# **Supporting Information**

# CO<sub>2</sub> Assisted Synthesis of Non-symmetric α-Diketones Directly from Aldehydes via C-C Bond Formation

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#### 1. Materials and methods

Unless otherwise stated, commercial reagents were used without purification. All liquid aldehyde starting materials were distilled and dried under nitrogen atmosphere. Reactions were run under a CO<sub>2</sub> atmosphere with exclusion of moisture from reagents using standard techniques for manipulating air-sensitive compounds. <sup>1</sup>H NMR spectra (300.14, 400.13 MHz and 500 MHz) and <sup>13</sup>C NMR spectra (75.58, 100.62 MHz and 125.71 MHz) were recorded using Bruker spectrometers AVANCE III 300, AVANCE III HD 400, AVANCE III 400, AVANCE III HD 500 and Varian spectrometers Mercury VX 300, VNMRS 300 and Inova 500 with CDCl<sub>3</sub>, acetone- $d_6$  and DMSO- $d_6$  as solvents. NMR spectra were calibrated using solvent residual signals (CDCl<sub>3</sub>:  $\delta^{-1}$ H = 7.26,  $\delta^{-13}$ C = 77.16; DMSO-*d*<sub>6</sub>:  $\delta^{-1}$ H = 2.50,  $\delta^{-13}$ C = 39.52; acetone-*d*<sub>6</sub>:  $\delta$  ${}^{1}\text{H} = 2.050$ ,  $\delta {}^{13}\text{C} = 206.26$ ). ESI mass spectra were recorded on BrukerDaltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). GC-MS mass spectra were recorded on ThermoFinnigan spectrometers TRACE (Varian GC Capillary Column; wcot fused silica coated CP-SIL 8CB for amines; 30 m x 0.25 mm x 0.25 µm) and DSQ (Varian FactorFour Capillary Column; VF-5ms 30 m x 0.25 mm x 0.25 µm). LC-ESI-MS spectra were recorded on a Accela HPLC system (Thermo Scientific), equipped with a Synergi 4u MAX-RP 80A column (150 x 2.0 mm; 4 um particle size), a Finnigan Surveyor PDA detector and an Orbitrap LTO XL mass spectrometer (Thermo Scientific). Gas chromatography was performed on an Agilent Technologies chromatograph 7890A GC System (Supelcowax 10 Fused Silica Capillary Column; 30 m x 0.32 mm x 0.25 µm). GC calibrations were carried out with authentic samples and dodecane as an internal standard. Gas-phase GC measurements were conducted by a Shimadzu GC-2014 equipped with a TCD detector and a ShinCarbon ST 80/100 Silco column.

#### 2. General procedure for the synthesis of symmetric α-diketones

A 10 mL two-necked flask containing a stirring bar was charged with 0.5 mmol substrate, 10 mol% of 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide and 0.75 mmol of  $K_2CO_3$ . After purging the flask three times with vacuum and two times with nitrogen the CO<sub>2</sub> atmosphere was incorporated through a CO<sub>2</sub> filled balloon. Afterwards, dry DMSO (2.5 mL) was added. The resulting mixture was stirred for 16–48 h at 55 °C. Then, the resulting mixture underwent an aqueous workup and was extracted three times with excess of ethyl acetate and the combined

organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. In general, products were purified by using silica gel chromatography with ethyl acetate and hexane as solvents and, if needed, 1 V% triethylamine.

# 3. Optimization table

**Table 1:** Optimization of synthesis of furil from furfural.



Entry	Catalyst	Solvent	Base	Base amount [eq]	Yield [%]
1	А	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	86
2	В	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	49
3	С	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	0
4	D	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	20
5	Е	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	1
6	А	DMSO	$Cs_2CO_3$	1.5	50
7	А	DMSO	КОН	1.5	43
8	А	DMSO	LiOH	1.5	18
9	А	DMSO	DBU	1.5	0
10	А	DMSO	DBN	1.5	15
11	А	DMSO	KO <i>t</i> Bu	1.5	26
12	А	DMSO	DMAP	1.5	0
13	А	DMSO	NEt <sub>3</sub>	1.5	1
14	А	DMSO	NaH	1.5	7
15	А	DMSO	Aniline	1.5	0
16	А	DMSO	Pyrimidine	1.5	0
17	А	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.0	57
18	А	DMSO	K <sub>2</sub> CO <sub>3</sub>	0.5	45
19	А	DMSO	-	-	0
20	-	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	0
21	А	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	$1^{[a]}$
22	А	DMSO	K <sub>2</sub> CO <sub>3</sub>	1.5	5 <sup>[b]</sup>

General reaction conditions: 55 °C, 16 h; <sup>[a]</sup>N<sub>2</sub> atmosphere; <sup>[b]</sup>O<sub>2</sub> atmosphere.



