

# First Studies Directed Towards the Diastereoselective Synthesis of the **BCD** Tricyclic Core of Brownin F

Fabien Rodier,<sup>a</sup> Jean-Luc Parrain,<sup>a</sup> Gaëlle Chouraqui,<sup>a\*</sup> Laurent Commeiras<sup>a\*</sup>

<sup>a</sup> Aix Marseille Université, CNRS, iSm2 UMR 7313, 13397 Marseille cedex 20, France  
Fax: (+33)-(0)4 91 28 91 87; Phone: (+33)-(0)4 91 28 91 88; e-mail: gaelle.chouraqui@univ-amu.fr and laurent.commeiras@univ-amu.fr

## Supporting Information

### Table of Contents

**S2** General Experimental

**S3** Procedure and analytical data

1. Preparation of furan <b>8</b> .....	S3
2. Preparation of $\gamma$ -alkylidenebutenolides <b>9</b> and <b>9b</b> .....	S11
3. Preparation of alcohols <b>6</b> and <b>b</b> .....	S15
4. Preparation of $\gamma$ -pyrones <b>10</b> and <b>10b</b> .....	S19
5. NMR data of hemiacetals <b>5a</b> and <b>5b</b> .....	S23
6. NMR data of cycloadducts <b>2a</b> and <b>2b</b> .....	S26
7. NMR data of tetracyclic structure <b>11</b> .....	S29
8. NMR data of diazo derivative <b>4a</b> and molecules involved in its preparation .....	S31
9. NMR data of cycloadduct <b>2c</b> .....	S39

**S41** Theoretical results

## General Experimental

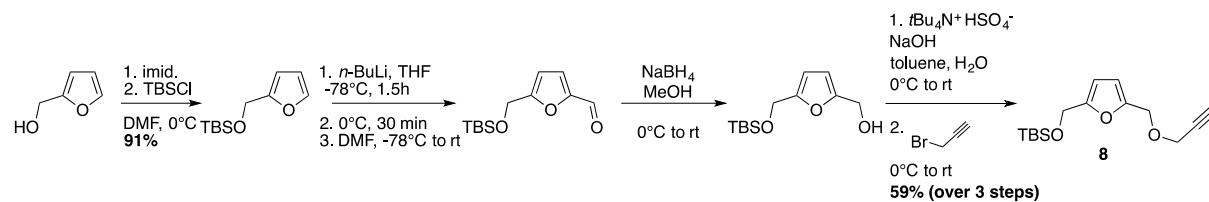
<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock at ambient temperature on the following instruments: Bruker AC400 (400 MHz). An internal reference of  $\delta_H$  7.26 ppm was used for the residual protons in CDCl<sub>3</sub>,  $\delta_H$  2.05 ppm in (CD<sub>3</sub>)<sub>2</sub>CO and  $\delta_H$  7.16 ppm in the case of C<sub>6</sub>D<sub>6</sub>. Data are presented as follows: chemical shift (in ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br means the signal is broad), coupling constant (*J* in Hz) and interpretation. <sup>13</sup>C NMR spectra were recorded on a Bruker AC300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.16 ppm in the case of CDCl<sub>3</sub>; peak at 29.84 and 206.26 ppm in the case of (CD<sub>3</sub>)<sub>2</sub>CO; peak at 128.06 ppm in the case of C<sub>6</sub>D<sub>6</sub>). NMR spectra were assigned using information ascertained from DEPT, HMQC, COSY, NOESY and NOE experiments. Infrared spectra were recorded on a Bruker VERTEX70 Fourier transform infrared spectrometer fitted with a single reflection diamond ATR Bruker A222 accessory. The measurements were done for pure samples. For each individual spectrum, about 30 scans were averaged at 4 cm<sup>-1</sup> resolution. The diamond crystal without sample served as reference. All the system was purged with dry air. The identification of peaks was done with the standard method proposed in OPUS 6.0 software. Wavelengths of maximum absorbance ( $\nu_{max}$ ) are quoted in cm<sup>-1</sup>. High-resolution mass spectra (HRMS) were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted. Samples were ionised by positive electrospray mode as follows: electrospray tension (ISV): 5500 V; opening tension (OR): 50 V; nebulisation gas pressure (air): 20 psi. Low resolution mass spectra were recorded on ion trap Brucker Esquire 6000, equipped with an electrospray source (methanolic sodium chloride solution). The parent ion (M<sup>+</sup>, [M+H]<sup>+</sup>, [M+Na]<sup>+</sup> or [M+NH<sub>4</sub>]<sup>+</sup>) is quoted. Analytical thin layer chromatography (TLC) was carried out on Merck® Kieselgel 60 F254 plates and achieved under a 254 nM UV light, visualized with a KMNO<sub>4</sub> solution. Flash column chromatography was carried out on Merck® Kieselgel 60 (230-400 mesh) silica gel according to W. C. Still method.<sup>1</sup> Anhydrous THF, dichloromethane, toluene and Et<sub>2</sub>O were obtained from a MBraun® SPS-800 solvent purification system. Reagents and solvents were purified by standard means.<sup>2</sup> All experiments were performed under anhydrous conditions and an inert atmosphere of argon and, except where stated, using dried apparatus and employing standard techniques for handling air-sensitive materials. Petroleum ether refers to the petroleum ether fraction boiling between 40°C and 65°C. All reagents were weighed and handled in air at room temperature. The reactions were magnetically stirred.

<sup>1</sup> Still, W. C.; Khan, M.; Mitra, A. J. J. Org. Chem. 1978 , 43 , 2423-2426.

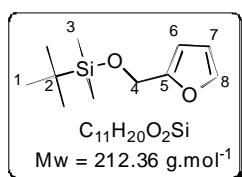
<sup>2</sup> Perrin, D. D.; Amarego, W. L.; Purification of Laboratory Chemicals; Pergamon Press, 1988.

## Procedure and analytical data

### 1. Preparation of furan 8



### Preparation of *t*-butyl(furan-2-ylmethoxy)dimethylsilane<sup>3</sup>



To a cooled (0°C) stirred solution of furfuryl alcohol (50 g, 510 mmol, 1 equiv) in anhydrous DMF (350 mL) was added imidazole (41.7 g, 612 mmol, 1.2 equiv) followed after dissolution by *t*-butyldimethylchlorosilane (92.2 g, 612 mmol, 1.2 equiv). Stirring at 0°C was allowed for 30 min and then 4 hours at room temperature. Petroleum Ether (1.5 L) was added and the organic layer was washed with water (3 x 800 mL). The aqueous phase was back extracted with Petroleum Ether and the combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The resulting oil was purified by distillation under reduced pressure (150°C, 3 mbar) to yield the desired protected alcohol (91.8 g, 460 mmol, 91 %).

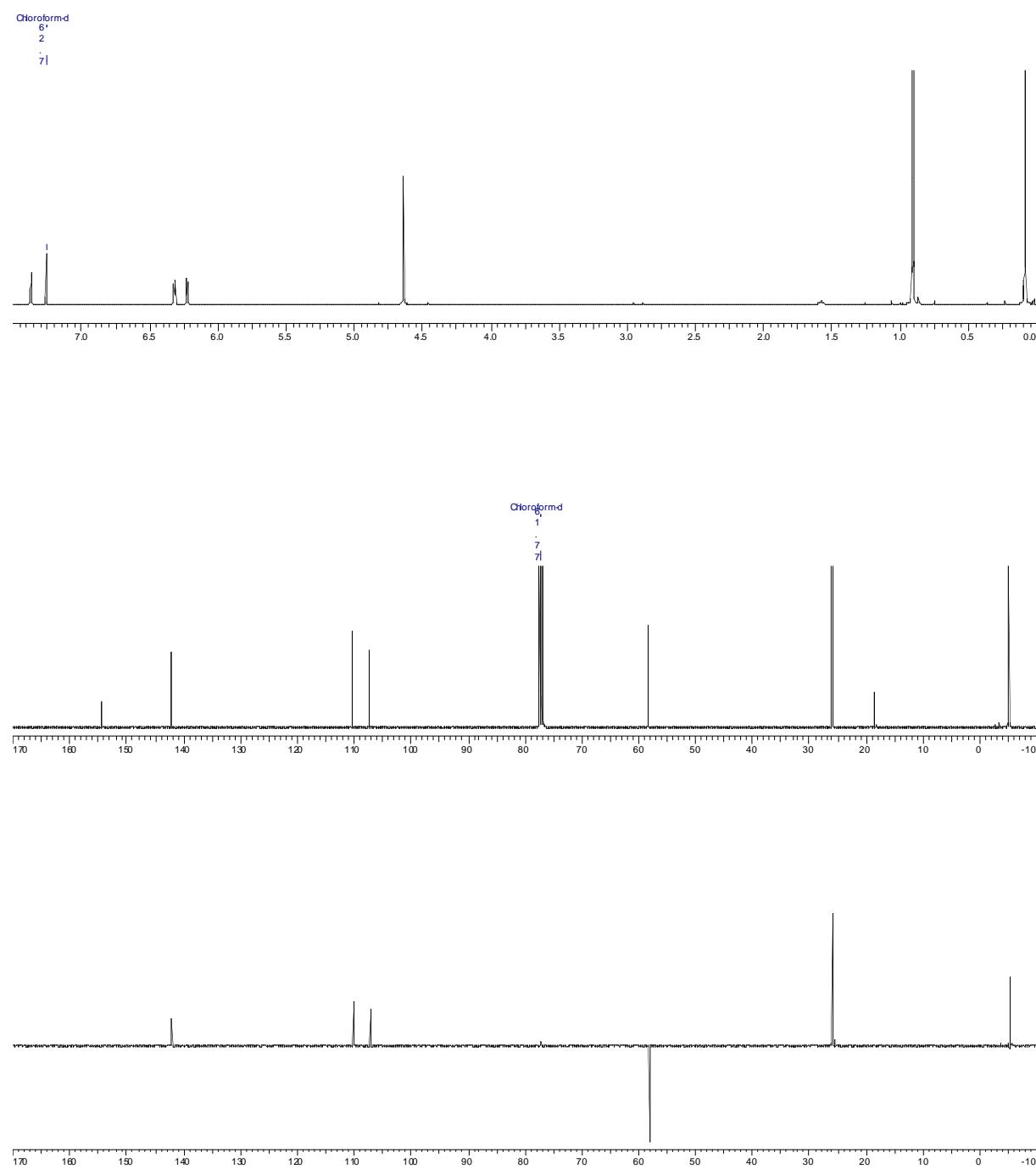
**Aspect:** colorless liquid

**Rf** (PE/EE : 9/1) = 0.86

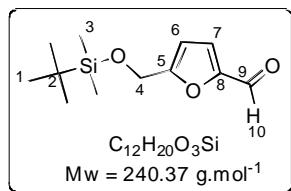
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 0.09 (6H, 2 x CH<sub>3</sub>, s, H<sub>3</sub>), 0.91 (9H, 3 x CH<sub>3</sub>, s, H<sub>1</sub>), 4.64 (2H, CH<sub>2</sub>, s, H<sub>4</sub>), 6.22 (1H, CH, d, *J* = 3.2 Hz, H<sub>6</sub>), 6.32 (1H, CH, dd, *J* = 3.2 Hz, *J* = 1.77 Hz, H<sub>7</sub>), 7.37 (1H, CH, d, *J* = 1.77 Hz, H<sub>8</sub>).

<sup>3</sup> The NMR data was consistent with that reported in the literature: S. Celanire, F. Marlin, J. E. Baldwin and R. M. Adlington. *Tetrahedron*. **2005**, *61*, 3025-3032.

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) -5.6 (2 x  $\text{CH}_3$ ,  $\text{C}_3$ ), 18.1 ( $\text{C}$ ,  $\text{C}_2$ ), 25.6 (3 x  $\text{CH}_3$ ,  $\text{C}_1$ ), 57.8 ( $\text{CH}_2$ ,  $\text{C}_4$ ), 106.9 ( $\text{CH}$ ,  $\text{C}_6$ ), 109.8 ( $\text{CH}$ ,  $\text{C}_7$ ), 141.7 ( $\text{CH}$ ,  $\text{C}_8$ ), 154.0 ( $\text{C}$ ,  $\text{C}_5$ ).



### Preparation of 5-(((*t*-butyldimethylsilyl)oxy)methyl)furan carbaldehyde<sup>3</sup>



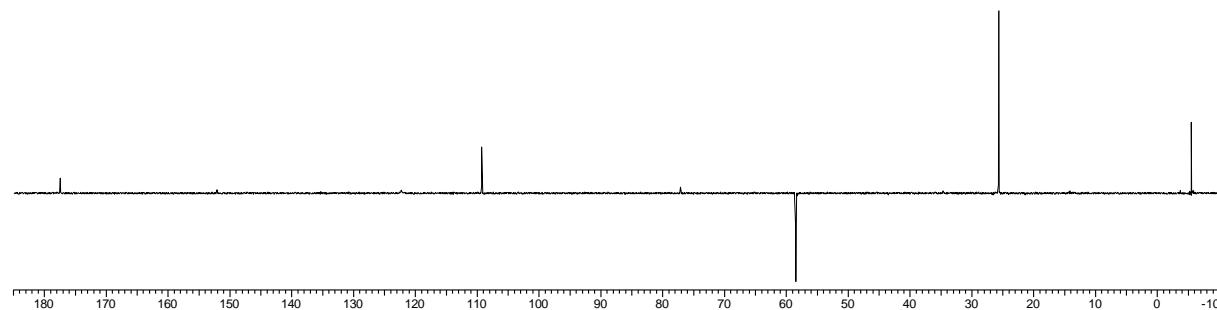
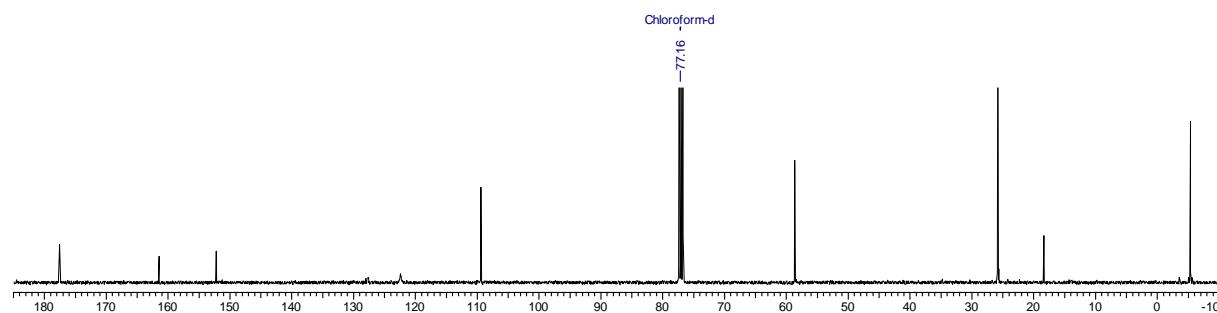
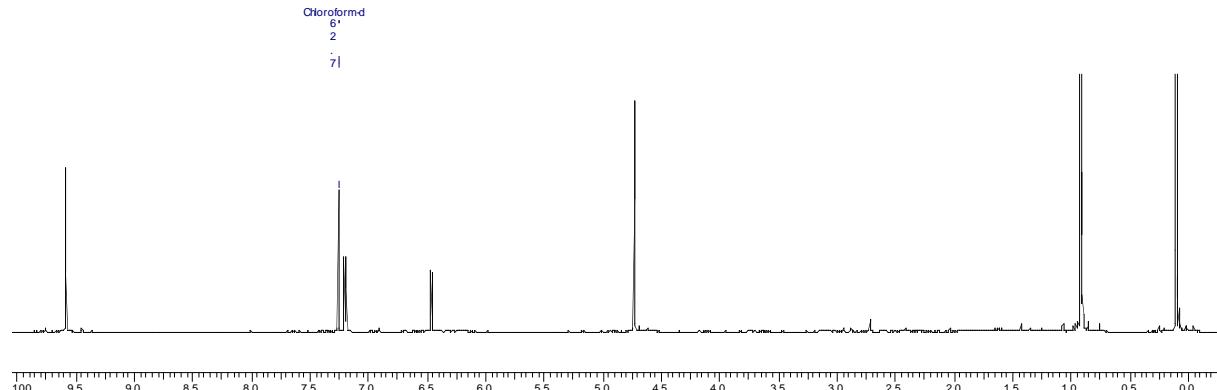
To a cooled (-78°C) solution of the previously prepared silylated ether (10 g, 47.2 mmol, 1 equiv) in anhydrous THF (80 mL) was added dropwise *n*-BuLi (22 mL of a 2.4 M solution in heptane, 52 mmol, 1.1 equiv). Stirring at -78°C was allowed for 1.5 hours and then at 0°C for 30 min. The reaction mixture was cooled back to -78°C and freshly distilled DMF (6.9 g, 94.2 mmol, 2 equiv) was added. Stirring at -78°C was allowed for 30 min and then for an additional 30 min at room temperature following which water (200 mL) was added to quench the reaction mixture. The aqueous phase was extracted with Et<sub>2</sub>O (3 x 200 mL) and the combined organic layers were washed with brine (3 x 200 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give the desired product as an orange oil (11.4 g, 47.3 mmol) which was used in the next step without further purification.

**Aspect:** orange liquid

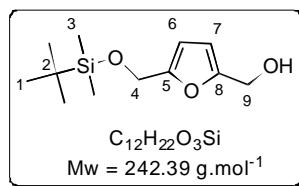
**Rf** (PE/EE : 9/1) = 0.35

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 0.11 (6H, 2 x CH<sub>3</sub>, s, H<sub>3</sub>), 0.92 (9H, 3 x CH<sub>3</sub>, s, H<sub>1</sub>), 4.73 (2H, CH<sub>2</sub>, s, H<sub>4</sub>), 6.47 (1H, CH, d, *J* = 3.6 Hz, H<sub>6</sub>), 7.20 (1H, CH, d, *J* = 3.6 Hz, H<sub>7</sub>), 9.59 (1H, CH, s, H<sub>10</sub>).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz): δ (ppm) -5.3 (2 x CH<sub>3</sub>, C<sub>3</sub>), 18.5 (C, C<sub>2</sub>), 25.9 (3 x CH<sub>3</sub>, C<sub>1</sub>), 58.7 (CH<sub>2</sub>, C<sub>4</sub>), 109.5 (CH, C<sub>6</sub>), 122.4 (CH, C<sub>7</sub>), 152.3 (C, C<sub>5</sub>), 161.6 (C, C<sub>8</sub>), 177.7 (C, C<sub>9</sub>).



