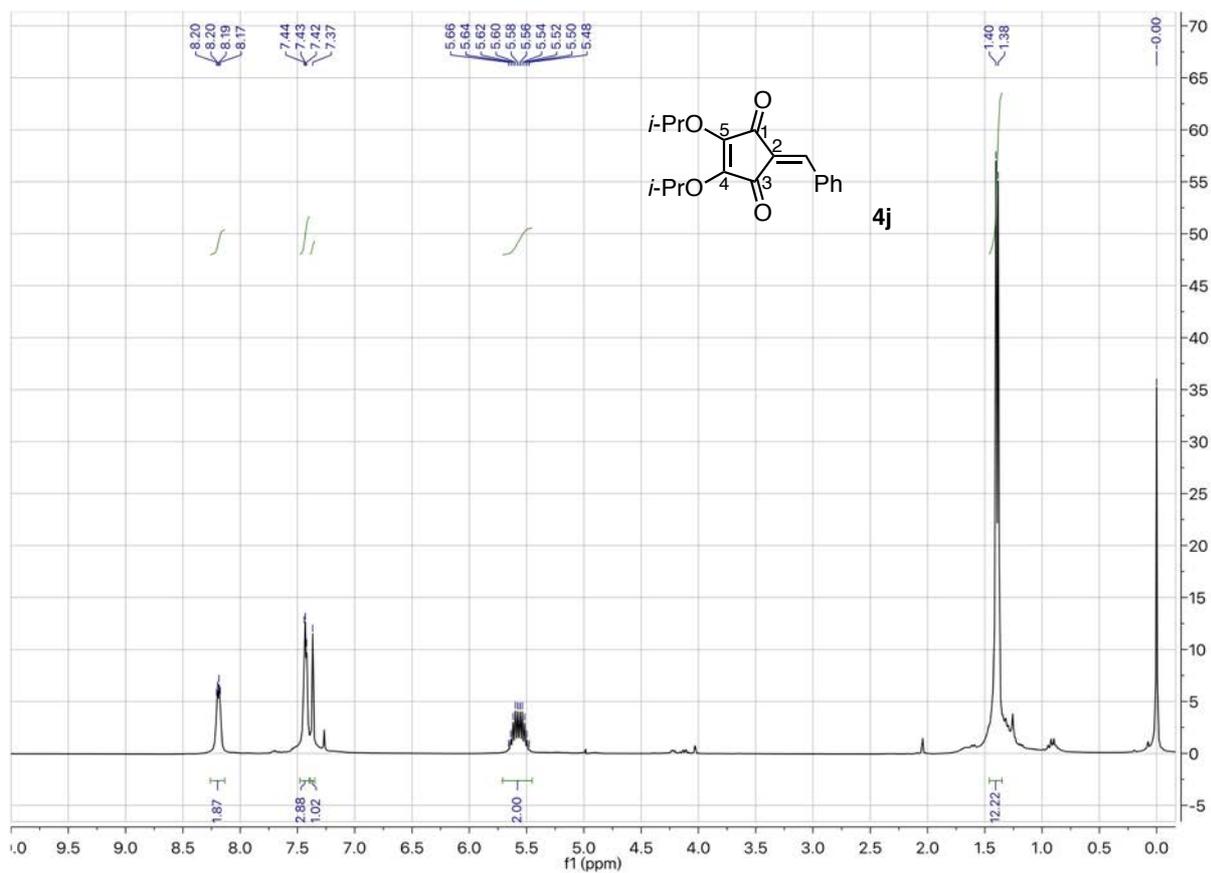
2,3-Diisopropoxycyclohexa-2,5-diene-1,4-dione (5)<sup>30</sup>:

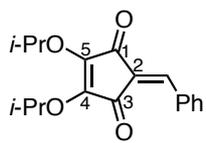


5-((3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-yl)methyl)-2,3-diisopropoxycyclohexa-2,5-diene-1,4-dione (6):

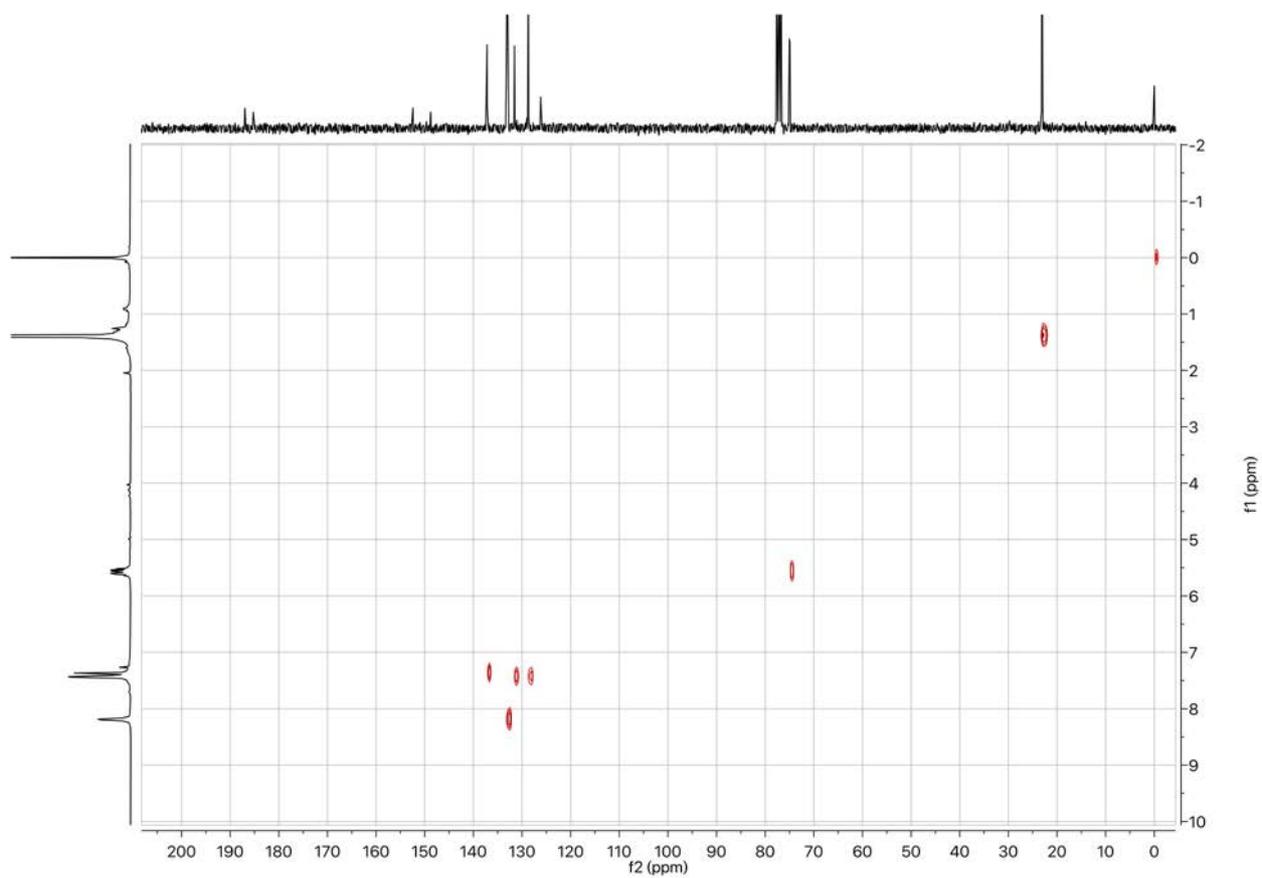


## 2-Benzylidene-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4j):

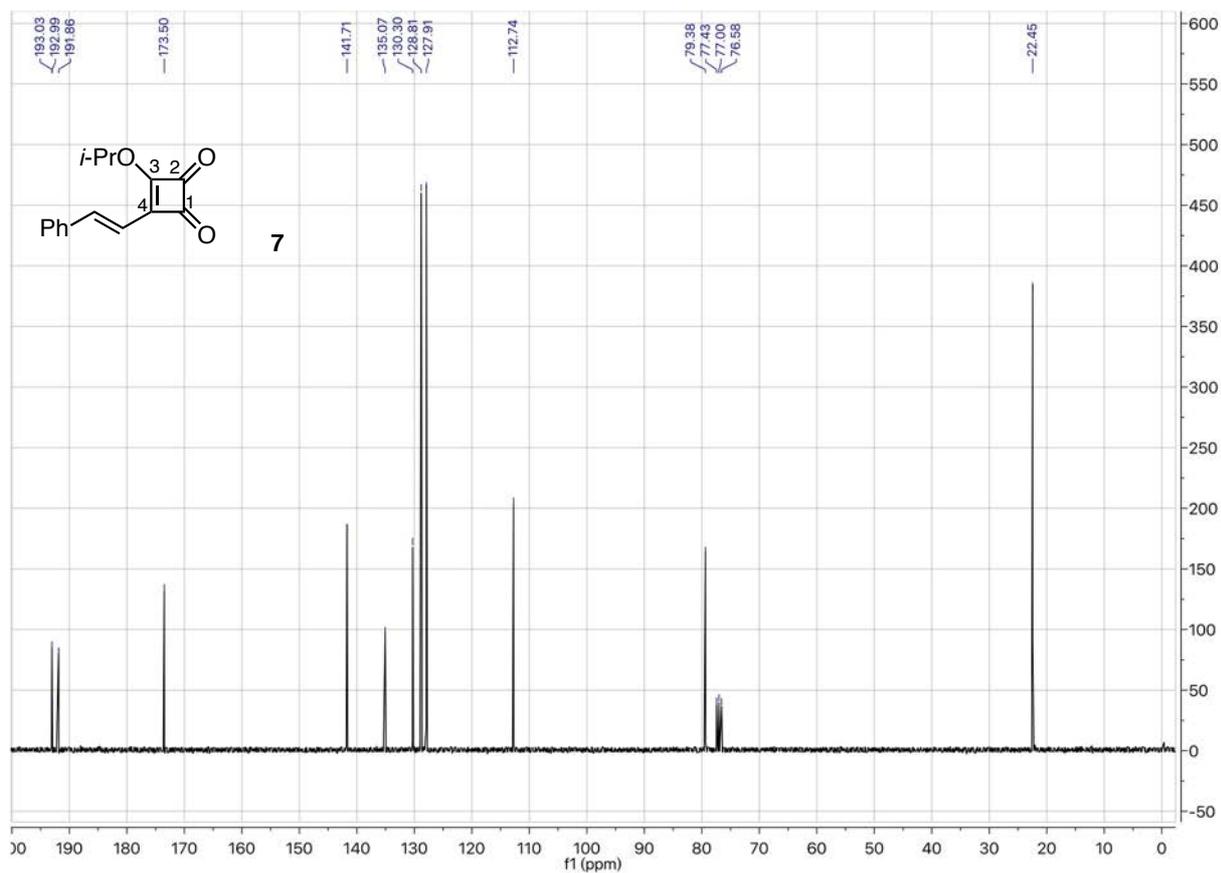
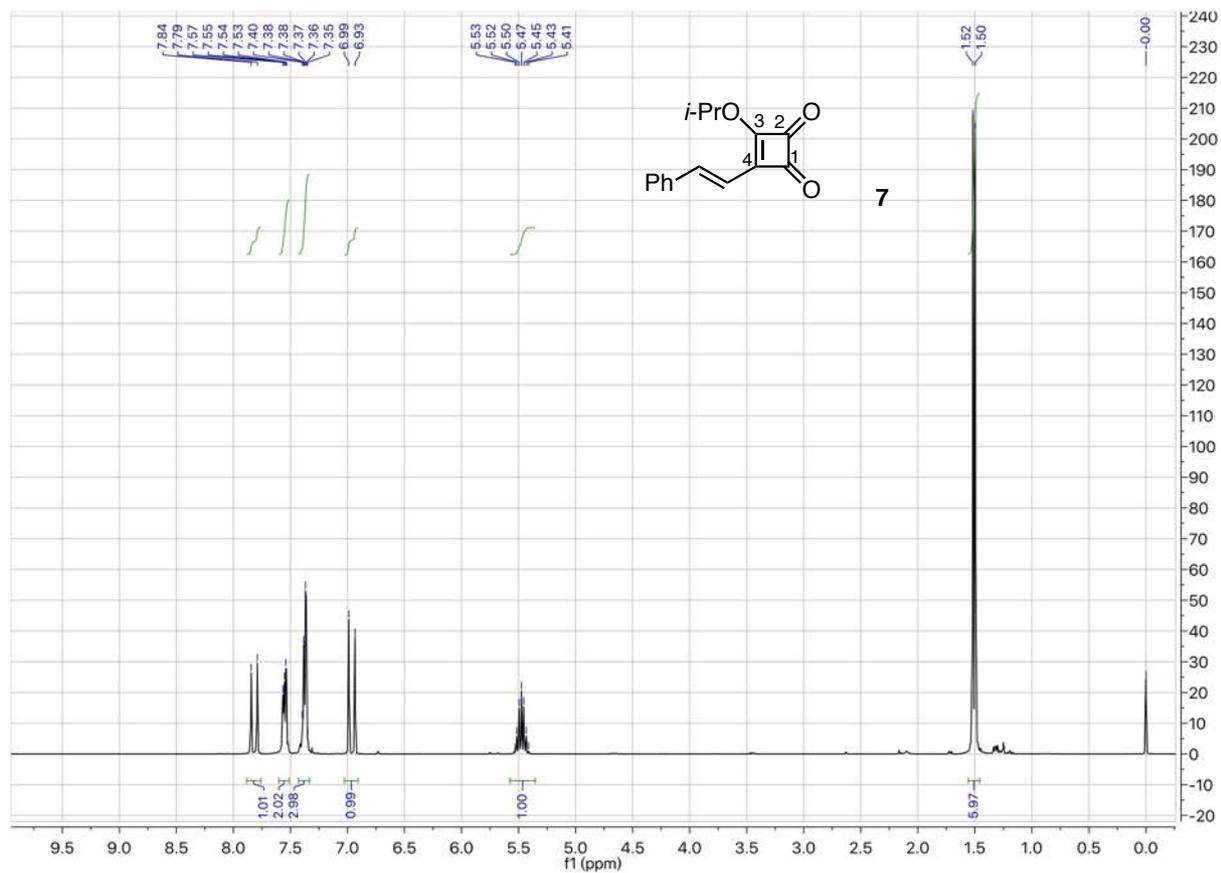