Figure 1: Conversion of furfural to furoin and furil under optimized reaction conditions.

#### 4. Procedures for the application of 4,4'-dichlorobenzil

5,6-Bis(4-chlorophenyl)-3-(methylthio)-1,2,4-triazine (14)<sup>[1]</sup>:



1.) 4,4'-Dichlorobenzil (0.5 mmol) was mixed with thiosemicarbazide (1 mmol) in 7 mL of ethanol. The mixture was refluxed for 40 h. The solvent was removed under vacuum and the product was dissolved in dichloromethane, then the organic layer was washed with water and dried with  $Na_2SO_4$ , filtered and the solvent was removed in vacuum to yield the crude product, which was purified by column chromatography to give 48% of 5,6-bis(4-chlorophenyl)-1,2,4-triazine-3-thiol.

2.) To a stirring solution of 5,6-bis(4-chlorophenyl)-1,2,4-triazine-3-thiol (0.09 mmol) in methanol (5 mL), methyl iodide (0.108 mmol), and triethylamine (0.65 mmol) were added and the mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure. Water and dichloromethane were added to the mixture. The organic phase was separated, dried over  $Na_2SO_4$ , filtered and evaporated under reduced pressure and the residue was crystallized from methanol to yield 72% (2 steps) of 5,6-bis(4-chlorophenyl)-3-(methylthio)-1,2,4-triazine.

# 5,5-Bis(4-chlorophenyl)-2-iminoimidazolidin-4-one (15)<sup>[2]</sup>:



1.) Cyclohexylthiourea (0,58 mmol) and 4,4'-dichlorobenzil (0,52 mmol) were heated up to 110 °C in 3 mL DMSO. Then, a solution of KOH (0,8 mmol) in 1.6 mL water was added dropwise and the mixture was stirred for 10 min. After cooling to room temperature, the product was extracted with dichloromethane. The organic phase was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the resulting crude product was used for the next reaction step without further purification.

2.) To a solution of 5,5-Bis(4-chlorophenyl)-2-thioxoimidazolidin-4-one (0,5 mmol), 2.8 mL  $NH_3$  (40% solution in water) and 0.7 mL hydroperoxide (70% solution in water) were added. The reaction mixture was stirred at room temperature overnight. The crude product was extracted

with dichloromethane and the solvent was removed under reduced pressure. After column chromatography, the product was obtained in 55% yield (after two steps).



2,5-Di([1,1'-biphenyl]-3-yl)-3,4-bis(4-chlorophenyl)cyclopenta-2,4-dien-1-one (16)<sup>[3]</sup>:

1.) To a solution of 3-(bromomethyl)-biphenyl (7,12 mmol),  $Fe(CO)_5$  (3,73 mmol) and benzyltriethylammonium chloride (0,237 mmol) in 17 mL dichloromethane was added a solution of KOH (30,8 mmol) in 1 mL water and the mixture was refluxed overnight. After cooling to room temperature, the mixture was quenched with HCl and the organic phase was concentrated *in vacuo*. The crude product was first purified by column chromatography and then dissolved in dichloromethane and reprecipitated by addition of methanol to give 38% of 1,3-di(biphenyl-3-yl)propan-2-on.

2.) To a degassed solution of 4,4'-dichlorobenzil (0,22 mmol) and 1,3-di(biphenyl-3-yl)propan-2on (0,22 mmol) in tert-butanol (2,3 mL) at 80 °C a methanol solution of tetrabutylammonium hydroxide (1.0 M, 0.22 mmol) was added. After stirring at 80 °C for 20 min, the reaction was quenched with water and the reaction mixture was extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to give a purple crude product. Purification by column chromatography gave 69 % of 2,5-di([1,1'biphenyl]-3-yl)-3,4-bis(4-chlorophenyl)cyclopenta-2,4-dien-1-one.