### Preparation of 5-(((*t*-butyldimethylsilyl)oxy)methyl)furanyl)methanol<sup>3</sup>



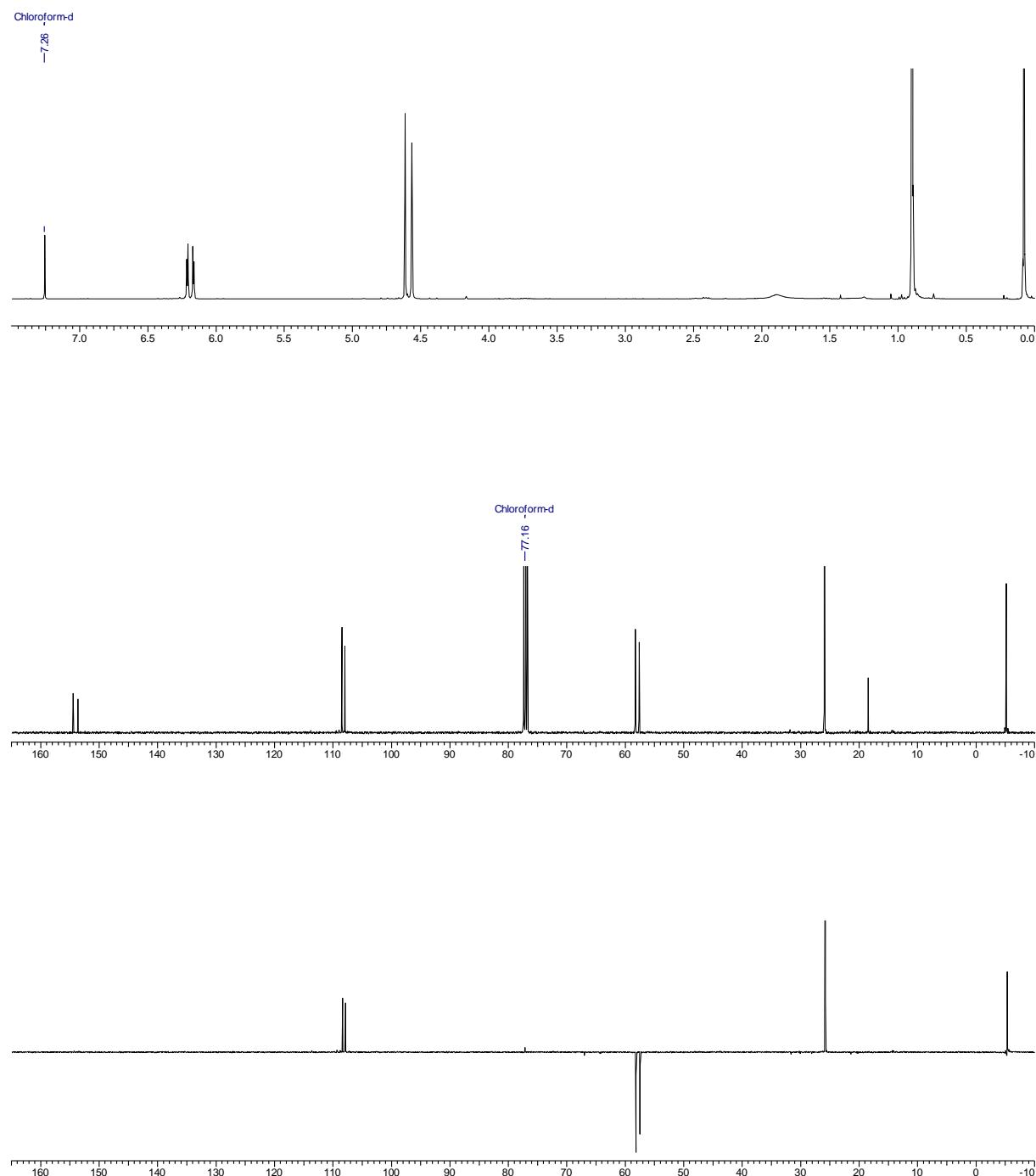
A three-neck round bottom flask equipped with a reflux condenser was charged with a solution of the previously prepared aldehyde (5 g, 20.8 mmol, 1 equiv) in methanol (220 mL). The reaction mixture was cooled to 0°C and NaBH<sub>4</sub> (1.3 g, 33 mmol, 1.6 equiv, powder) was added portionwise. Stirring was allowed at this temperature for 10 min and for an additional 10 min at room temperature. Then the solvent was removed *in vacuo* and water (50 mL) followed by ethylacetate (50 mL) were added. The aqueous layer was adjusted to pH 9 by adding an aqueous NaOH solution (1N). Then the aqueous phase was extracted with ethylacetate (3 x 200 mL) and the combined organic layers were washed with brine (3 x 200 mL), dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give a yellow oil (5.4 g, 0.022 mol) which was used without further purification in the next step.

**Aspect:** yellow oil

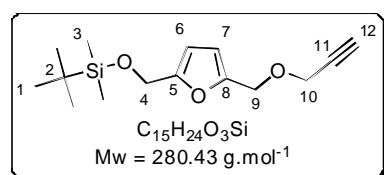
**Rf** (PE/EE : 8/2) = 0.22

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 0.08 (6H, 2 x CH<sub>3</sub>, s, H<sub>3</sub>), 0.90 (9H, 3 x CH<sub>3</sub>, s, H<sub>1</sub>), 4.57 (2H, CH<sub>2</sub>, s, H<sub>4</sub>), 4.62 (2H, CH<sub>2</sub>, s, H<sub>9</sub>), 6.17 (1H, CH, d, *J* = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>), 6.21 (1H, CH, d, *J* = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz): δ (ppm) -5.10 (2 x CH<sub>3</sub>, C<sub>3</sub>), 18.6 (C, C<sub>2</sub>), 26.0 (3 x CH<sub>3</sub>, C<sub>1</sub>), 57.7 (CH<sub>2</sub>, C<sub>4</sub>), 58.4 (CH<sub>2</sub>, C<sub>9</sub>), 108.1 (CH, C<sub>6</sub> or C<sub>7</sub>), 108.6 (CH, C<sub>6</sub> or C<sub>7</sub>), 153.7 (C, C<sub>5</sub> or C<sub>8</sub>), 154.5 (C, C<sub>5</sub> or C<sub>8</sub>).



**Preparation of 5-*t*-butyldimethylsilyloxymethyl-8-[(2-propynyl-oxy)-methyl]furan (**8**)<sup>3</sup>**



To a vigourously stirred cooled (0°C) solution of the previously prepared alcohol (10.3 g, 43 mmol, 1 equiv) in toluene (44 mL) were added water (17 mL), tetrabutylammonium hydrogen-sulfate (0.73 g, 2.1 mmol, 0.05 equiv) and sodium hydroxide portionwise (6.8 g, 17.0 mol, 4 equiv, pearl). Stirring was allowed for 15 min at 0°C and for an additional hour at room temperature. Then the mixture was cooled to 0°C and a solution of propargyl bromide in toluene (80% w/w, 0.064 mol, 1.5 equiv, 5.7 mL) was added dropwise. Stirring at 0°C was allowed for 30 min and then at room temperature until completion of the reaction by TLC. The solution was diluted with Et<sub>2</sub>O (100 mL) followed by the addition of water (30 mL). Then the aqueous phase was extracted with Et<sub>2</sub>O (3 x 100 mL) and the combined organic layers were washed with a saturated aqueous solution of NH<sub>4</sub>Cl (2 x 100 mL) followed by brine (2 x 100 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The resulting oil was purified by flash chromatography on silica gel (PE/AcOEt : 95/5). Fractions that contained the pure product were gathered and concentrated *in vacuo* to give **8** as a pale yellow oil (7.81 g, 27.8 mmol, 59 % over 3 steps).

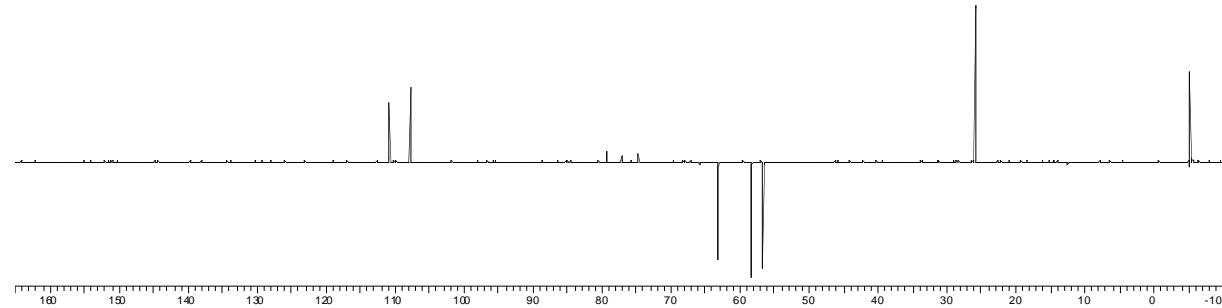
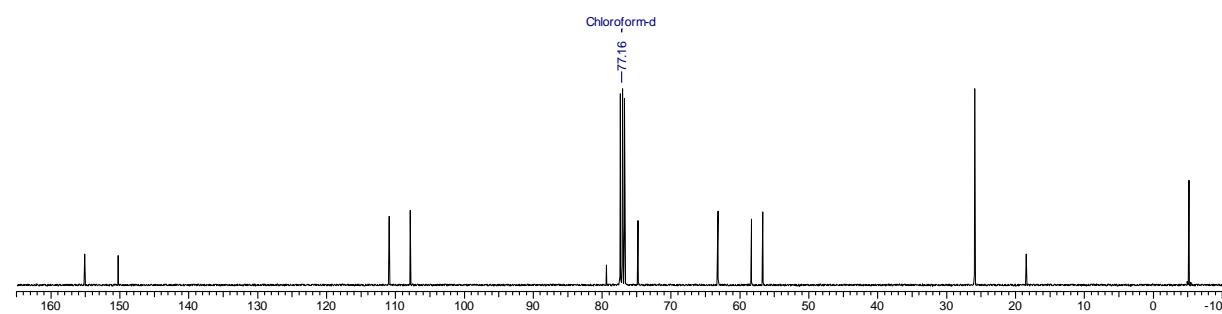
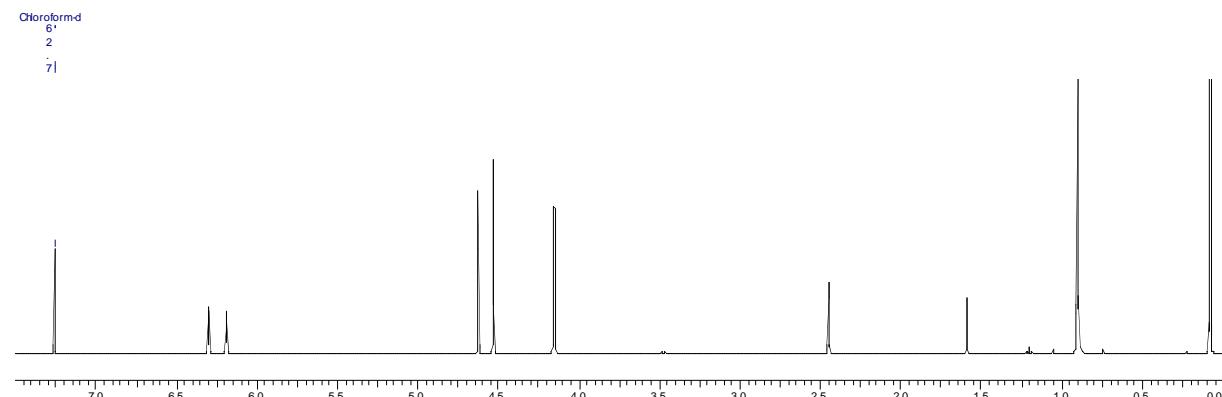
**Aspect:** yellow oil

**Rf** (PE/AcOEt : 95/5) = 0.3

**HRMS (ES)** m/z calcd for C<sub>15</sub>H<sub>24</sub>O<sub>3</sub>Si + NH<sub>4</sub><sup>+</sup>: 298.1833, [M+NH<sub>4</sub><sup>+</sup>], found 298.1897

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ (ppm) 0.08 (6H, 2 x CH<sub>3</sub>, s, H<sub>3</sub>), 0.90 (9H, 3 x CH<sub>3</sub>, s, H<sub>1</sub>), 2.45 (1H, CH, t, *J* = 2.5 Hz, H<sub>12</sub>), 4.15 (2H, CH<sub>2</sub>, d, *J* = 2.5 Hz, H<sub>10</sub>), 4.54 (2H, CH<sub>2</sub>, s, H<sub>4</sub> or H<sub>9</sub>), 4.64 (2H, CH<sub>2</sub>, s, H<sub>4</sub> or H<sub>9</sub>), 6.19 (1H, CH, d, *J* = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>), 6.30 (1H, CH, d, *J* = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>).

**$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):**  $\delta$  (ppm) -5.3 (2 x  $\text{CH}_3$ ,  $\text{C}_3$ ), 18.4 ( $\text{C}$ ,  $\text{C}_2$ ), 25.9 (3 x  $\text{CH}_3$ ,  $\text{C}_1$ ), 56.6 ( $\text{CH}_2$ ,  $\text{C}_{10}$ ), 58.3 ( $\text{CH}_2$ ,  $\text{C}_4$  or  $\text{C}_9$ ), 63.1 ( $\text{CH}_2$ ,  $\text{C}_4$  or  $\text{C}_9$ ), 74.7 ( $\text{CH}$ ,  $\text{C}_{12}$ ), 79.3 ( $\text{C}$ ,  $\text{C}_{11}$ ), 107.8 ( $\text{C}$ ,  $\text{C}_6$  or  $\text{C}_7$ ), 110.9 ( $\text{C}$ ,  $\text{C}_6$  or  $\text{C}_7$ ), 150.2 ( $\text{C}$ ,  $\text{C}_5$  or  $\text{C}_8$ ), 155.1 ( $\text{C}$ ,  $\text{C}_5$  or  $\text{C}_8$ ).

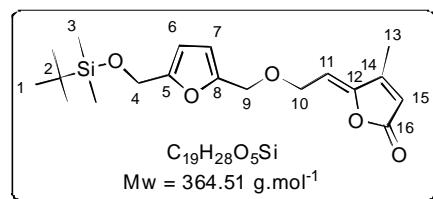


## 2. Preparation of $\gamma$ -alkylidenebutenolides 9, 9b

### General procedure

A dry Schlenk tube equipped with a Teflon-coated magnetic stirrer was charged with  $K_2CO_3$  (3 equiv) and (*Z*)-3-iodobut-2-enoic acid (2 equiv). The vessel was evacuated and backfilled with argon. Anhydrous DMF ( $c = 1.9$  M) was added and the suspension was stirred for 15 min. Then the reaction mixture was degassed at  $0^\circ C$  for 5 min under *vacuum* and backfilled with argon. After reaching room temperature, the previously prepared alkyne (1 equiv) and CuI (1 equiv) were successively added. The Schlenk tube was sealed and then placed in a preheated oil bath at  $55^\circ C$  for 4 hours, following which, the Schlenk tube was placed in an ice bath and a saturated aqueous solution of  $NH_4Cl$  was added. Stirring at  $0^\circ C$  was allowed for 10 min and the reaction mixture was diluted in diethyl ether and filtered through a short pad of celite. The filtrate was washed with brine and the combined organic layers were dried over anhydrous  $MgSO_4$ , filtered and concentrated *in vacuo*.

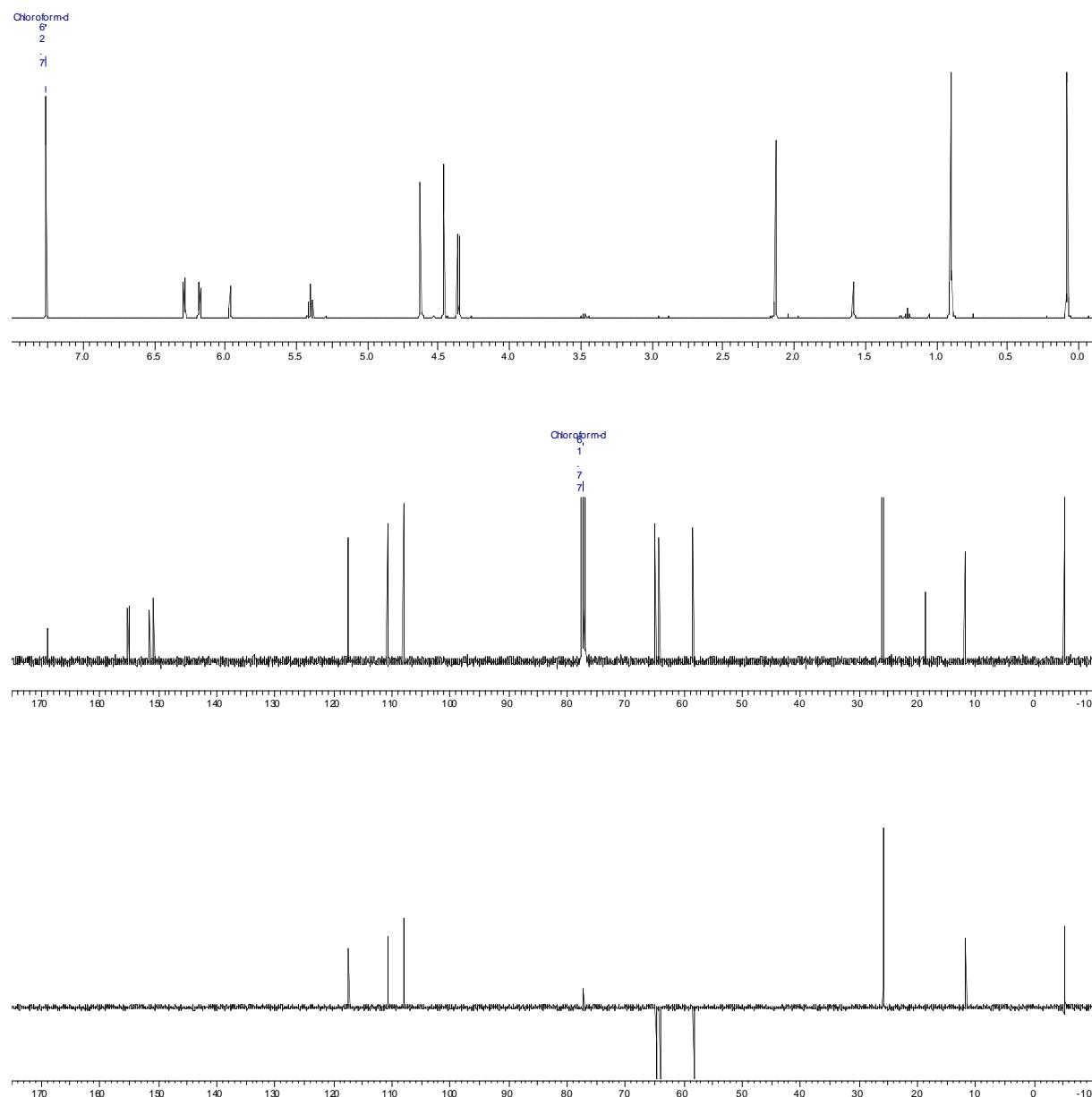
### (*Z*)-5-((2-((*t*-butyldimethylsiloxy)methyl)furan-2-yl)methoxy)ethylidene)-4-methyl furan-2(5H)-one (9)



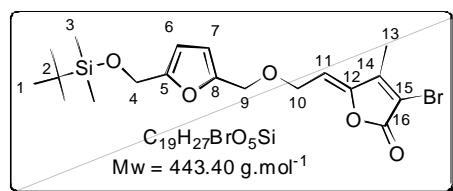
See Full Paper

**$^1H$  NMR** ( $CDCl_3$ , 400 MHz):  $\delta$  (ppm) 0.08 (6H, 2 x  $CH_3$ , s,  $H_3$ ), 0.90 (9H, 3 x  $CH_3$ , s,  $H_1$ ), 2.13 (3H,  $CH_3$ , d,  $J = 1.5$  Hz,  $H_{13}$ ), 4.35 (2H,  $CH_2$ , d,  $J = 7.0$  Hz,  $H_{10}$ ), 4.46 (2H,  $CH_2$ , s,  $H_4$  or  $H_9$ ), 4.62 (2H,  $CH_2$ , s,  $H_4$  or  $H_9$ ), 5.4 (1H,  $CH$ , t,  $J = 6.3$  Hz,  $H_{11}$ ), 5.97 (1H,  $CH$ , br s,  $H_{15}$ ), 6.18 (1H,  $CH$ , d,  $J = 3.3$  Hz,  $H_6$  or  $H_7$ ), 6.29 (1H,  $CH$ , d,  $J = 3.3$  Hz,  $H_6$  or  $H_7$ ).

**$^{13}C$  NMR** ( $CDCl_3$ , 100 MHz):  $\delta$  (ppm) -5.3 (2 x  $CH_3$ ,  $C_3$ ), 11.7 ( $CH_3$ ,  $C_{13}$ ), 18.4 ( $C$ ,  $C_2$ ), 25.9 (3 x  $CH_3$ ,  $C_1$ ), 58.3 ( $CH_2$ ,  $C_4$  or  $C_9$ ), 64.0 ( $CH_2$ ,  $C_{10}$ ), 64.7 ( $CH_2$ ,  $C_4$  or  $C_9$ ), 107.9 (2 x  $CH$ ,  $C_{11}$  and  $C_6$  or  $C_7$ ), 110.6 ( $CH$ ,  $C_6$  or  $C_7$ ), 117.3 ( $CH$ ,  $C_{15}$ ), 150.5 ( $C$ ,  $C_5$  or  $C_8$ ), 151.2 ( $C$ ,  $C_{12}$ ), 154.6 ( $C$ ,  $C_{14}$ ), 155.0 ( $C$ ,  $C_5$  or  $C_8$ ), 168.7 ( $C$ ,  $C_{16}$ )



**(Z)-3-bromo-5-((2-(((5-((t-butyldimethylsilyl)oxy)methyl)furan-2-yl)methoxy)ethylidene)-4-methylfuran-2(5H)-one (9b)**



The expected  $\gamma$ -alkylidenebutenolide **9b** was used in the next step without further purification.