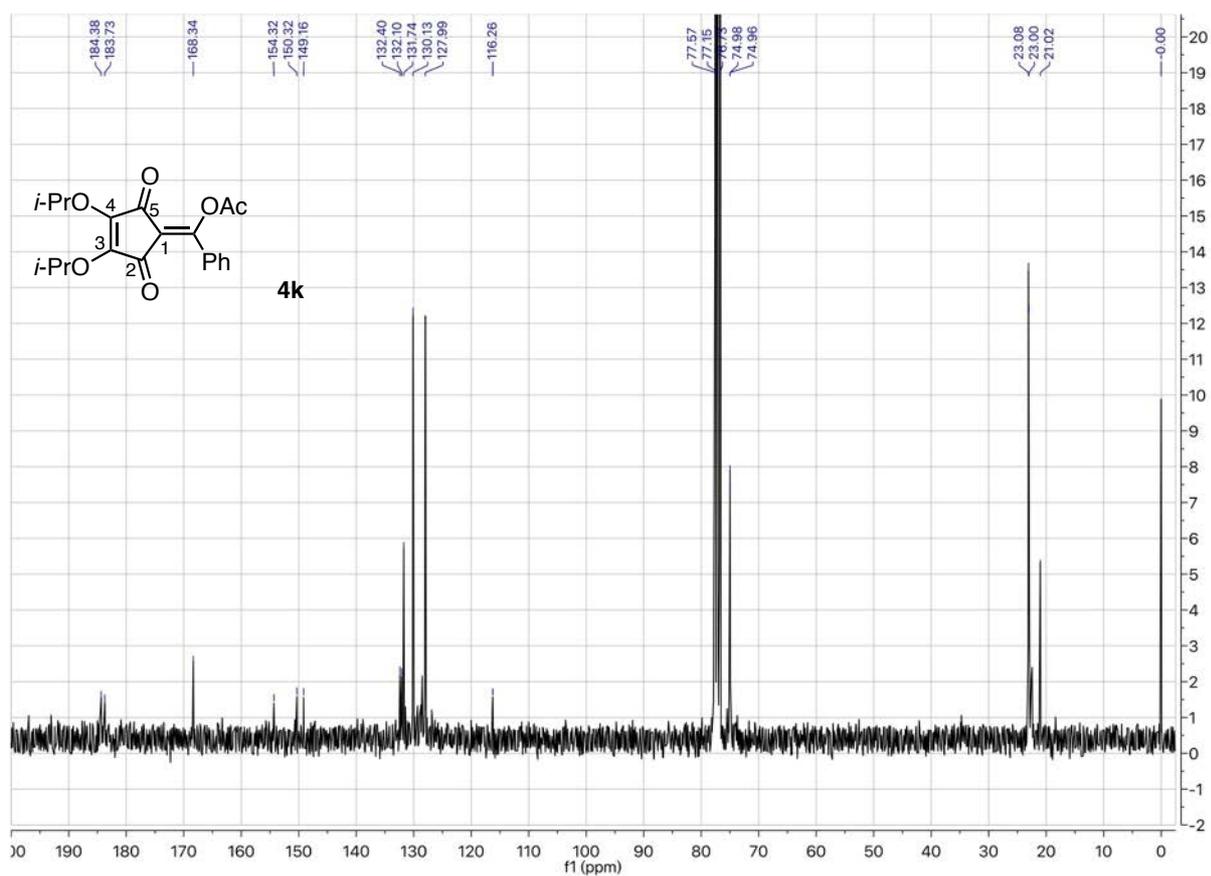
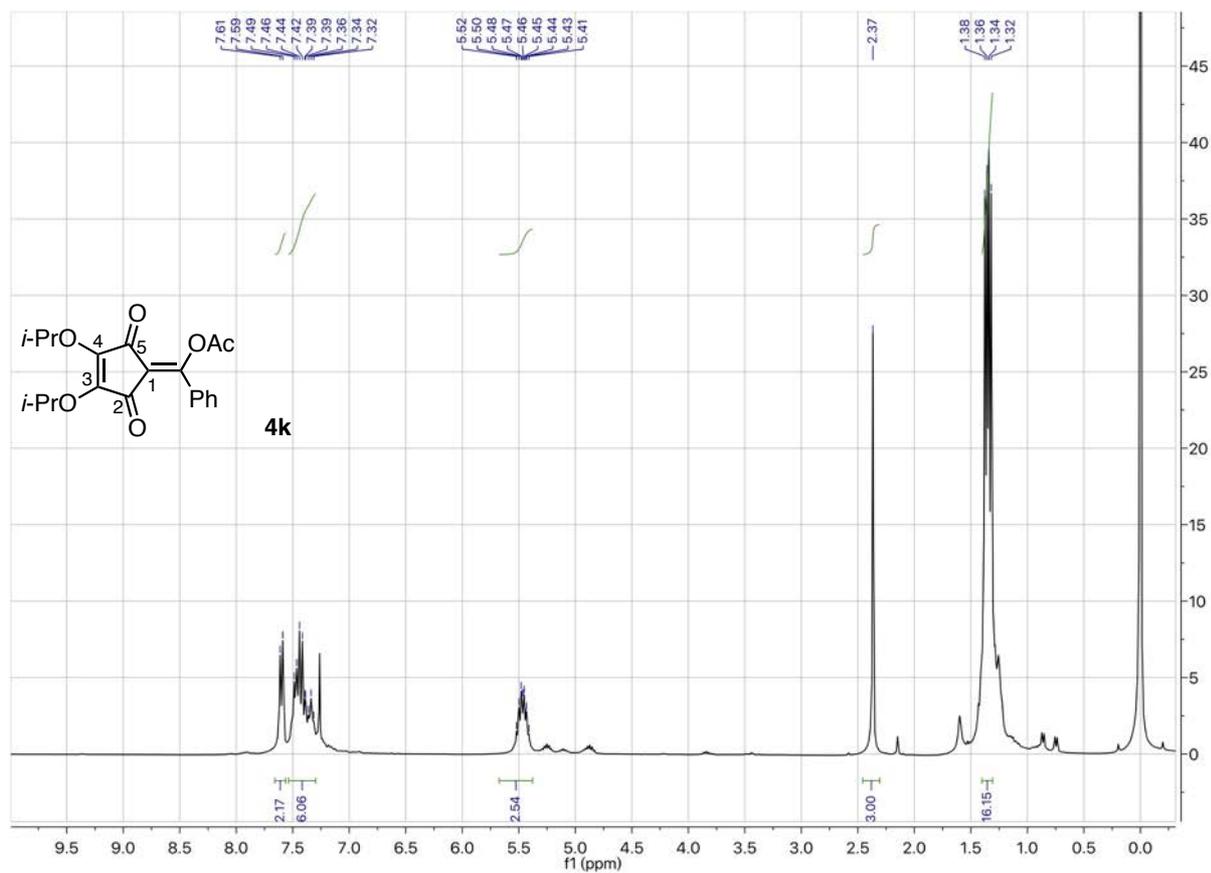
4j



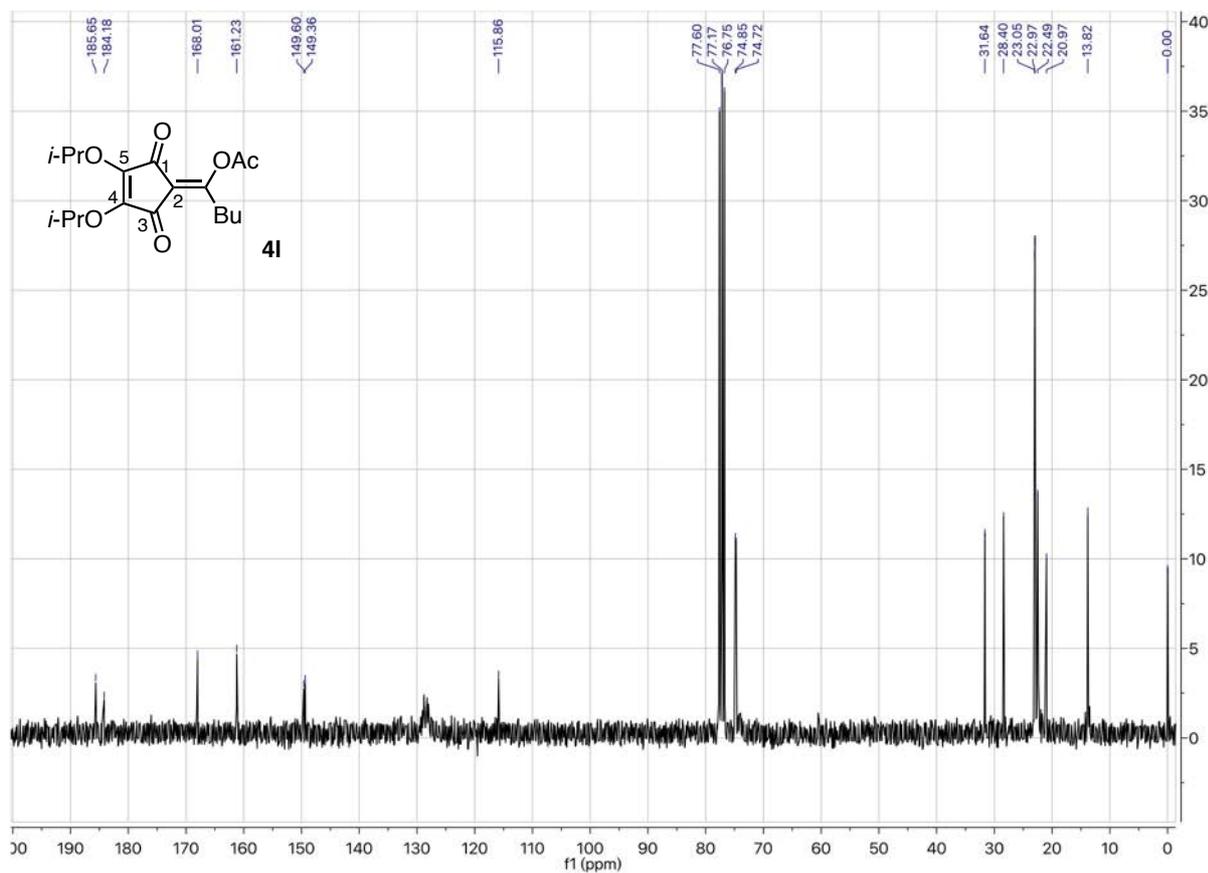
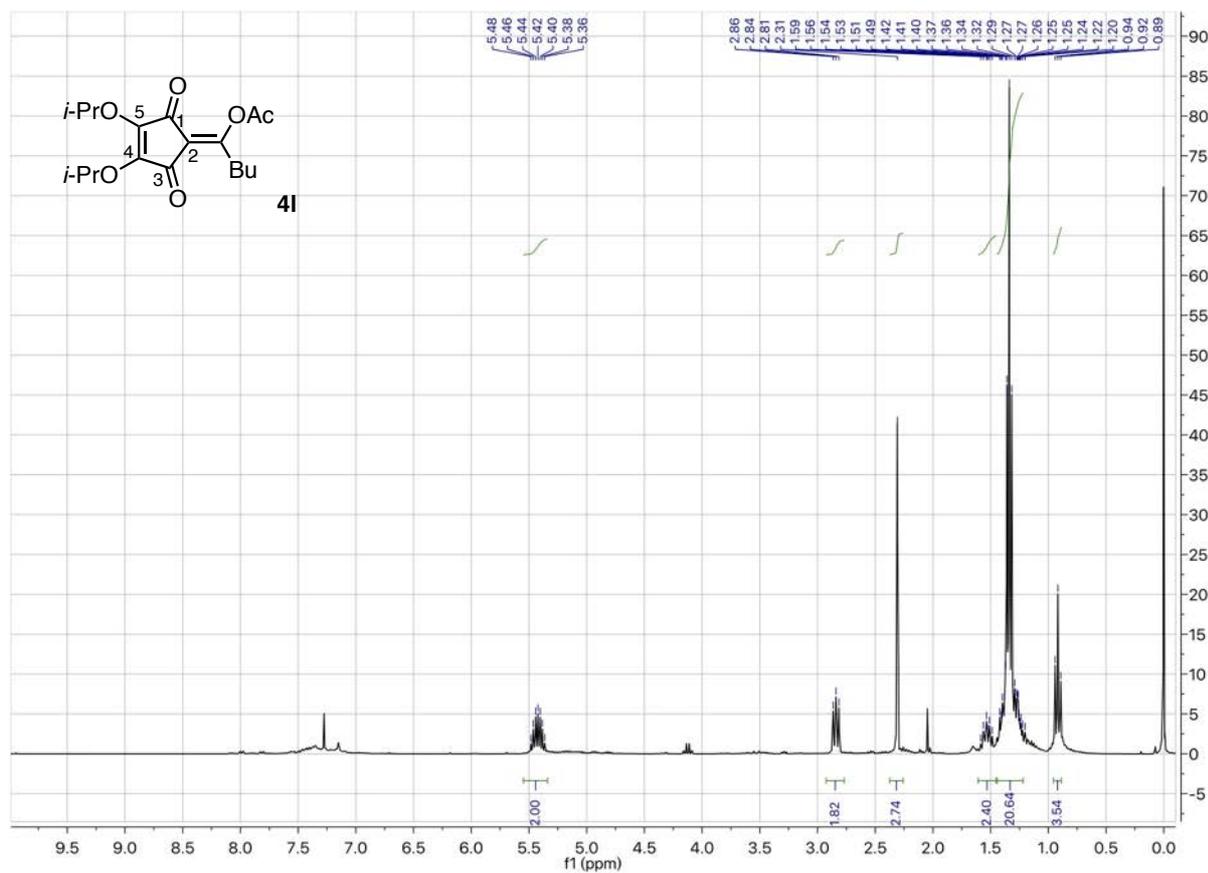
**(E)-3-Isopropoxy-4-styrylcyclobut-3-ene-1,2-dione (7)<sup>31</sup>:**