#### 5. Procedures for the application of furil

#### 2,3-Di(furan-2-yl)quinoxaline (17)<sup>[4]</sup>:



A solution of *o*-phenylenediamine (0.25 mmol) and furil (0.25 mmol) in ethanol:water (7:3, 2.5 mL) was stirred at room temperature in the presence of catalytic amount of phenol (20 mol%, 0.05 mmol). The progress of the reaction was monitored by TLC (ethyl acetate:n-hexane 5:95). After completion of the reaction, water (5 mL) was added to the mixture and was allowed to stand at room temperature for 30 min. During this time, crystals of the pure product were formed which were collected by filtration and dried. For further purification, the product was recrystallized from hot ethanol to yield 90% of 2,3-di(furan-2-yl)quinoxaline.

5,6-Di(furan-2-yl)-2,3-dihydropyrazine (18)<sup>[5]</sup>:



0.53 mmol of furil was dissolved in 1 mL of methanol and was made homogeneous by stirring with a magnetic spinning bar. To this 0.53 mmol of ethylene diamine and 0.0212 mmol t-BuOK were added. Stirring was continued until the reaction is completed (checked by TLC, 15 h). Methanol was evaporated under reduced pressure, and the crude product was purified by column chromatography yielding 77% of 5,6-di(furan-2-yl)-2,3-dihydropyrazine.

4,5-Di(furan-2-yl)-2-phenyloxazole (19)<sup>[6]</sup>:



To a solution of Furil (0.275 mmol) in 1.5 mL dry DMA, CuI (0.0826 mmol) and 4 Å molecular sieves (140 mg) were added after it. Finally, benzylamine (0.826 mmol) was added in two portions and stirring was continued for 21 h. After that, the reaction mixture was extracted with EtOAc, dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. Then, the solvent was removed under reduced pressure and the product was purified by silica gel column chromatography to afford 53% of 4,5-di(furan-2-yl)-2-phenyloxazole.

# 1-(4-Bromophenyl)-3-(2,3-di(furan-2-yl)quinoxalin-6-yl)urea (20)<sup>[7]</sup>:



1.) 1 mmol of furil and 1 mmol of 4-nitrobenzene-1,2-diamine were dissolved in 10 mL ethanol and refluxed for 63 h. The solvent was removed under reduced pressure and recrystallization gave 2,3-di(furan-2-yl)-6-nitroquinoxaline in 60% yield.

2.) 0.592 mmol of 2,3-di(furan-2-yl)-6-nitroquinoxaline and 12 mg of Pd/C (5%) were loaded into a two-necked flask. After purging the flask thrice with vacuum and twice with nitrogen, the flask was filled with an H<sub>2</sub> atmosphere *via* a balloon (1 atm pressure) and 3.5 mL ethanol were loaded. The reaction mixture was stirred at room temperature for 16 h. After that, the reaction mixture was dissolved in dichloromethane and filtered through a plug of cotton. The solvents were removed under reduced pressure to yield 92% of pure 2,3-di(furan-2-yl)quinoxalin-6-amine.

3.) 0.527 mmol of 2,3-di(furan-2-yl)quinoxalin-6-amine, 0.79 mmol of 1-bromo-4isocyanatobenzene and 1.58 mmol of *N*-ethyl-*N*-isopropylpropan-2-amine were dissolved in 15 mL dichloromethane and stirred for 48 h at room temperature. The resulting mixture was treated with water. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The product was purified by column chromatography in 58% yield.

4,5-Di(furan-2-yl)-2-phenyl-1H-imidazole (21)<sup>[8]</sup>:



Furil (0.254 mmol), benzaldehyde (0.254 mmol), and ammonium acetate (0.588 mmol) were dissolved in 2 mL 2,2,2-trifluoroethanol and refluxed for 8 h. During that time, a precipitation of light-yellow crystals occurred gradually. The mixture was cooled to room temperature and the precipitate was filtered. The crude product was purified by column chromatography (ethyl acetate, hexane) to yield 4,5-di(furan-2-yl)-2-phenyl-1*H*-imidazole in 82% yield.

# 6. Mechanistic Experiments

Figure 2: Gas GC measurement of the gas phase of a reaction from furfurladehyde to furil. In the middle of the reaction time (8 h) and in the end (16 h) the curves are same. The source of  $N_2$  gas is the front part of the needle of the used gas-tight syringe; 7.5 min:  $N_2$ , 29.5 min: CO<sub>2</sub>.