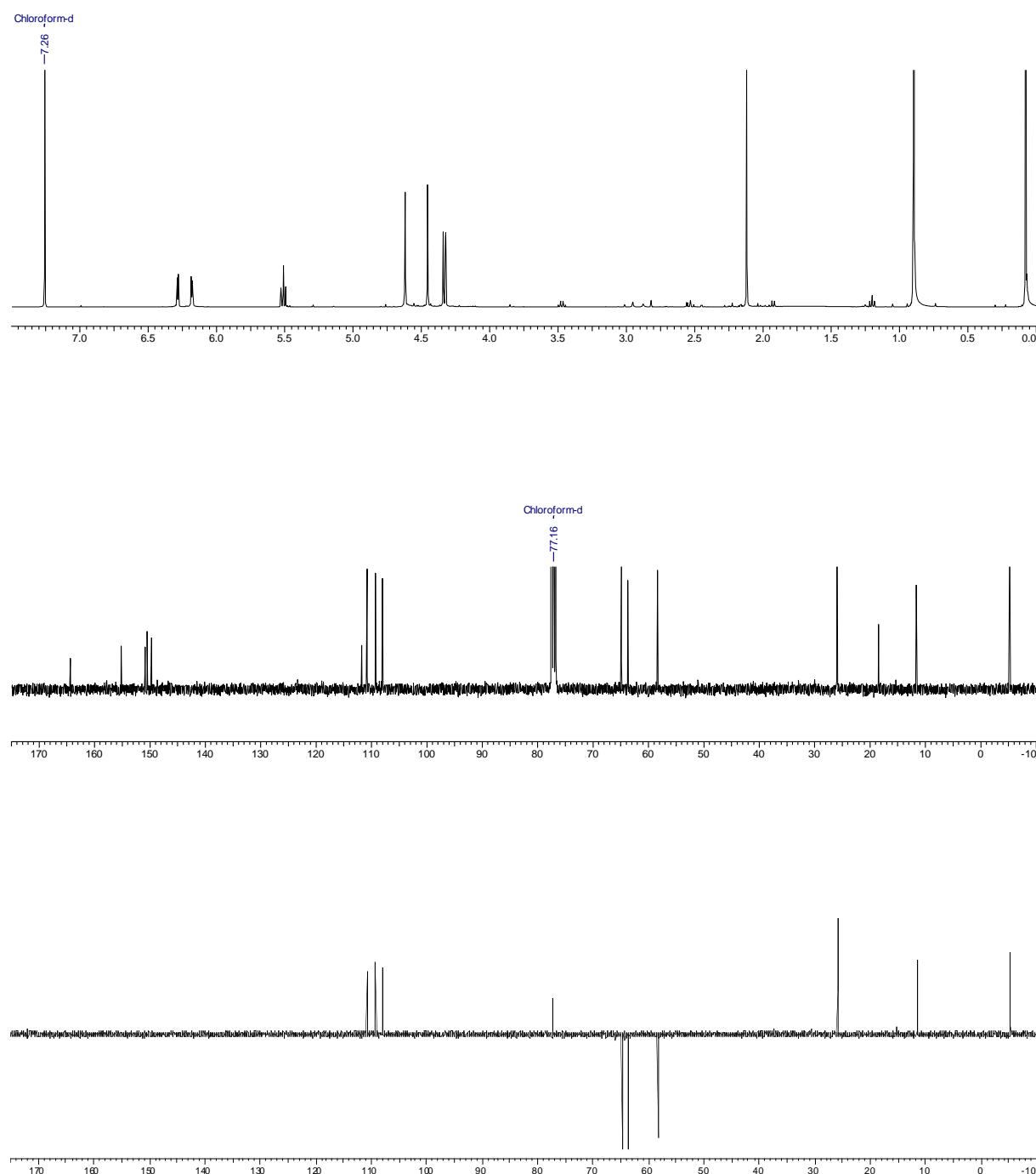
**Aspect:** dark brown oil

**Rf** (PE/AcOEt : 9/1) = 0.33

**HRMS (ES)** m/z calcd for  $C_{19}H_{27}O_5SiBr + NH_4^+$ : 460.1149,  $[M+NH_4^+]$ , found 460.1151

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 0.08 (6H, 2 x  $\text{CH}_3$ , s, H<sub>3</sub>), 0.90 (9H, 3 x  $\text{CH}_3$ , s, H<sub>1</sub>), 2.12 (3H,  $\text{CH}_3$ , s, H<sub>13</sub>), 4.33 (2H,  $\text{CH}_2$ , d,  $J$  = 6.8 Hz, H<sub>10</sub>), 4.46 (2H,  $\text{CH}_2$ , s, H<sub>4</sub> or H<sub>9</sub>), 4.62 (2H,  $\text{CH}_2$ , s, H<sub>4</sub> or H<sub>9</sub>), 5.50 (1H, CH, t,  $J$  = 6.8 Hz, H<sub>11</sub>), 6.18 (1H, CH, d,  $J$  = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>), 6.28 (1H, CH, d,  $J$  = 3.3 Hz, H<sub>6</sub> or H<sub>7</sub>).

**<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) -5.3 (2 x  $\text{CH}_3$ ,  $\text{C}_3$ ), 11.6 ( $\text{CH}_3$ ,  $\text{C}_{13}$ ), 18.4 ( $\text{C}$ ,  $\text{C}_2$ ), 25.9 (3 x  $\text{CH}_3$ ,  $\text{C}_1$ ), 58.3 ( $\text{CH}_2$ ,  $\text{C}_4$  or  $\text{C}_9$ ), 63.6 ( $\text{CH}_2$ ,  $\text{C}_{10}$ ), 64.8 ( $\text{CH}_2$ ,  $\text{C}_4$  or  $\text{C}_9$ ), 107.9 ( $\text{CH}$ ,  $\text{C}_6$  or  $\text{C}_7$ ), 109.2 ( $\text{CH}$ ,  $\text{C}_{11}$ ), 110.7 ( $\text{CH}$ ,  $\text{C}_6$  or  $\text{C}_7$ ), 111.7 ( $\text{C}$ ,  $\text{C}_{15}$ ), 149.6 ( $\text{C}$ ,  $\text{C}_{12}$ ), 150.4 ( $\text{C}$ ,  $\text{C}_5$  or  $\text{C}_8$ ), 150.8 ( $\text{C}$ ,  $\text{C}_{14}$ ), 155.1 ( $\text{C}$ ,  $\text{C}_5$  or  $\text{C}_8$ ), 164.3 ( $\text{C}$ ,  $\text{C}_{16}$ ).

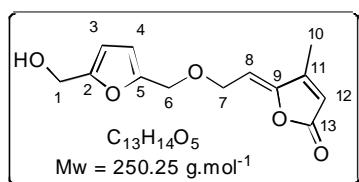


### 3. Preparation of alcohols **6** and **6b**

#### General procedure

To a cooled ( $0^{\circ}\text{C}$ ) solution of the  $\gamma$ -alkyldenebutenolide **9** (or **9b**) (1 equiv) in anhydrous THF ( $c = 0.27\text{ M}$ ) was added a solution of HF•pyridine (HF 70 %• pyridine 30 %) (2 equiv). Stirring at room temperature was allowed until completion of the reaction by TLC at which time a saturated aqueous solution of  $\text{NaHCO}_3$  was carefully added to quench the reaction. The aqueous phase was extracted with  $\text{Et}_2\text{O}$  and the combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The resulting oil was purified by flash chromatography on silica gel (PE/AcOEt : 1/1).

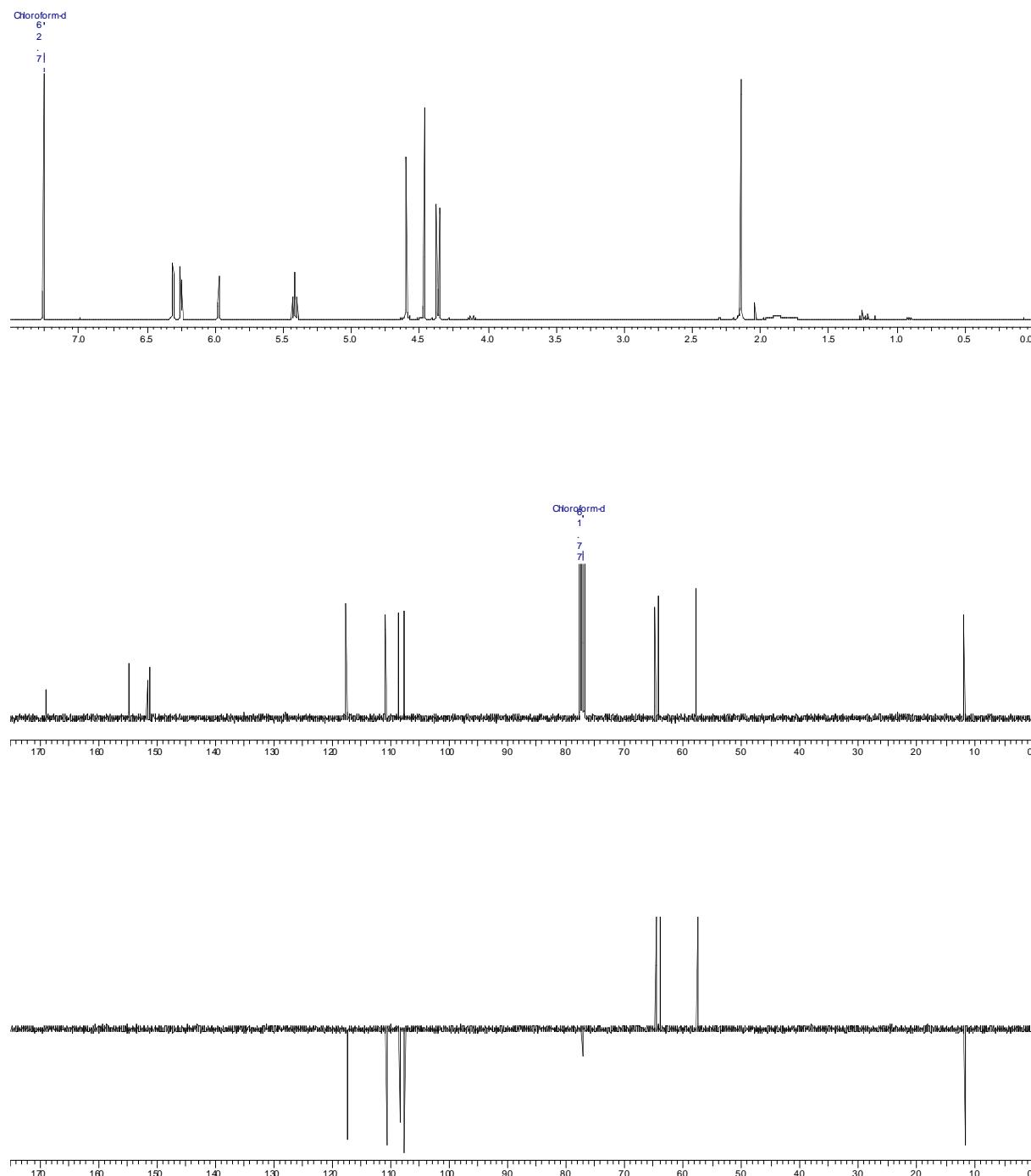
#### (Z)-5-((2-((5-(hydroxymethyl)furan-2-yl)methoxy)ethylidene)-4-methylfuran-2(5H)-one (**6**)



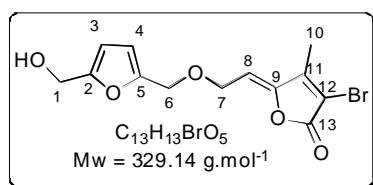
See Full Paper

**$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 2.14 (3H, 3 x  $\text{CH}_3$ , s,  $\text{H}_{10}$ ), 4.36 (2H,  $\text{CH}_2$ , dd,  $J = 7.0$  Hz,  $\text{H}_7$ ), 4.47 (2H,  $\text{CH}_2$ , s,  $\text{H}_1$  or  $\text{H}_6$ ), 4.60 (2H,  $\text{CH}_2$ , s,  $\text{H}_1$  or  $\text{H}_6$ ), 5.40 (1H,  $\text{CH}$ , t,  $J = 7.0$  Hz,  $J = 0.5$  Hz,  $\text{H}_8$ ), 5.98 (1H,  $\text{CH}$ , s,  $\text{H}_{12}$ ), 6.25 (1H,  $\text{CH}$ , d,  $J = 3.1$  Hz,  $\text{H}_3$  or  $\text{H}_4$ ), 6.31 (1H,  $\text{CH}$ , d,  $J = 3.1$  Hz,  $\text{H}_3$  or  $\text{H}_4$ ).

**$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 11.9 ( $\text{CH}_3$ ,  $\text{C}_{10}$ ), 57.7 ( $\text{CH}_2$ ,  $\text{C}_1$  or  $\text{C}_6$ ), 64.1 ( $\text{CH}_2$ ,  $\text{C}_7$ ), 64.7 ( $\text{CH}_2$ ,  $\text{C}_1$  or  $\text{C}_6$ ), 107.8 ( $\text{CH}$ ,  $\text{C}_8$ ), 108.7 ( $\text{CH}$ ,  $\text{C}_3$  or  $\text{C}_4$ ), 110.8 ( $\text{CH}$ ,  $\text{C}_3$  or  $\text{C}_4$ ), 117.6 ( $\text{CH}$ ,  $\text{C}_{12}$ ), 151.3 ( $\text{C}$ ,  $\text{C}_2$  or  $\text{C}_5$ ), 151.7 ( $\text{C}$ ,  $\text{C}_{11}$ ), 154.8 (2C,  $\text{C}_9$  and  $\text{C}_2$  or  $\text{C}_5$ ), 168.9 ( $\text{C}$ ,  $\text{C}_{13}$ )



**(Z)-3-bromo-5-(2-((5-(hydroxymethyl)furan-2-yl)methoxy)ethylidene)-4-methylfuran-2-(5H)-one (6b)**



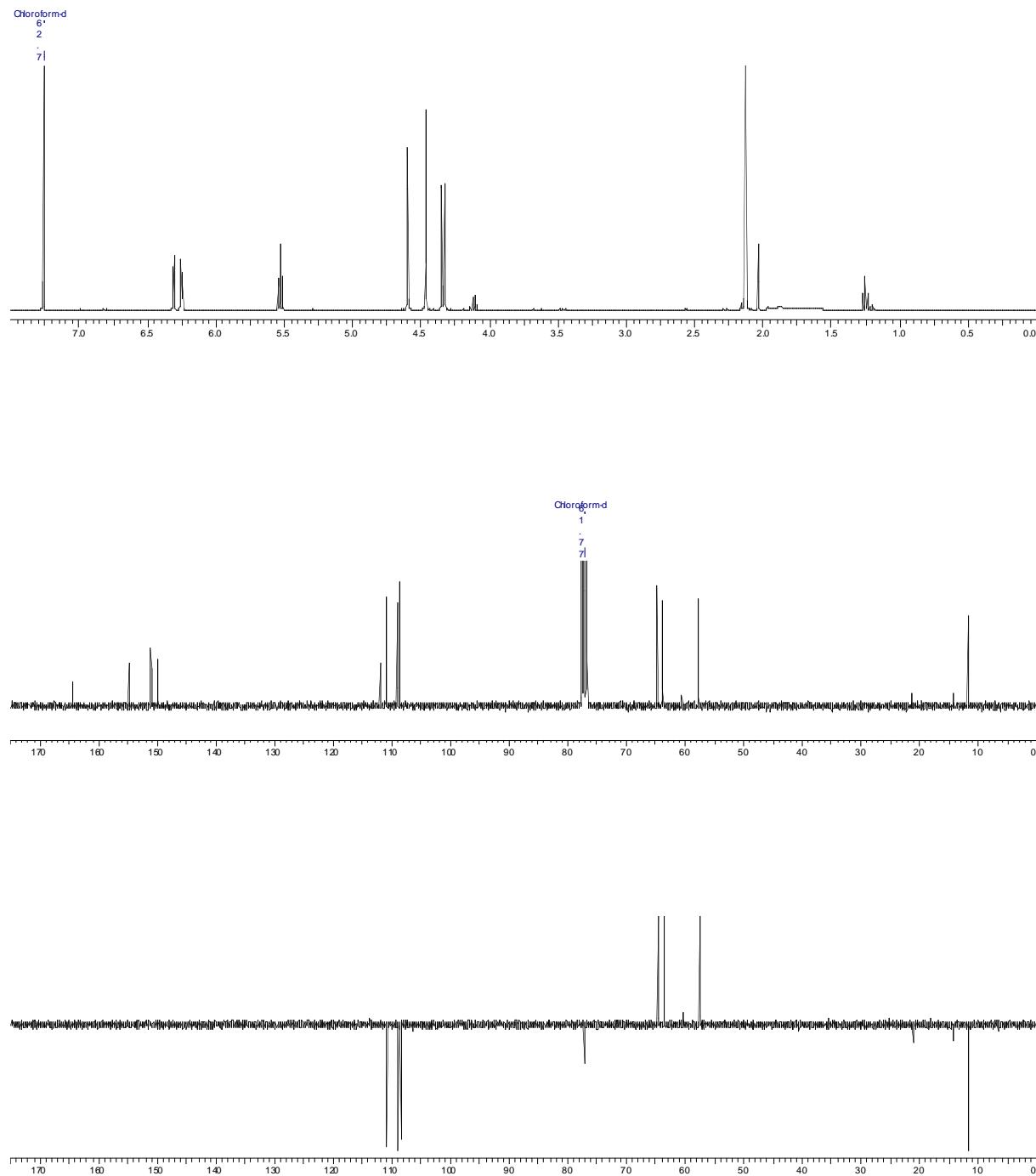
Fractions that contained the desired product were gathered and concentrated under reduced pressure to give the alcohol **6b** in 72 % yield (over 2 steps) as an orange oil.

**R<sub>f</sub>** (PE/AcOEt : 1/1) = 0.37

**HRMS (ES)** m/z calcd for  $\text{C}_{13}\text{H}_{13}\text{O}_5\text{Br} + \text{NH}_4^+$ : 346.0285, [ $\text{M}+\text{NH}_4^+$ ], found 346.0284

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 2.13 (3H,  $\text{CH}_3$ , s,  $\text{H}_{10}$ ), 4.33 (2H,  $\text{CH}_2$ , d,  $J$  = 7.0 Hz,  $\text{H}_7$ ), 4.47 (2H,  $\text{CH}_2$ , s,  $\text{H}_1$  or  $\text{H}_6$ ), 4.60 (2H,  $\text{CH}_2$ , s,  $\text{H}_1$  or  $\text{H}_6$ ), 5.51 (1H,  $\text{CH}$ , t,  $J$  = 7.0 Hz,  $\text{H}_8$ ), 6.25 (1H,  $\text{CH}$ , d,  $J$  = 3.2 Hz,  $\text{H}_3$  or  $\text{H}_4$ ), 6.30 (1H,  $\text{CH}$ , d,  $J$  = 3.2 Hz,  $\text{H}_3$  or  $\text{H}_4$ ).

**<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 11.8 ( $\text{CH}_3$ ,  $\text{C}_{10}$ ), 57.7 ( $\text{CH}_2$ ,  $\text{C}_1$  or  $\text{C}_6$ ), 63.7 ( $\text{CH}_2$ ,  $\text{C}_7$ ), 64.8 ( $\text{CH}_2$ ,  $\text{C}_1$  or  $\text{C}_6$ ), 108.7 ( $\text{CH}$ ,  $\text{C}_3$  or  $\text{C}_4$ ), 109.0 ( $\text{CH}$ ,  $\text{C}_8$ ), 110.9 ( $\text{CH}$ ,  $\text{C}_3$  or  $\text{C}_4$ ), 111.9 ( $\text{C}$ ,  $\text{C}_{12}$ ), 150.0 ( $\text{C}$ ,  $\text{C}_9$ ), 151.0 ( $\text{C}$ ,  $\text{C}_2$  or  $\text{C}_5$  or  $\text{C}_{11}$ ), 151.2 ( $\text{C}$ ,  $\text{C}_2$  or  $\text{C}_5$  or  $\text{C}_{11}$ ), 154.9 ( $\text{C}$ ,  $\text{C}_2$  or  $\text{C}_5$  or  $\text{C}_{11}$ ), 146.5 ( $\text{C}$ ,  $\text{C}_{13}$ ).