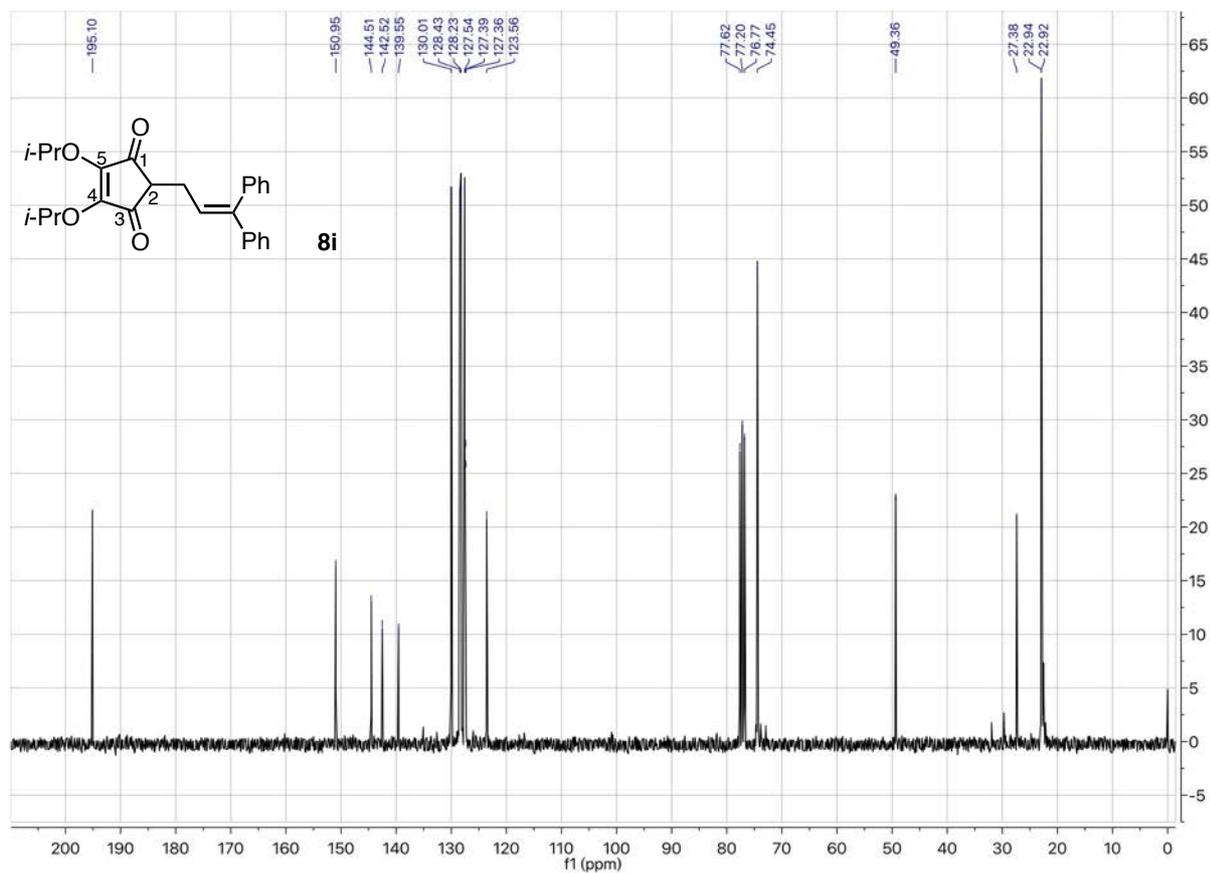
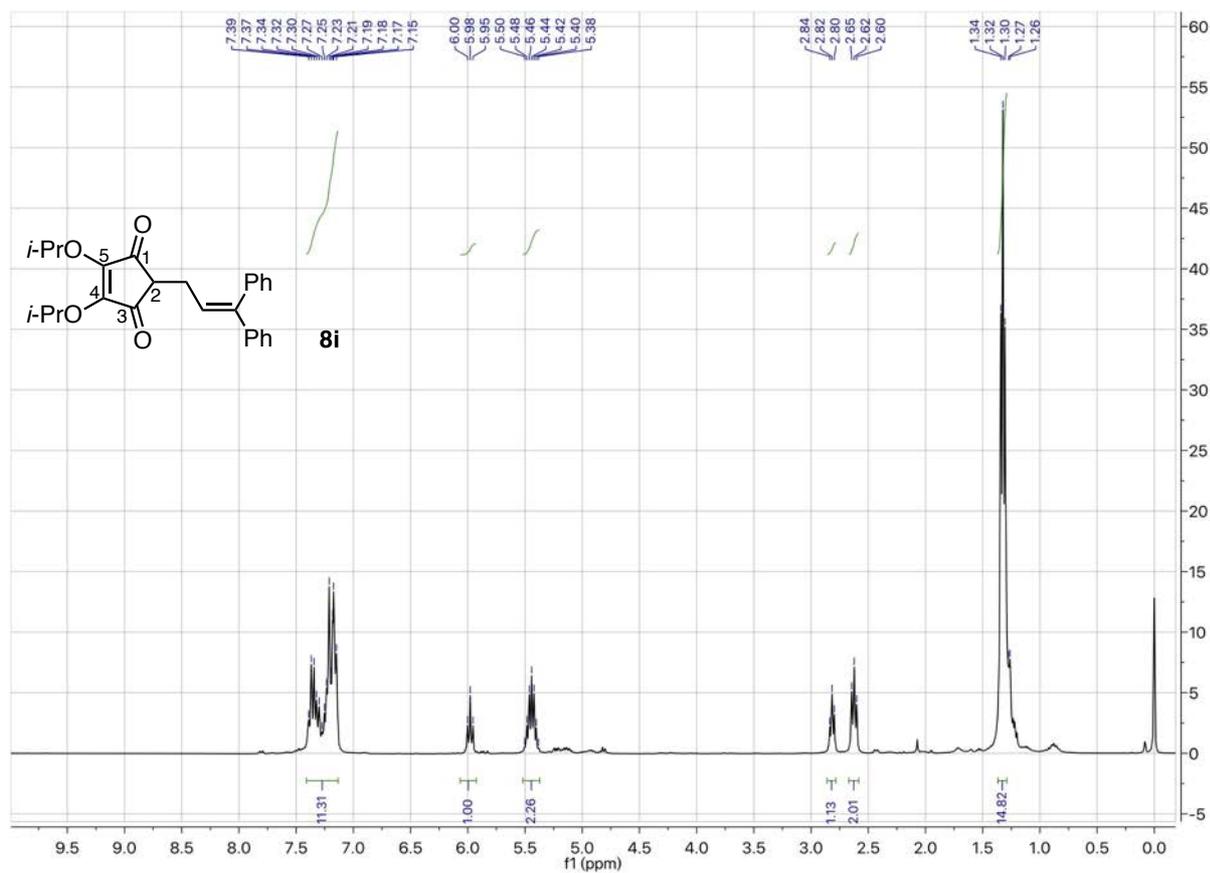
**(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)(phenyl)methyl acetate (4k):**



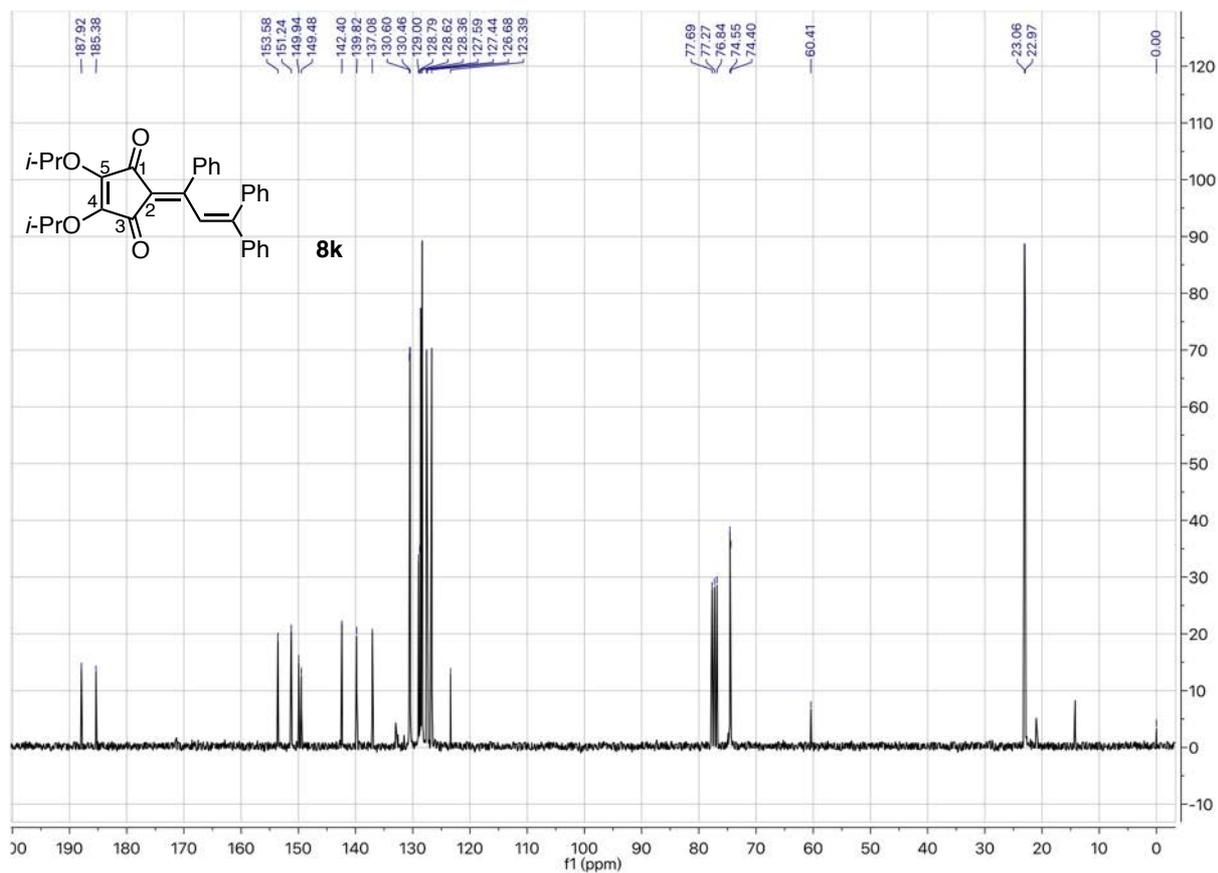
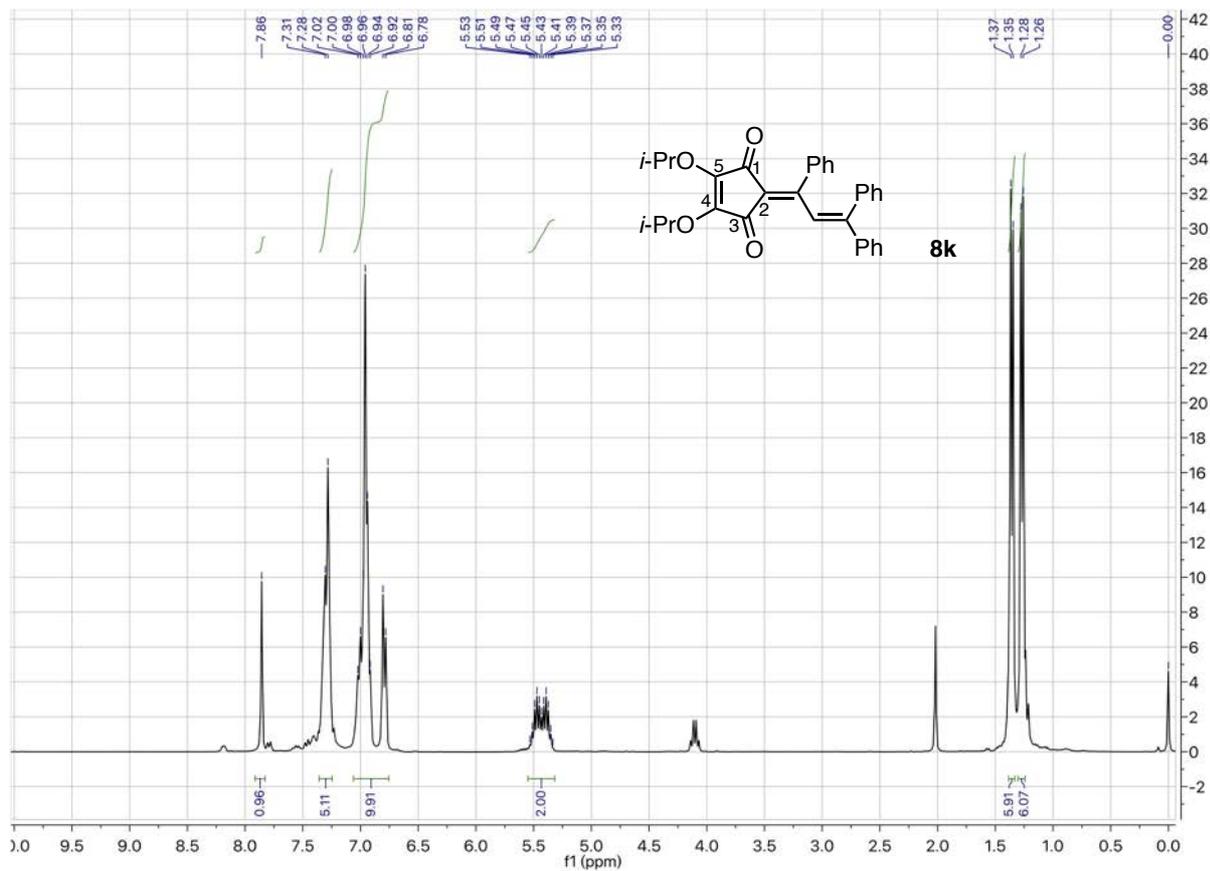
**1-(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)pentyl acetate (4I):**