GC after 16 h.

Trapping of the carboxylated alcohol intermediate with CO<sub>2</sub> and <sup>13</sup>C-labelled CO<sub>2</sub>:



**LC-ESI-HRMS:** m/z calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>6</sub> [M+H<sup>+</sup>]: 265.0707, found: 265.0704; m/z calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>6</sub> [M+Na<sup>+</sup>]: 287.0526, found: 287.0545.



**LC-ESI-HRMS:** m/z calcd. for  $C_{12}^{13}C_1H_{12}O_6$  [M+H<sup>+</sup>]: 266.0740, found: 266.0737; m/z calcd. for  $C_{12}^{13}C_1H_{12}O_6$  [M+Na<sup>+</sup>]: 288.0559, found: 288.0555.

#### 7. General procedure for the synthesis of non-symmetric α-diketones

A 10 mL two-necked flask containing a stirring bar was charged with 0.25 mmol of one substrate and 0.375 mmol of the other substrate: In the case of compound 22, 23, 24, 25, 27, 28, 30, 32 and 33, 0.25 mmol of 2-furfuraldehyde was taken; for compound 26, 4-methyl benzaldehyde, for compound 29, 5-methyl furfuraldehyde and for compound 31 2-pyridine carboxaldehyde were taken in 0.25 mmol amounts. Additionally, 10 mol% 3-ethyl-5-(2-hydroxyethyl)-4methylthiazolium bromide and 0.75 mmol of K<sub>2</sub>CO<sub>3</sub> were loaded into the flask. After purging the flask three times with vacuum and two times with nitrogen, the CO<sub>2</sub> atmosphere was incorporated through a CO<sub>2</sub> filled balloon. Afterwards, dry DMSO (2.5 mL) was added. The resulting mixture was stirred for 36–48 h at 55 °C. Then, the resulting mixture underwent an aqueous workup and was extracted three times with excess of ethyl acetate and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. In general, products were purified by using silica gel chromatography with ethyl acetate and hexane as solvents and, if needed, 1 V% triethylamine.

# 8. Characterization of products



**1,2-Di(furan-2-yl)ethane-1,2-dione (1):** 16 h; **Yield:** 86%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$ 7.78 (dd, J = 1.7, 0.7 Hz, 2H), 7.64 (dd, J = 3.7, 0.7 Hz, 2H), 6.63 (dd, J = 3.7, 1.7 Hz, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  177.00, 149.60, 149.49, 124.78, 113.19; **HRMS:** *m*/*z* calcd. for C<sub>10</sub>H<sub>6</sub>O<sub>4</sub> [M+Na<sup>+</sup>]: 213.0158, found: 213.0159.



**1,2-Di(pyridin-2-yl)ethane-1,2-dione (2):**<sup>[1]</sup> 25 h; Yield: 79%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.63 – 8.54 (m, 2H), 8.25 – 8.16 (m, 2H), 7.98 – 7.86 (m, 2H), 7.53 – 7.42 (m, 2H); <sup>13</sup>C NMR

(75 MHz, CDCl<sub>3</sub>): δ 197.02, 151.94, 149.63, 137.30, 127.98, 122.51; **MS (GC-MS)**: *m/z* 212 (M<sup>+</sup>).



**1,2-Di(furan-3-yl)ethane-1,2-dione (3):** 16 h; **Yield:** 85%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.52 (dd, J = 1.4, 0.8 Hz, 2H), 7.49 (dd, J = 2.0, 1.4 Hz, 2H), 6.92 (dd, J = 1.9, 0.7 Hz, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  184.27, 152.04, 144.13, 123.11, 109.26; **HRMS:** *m*/*z* calcd. for C<sub>10</sub>H<sub>6</sub>O<sub>4</sub> [M+Na<sup>+</sup>]: 213.0158, found: 213.0160.



**1,2-Bis(4-fluorophenyl)ethane-1,2-dione (4):**<sup>[2]</sup> 40 h; Yield: 76%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.14 – 8.02 (m, 2H), 7.33 – 7.21 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  192.18, 167.91, 165.86, 132.82, 129.45, 116.45; MS (GC-MS): *m/z* 246 (M<sup>+</sup>).