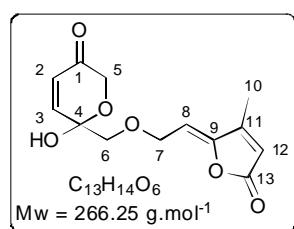


## 4. Preparation of $\gamma$ -pyrones 10 and 10b

### General procedure for the Achmatowicz reaction

To a cooled (-78°C) solution of alcohol **6** or (**6b**) (1 equiv) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (c = 0.13 M) was added *m*-CPBA (1.1 equiv). The reaction mixture was allowed to warm to room temperature over a period of an hour and was stirred until completion of the reaction by TLC. Then the reaction mixture was diluted with dichloromethane and the organic layer was washed with a saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub>, followed by an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 %). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo* to give the expected  $\gamma$ -pyrone which was used in the next step without further purification.

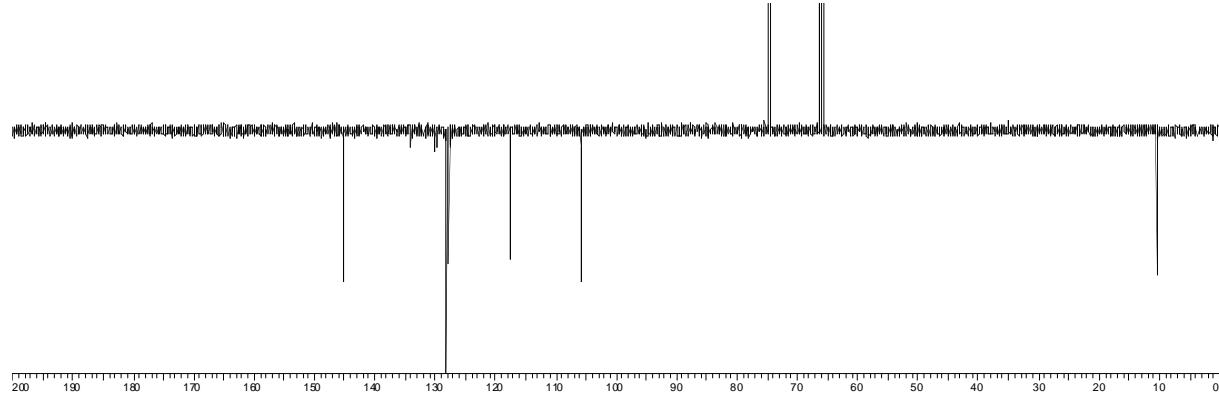
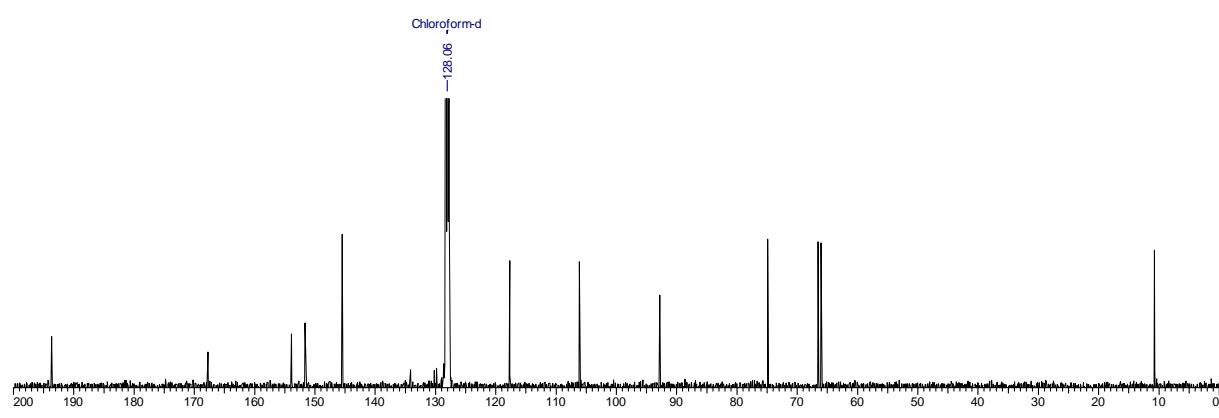
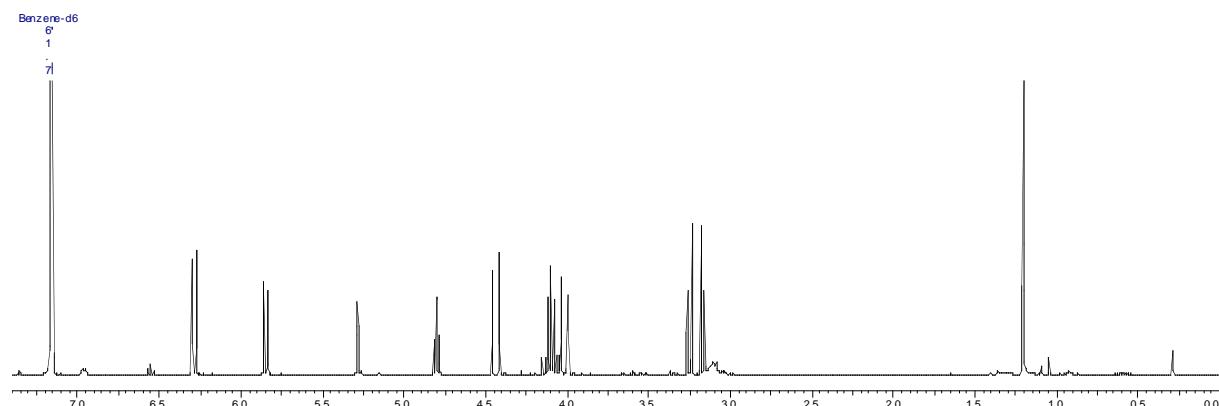
### (Z)-6-hydroxy-6-((2-(3-methyl-5-oxofuran-2(5H)-ylidene)ethoxy)methyl)-2H-pyran-3 (6H)-one (10)



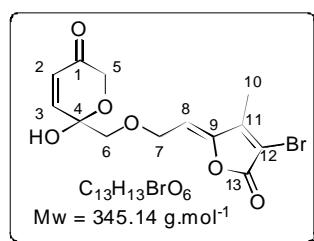
See Full Paper

**<sup>1</sup>H NMR** (benzene-*d*<sup>6</sup>, 400 MHz):  $\delta$  (ppm) 1.21 (3H, CH<sub>3</sub>, d, *J* = 1.3 Hz, H<sub>10</sub>), 3.17 (1H, CH<sub>2</sub>, d, *J* = 10.0 Hz, H<sub>5a</sub>), 3.24 (1H, CH<sub>2</sub>, d, *J* = 10.0 Hz, H<sub>5b</sub>), 4.00 (1H, CH<sub>2</sub>, d, *J* = 16.8 Hz, H<sub>6a</sub>), 4.08 (2H, CH<sub>2</sub>, m, H<sub>7</sub>), 4.42 (1H, CH<sub>2</sub>, d, *J* = 16.8 Hz, H<sub>6b</sub>), 4.78 (1H, CH, t, *J* = 6.5 Hz, H<sub>8</sub>), 5.29 (1H, CH, br s, H<sub>12</sub>), 5.84 (1H, CH, d, *J* = 10.0 Hz, H<sub>2</sub>), 6.27 (1H, CH, d, *J* = 10.0 Hz, H<sub>3</sub>).

**<sup>13</sup>C NMR** (benzene-*d*<sup>6</sup>, 100 MHz):  $\delta$  (ppm) 11.1 (CH<sub>3</sub>, C<sub>10</sub>), 66.4 (CH<sub>2</sub>, C<sub>7</sub>), 66.9 (CH<sub>2</sub>, C<sub>6</sub>), 75.2 (CH<sub>2</sub>, C<sub>5</sub>), 93.1 (C, C<sub>4</sub>), 106.4 (CH, C<sub>8</sub>), 118.0 (CH, C<sub>12</sub>), 128.1 (CH, C<sub>2</sub>), 145.8 (CH, C<sub>3</sub>), 152.0 (C, C<sub>11</sub>), 154.2 (C, C<sub>9</sub>), 168.1 (C, C<sub>13</sub>), 194.0 (C, C<sub>1</sub>).



**(Z)-6-((2-(4-bromo-3-methyl-5-oxofuran-2(5H)-ylidene)ethoxy)methyl)-6-hydroxy-2H-pyran-3(6H)-one (10b)**



**Aspect:** orange oil

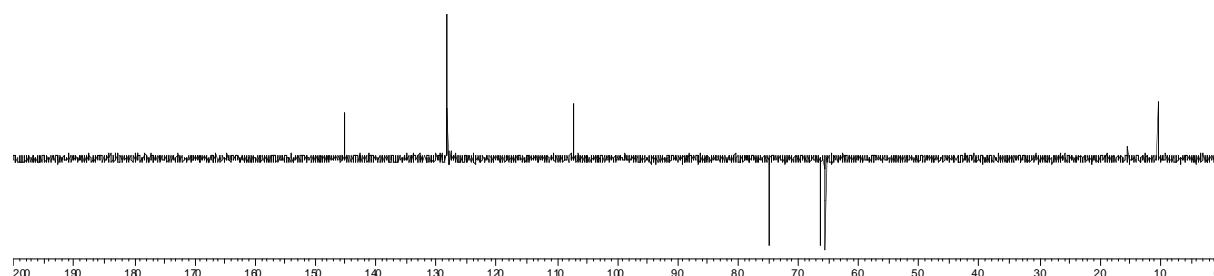
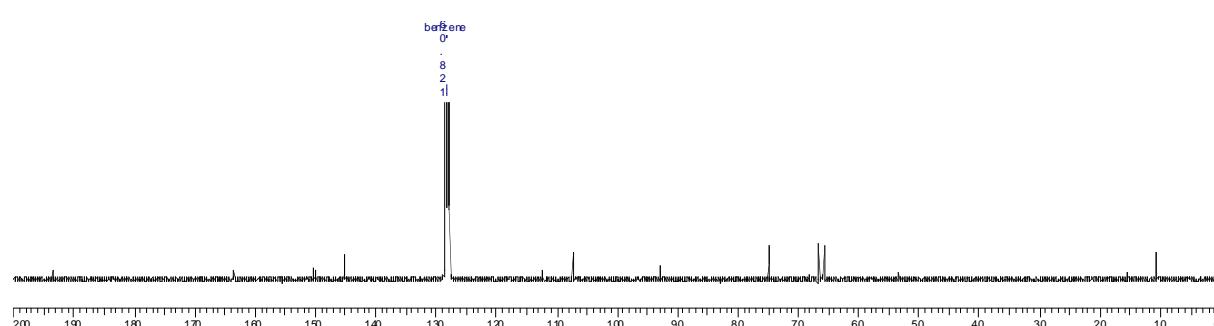
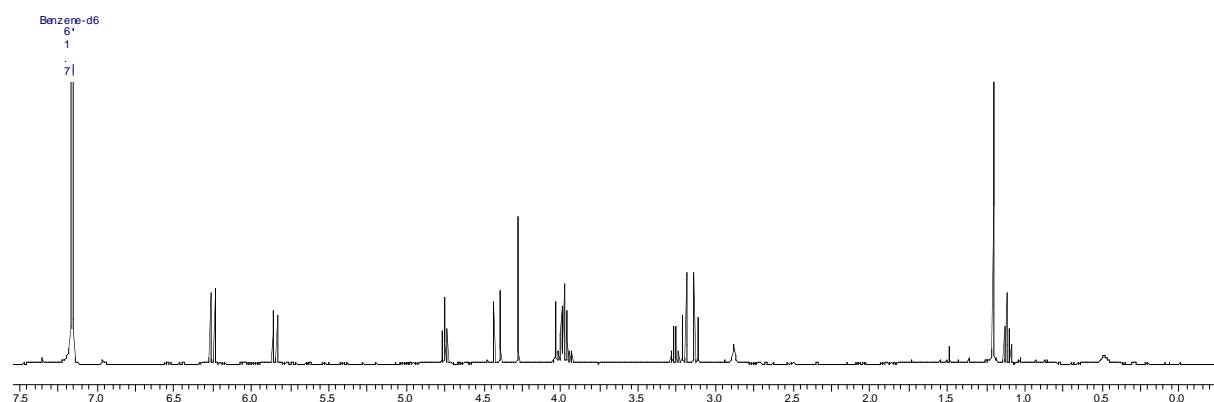
**Yield** = 72 %

**Rf** (PE/AcOEt : 1/1) = 0.44

**HRMS (ES)** m/z calcd for C<sub>13</sub>H<sub>13</sub>O<sub>6</sub>Br + NH<sub>4</sub><sup>+</sup>: 362.0234, [M+NH<sub>4</sub><sup>+</sup>], found 362.0234

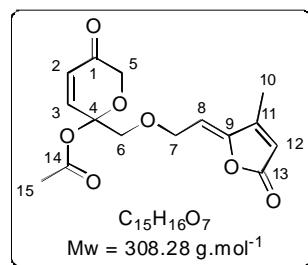
**<sup>1</sup>H NMR** (benzene-*d*<sup>6</sup>, 400 MHz): δ (ppm) 1.20 (3H, CH<sub>3</sub>, s, H<sub>10</sub>), 3.12 (1H, CH, d, *J* = 10.2 Hz, H<sub>5a</sub>), 3.20 (1H, CH, d, *J* = 10.2 Hz, H<sub>5b</sub>), 3.96-4.03 (3H, CH<sub>2</sub> and CH<sub>2</sub>, m, H<sub>6a</sub> and H<sub>7</sub>), 4.41 (1H, CH, d, *J* = 16.5 Hz, H<sub>6b</sub>), 4.75 (1H, CH, t, *J* = 7.0 Hz, H<sub>8</sub>), 5.85 (1H, CH, d, *J* = 10.3 Hz, H<sub>2</sub>), 6.25 (1H, CH, d, *J* = 10.3 Hz, H<sub>3</sub>).

**<sup>13</sup>C NMR** (benzene-*d*<sup>6</sup>, 100 MHz): δ (ppm) 10.7 (CH<sub>3</sub>, C<sub>10</sub>), 65.7 (CH<sub>2</sub>, C<sub>7</sub>), 66.6 (CH<sub>2</sub>, C<sub>6</sub>), 75.0 (CH<sub>2</sub>, C<sub>5</sub>), 92.8 (C, C<sub>4</sub>), 107.4 (CH, C<sub>8</sub>), 112.4 (C, C<sub>12</sub>), 128.1 (CH, C<sub>2</sub>), 145.3 (CH, C<sub>3</sub>), 150.0 (C, C<sub>9</sub> or C<sub>11</sub>), 150.3 (C, C<sub>9</sub> or C<sub>11</sub>), 163.5 (C, C<sub>13</sub>), 193.5 (C, C<sub>1</sub>).



## 5. NMR data of **heterocyclics 5a and 5b**

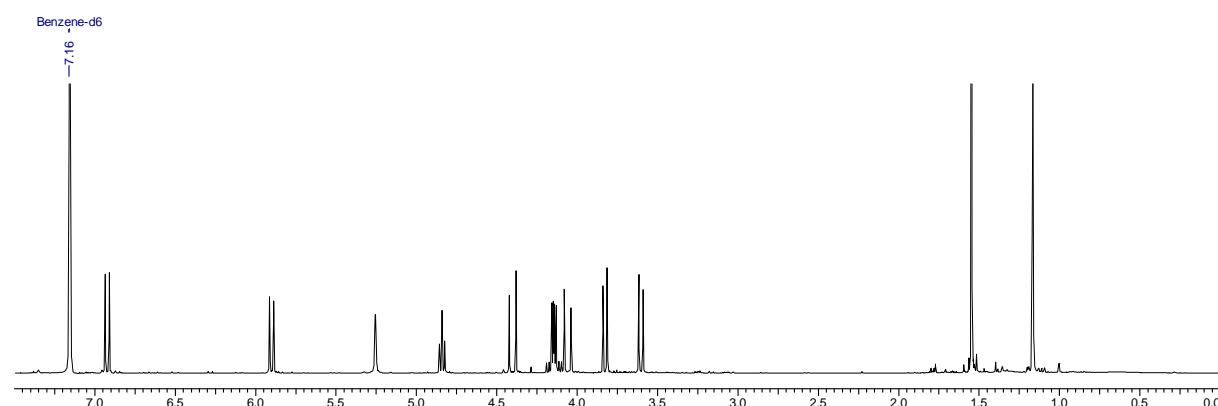
**(Z)-2-((2-(3-methyl-5-oxofuran-2(5H)-ylidene)ethoxy)methyl)-5-oxo-5,6-dihydro-2H-pyran-2-yl acetate (5a)**

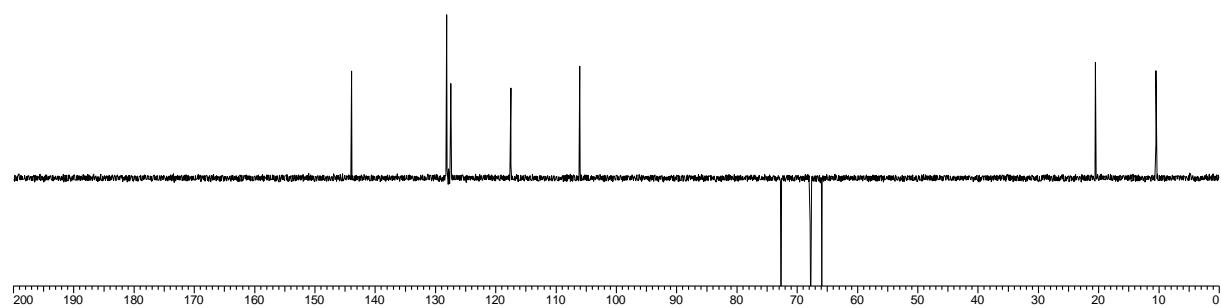
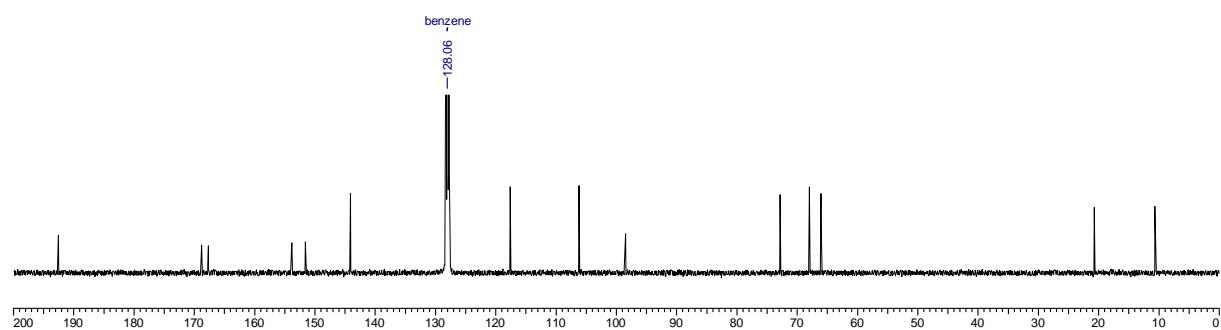


See Full Paper

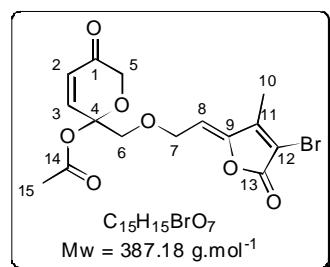
**$^1\text{H}$  NMR** (benzene- $d^6$ , 400 MHz):  $\delta$  (ppm) 1.1 (3H,  $\text{CH}_3$ , d,  $J = 1.5$  Hz, H<sub>10</sub>), 1.55 (3H,  $\text{CH}_3$ , s, H<sub>15</sub>), 3.61 (1H, CH, d,  $J = 10.5$  Hz, H<sub>5a</sub>), 3.83 (1H, CH, d,  $J = 10.5$  Hz, H<sub>5b</sub>), 4.06 (1H, CH, d,  $J = 16.8$  Hz, H<sub>6a</sub>), 4.10-4.20 (2H,  $\text{CH}_2$ , m, H<sub>7</sub>), 4.41 (1H, CH, d,  $J = 16.1$  Hz, H<sub>6b</sub>), 4.81 (1H, CH, t,  $J = 6.6$  Hz, H<sub>8</sub>), 5.26 (1H, CH, br s, H<sub>12</sub>), 5.89 (1H, CH, d,  $J = 10.5$  Hz, H<sub>2</sub>), 6.91 (1H, CH, d,  $J = 10.5$  Hz, H<sub>3</sub>).