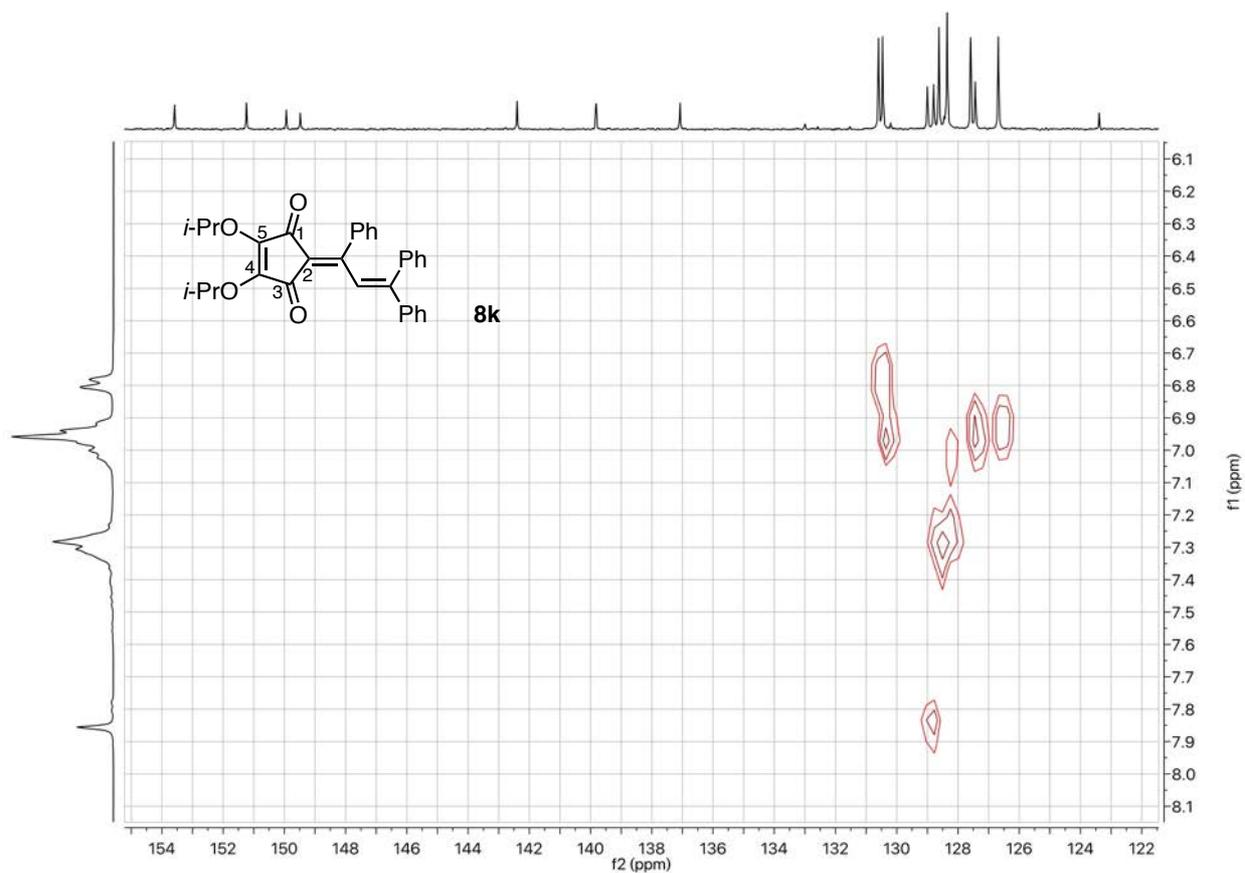
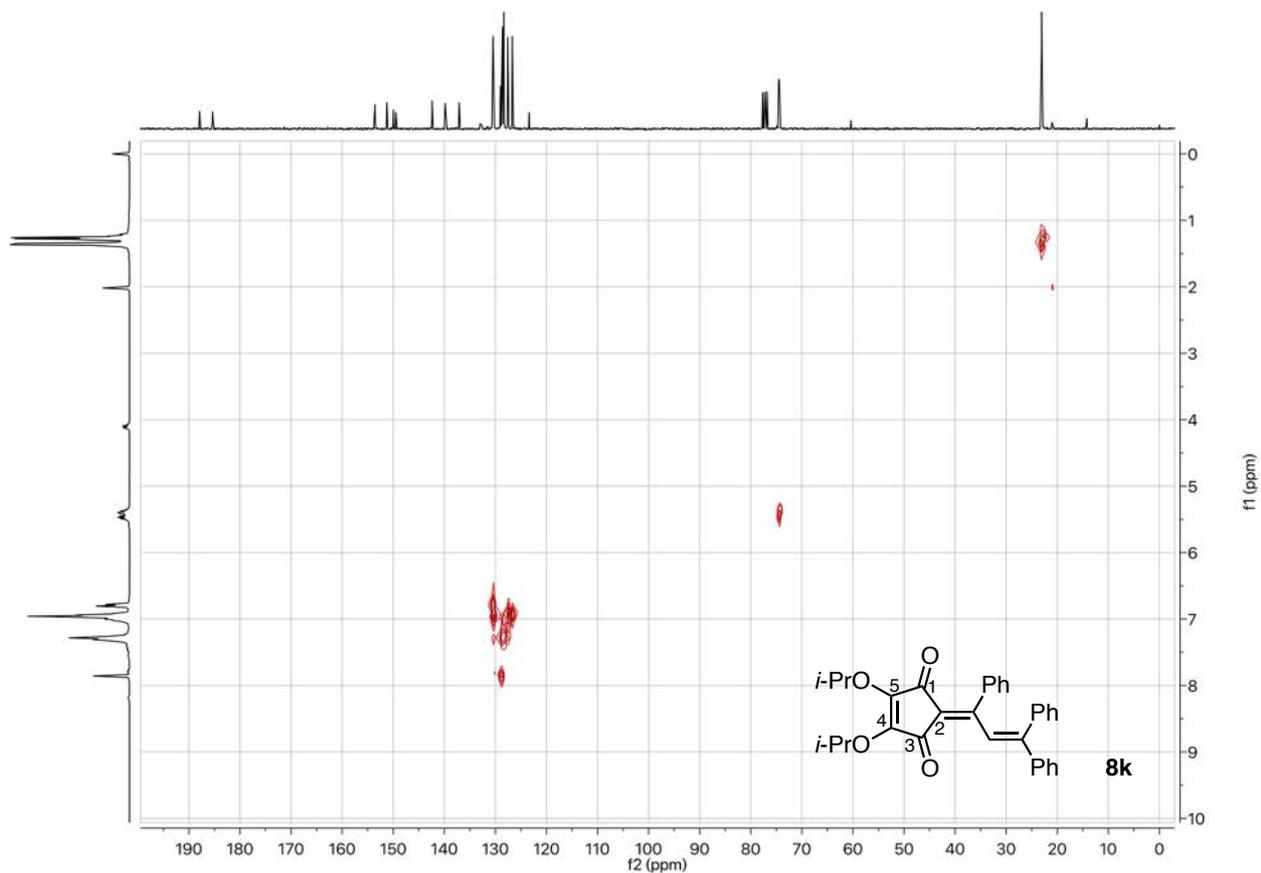


2-(3,3-diphenylallyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (**8i**):

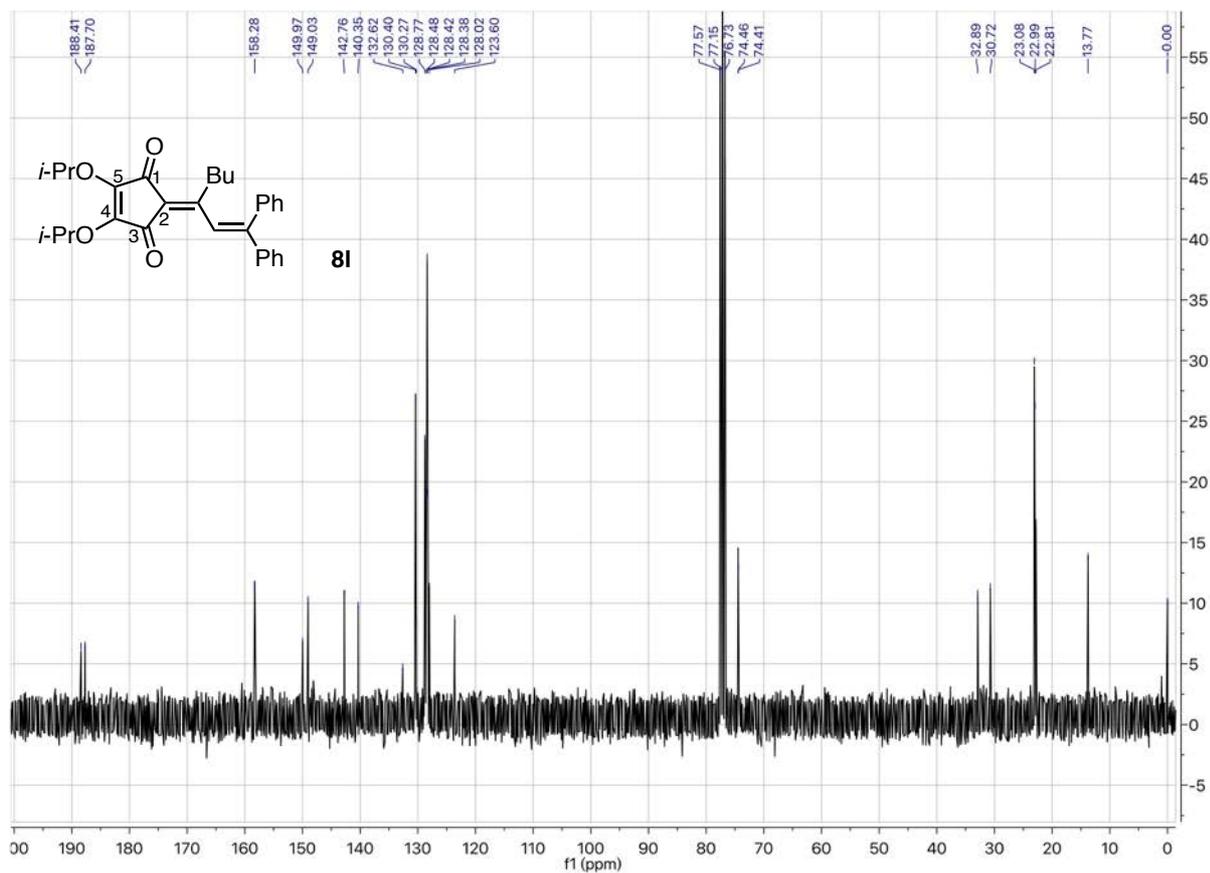
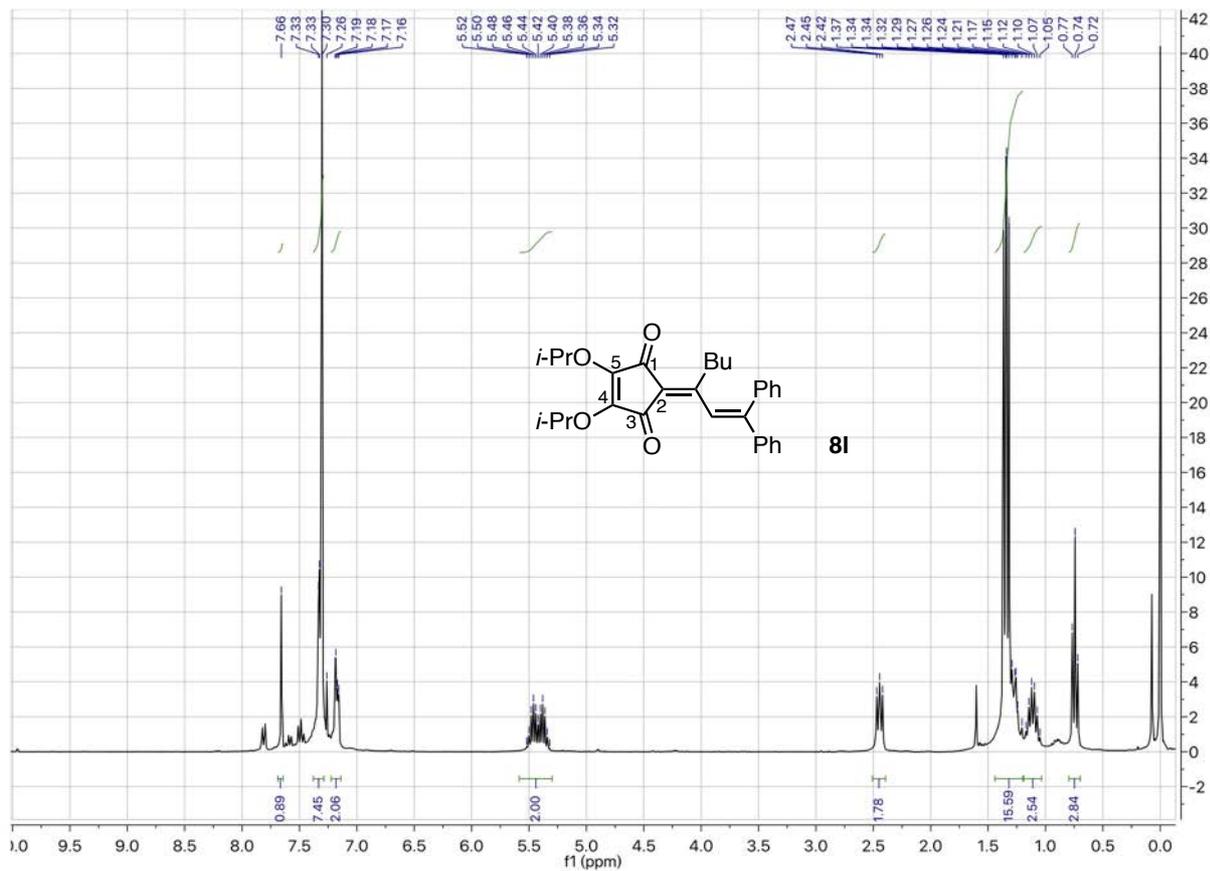


4,5-Diisopropoxy-2-(1,3,3-triphenylallylidene)cyclopent-4-ene-1,3-dione (**8k**):