**1,2-Bis(4-chlorophenyl)ethane-1,2-dione (5):**<sup>[3]</sup> 20 h; Yield: 83%; <sup>1</sup>H NMR (300 MHz, Acetone- $d_6$ ):  $\delta$  7.88 (d, J = 8.9 Hz, 4H), 7.54 (d, J = 8.9 Hz, 4H); <sup>13</sup>C NMR (126 MHz, Acetone- $d_6$ ):  $\delta$  193.35, 141.79, 132.20, 130.28; MS (GC-MS): m/z 278 (M<sup>+</sup>).



**1,2-Di-p-tolylethane-1,2-dione (6):**<sup>[3]</sup> 40 h; **Yield:** 74%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.08 – 7.73 (m, 4H), 7.40 – 7.21 (m, 4H), 2.43 (s, 6H); <sup>13</sup>**C NMR** (126 MHz, CDCl<sub>3</sub>): δ 194.42, 146.07, 130.76, 130.03, 129.73, 22.10; **MS (GC-MS):** *m/z* 238 (M<sup>+</sup>).



**1,2-Di(thiophen-3-yl)ethane-1,2-dione (7):**<sup>[4]</sup> 16 h; Yield: 71%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ 8.36 (dd, J = 2.9, 1.2 Hz, 2H), 7.70 (dd, J = 5.1, 1.2 Hz, 2H), 7.39 (dd, J = 5.1, 2.9 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  185.90, 137.80, 137.50, 127.71, 127.01; MS (GC-MS): m/z 222 (M<sup>+</sup>).



**1,2-Di(thiophen-2-yl)ethane-1,2-dione (8):** 24 h; **Yield:** 70%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$ 8.07 (dd, J = 3.9, 1.2 Hz, 2H), 7.84 (dd, J = 4.9, 1.2 Hz, 2H), 7.21 (dd, J = 4.9, 3.9 Hz, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  182.55, 138.77, 137.60, 137.39, 128.80; **HRMS:** *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>S<sub>2</sub> [M+Na<sup>+</sup>]: 244.9701, found: 244.9703.



**1,2-Bis(4-methylthiazol-2-yl)ethane-1,2-dione (9):** 16 h; **Yield:** 82%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (d, J = 0.9 Hz, 2H), 2.51 (s, 6H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  184.67, 161.83, 157.12, 123.21, 17.26; HRMS: m/z calcd. for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [M+H<sup>+</sup>]: 253.0100, found: 253.0103.



**1,2-Di(pyridin-3-yl)ethane-1,2-dione (10):** 24 h; **Yield:** 80%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$ 9.22 (d, J = 2.7 Hz, 2H), 8.90 (d, 2H), 8.36 (d, 2H), 7.66 – 7.41 (m, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  <sup>13</sup>**C** NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  189.92, 154.08, 150.48, 136.08, 127.31, 122.93; **HRMS:** m/z calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> [M+H<sup>+</sup>]: 213.0659, found: 213.0658.



**1,2-Bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione (11):** 24 h; Yield: 74%; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.57 (d, J = 3.6 Hz, 2H), 6.65 (d, J = 3.7 Hz, 2H), 5.61 (t, J = 6.0 Hz, 2H), 4.55 (d, J = 5.9 Hz, 4H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  177.63, 164.03, 147.85, 126.02, 110.30, 55.98; HRMS: *m*/*z* calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>6</sub> [M+Na<sup>+</sup>]: 273.0370, found: 273.0363.



**1,2-Di(benzofuran-2-yl)ethane-1,2-dione (12):** 24 h; **Yield:** 79%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.03 (d, J = 1.0 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.70 – 7.61 (m, 2H), 7.61 – 7.53 (m, 2H), 7.43 – 7.31 (m, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  178.79, 156.84, 149.41, 130.15, 127.17, 124.61, 124.41, 121.17, 112.85; **HRMS:** *m/z* calcd. for C<sub>18</sub>H<sub>10</sub>O<sub>4</sub> [M+H<sup>+</sup>]: 291.0652, found: 291.0645.



**1,2-Bis(5-methylfuran-2-yl)ethane-1,2-dione (13):** 24 h; **Yield:** 75%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): $\delta$  7.52 (dd, J = 3.6, 0.6 Hz, 2H), 6.25 (dd, J = 3.6, 0.9 Hz, 2H), 2.54 – 2.33 (s, 6H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  176.84, 161.37, 148.77, 126.85, 110.28, 14.40; **HRMS:** m/z calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>4</sub> [M+Na<sup>+</sup>]: 241.0471, found: 241.0471.