**$^{13}\text{C}$  NMR** (benzene- $d^6$ , 100 MHz):  $\delta$  (ppm) 10.8 ( $\text{CH}_3$ , C<sub>10</sub>), 20.8 ( $\text{CH}_3$ , C<sub>15</sub>), 66.1 ( $\text{CH}_2$ , C<sub>7</sub>), 68.1 ( $\text{CH}_2$ , C<sub>6</sub>), 72.9 ( $\text{CH}_2$ , C<sub>5</sub>), 98.5 (C, C<sub>4</sub>), 106.3 (CH, C<sub>8</sub>), 117.7 (CH, C<sub>12</sub>), 128.1 (CH, C<sub>2</sub>), 144.2 (CH, C<sub>3</sub>), 151.6 (C, C<sub>9</sub> or C<sub>11</sub>), 153.9 (C, C<sub>9</sub> or C<sub>11</sub>), 167.7 (C, C<sub>13</sub>), 168.9 (C, C<sub>14</sub>), 192.6 (C, C<sub>1</sub>).

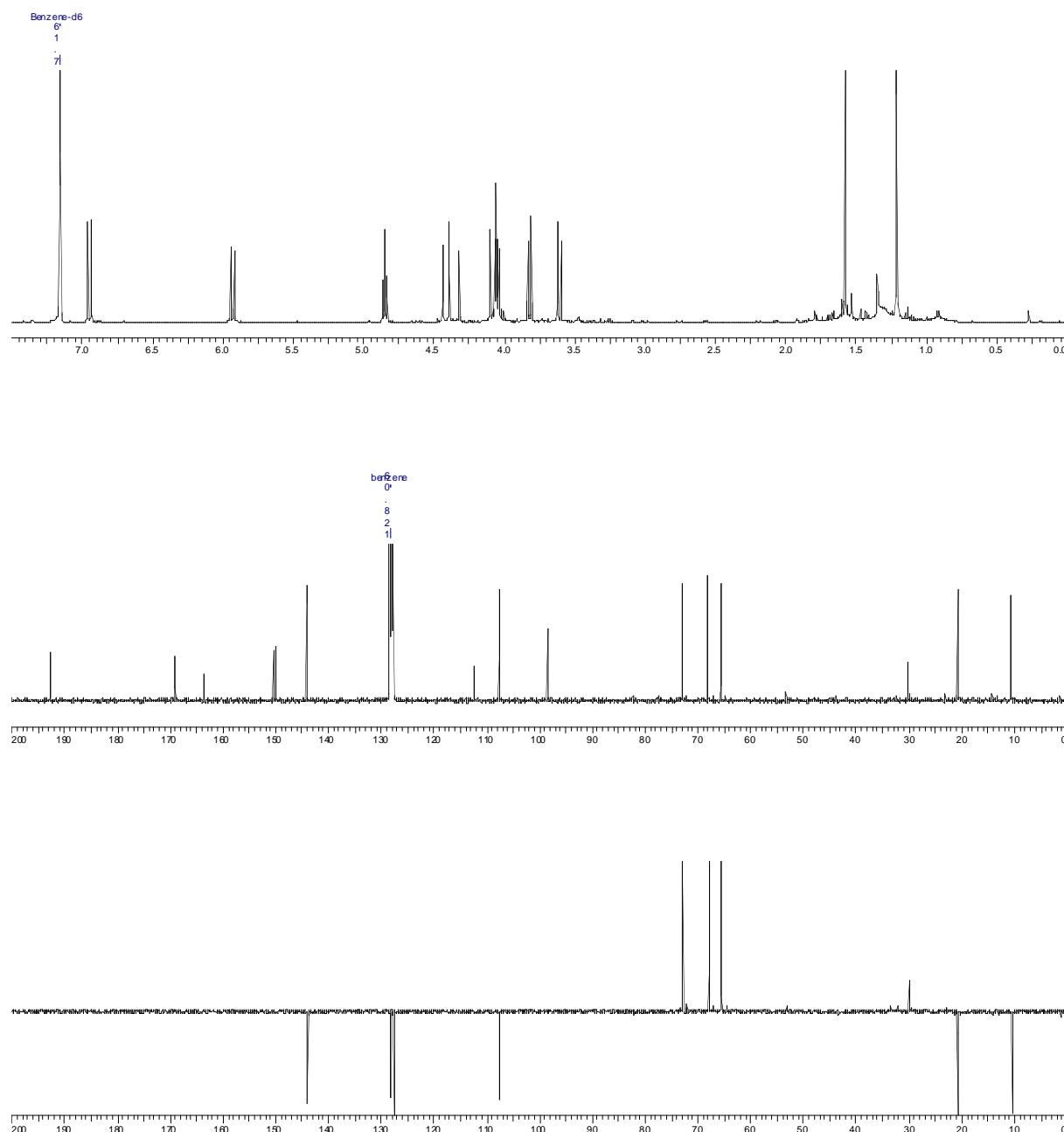




**(Z)-2-((2-(4-bromo-3-methyl-5-oxofuran-2(5H)-ylidene)ethoxy)methyl)-5-oxo-5,6-dihydro-2H-pyran-2-yl acetate (5b)**

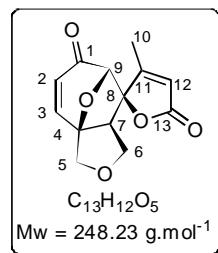


See Full Paper



## 6. NMR data of cycloadducts 2a and 2b

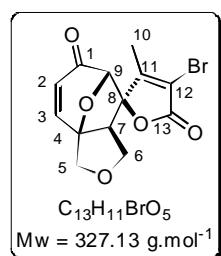
### Cycloadduct 2a.



See Full Paper

**<sup>1</sup>H NMR** (acetone-*d*<sup>6</sup>, 400 MHz): δ (ppm) 1.88 (3H, CH<sub>3</sub>, d, *J* = 1.5 Hz, H<sub>10</sub>), 3.42 (1H, CH, dd, *J* = 8.3 Hz, *J* = 4.02 Hz, H<sub>7</sub>), 3.76-3.82 (1H, CH<sub>2</sub>, m, H<sub>6a</sub>), 3.89 (1H, CH<sub>2</sub>, d, *J* = 10.5 Hz, H<sub>5a</sub>), 4.00-4.03 (1H, CH<sub>2</sub>, m, H<sub>6b</sub>), 4.15 (1H, CH<sub>2</sub>, d, *J* = 10.5 Hz, H<sub>5b</sub>), 4.54 (1H, CH, s, H<sub>9</sub>), 6.00-6.02 (1H, CH, br s, H<sub>12</sub>), 6.18 (1H, CH, dd, *J* = 9.8 Hz, *J* = 1.0 Hz, H<sub>2</sub>), 7.83 (1H, CH, d, *J* = 9.8 Hz, H<sub>3</sub>).

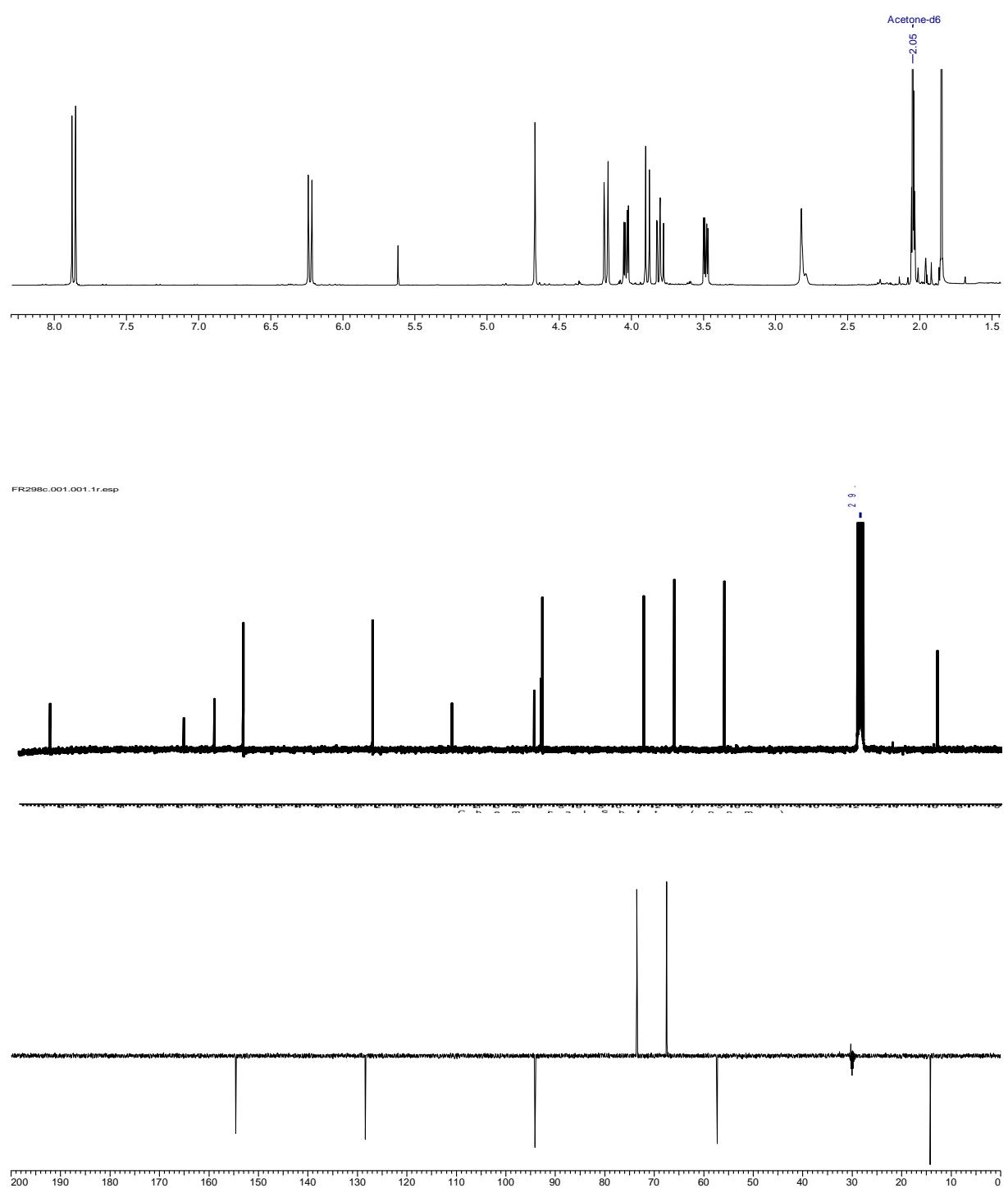
### Cycloadduct 2b.



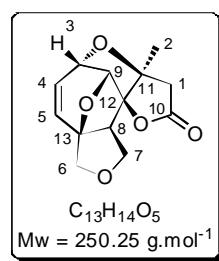
See Full Paper

**<sup>1</sup>H NMR** (acetone-*d*<sup>6</sup>, 400 MHz): δ (ppm) 1.85 (3H, CH<sub>3</sub>, s, H<sub>10</sub>), 3.47 (1H, CH, dd, *J* = 3.8 Hz, *J* = 8.5 Hz, H<sub>7</sub>), 3.78-3.83 (1H, CH, m, H<sub>6a</sub>), 3.90 (1H, CH, d, *J* = 10.7 Hz, H<sub>5a</sub>), 4.04 (1H, CH, dd, *J* = 9.8 Hz, *J* = 3.8 Hz, H<sub>6b</sub>), 4.18 (1H, CH, d, *J* = 10.7 Hz, H<sub>5b</sub>), 4.67 (1H, CH, s, H<sub>9</sub>), 6.23 (1H, CH, dd, *J* = 9.8 Hz, *J* = 1.0 Hz, H<sub>2</sub>), 7.87 (1H, CH, d, *J* = 9.8 Hz, H<sub>3</sub>).

**<sup>13</sup>C NMR** (acetone-*d*<sup>6</sup>, 100 MHz): δ (ppm) 14.4 (CH<sub>3</sub>, C<sub>10</sub>), 57.4 (CH, C<sub>7</sub>), 67.6 (CH<sub>2</sub>, C<sub>6</sub>), 73.7 (CH<sub>2</sub>, C<sub>5</sub>), 94.2 (CH, C<sub>9</sub>), 94.5 (C, C<sub>8</sub> or C<sub>4</sub>), 95.8 (C, C<sub>8</sub> or C<sub>4</sub>), 112.4 (C, C<sub>12</sub>), 128.5 (CH, C<sub>2</sub>), 154.7 (CH, C<sub>3</sub>), 160.5 (C, C<sub>11</sub>), 166.7 (C, C<sub>13</sub>), 193.7 (C, C<sub>1</sub>).



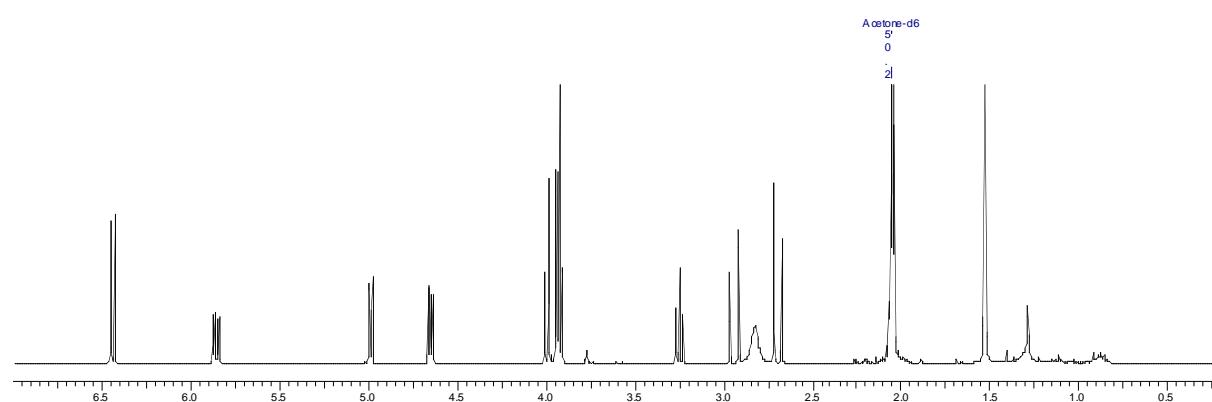
## 7. NMR data of tetracyclic structure 11

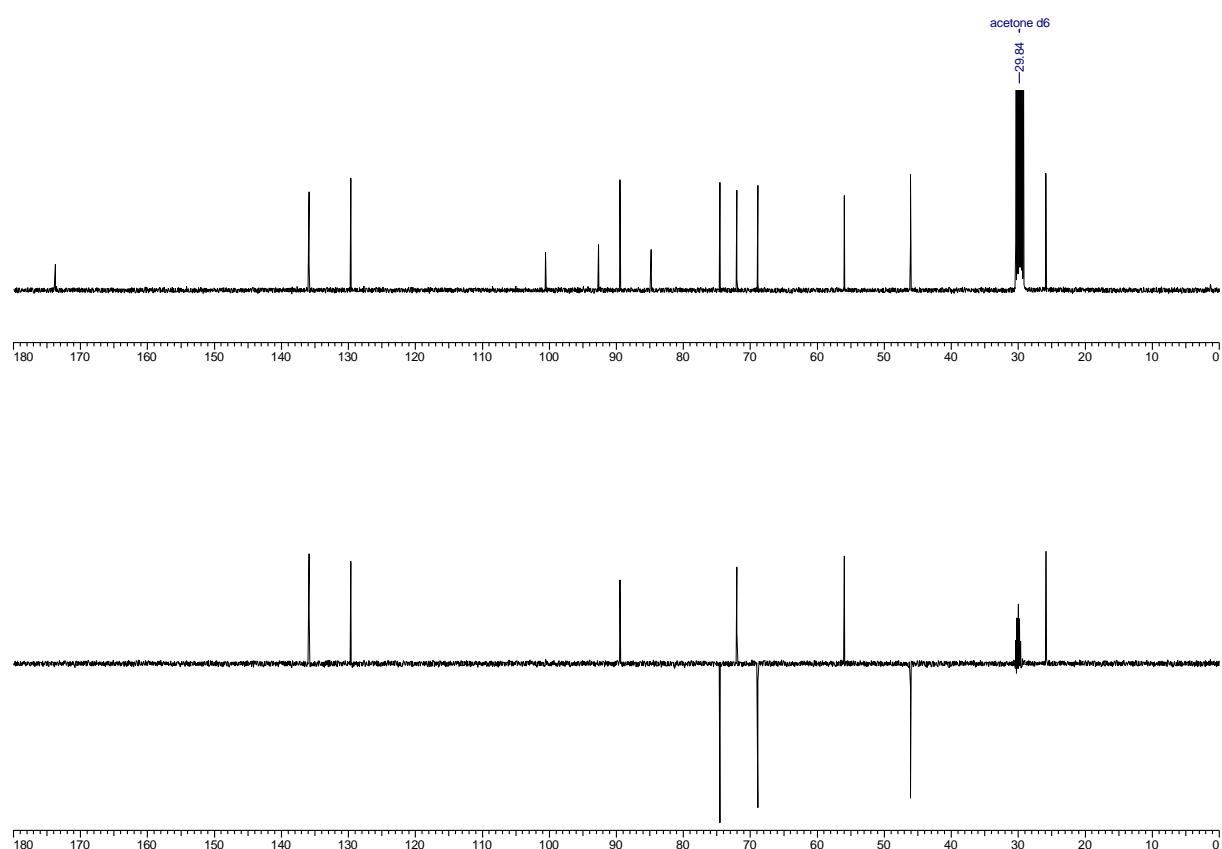


See Full Paper

**$^1\text{H}$  NMR** (acetone- $d^6$ , 400 MHz):  $\delta$  (ppm) 1.53 (3H,  $\text{CH}_3$ , s,  $\text{H}_2$ ), 2.70 (1H,  $\text{CH}$ , d,  $J = 19.0$  Hz,  $\text{H}_{1a}$ ), 2.94 (1H,  $\text{CH}$ , d,  $J = 19.0$  Hz,  $\text{H}_{1b}$ ), 3.25 (1H,  $\text{CH}$ , t,  $J = 9.0$  Hz,  $\text{H}_8$ ), 3.91-3.95 (3H,  $\text{CH}_2$  and  $\text{CH}_2$ , m,  $\text{H}_{6a}$  and  $\text{H}_7$ ), 4.0 (1H,  $\text{CH}$ , d,  $J = 10.3$  Hz,  $\text{H}_{6b}$ ), 4.65 (1H,  $\text{CH}$ , dd,  $J = 3.8$  Hz,  $J = 6.8$  Hz  $\text{H}_3$ ), 4.98 (1H,  $\text{CH}$ , d,  $J = 6.8$  Hz,  $\text{H}_9$ ), 5.86 (1H,  $\text{CH}$ , ddd,  $J = 3.8$  Hz,  $J = 9.5$  Hz,  $J = 0.8$  Hz,  $\text{H}_4$ ), 6.44 (1H,  $\text{CH}$ , d,  $J = 9.5$  Hz,  $\text{H}_5$ ).