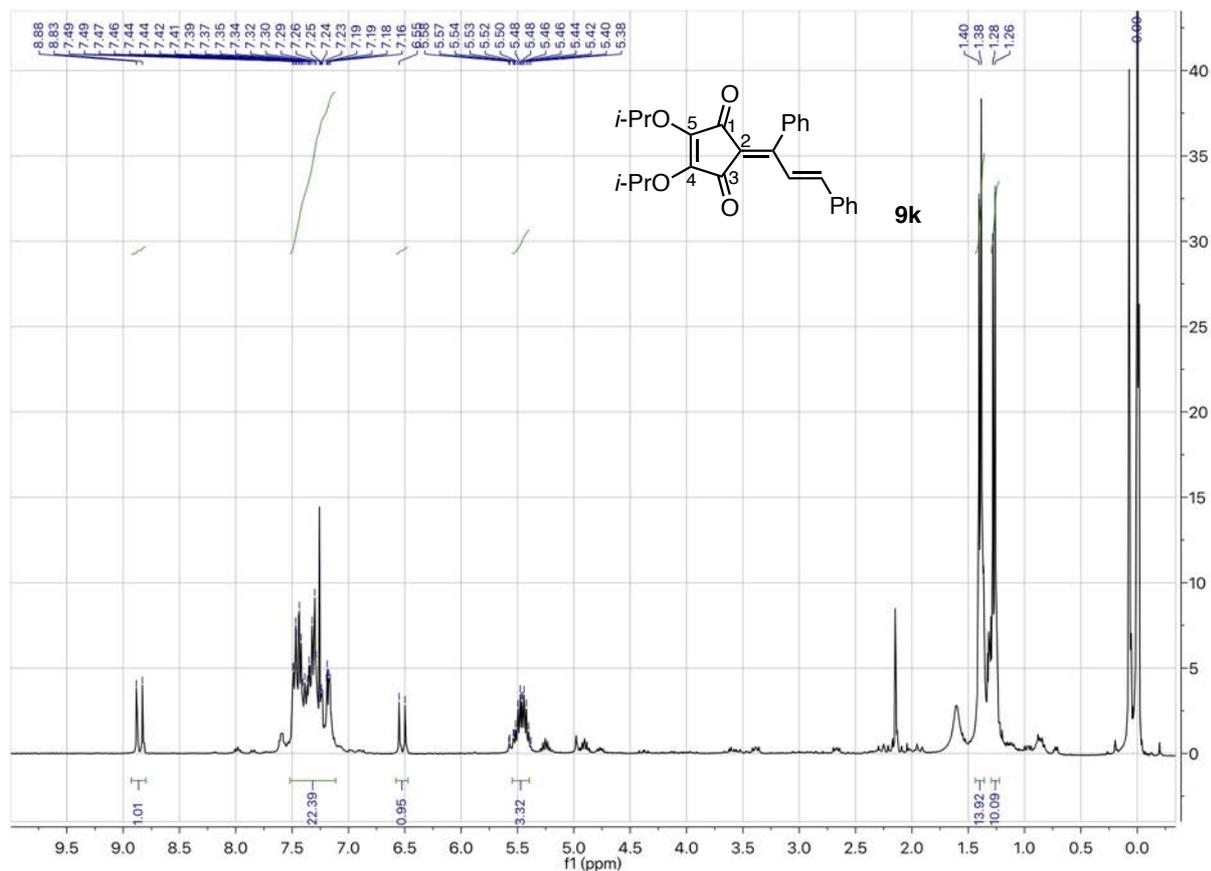




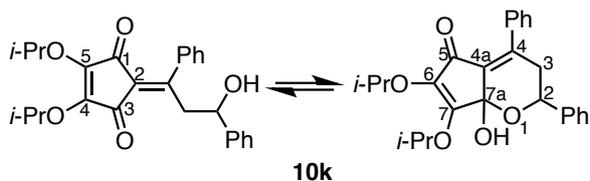
2-(1,1-Diphenylhept-1-en-3-ylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (**8I**):