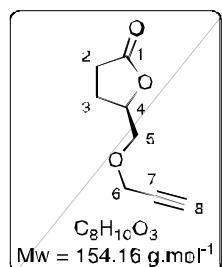
**$^{13}\text{C}$  NMR** (acetone- $d^6$ , 100 MHz):  $\delta$  (ppm) 25.9 ( $\text{CH}_3$ ,  $\text{C}_2$ ), 46.1 ( $\text{CH}_2$ ,  $\text{C}_1$ ), 56.0 ( $\text{CH}$ ,  $\text{C}_8$ ), 68.9 ( $\text{CH}_2$ ,  $\text{C}_7$ ), 72.1 ( $\text{CH}$ ,  $\text{C}_3$ ), 74.6 ( $\text{CH}_2$ ,  $\text{C}_6$ ), 84.9 (C,  $\text{C}_{11}$  or  $\text{C}_{12}$  or  $\text{C}_{13}$ ), 89.5 ( $\text{CH}$ ,  $\text{C}_9$ ), 92.7 (C,  $\text{C}_{11}$  or  $\text{C}_{12}$  or  $\text{C}_{13}$ ), 100.6 (C,  $\text{C}_{11}$  or  $\text{C}_{12}$  or  $\text{C}_{13}$ ), 129.7 ( $\text{CH}$ ,  $\text{C}_4$ ), 153.9 ( $\text{CH}$ ,  $\text{C}_5$ ), 173.8 (C,  $\text{C}_{10}$ ).





## 8. NMR data of compounds 4a and molecules involved in its preparation

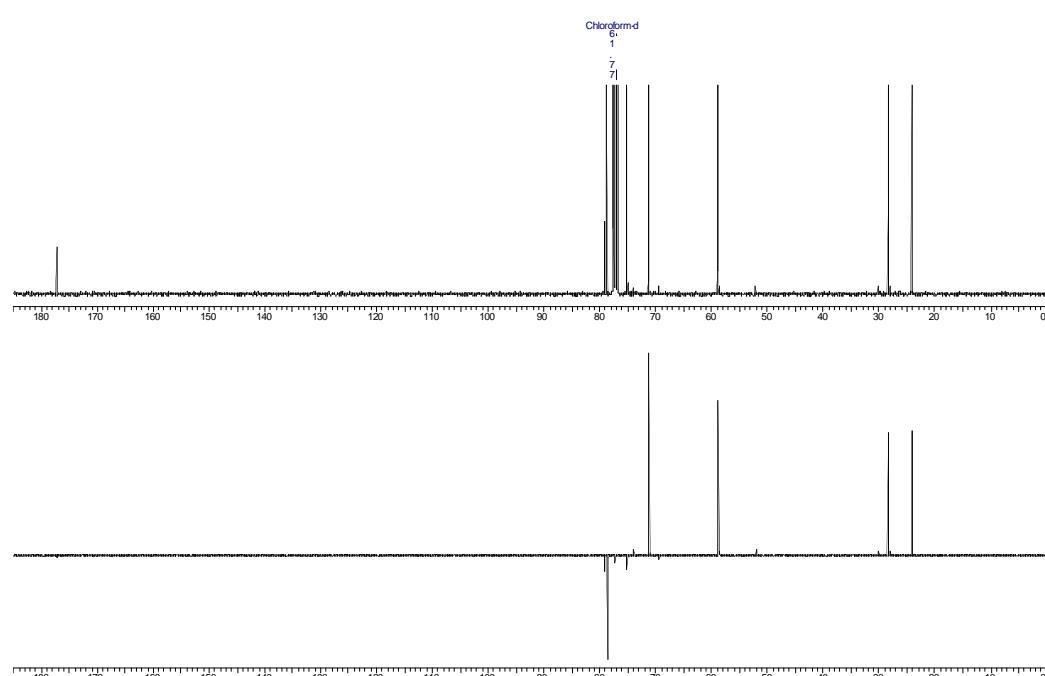
### (R)-5-((prop-2-yn-1-yloxy)methyl)dihydrofuran-2(3H)-one (12)



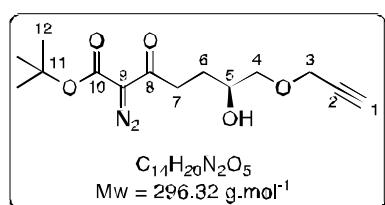
See Full Paper

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 2.09-2.05 (1H,  $\text{CH}_2$ , m, H<sub>3a</sub>), 2.26-2.35 (1H,  $\text{CH}_2$ , m, H<sub>3b</sub>), 2.44-2.52 (2H, CH and  $\text{CH}_2$ , m, H<sub>8</sub> and H<sub>2a</sub>), 2.56-2.65 (1H,  $\text{CH}_2$ , m, H<sub>2b</sub>), 3.71 (2H,  $\text{CH}_2$ , ddd,  $J$  = 3.5 Hz,  $J$  = 4.3 Hz,  $J$  = 10.6 Hz, H<sub>5</sub>), 4.20 (2H,  $\text{CH}_2$ , ddd,  $J$  = 2.3 Hz,  $J$  = 2.5 Hz,  $J$  = 15.8 Hz, H<sub>6</sub>), 4.64-4.69 (2H,  $\text{CH}_2$ , m, H<sub>4</sub>).

**<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 24.0 ( $\text{CH}_2$ , C<sub>3</sub>), 28.3 ( $\text{CH}_2$ , C<sub>2</sub>), 58.7 ( $\text{CH}_2$ , C<sub>6</sub>), 71.1 ( $\text{CH}_2$ , C<sub>5</sub>), 75.0 (CH, C<sub>8</sub>), 78.6 (CH, C<sub>4</sub>), 79.0 (C, C<sub>7</sub>), 177.1 (C, C<sub>1</sub>).



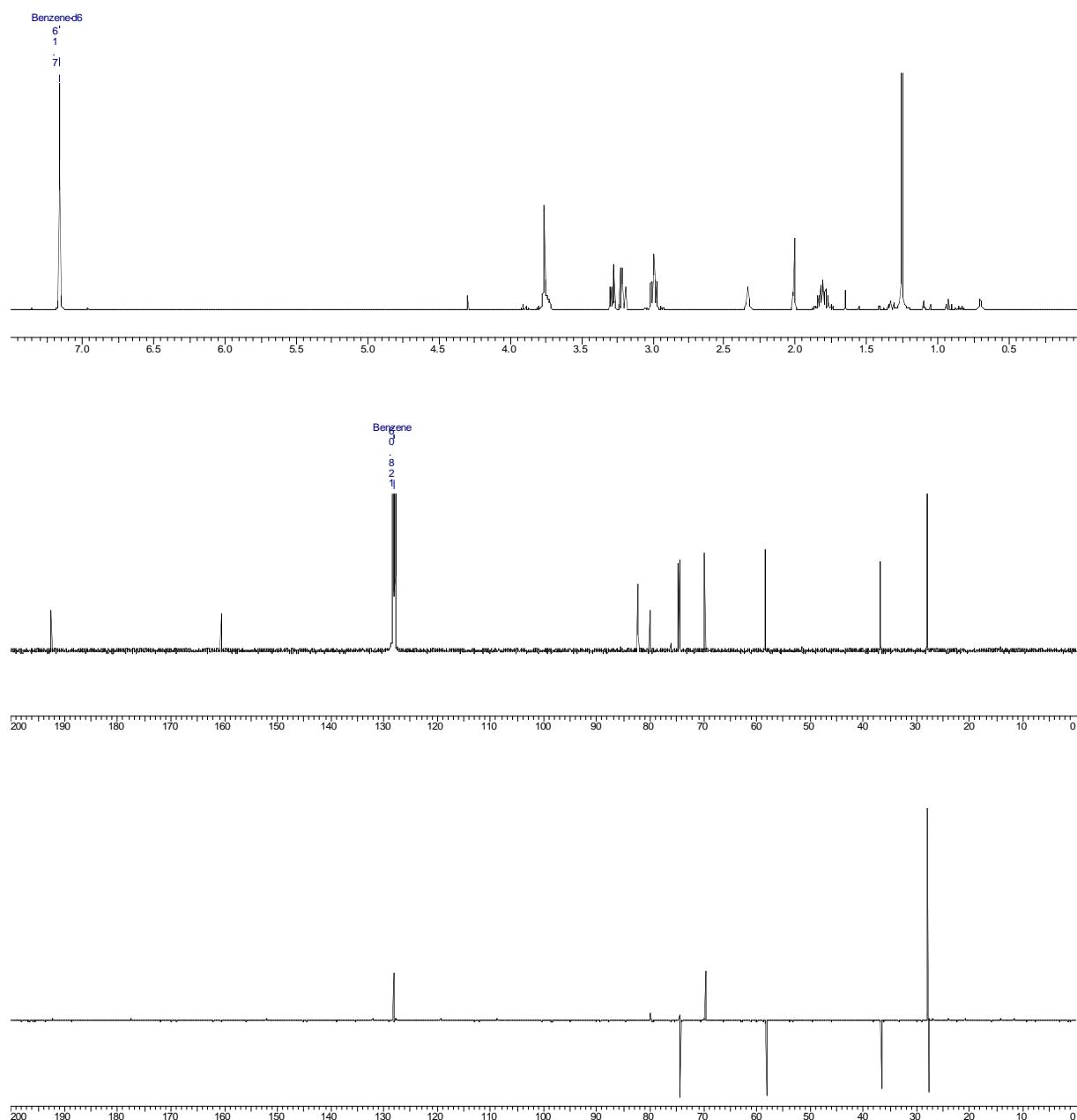
**(S)-*t*-butyl 2-diazo-6-hydroxy-3-oxo-7-(prop-2-yn-1-yloxy)heptanoate (14)**



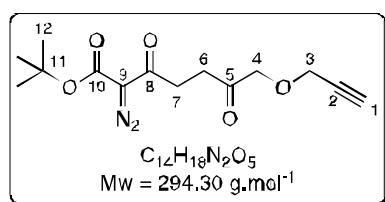
**<sup>1</sup>H NMR** (benzene-*d*<sup>6</sup>, 400 MHz):  $\delta$  (ppm) 1.25 (9H, CH<sub>3</sub>, s, H<sub>12</sub>), 1.75-1.86 (2H, CH<sub>2</sub>, m, H<sub>6</sub>), 2.01 (1H, CH, t, *J* = 2.5 Hz, H<sub>1</sub>), 2.33 (1H, OH, m), 2.98 (2H, CH<sub>2</sub>, td, *J* = 7.3 Hz, *J* = 2.0 Hz, H<sub>7</sub>), 3.19-3.23 (1H, CH<sub>2</sub>, m, H<sub>4a</sub>), 3.27-3.30 (1H, CH<sub>2</sub>, m, H<sub>4b</sub>), 3.71-3.77 (3H, CH and CH<sub>2</sub>, m, H<sub>3</sub> and H<sub>5</sub>).

**<sup>13</sup>C NMR** (benzene-*d*<sup>6</sup>, 100 MHz):  $\delta$  (ppm) 28.0 (CH<sub>2</sub>, C<sub>6</sub>), 28.1 (3 x CH<sub>3</sub>, C<sub>12</sub>), 36.8 (CH<sub>2</sub>, C<sub>7</sub>), 58.4 (CH<sub>2</sub>, C<sub>3</sub>), 69.8 (CH, C<sub>5</sub>), 74.5 (CH<sub>2</sub>, C<sub>4</sub>), 74.7 (CH, C<sub>1</sub>), 80.1 (C, C<sub>2</sub> or C<sub>11</sub>), 82.3 (C, C<sub>2</sub> or C<sub>11</sub>), 160.6 (C, C<sub>10</sub>), 192.4 (C, C<sub>8</sub>), (C=N<sub>2</sub> was not observed).<sup>4</sup>

<sup>4</sup> This is consistent with data previously reported, see for example : a) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, 122, 3063-3070; b) Davis, F. A.; Yang, B.; Deng J. *J. Org. Chem.* **2003**, 68, 5147-5152.; c) Peddibhotla, S.; Dang, Y.; Liu, J. O.; Romo, D. *J. Am. Chem. Soc* **2007**, 129, 12222-12231.



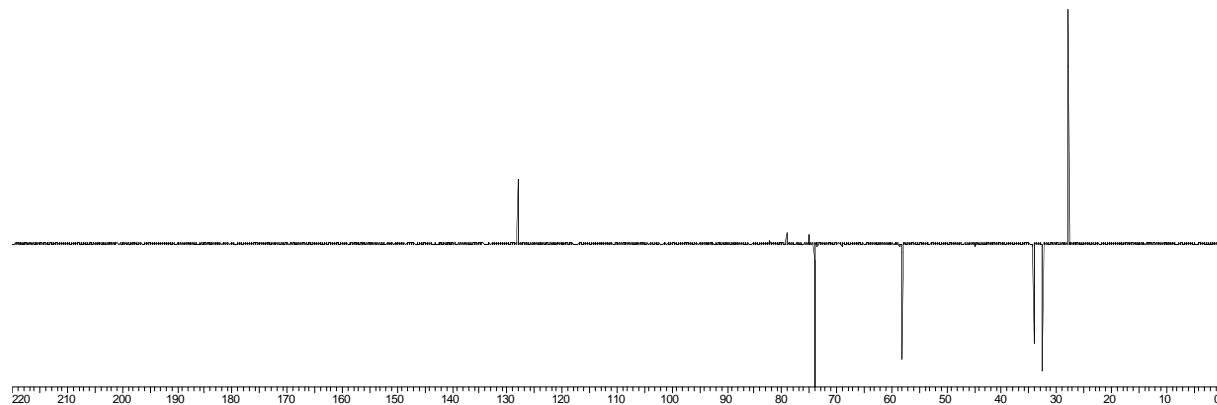
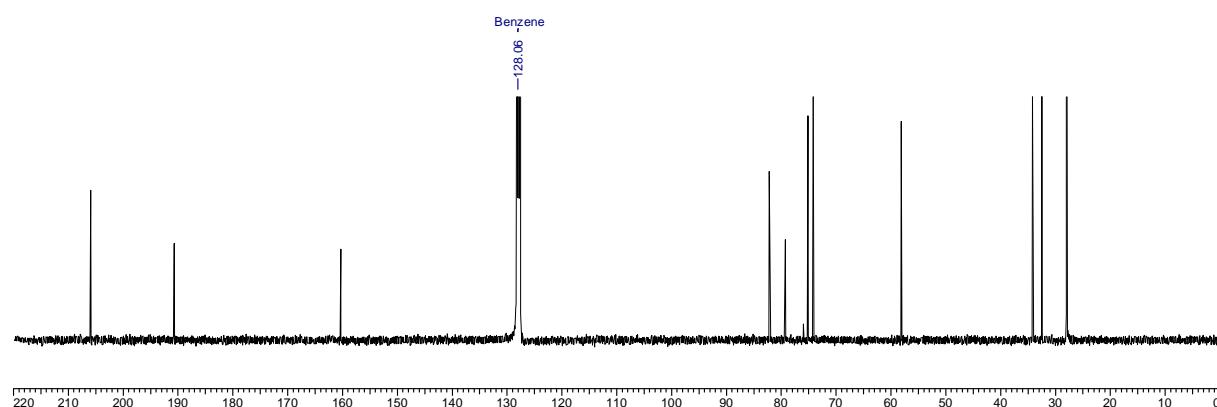
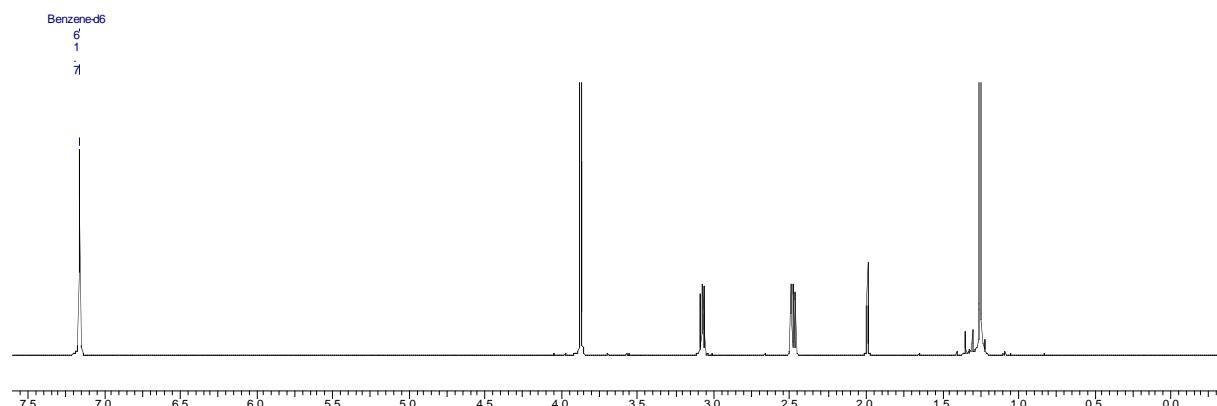
**t-Butyl 2-diazo-3,6-dioxo-7-(prop-2-yn-1-yloxy)heptanoate (15)**



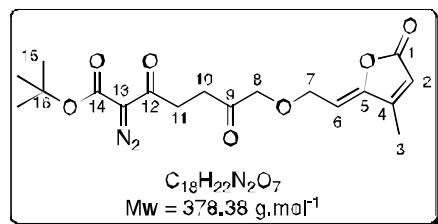
See Full Paper

**$^1\text{H NMR}$**  (benzene- $d^6$ , 400 MHz):  $\delta$  (ppm) 1.25 (9H,  $\text{CH}_3$ , s, H<sub>12</sub>), 1.99 (1H,  $\text{CH}_2$ , t,  $J = 2.3$  Hz, H<sub>1</sub>), 2.46-2.49 (2H,  $\text{CH}_2$ , m, H<sub>6</sub>), 3.06-3.09 (2H,  $\text{CH}_2$ , m, H<sub>7</sub>), 3.87 (2H,  $\text{CH}_2$ , s, H<sub>4</sub>), 3.87 (2H,  $\text{CH}_2$ , d,  $J = 2.3$  Hz, H<sub>3</sub>).