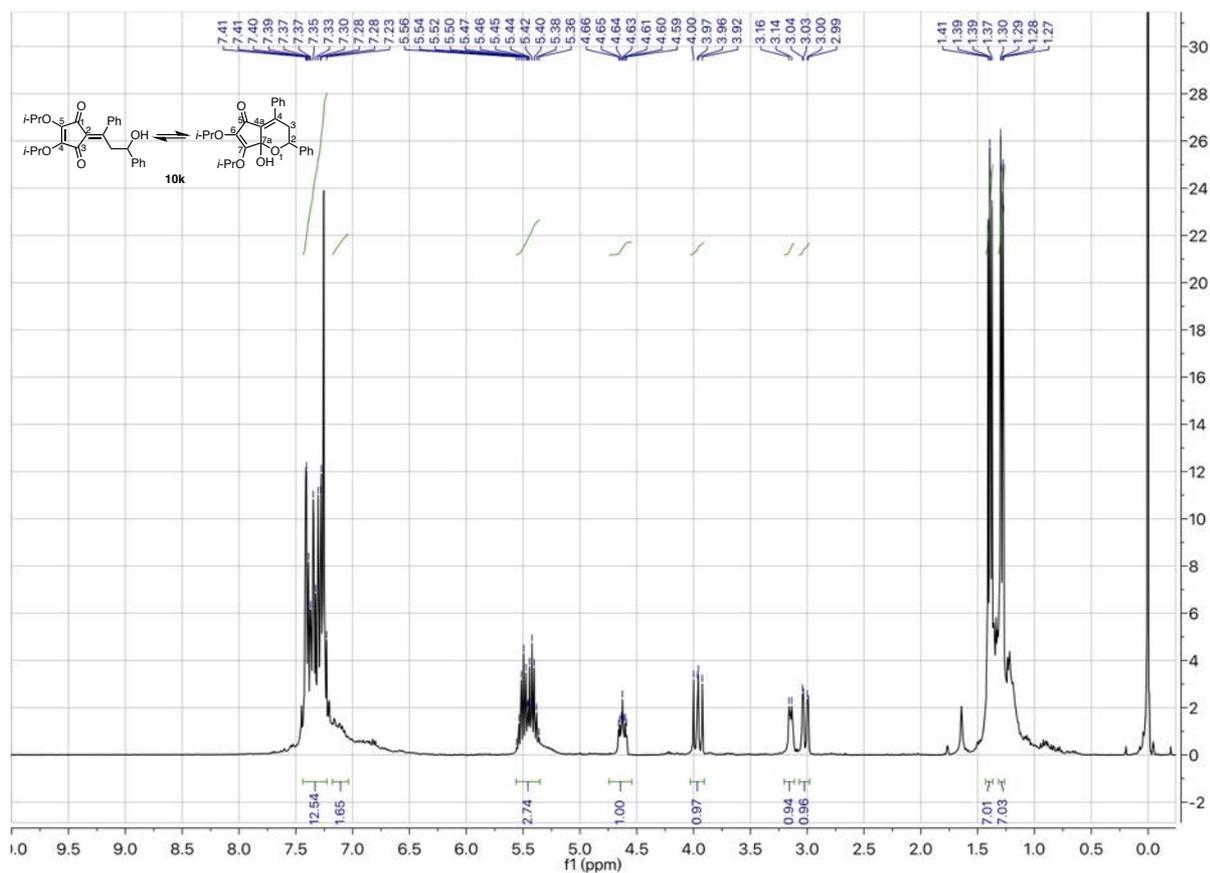


**(E)-2-(1,3-Diphenylallylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (9k):**

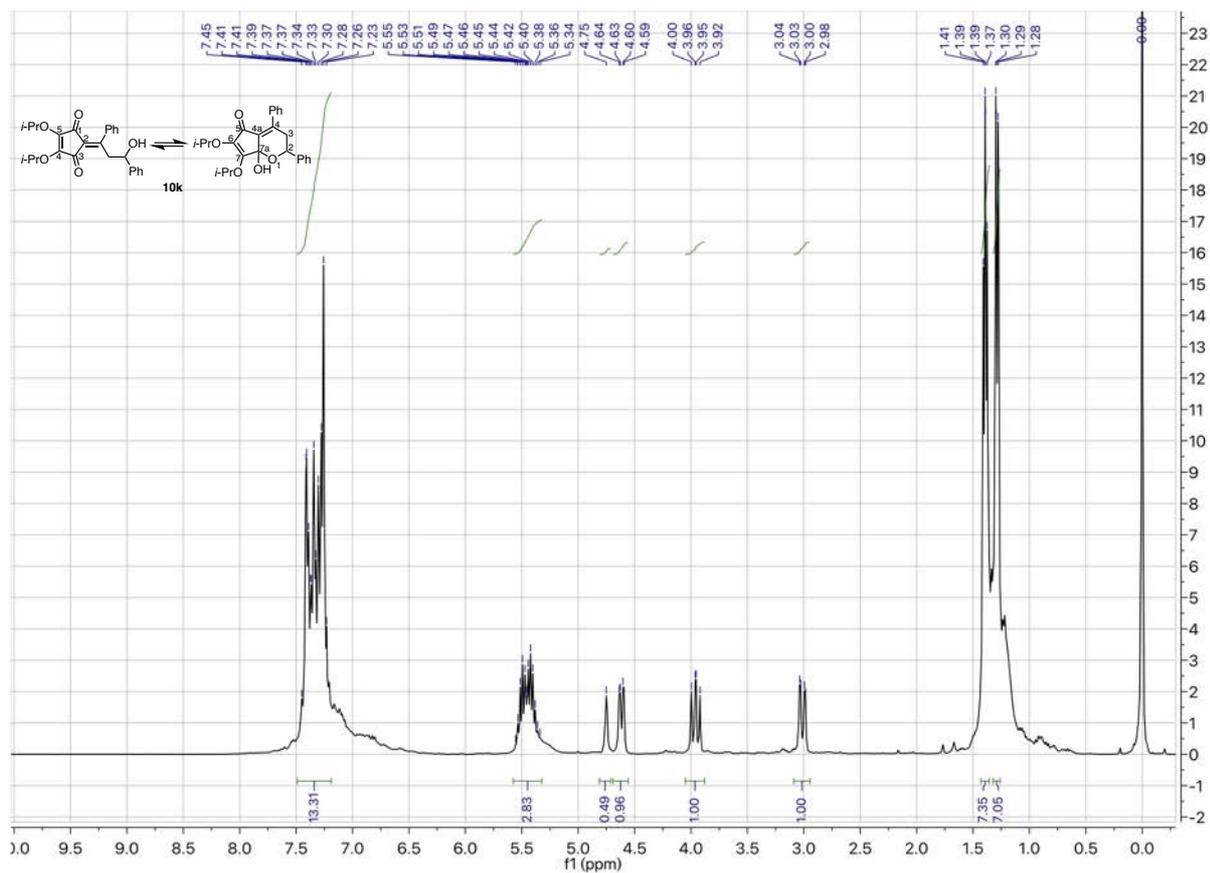


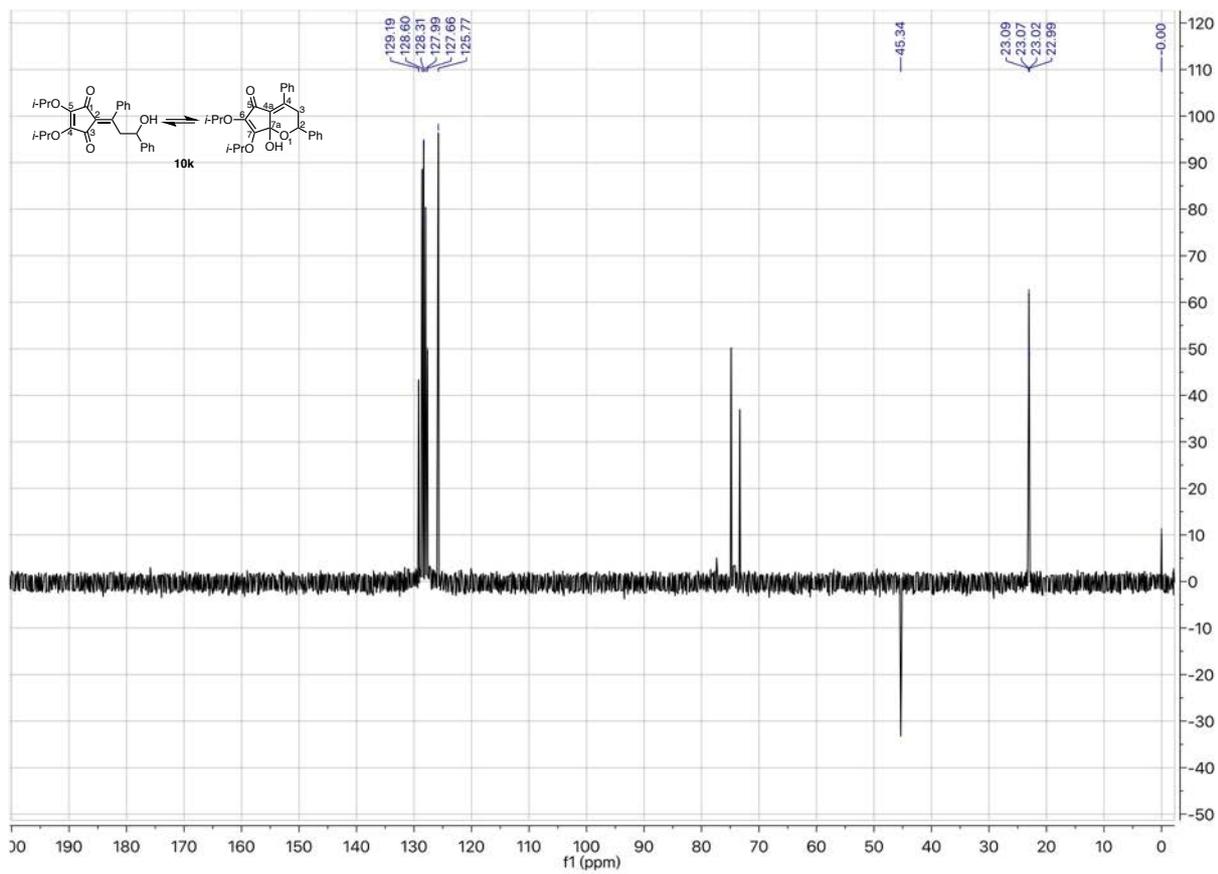
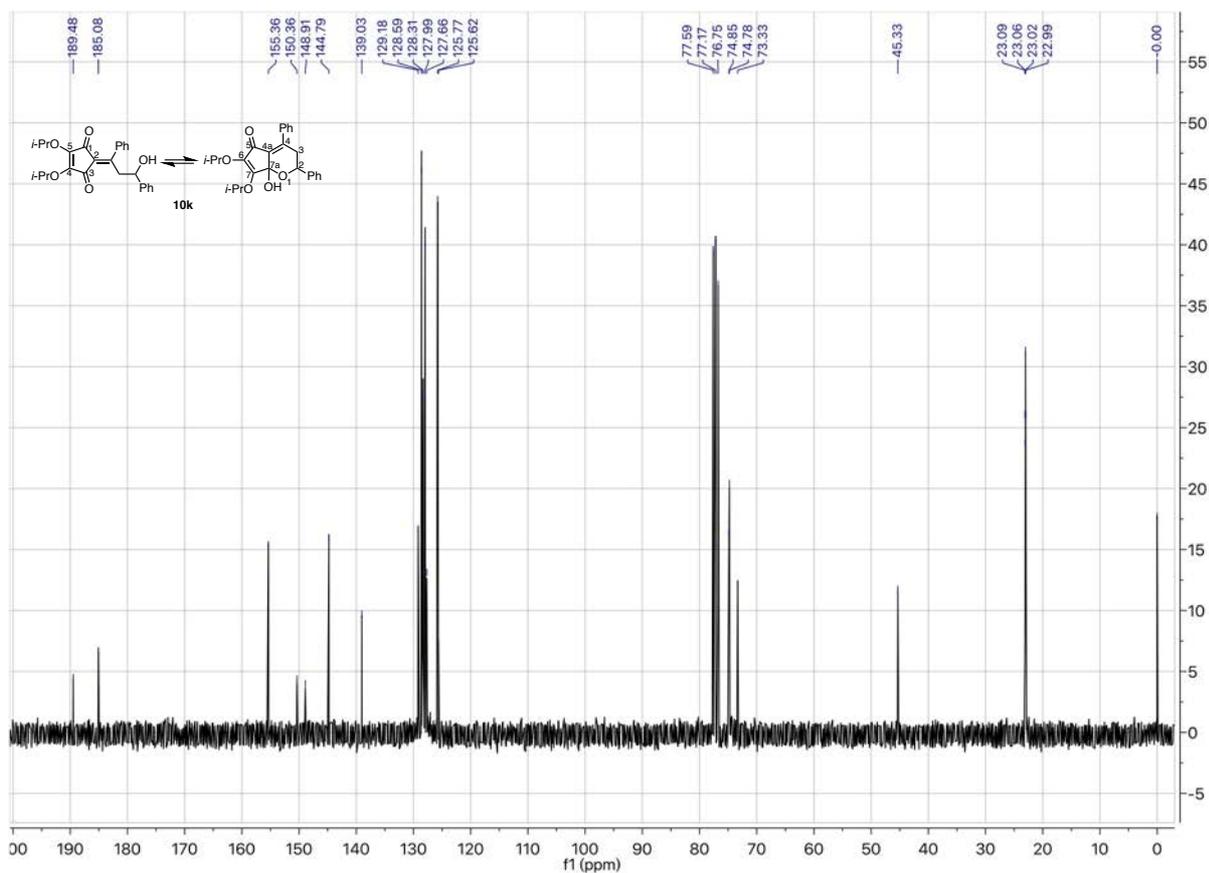
**An equilibrium mixture of 2-(3-hydroxy-1,3-diphenylpropylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione and 7a-hydroxy-6,7-diisopropoxy-2,4-diphenyl-3,7a-dihydrocyclopenta[b]pyran-5(2H)-one (10k):**



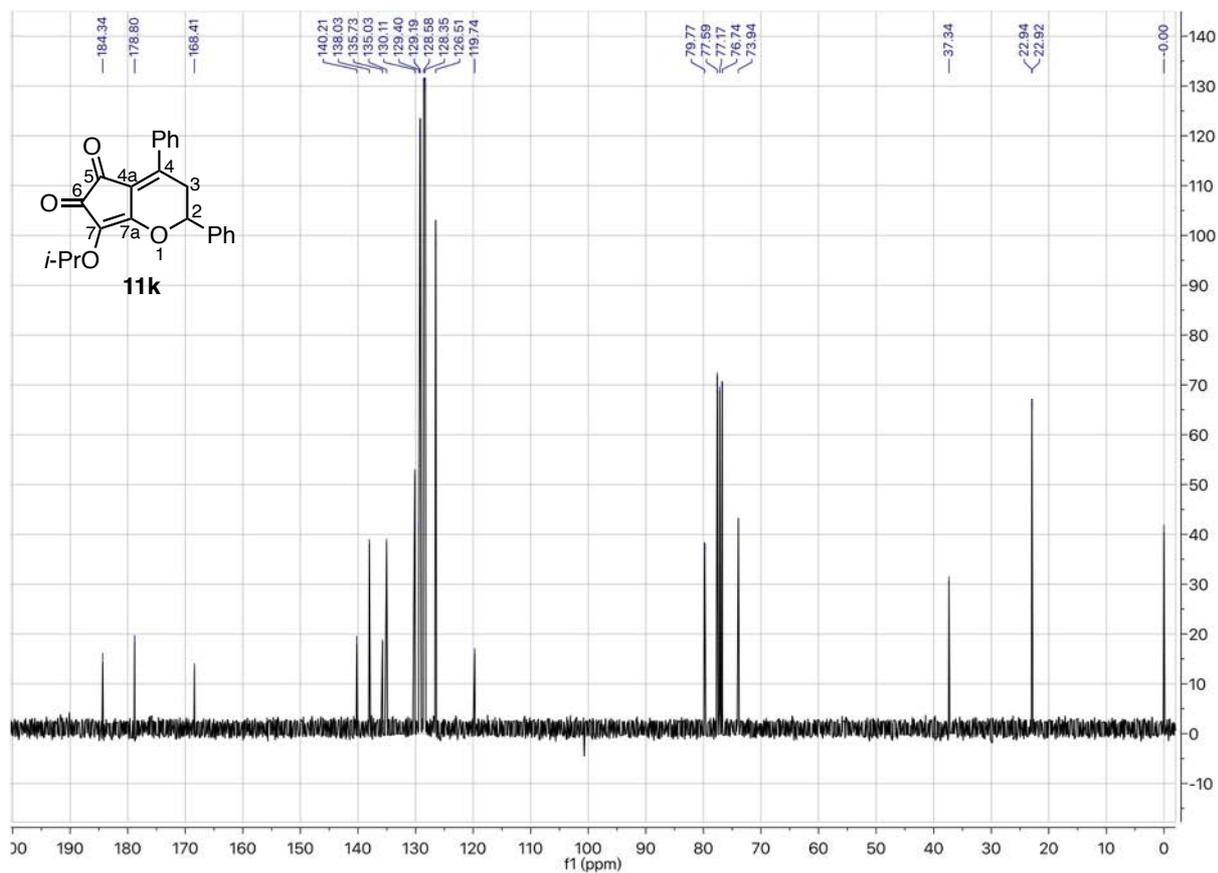
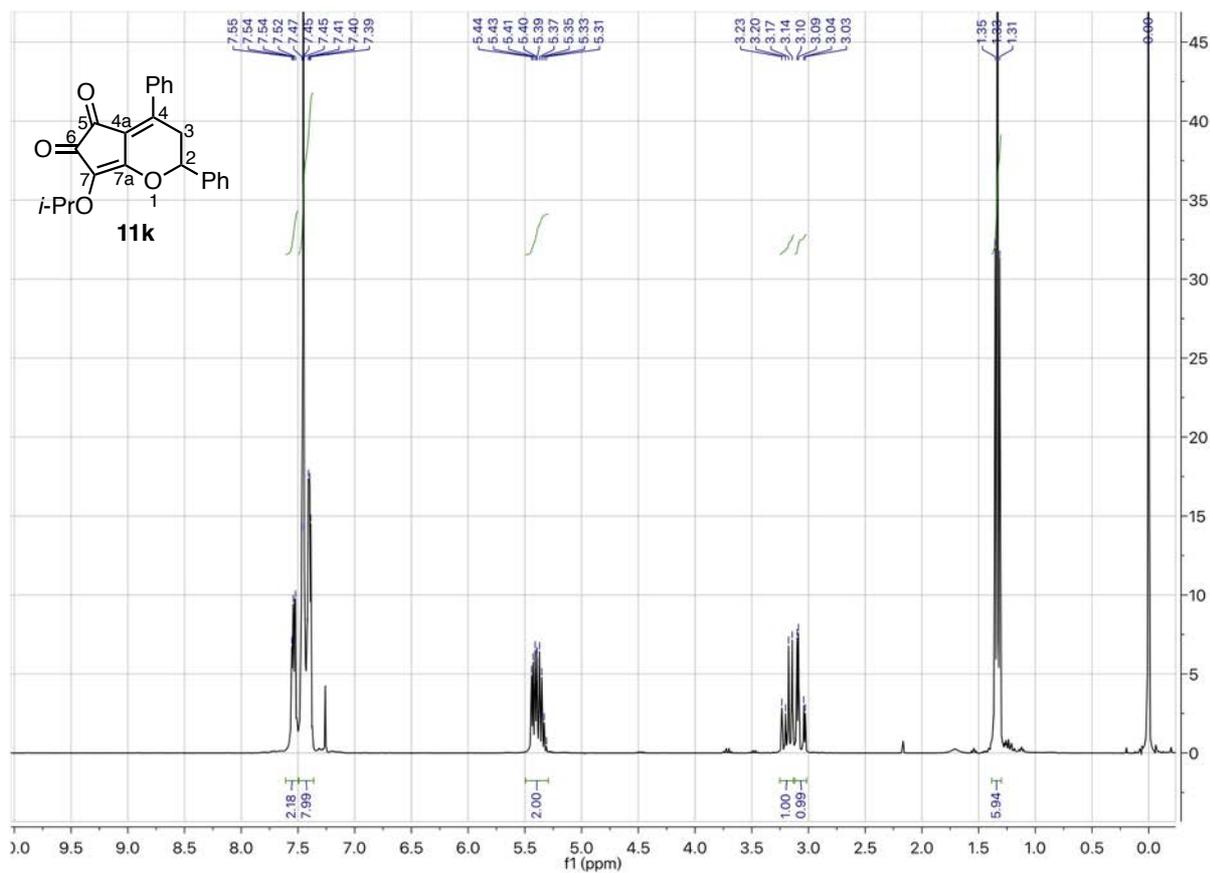


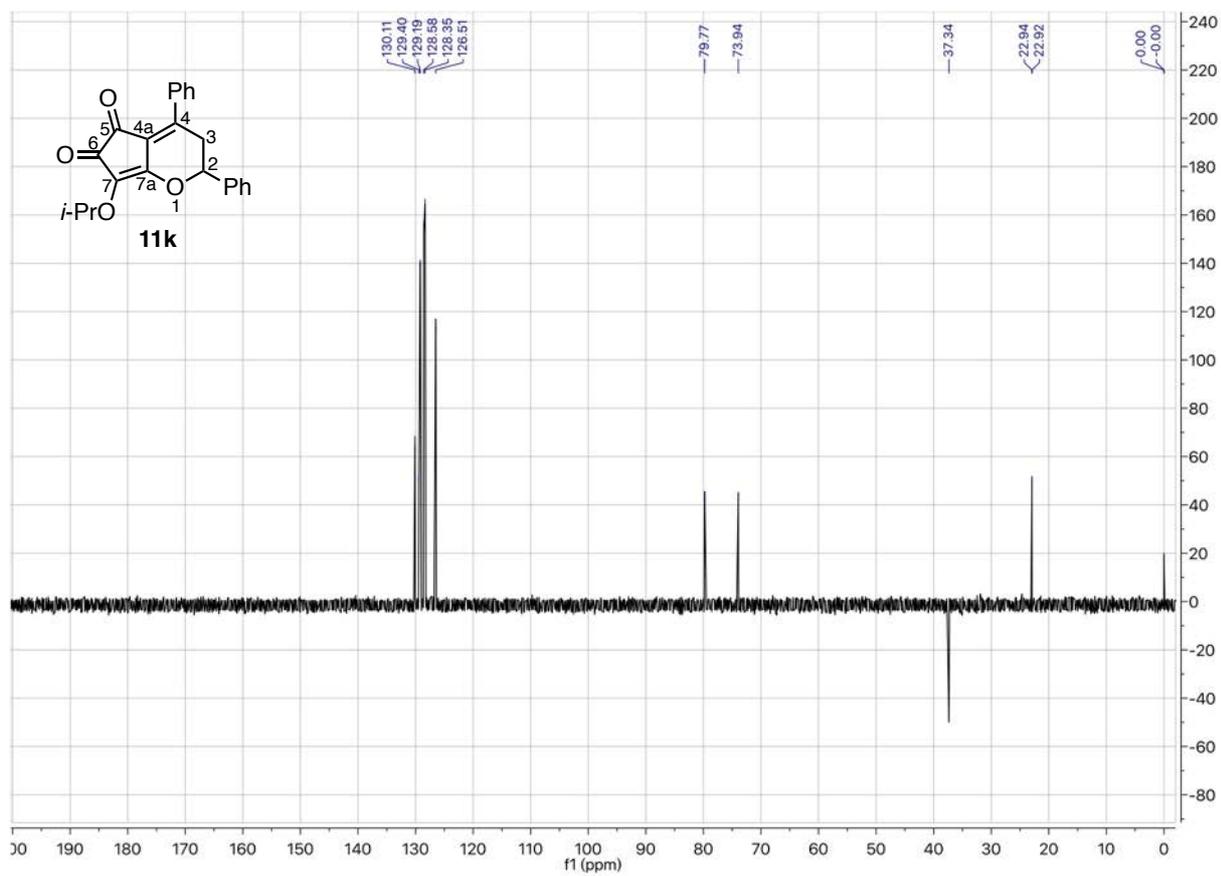
**D<sub>2</sub>O Exchange Experiment of 10k:**