**$^{13}\text{C NMR}$**  (benzene- $d^6$ , 100 MHz):  $\delta$  (ppm) 28.1 (3 x  $\text{CH}_3$ , C<sub>12</sub>), 32.6 ( $\text{CH}_2$ , C<sub>6</sub>), 34.3 ( $\text{CH}_2$ , C<sub>7</sub>), 58.3 ( $\text{CH}_2$ , C<sub>3</sub>), 74.4 ( $\text{CH}_2$ , C<sub>4</sub>), 75.3 (CH, C<sub>1</sub>), 79.4 (C, C<sub>2</sub>), 82.3 (C, C<sub>11</sub>), 160.5 (C, C<sub>10</sub>), 190.8 (C, C<sub>8</sub>), 206.1 (C, C<sub>5</sub>), (C=N<sub>2</sub> was not observed).<sup>4</sup>



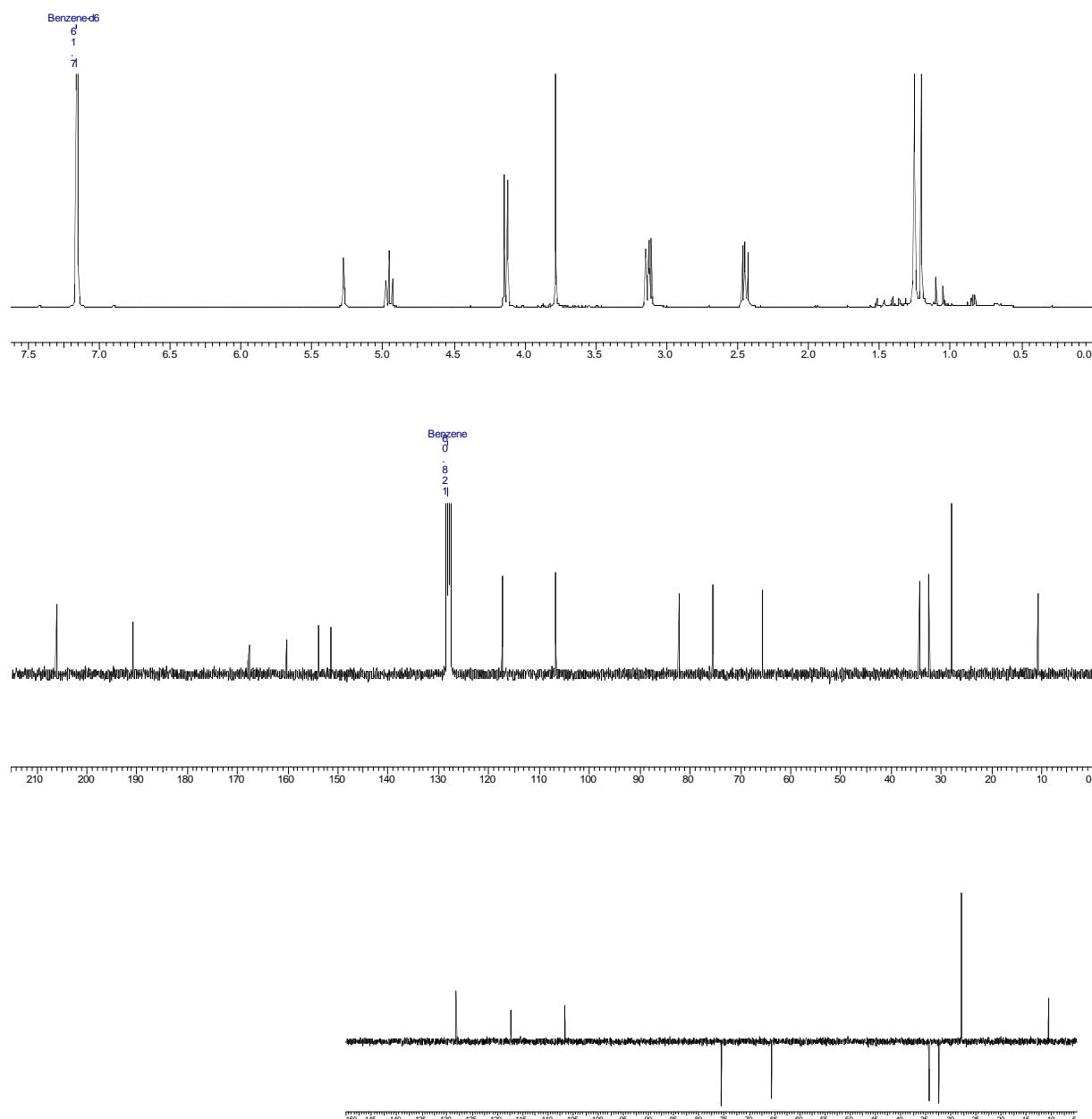
**(Z)-*t*-butyl 2-diazo-7-(2-(3-methyl-5-oxofuran-2(5H)-ylidene)ethoxy)-3,6-dioxoheptanoate (4a)**

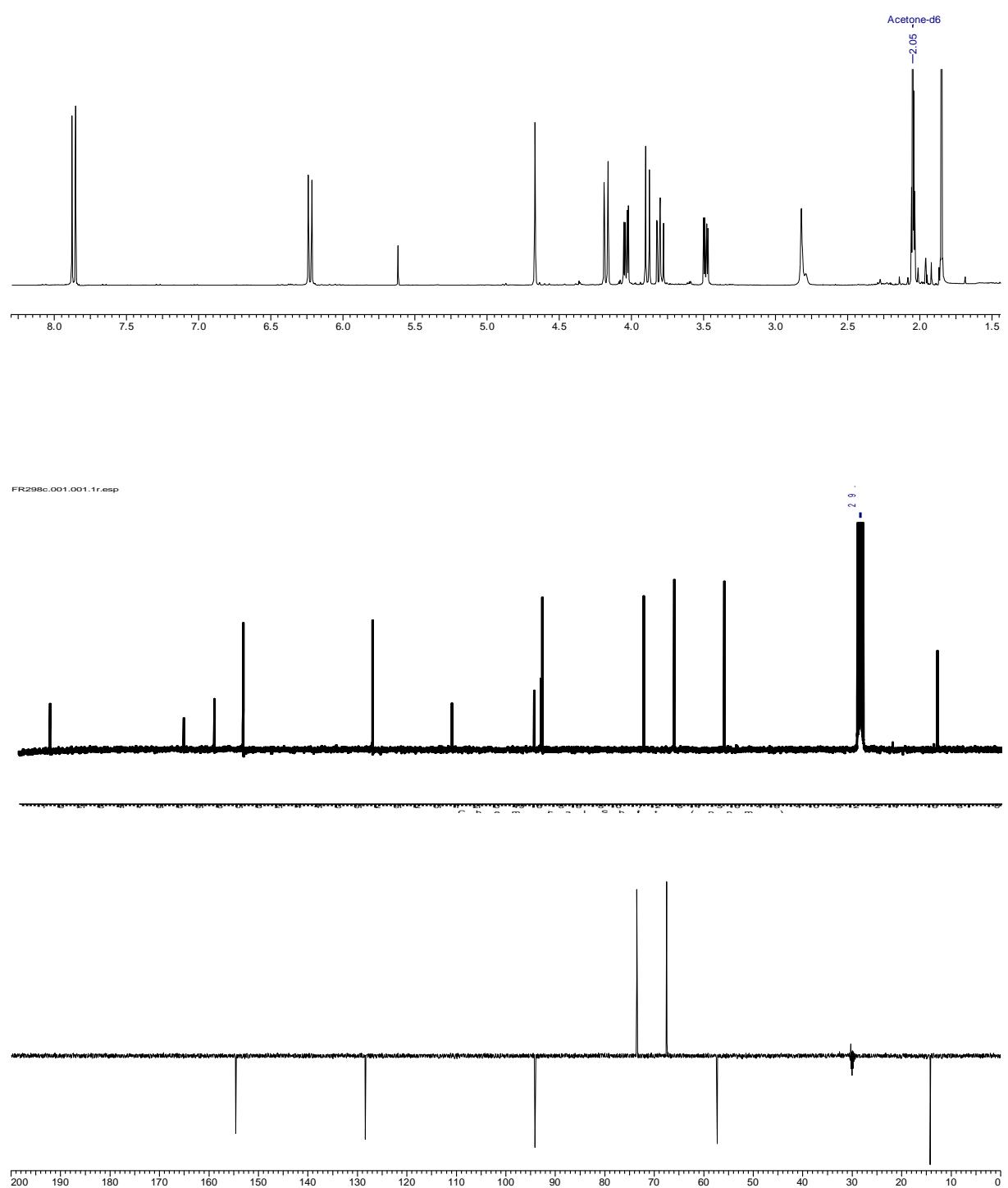


See Full Paper

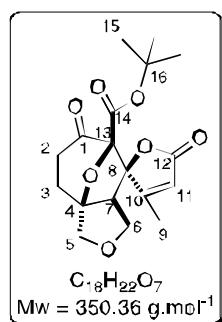
**$^1\text{H NMR}$**  (benzene- $d^6$ , 400 MHz):  $\delta$  (ppm) 1.20 (3H, CH<sub>3</sub>, d,  $J$  = 1.32 Hz, H<sub>3</sub>), 1.25 (9H, CH<sub>3</sub>, s, H<sub>15</sub>), 2.43-2.47 (2H, CH<sub>2</sub>, m, H<sub>10</sub>), 3.11-3.15 (1H, CH<sub>2</sub>, m, H<sub>11</sub>), 3.78 (2H, CH<sub>2</sub>, s, H<sub>8</sub>), 4.13 (1H, CH<sub>2</sub>, d,  $J$  = 6.80 Hz, H<sub>7</sub>), 4.96 (1H, CH, t,  $J$  = 6.80 Hz, H<sub>6</sub>), 5.28 (1H, CH, br s, H<sub>2</sub>).

**$^{13}\text{C NMR}$**  (benzene- $d^6$ , 100 MHz):  $\delta$  (ppm) 10.8 (CH<sub>3</sub>, C<sub>3</sub>), 28.1 (3 x CH<sub>3</sub>, C<sub>15</sub>), 32.5 (CH<sub>2</sub>, C<sub>10</sub>), 34.5 (CH<sub>2</sub>, C<sub>11</sub>), 65.7 (CH<sub>2</sub>, C<sub>7</sub>), 75.7 (CH<sub>2</sub>, C<sub>8</sub>), 82.4 (C, C<sub>16</sub>), 106.8 (CH, C<sub>6</sub>), 117.5 (CH, C<sub>2</sub>), 150.5 (C, C<sub>4</sub> or C<sub>5</sub>), 154.0 (C, C<sub>4</sub> or C<sub>5</sub>), 160.5 (C, C<sub>14</sub>), 167.9 (C, C<sub>1</sub>), 190.9 (C, C<sub>12</sub>), 206.0 (C, C<sub>9</sub>), (C=N<sub>2</sub> was not observed).<sup>4</sup>





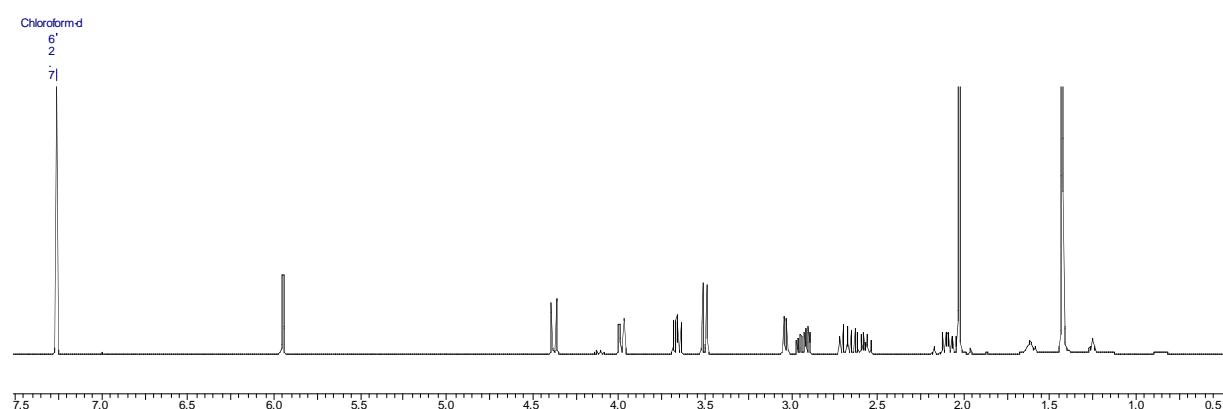
## 9. NMR data of cycloadduct 2c

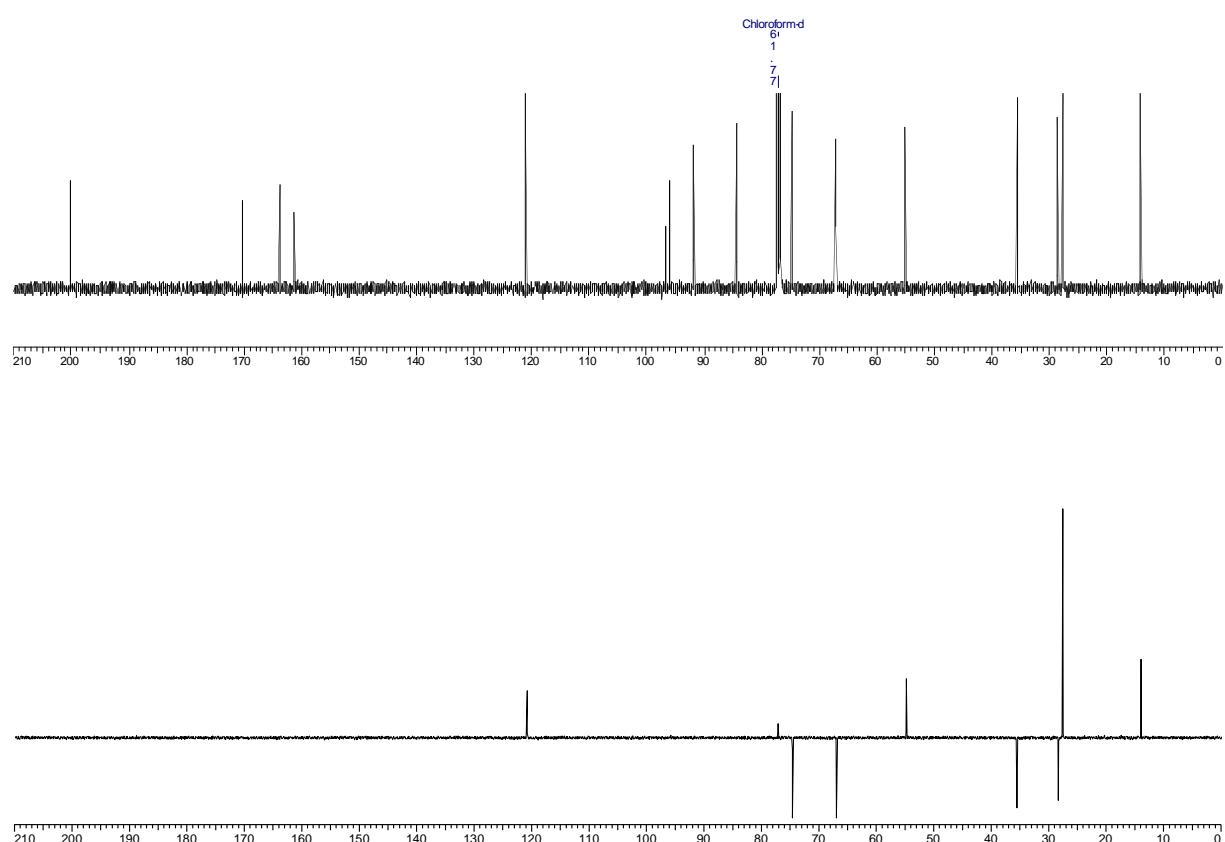


See Full Paper

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 1.44 (9H, 3 x  $\text{CH}_3$ , s, H<sub>15</sub>), 1.20 (3H,  $\text{CH}_3$ , d,  $J$  = 1.5 Hz, H<sub>9</sub>), 2.06-2.12 (1H,  $\text{CH}_2$ , m, H<sub>3a</sub>), 2.54-2.72 (2H, 2 x  $\text{CH}_2$ , m, H<sub>2a</sub> and H<sub>3b</sub>), 2.89-2.97 (1H,  $\text{CH}_2$ , m, H<sub>2b</sub>), 3.03 (1H, CH, dd,  $J$  = 1.8 Hz,  $J$  = 7.3 Hz, H<sub>7</sub>), 3.51 (1H,  $\text{CH}_2$ , d,  $J$  = 10.5 Hz, H<sub>5a</sub>), 3.66 (1H,  $\text{CH}_2$ , dd,  $J$  = 7.3 Hz,  $J$  = 10.0 Hz, H<sub>6a</sub>), 3.98 (1H,  $\text{CH}_2$ , dd,  $J$  = 1.8 Hz,  $J$  = 10.0 Hz, H<sub>6b</sub>), 4.37 (1H,  $\text{CH}_2$ , d,  $J$  = 10.5 Hz, H<sub>5b</sub>), 5.95 (1H, CH, q,  $J$  = 1.5 Hz, H<sub>11</sub>).

**<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm) 14.0 ( $\text{CH}_3$ , C<sub>9</sub>), 27.6 (3 x  $\text{CH}_3$ , C<sub>15</sub>), 28.4 ( $\text{CH}_2$ , C<sub>3</sub>), 35.6 ( $\text{CH}_2$ , C<sub>2</sub>), 54.9 (CH, C<sub>7</sub>), 67.0 ( $\text{CH}_2$ , C<sub>6</sub>), 74.7 ( $\text{CH}_2$ , C<sub>5</sub>), 84.4 (C, C<sub>4</sub> or C<sub>8</sub> or C<sub>13</sub> or C<sub>16</sub>), 91.7 (C, C<sub>4</sub> or C<sub>8</sub> or C<sub>13</sub> or C<sub>16</sub>), 95.8 (C, C<sub>4</sub> or C<sub>8</sub> or C<sub>13</sub> or C<sub>16</sub>), 96.6 (C, C<sub>4</sub> or C<sub>8</sub> or C<sub>13</sub> or C<sub>16</sub>), 120.8 (CH, C<sub>11</sub>), 161.1 (C, C<sub>10</sub>), 163.7 (C, C<sub>14</sub>), 170.1 (C, C<sub>12</sub>), 200.0 (C, C<sub>1</sub>).

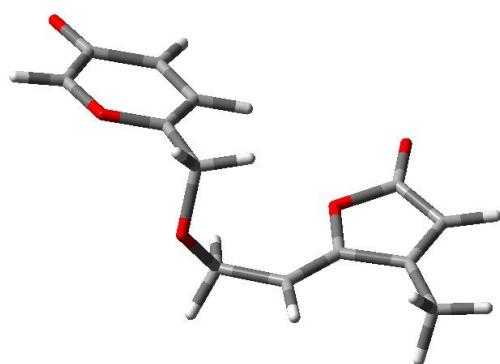




## Theoretical Results

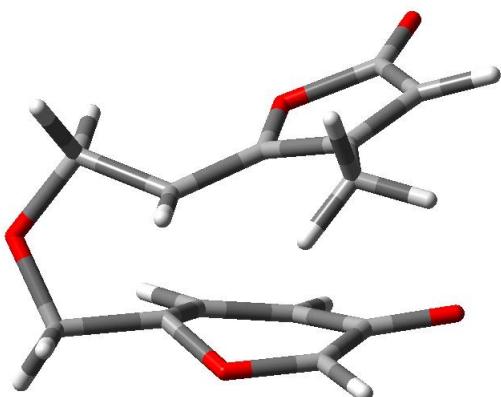
### Theoretical Results for 2a

Cartesian coordinates of optimized structure of reactant – B3LYP/6-311G++(d,p)



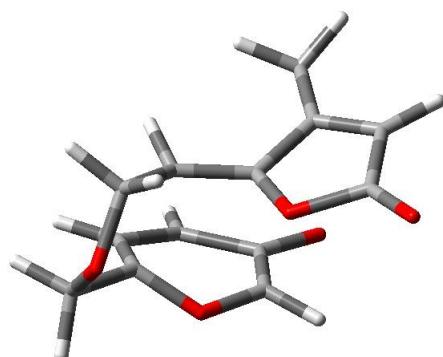
C	3.270181	0	1.869852	0	0.000000	0
C	3.817201	1	0.692115	0	0.326412	0
C	6.463837	1	0.622378	1	-1.259556	0
C	7.572311	1	1.564227	1	-0.911148	1
C	9.876546	1	1.621125	1	-0.490394	1
C	9.921390	1	3.029056	1	-0.182828	1
O	10.976366	1	3.601541	1	0.127833	1
O	8.772805	1	0.977156	1	-0.824071	1
C	8.615196	1	3.647853	1	-0.291001	1
C	7.490847	1	2.923297	1	-0.641974	1
C	1.916038	1	2.170978	1	-0.478066	1
O	3.980860	1	3.053191	1	0.080478	1
C	1.848568	1	3.503185	1	-0.666106	1
H	1.012075	1	4.091986	1	-1.010414	1
C	3.144803	1	4.104218	1	-0.330055	1
O	3.539028	1	5.233158	1	-0.365907	1
H	3.204982	1	-0.195347	1	0.211159	1
C	5.225939	1	0.496943	1	0.810547	1
H	5.677953	1	1.450445	1	1.096721	1
H	5.230138	1	-0.156391	1	1.685488	1
O	6.032335	1	-0.186316	1	-0.158406	1
H	5.626936	1	1.192300	1	-1.676982	1
H	6.807384	1	-0.089335	1	-2.012188	1
C	0.855021	1	1.142748	1	-0.691452	1
H	-0.064249	1	1.601961	1	-1.055514	1
H	1.177927	1	0.393501	1	-1.420163	1
H	0.630862	1	0.614767	1	0.239974	1
H	6.520694	1	3.402080	1	-0.705415	1
H	8.544126	1	4.709698	1	-0.083824	1
H	10.752084	1	0.985845	1	-0.476484	1

Cartesian coordinates of optimized structure of *exo* TS – B3LYP/6-311G++(d,p)