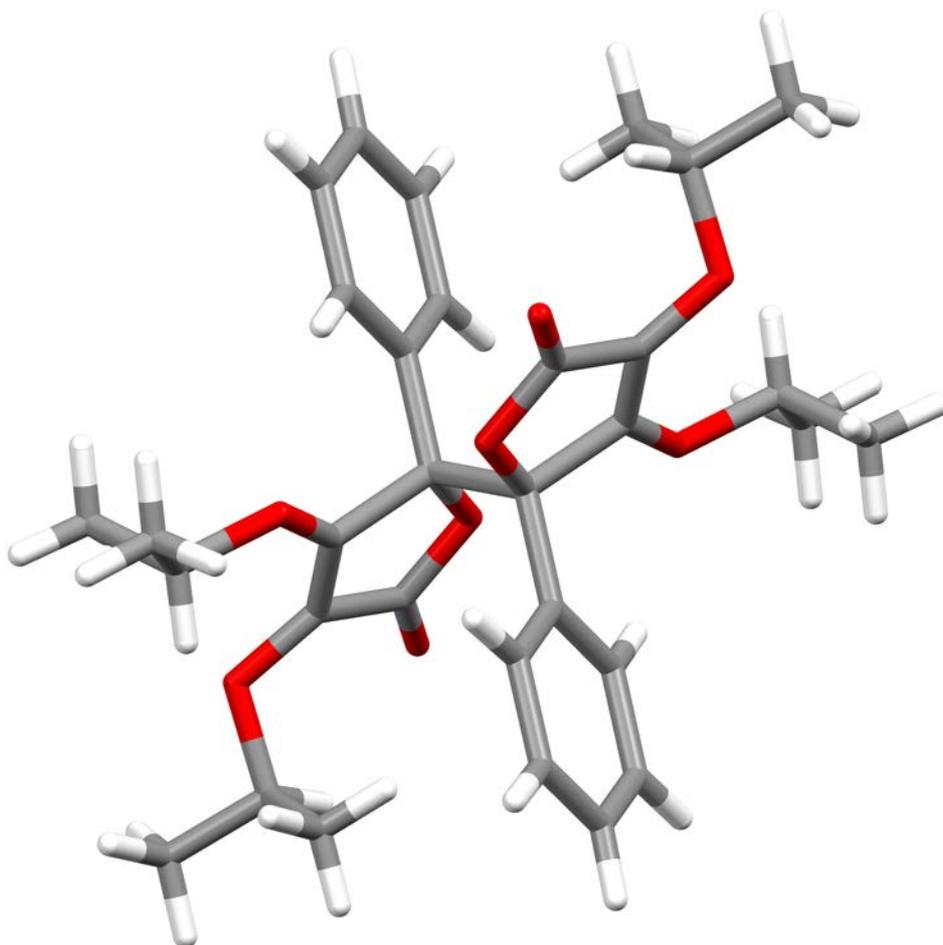
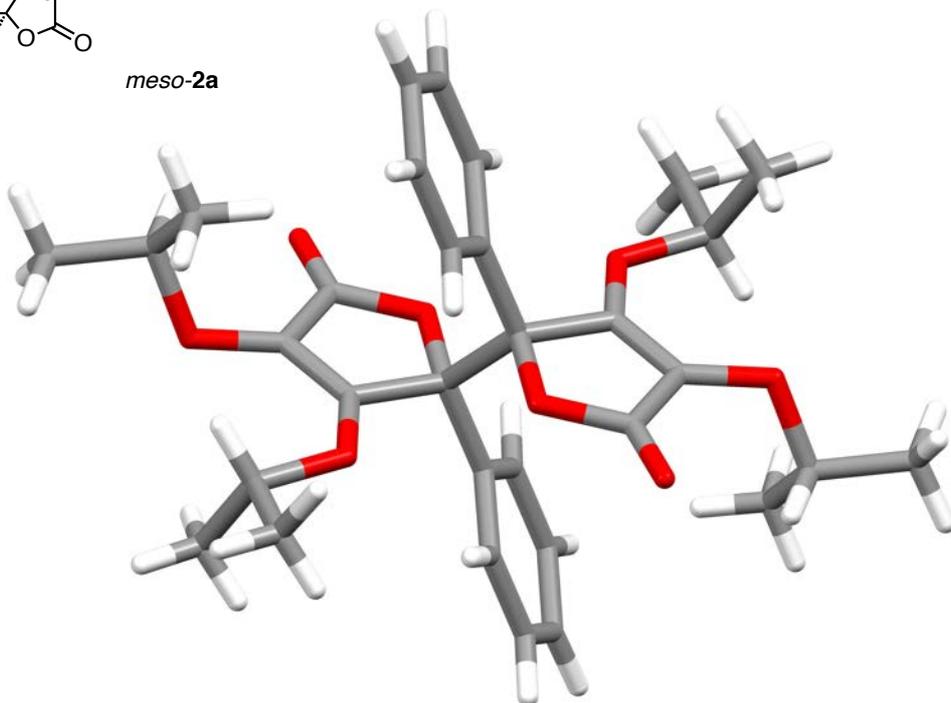
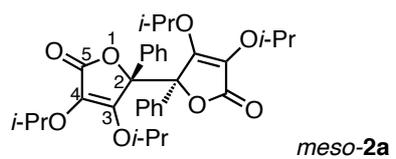


7-Isopropoxy-2,4-diphenyl-2,3-dihydrocyclopenta[*b*]pyran-5,6-dione (11k):

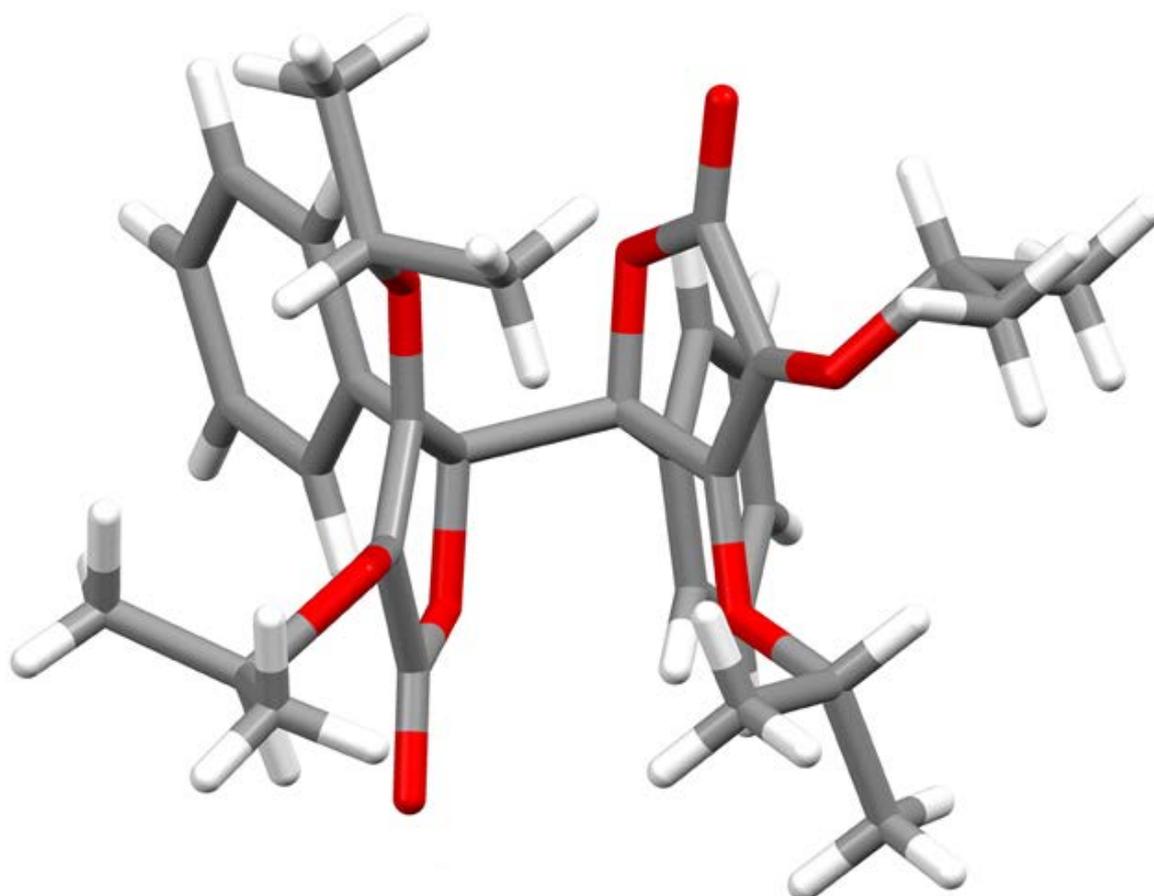
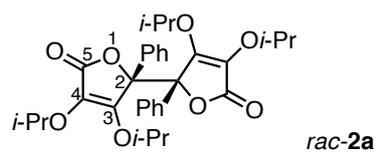


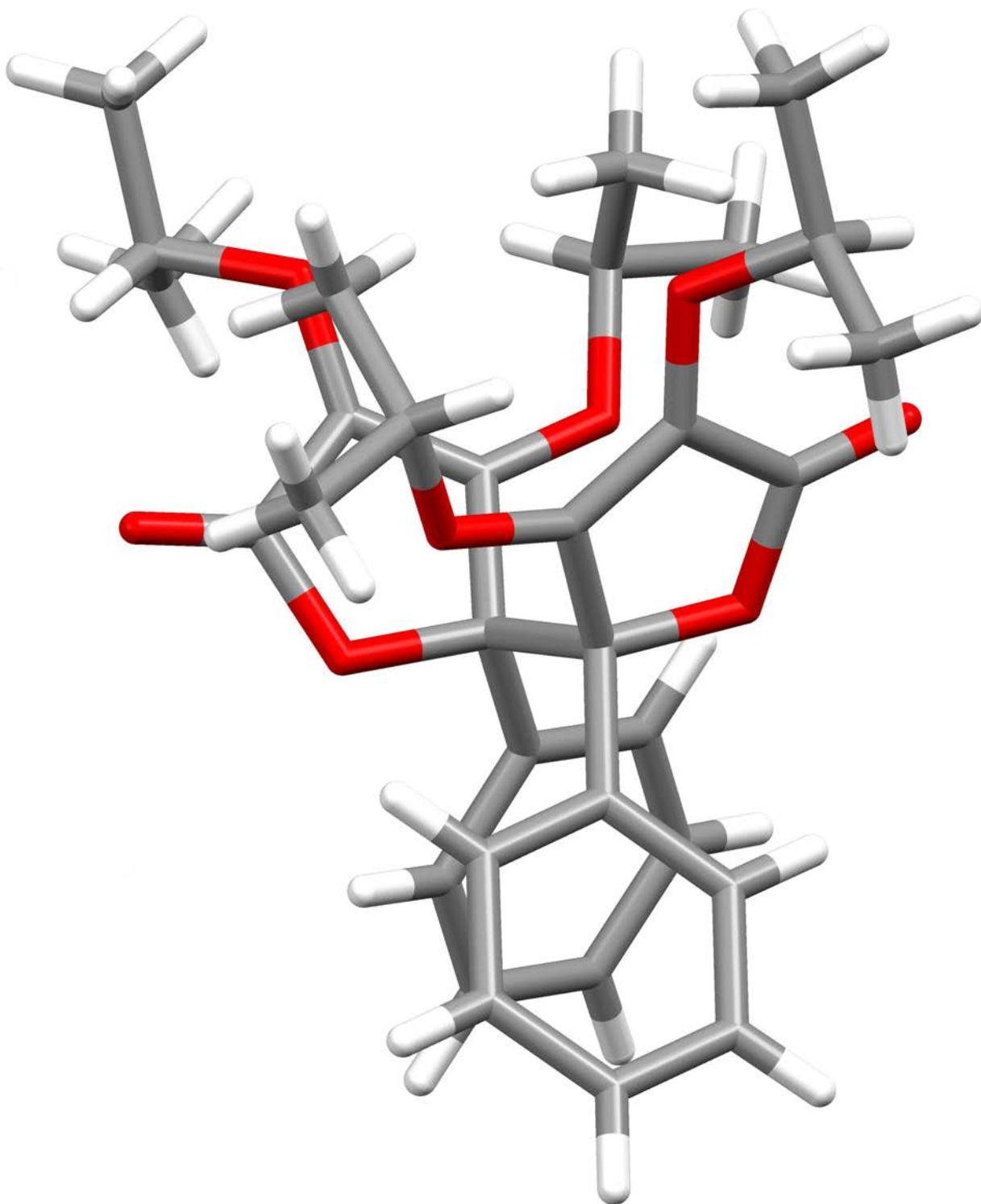
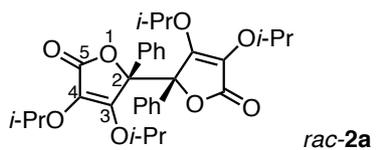