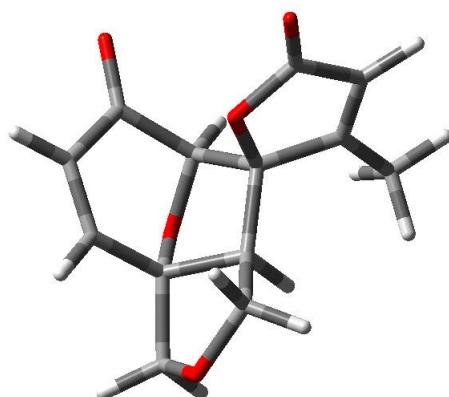
C	-0.485997	0	1.457990	0	0.000000	0
C	0.891678	1	1.315087	0	0.216931	0
C	3.165386	1	2.322155	1	-0.159305	0
H	3.945417	1	2.876459	1	-0.684766	1
C	1.800608	1	2.954120	1	-0.302565	1
C	0.179324	1	4.287985	1	0.663660	1
C	-0.547339	1	4.460332	1	-0.562450	1
O	-1.712671	1	4.882226	1	-0.584128	1
O	1.405607	1	3.758216	1	0.729215	1
C	0.231220	1	4.100929	1	-1.750618	1
C	1.352392	1	3.359533	1	-1.617357	1
C	-1.565063	1	1.708977	1	0.931591	1
H	3.433803	1	2.256173	1	0.902672	1
O	-0.984527	1	1.299686	1	-1.250152	1
C	-2.716016	1	1.729697	1	0.207152	1
H	-3.721049	1	1.904911	1	0.556177	1
C	-2.413383	1	1.465945	1	-1.187984	1
O	-3.071575	1	1.347000	1	-2.178170	1
H	1.147090	1	1.328237	1	1.273557	1
C	1.791383	1	0.422981	1	-0.611054	1
H	1.366107	1	0.236919	1	-1.598570	1
H	1.945057	1	-0.535626	1	-0.106341	1
C	-1.427857	1	1.824872	1	2.418990	1
H	-2.193547	1	2.489359	1	2.822715	1
H	-1.558162	1	0.844914	1	2.889700	1
H	-0.451804	1	2.209150	1	2.718048	1
O	3.085327	1	1.044666	1	-0.779754	1
H	-0.143101	1	4.742211	1	1.590946	1
H	-0.149271	1	4.410246	1	-2.716991	1
H	1.912041	1	2.995671	1	-2.471177	1

Cartesian coordinates of optimized structure of *endo* TS – B3LYP/6-311G++(d,p)



C	1.210873	0	4.406919	0	0.000000	0
C	-0.017351	1	4.039346	0	0.570565	0
C	-2.281458	1	3.371701	1	-0.688874	0
C	-1.513856	1	4.666388	1	-0.713336	1
C	0.128538	1	5.798861	1	-1.852168	1
C	-0.113771	1	7.057041	1	-1.173444	1
O	0.656222	1	8.020362	1	-1.271717	1
O	-0.756475	1	4.802040	1	-1.832563	1
C	-1.339430	1	7.057698	1	-0.375246	1
C	-1.989830	1	5.892857	1	-0.133240	1
C	2.210004	1	5.367552	1	0.467019	1
O	1.809882	1	3.531361	1	-0.870240	1
C	3.381379	1	5.038388	1	-0.128021	1
H	4.340797	1	5.519347	1	-0.018208	1
C	3.175442	1	3.891918	1	-1.001898	1
O	3.901327	1	3.278784	1	-1.731408	1
H	-0.277381	1	4.607508	1	1.455376	1
C	-0.485751	1	2.584772	1	0.559476	1
H	0.350773	1	1.897347	1	0.442927	1
H	-0.995312	1	2.377173	1	1.510282	1
O	-1.371505	1	2.304793	1	-0.525094	1
H	-3.012329	1	3.410731	1	0.133001	1
H	-2.812154	1	3.196018	1	-1.626370	1
C	1.955379	1	6.484459	1	1.423541	1
H	2.877885	1	6.767724	1	1.932471	1
H	1.587299	1	7.363225	1	0.883458	1
H	1.213806	1	6.215122	1	2.179065	1
H	-2.839912	1	5.843445	1	0.539047	1
H	-1.670314	1	8.002165	1	0.041100	1
H	0.842989	1	5.726413	1	-2.661927	1

Cartesian coordinates of optimized structure of *exo* cycloadduct – B3LYP/6-311G++(d,p)



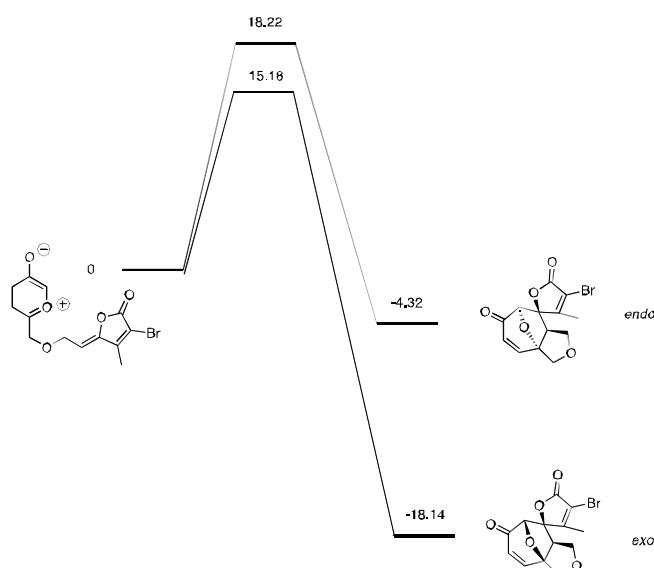
C	-1.210873	0	3.220758	0	0.000000	0
C	0.123605	1	2.520651	0	-0.276277	0
C	2.424288	1	2.779391	1	-0.092130	0
H	3.339486	1	3.341174	1	-0.279792	1
C	1.162755	1	3.621980	1	0.034925	1
C	-0.694108	1	4.387058	1	0.988425	1
C	-0.709967	1	5.734401	1	0.251657	1
O	-1.534355	1	6.590984	1	0.482160	1
O	0.674931	1	4.066229	1	1.303215	1
C	0.356391	1	5.832690	1	-0.765305	1
C	1.185553	1	4.794327	1	-0.926051	1
C	-2.309738	1	2.367213	1	0.600733	1
H	2.560254	1	2.139166	1	0.786425	1
O	-1.794315	1	3.776134	1	-1.184459	1
C	-3.397391	1	2.474115	1	-0.169158	1
H	-4.363838	1	2.013328	1	-0.028138	1
C	-3.106986	1	3.346676	1	-1.319234	1
O	-3.788697	1	3.673041	1	-2.247239	1
H	0.259021	1	1.804766	1	0.540229	1
C	0.704633	1	1.890688	1	-1.525241	1
H	0.453294	1	2.432617	1	-2.439672	1
H	0.461592	1	0.834339	1	-1.649607	1
C	-2.133536	1	1.575129	1	1.853748	1
H	-1.444406	1	0.738655	1	1.696219	1
H	-1.711346	1	2.184299	1	2.658600	1
H	-3.085957	1	1.166001	1	2.192183	1
O	2.144228	1	2.000149	1	-1.280894	1
H	1.914515	1	4.769396	1	-1.729254	1
H	0.385916	1	6.718985	1	-1.388066	1
H	-1.259024	1	4.459198	1	1.915223	1

Cartesian coordinates of optimized structure of *endo* cycloadduct – B3LYP/6-311G++(d,p)

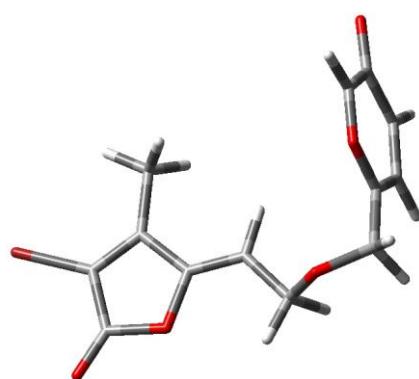


C	-2.034596	0	2.512356	0	0.000000	0
C	-3.106193	1	1.739305	0	0.833049	0
C	-5.044881	1	0.537728	1	-0.008671	0
C	-4.416104	1	1.924385	1	-0.019213	1
C	-2.924742	1	3.205171	1	-1.097945	1
C	-3.612533	1	4.513500	1	-0.668523	1
O	-3.131345	1	5.600567	1	-0.920583	1
O	-3.921995	1	2.221783	1	-1.330861	1
C	-4.869648	1	4.334230	1	0.090771	1
C	-5.239897	1	3.096034	1	0.449652	1
C	-1.066261	1	3.370348	1	0.801889	1
O	-1.189292	1	1.594739	1	-0.711141	1
C	0.176860	1	2.954012	1	0.537393	1
H	1.103467	1	3.334036	1	0.941756	1
C	0.139935	1	1.840012	1	-0.422076	1
O	1.026955	1	1.198896	1	-0.910608	1
H	-3.202768	1	2.191501	1	1.819421	1
C	-2.986415	1	0.202581	1	0.954712	1
H	-2.011043	1	-0.184268	1	0.667649	1
H	-3.210040	1	-0.100324	1	1.986490	1
O	-3.951667	1	-0.360137	1	0.065568	1
H	-5.708501	1	0.433284	1	0.864686	1
H	-5.605882	1	0.326105	1	-0.918936	1
C	-1.466449	1	4.471675	1	1.729999	1
H	-0.634643	1	4.737471	1	2.383699	1
H	-1.757784	1	5.364488	1	1.170731	1
H	-2.318079	1	4.191663	1	2.356595	1
H	-6.098858	1	2.920068	1	1.091217	1
H	-5.414485	1	5.226655	1	0.376721	1
H	-2.353422	1	3.374972	1	-2.008614	1

## Theoretical Results for 2b



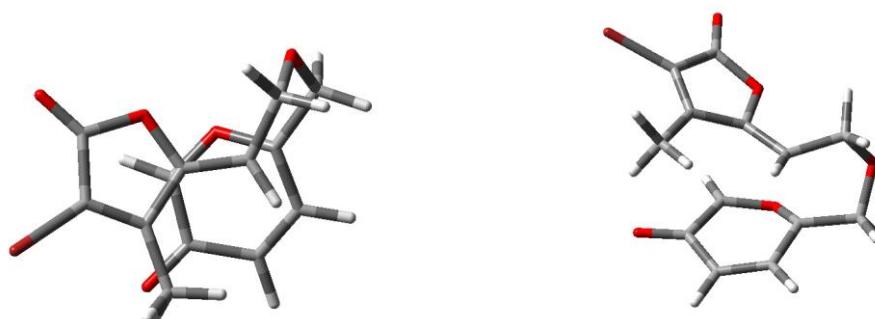
Cartesian coordinates of optimized structure of reactant – B3LYP/6-311G++(d,p)



C	-1.622296	0	0.773710	0	0.000000	0
C	-0.559471	1	0.282510	0	-1.032327	0
C	1.694993	1	-0.495866	1	-0.559593	0
C	0.800720	1	0.721874	1	-0.371388	1
C	-0.738153	1	1.613383	1	0.994243	1
C	-0.428901	1	3.051570	1	0.539008	1
O	-1.098358	1	3.994575	1	0.910015	1
O	0.467030	1	0.865627	1	1.015333	1
C	0.709832	1	3.174366	1	-0.398228	1
C	1.277335	1	2.058308	1	-0.879428	1
C	-2.859058	1	1.432663	1	-0.585736	1
O	-2.125875	1	-0.333648	1	0.769874	1
C	-3.921069	1	0.743879	1	-0.149091	1
C	-3.499279	1	-0.379643	1	0.717974	1
O	-4.143821	1	-1.207751	1	1.288997	1
H	-0.720428	1	0.776967	1	-1.989539	1
C	-0.367723	1	-1.238292	1	-1.238039	1
H	-1.185746	1	-1.841624	1	-0.850458	1
H	-0.238023	1	-1.445863	1	-2.308703	1
O	0.813871	1	-1.604891	1	-0.526786	1
H	2.219650	1	-0.430337	1	-1.526123	1

H	2.423472	1	-0.607927	1	0.243326	1
C	-2.849290	1	2.624468	1	-1.483450	1
H	-3.682155	1	2.575790	1	-2.186998	1
H	-2.958602	1	3.541807	1	-0.897258	1
H	-1.917715	1	2.709025	1	-2.046385	1
H	2.048367	1	2.093265	1	-1.643963	1
H	1.002682	1	4.172328	1	-0.703735	1
H	-1.180418	1	1.631934	1	1.988628	1
Br	-5.736528	1	1.057547	1	-0.524263	1

Cartesian coordinates of optimized structure of *endo* TS – B3LYP/6-311G++(d,p)



C	-1.638935	0	1.555740	0	0.000000	0
C	-2.867508	1	1.416938	0	0.663738	0
C	-5.297771	1	1.137366	1	-0.425143	0
C	-4.322959	1	2.279005	1	-0.534061	1
C	-2.591985	1	3.090905	1	-1.806547	1
C	-2.561297	1	4.380459	1	-1.140812	1
O	-1.643938	1	5.190154	1	-1.315343	1
O	-3.632474	1	2.265604	1	-1.703612	1
C	-3.709154	1	4.606097	1	-0.262773	1
C	-4.535017	1	3.576563	1	0.047898	1
C	-0.460692	1	2.329705	1	0.371289	1
O	-1.271126	1	0.565878	1	-0.884835	1
C	0.580916	1	1.770583	1	-0.295256	1
C	0.113800	1	0.655081	1	-1.120614	1
O	0.670244	1	-0.090029	1	-1.871089	1
H	-2.959971	1	2.034807	1	1.548453	1
C	-3.583575	1	0.068010	1	0.724286	1
H	-2.891451	1	-0.759505	1	0.575813	1
H	-4.055821	1	-0.028407	1	1.711346	1
O	-4.575360	1	-0.068785	1	-0.293219	1
H	-5.952206	1	1.314415	1	0.441594	1
H	-5.914228	1	1.042112	1	-1.320830	1
C	-0.438203	1	3.494964	1	1.298475	1
H	0.485456	1	3.501384	1	1.879816	1
H	-0.478474	1	4.425490	1	0.721091	1
H	-1.286121	1	3.486669	1	1.985195	1

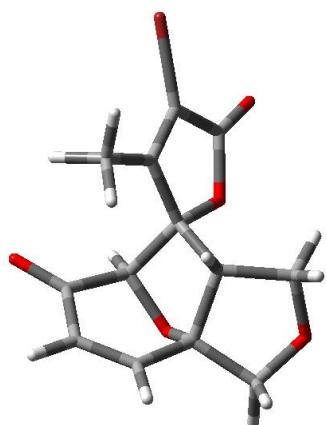
H	-5.332489	1	3.684851	1	0.775479	1
H	-3.840400	1	5.598759	1	0.152087	1
H	-1.962530	1	2.888292	1	-2.663579	1
Br	2.385817	1	2.283978	1	-0.254164	1

Cartesian coordinates of optimized structure of *exo* TS – B3LYP/6-311G++(d,p)



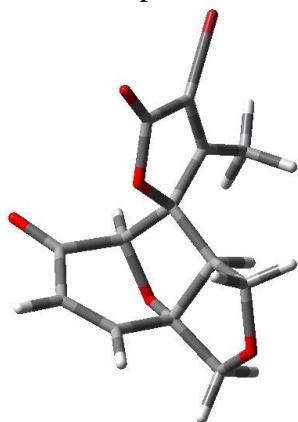
C	-2.204659	0	2.287854	0	0.000000	0
C	-3.512329	1	2.000325	0	-0.414105	0
C	-5.905819	1	2.775786	1	-0.455435	0
H	-6.811023	1	3.266383	1	-0.092682	1
C	-4.651142	1	3.556521	1	-0.143083	1
C	-3.036374	1	5.008218	1	-0.935167	1
C	-2.526818	1	5.305128	1	0.376048	1
O	-1.423606	1	5.840949	1	0.547510	1
O	-4.175053	1	4.345869	1	-1.151980	1
C	-3.446910	1	4.927357	1	1.451475	1
C	-4.458173	1	4.068923	1	1.195839	1
C	-1.014297	1	2.568393	1	-0.763352	1
H	-5.992719	1	2.631792	1	-1.539818	1
O	-1.906320	1	2.233389	1	1.329310	1
C	-0.005114	1	2.694851	1	0.144735	1
C	-0.515237	1	2.487325	1	1.496672	1
O	-0.012185	1	2.470927	1	2.578238	1
H	-3.598414	1	1.939476	1	-1.495743	1
C	-4.441979	1	1.056416	1	0.319368	1
H	-4.163538	1	0.960144	1	1.369910	1
H	-4.418316	1	0.065748	1	-0.144640	1
C	-0.901811	1	2.639881	1	-2.251551	1
H	-0.385671	1	3.555078	1	-2.550130	1
H	-0.309410	1	1.799547	1	-2.626115	1
H	-1.875339	1	2.616328	1	-2.741168	1
O	-5.799748	1	1.544970	1	0.249469	1
H	-2.618655	1	5.452168	1	-1.828905	1
H	-3.254828	1	5.321059	1	2.442619	1
H	-5.109450	1	3.690749	1	1.975216	1
Br	1.806309	1	3.030644	1	-0.196548	1

Cartesian coordinates of optimized structure of *endo* cycloadduct – B3LYP/6-311G++(d,p)



C	-1.056572	0	1.455907	0	0.000000	0
C	0.006253	1	0.964707	0	-1.032327	0
C	2.260717	1	0.186331	1	-0.559593	0
C	1.366444	1	1.404071	1	-0.371388	1
C	-0.172429	1	2.295580	1	0.994243	1
C	0.136823	1	3.733767	1	0.539008	1
O	-0.532634	1	4.676772	1	0.910015	1
O	1.032754	1	1.547824	1	1.015333	1
C	1.275556	1	3.856563	1	-0.398228	1
C	1.843059	1	2.740505	1	-0.879428	1
C	-2.293334	1	2.114860	1	-0.585736	1
O	-1.560151	1	0.348549	1	0.769874	1
C	-3.355345	1	1.426076	1	-0.149091	1
C	-2.933555	1	0.302554	1	0.717974	1
O	-3.578097	1	-0.525554	1	1.288997	1
H	-0.154704	1	1.459164	1	-1.989539	1
C	0.198001	1	-0.556095	1	-1.238039	1
H	-0.620022	1	-1.159427	1	-0.850458	1
H	0.327701	1	-0.763666	1	-2.308703	1
O	1.379595	1	-0.922694	1	-0.526786	1
H	2.785374	1	0.251860	1	-1.526123	1
H	2.989196	1	0.074270	1	0.243326	1
C	-2.283566	1	3.306665	1	-1.483450	1
H	-3.116431	1	3.257987	1	-2.186998	1
H	-2.392878	1	4.224004	1	-0.897258	1
H	-1.351991	1	3.391222	1	-2.046385	1
H	2.614091	1	2.775462	1	-1.643963	1
H	1.568406	1	4.854525	1	-0.703735	1
H	-0.614694	1	2.314131	1	1.988628	1
Br	-5.170804	1	1.739744	1	-0.524263	1

Cartesian coordinates of optimized structure of *exo* cycloadduct – B3LYP/6-311G++(d,p)



C	-2.554077	0	2.903494	0	0.000000	0
C	-1.492999	1	1.831366	0	-0.267577	0
C	0.764310	1	1.354529	1	-0.002792	0
H	1.815730	1	1.608654	1	-0.137661	1
C	-0.177208	1	2.544782	1	0.121504	1
C	-1.741663	1	3.824294	1	1.047085	1
C	-1.307460	1	5.129533	1	0.362384	1
O	-1.836782	1	6.192423	1	0.598671	1
O	-0.556291	1	3.082315	1	1.390778	1
C	-0.221678	1	4.918370	1	-0.615683	1
C	0.249083	1	3.677751	1	-0.791121	1
C	-3.878736	1	2.409942	1	0.540615	1
H	0.657118	1	0.675192	1	0.849896	1
O	-2.889955	1	3.648884	1	-1.180745	1
C	-4.841930	1	2.873861	1	-0.264258	1
C	-4.255822	1	3.657373	1	-1.377769	1
O	-4.772663	1	4.204376	1	-2.303626	1
H	-1.622187	1	1.084234	1	0.521441	1
C	-1.084077	1	1.092089	1	-1.524808	1
H	-1.116815	1	1.714047	1	-2.422152	1
H	-1.636611	1	0.168202	1	-1.702131	1
C	-3.995054	1	1.561461	1	1.760236	1
H	-3.792631	1	0.511536	1	1.519899	1
H	-3.277014	1	1.860819	1	2.528036	1
H	-5.001735	1	1.616060	1	2.175176	1
O	0.306936	1	0.741620	1	-1.233030	1
H	0.967053	1	3.448299	1	-1.571554	1
H	0.108863	1	5.768239	1	-1.201025	1
H	-2.295269	1	4.043607	1	1.957407	1
Br	-6.700301	1	2.625486	1	-0.122150	1