### X-ray Crystal Structure of *meso*-2a:

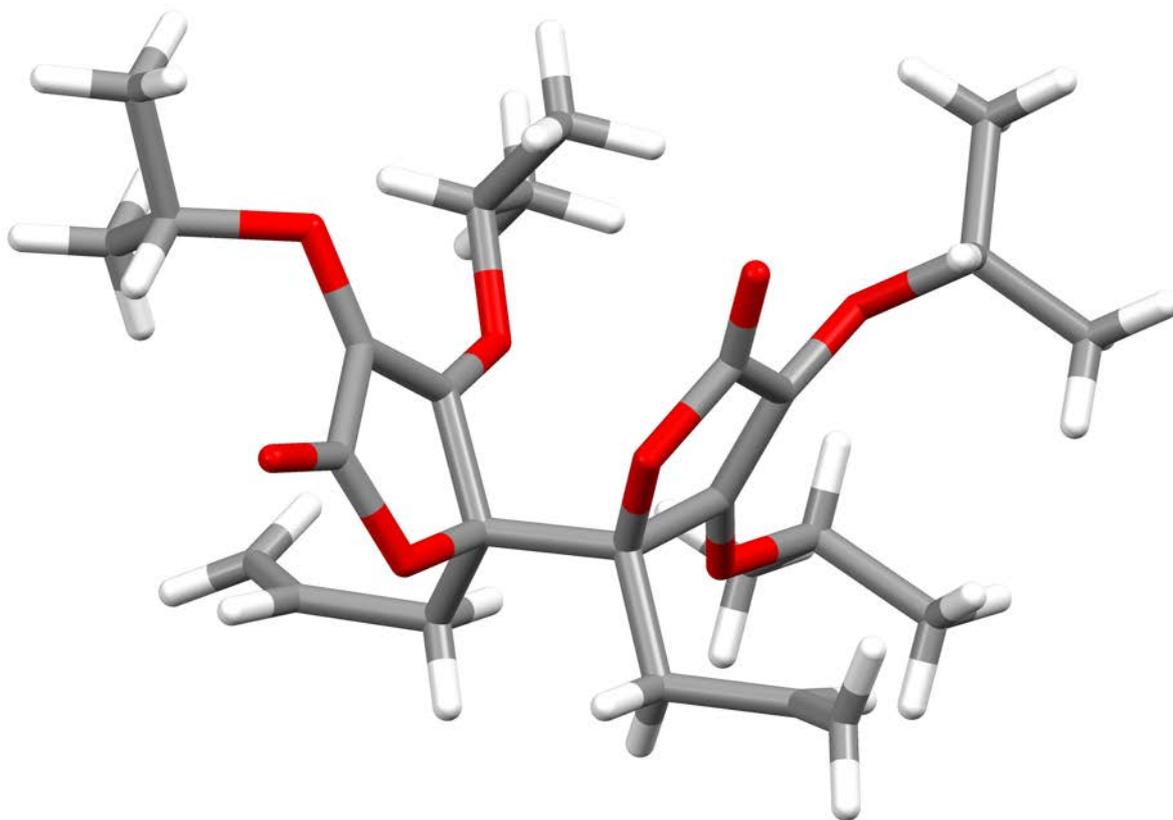
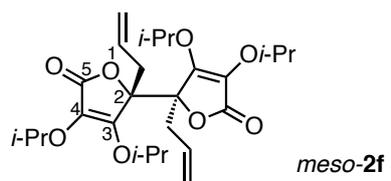


### X-ray Crystal Structure of *rac-2a*:

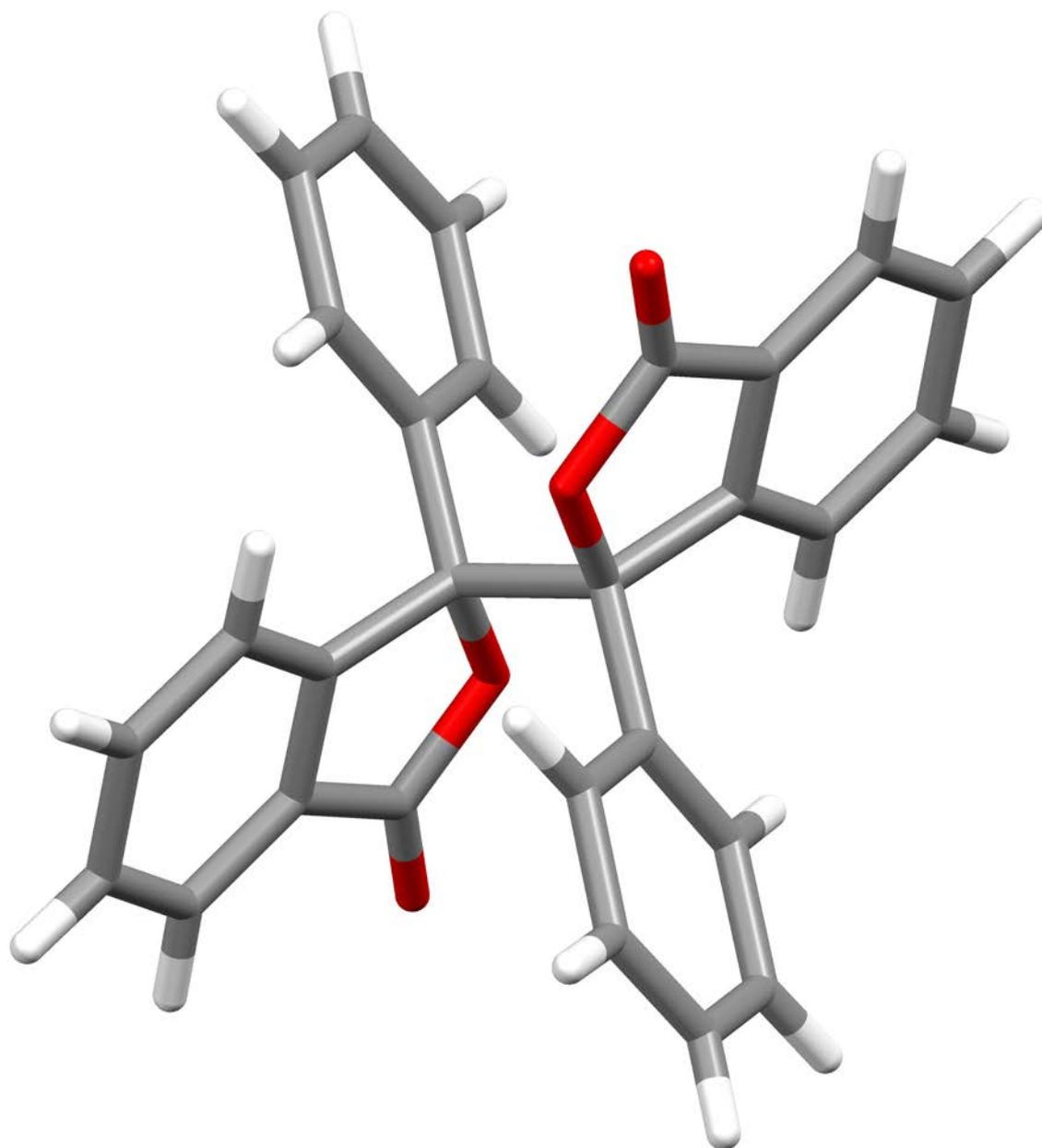
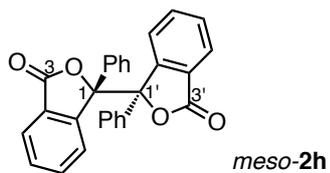




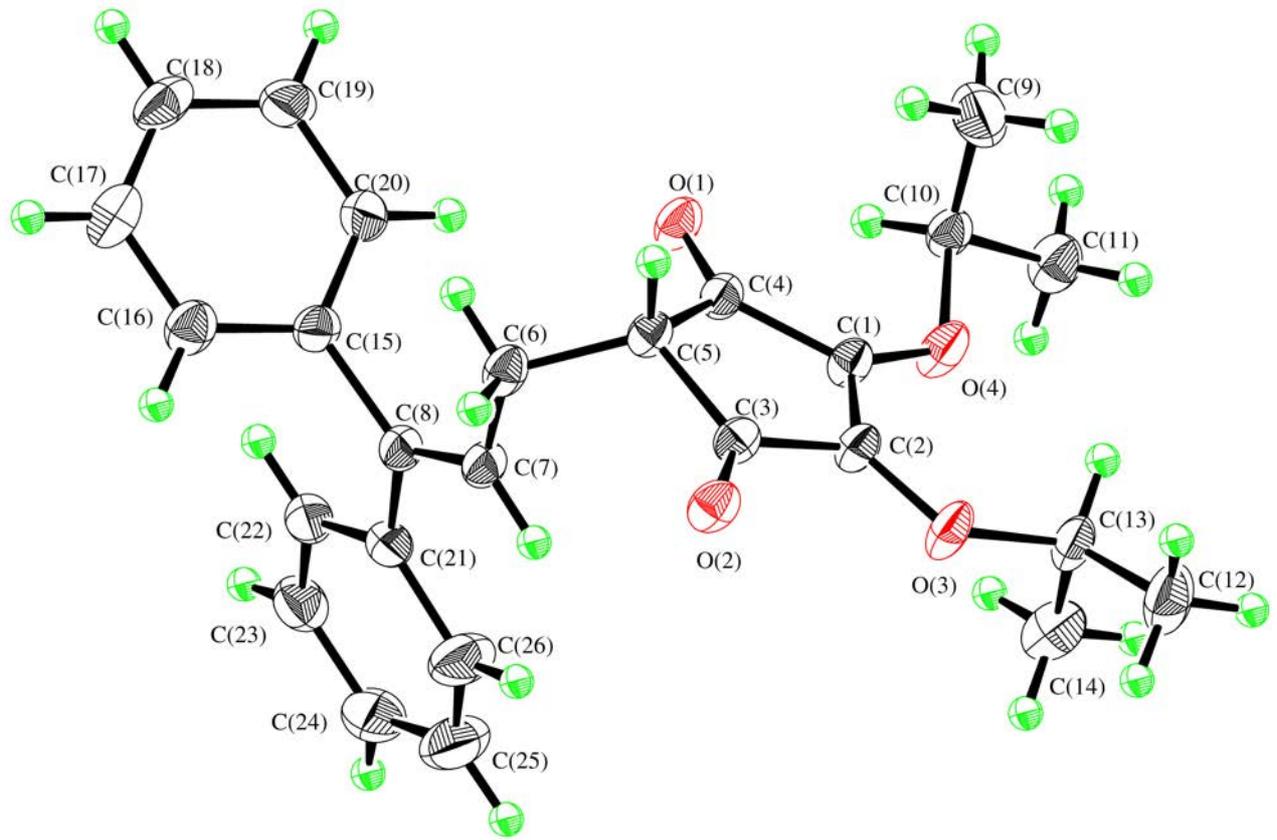
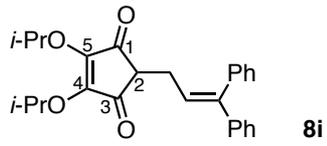
**X-ray Crystal Structure of *meso*-2f:**

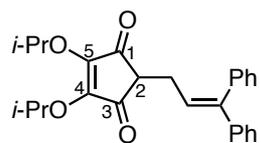
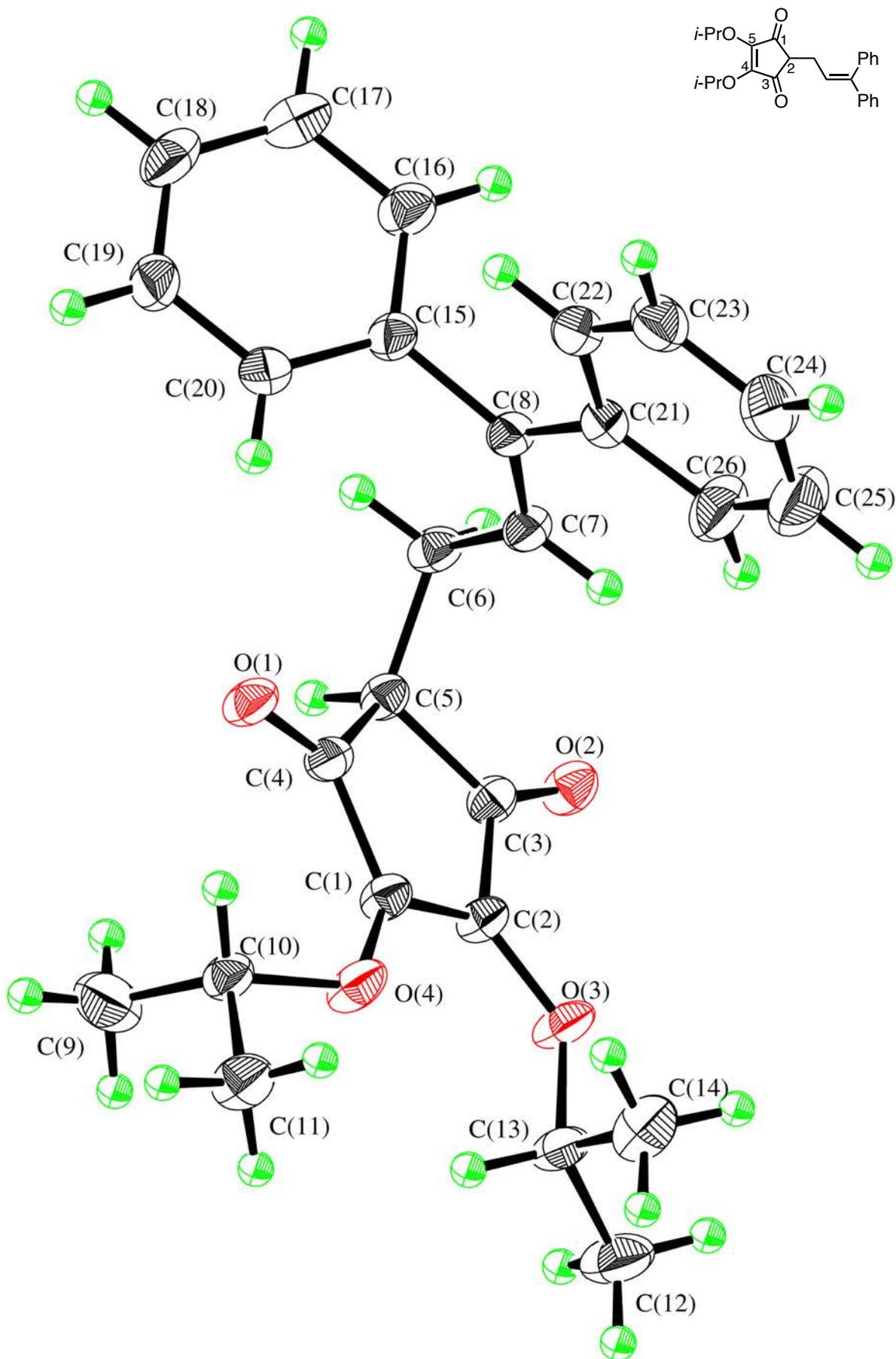


X-ray Crystal Structure of *meso*-2h:



### X-ray Crystal Structure of 8i:





8i