**5,6-Bis(4-chlorophenyl)-3-(methylthio)-1,2,4-triazine (14):**<sup>[1]</sup> <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.93 – 7.87 (m, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.37 (m, 2H), 7.30 – 7.24 (m, 2H), 3.23 (s, 3H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  158.39, 148.08, 144.01, 138.17, 128.92, 128.07, 127.79, 114.55, 112.33, 43.34; **HRMS:** *m*/*z* calcd. for C<sub>16</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>3</sub>S [M-H<sup>-</sup>]: 345.9972, found: 345.9963.



**5,5-Bis(4-chlorophenyl)-2-iminoimidazolidin-4-one (15):**<sup>[2]</sup> <sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ 8.01 (s, 1H), 7.35 (d, J = 8.7 Hz, 4H), 7.21 (d, J = 8.8 Hz, 4H), 4.54 (t, J = 12.4 Hz, 1H), 2.41 – 1.13 (m, 10H); **HRMS:** *m/z* calcd. for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>Cl<sub>2</sub>O [M+H<sup>+</sup>]: 402.1134, found: 402.1121.



**2,5-Di([1,1'-biphenyl]-3-yl)-3,4-bis(4-chlorophenyl)cyclopenta-2,4-dien-1-one** (16):<sup>[3]</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 – 7.26 (m, 18H), 7.25 – 7.17 (m, 4H), 6.99 – 6.92 (m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  199.75, 153.10, 141.17, 140.84, 135.11, 131.49, 130.89, 130.72, 129.22, 128.98, 128.87, 128.84, 127.49, 127.19, 126.76, 125.99; HRMS: *m/z* calcd. for C<sub>41</sub>H<sub>26</sub>Cl<sub>2</sub>O [M+H<sup>+</sup>]: 605.1433, found: 605.1402.



**2,3-Di(furan-2-yl)quinoxaline (17):**<sup>[4]</sup> <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.20 – 8.07 (m, 2H), 7.81 – 7.67 (m, 2H), 7.62 (dd, *J* = 1.8, 0.8 Hz, 2H), 6.66 (dd, *J* = 3.5, 0.8 Hz, 2H), 6.56 (dd, *J* = 3.5, 1.8 Hz, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>): δ 150.96, 144.34, 142.79, 140.77, 130.52, 129.26, 113.11, 112.04; **MS (GC-MS):** *m/z* 262 (M<sup>+</sup>).



**5,6-Di(furan-2-yl)-2,3-dihydropyrazine (18):**<sup>[5]</sup> <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (dd, J = 1.8, 0.8 Hz, 2H), 6.47 (dd, J = 3.5, 0.8 Hz, 2H), 6.39 (dd, J = 3.5, 1.8 Hz, 2H), 3.60 (s, 4H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  150.42, 149.41, 144.49, 114.15, 111.46, 45.04; **MS (GC-MS):** m/z 214 (M<sup>+</sup>).



**4,5-Di(furan-2-yl)-2-phenyloxazole (19):**<sup>[6]</sup> <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.33 (dd, *J* = 1.8, 0.8 Hz, 2H), 7.30 – 7.15 (m, 5H), 7.06 (dd, *J* = 3.5, 0.8 Hz, 2H), 6.41 (dd, *J* = 3.5, 1.8 Hz, 2H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>): δ 158.39, 148.08, 144.01, 138.17, 128.92, 128.74, 128.42, 128.07, 127.79, 114.55, 112.33; **MS (GC-MS):** *m/z* 277 (M<sup>+</sup>).



**1-(4-Bromophenyl)-3-(2,3-di(furan-2-yl)quinoxalin-6-yl)urea (20):**<sup>[7]</sup> <sup>1</sup>**H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  9.21 (dd, J = 7.5, 1.5 Hz, 1H), 8.14 – 7.95 (m, 2H), 7.90 – 7.78 (m, 2H), 7.58 (s, 1H), 7.39 (s, 1H), 7.30 (d, J = 7.5 Hz, 2H), 7.26 – 7.16 (m, 2H), 7.09 (d, J = 7.6 Hz, 2H), 6.91 – 6.75 (m, 2H); <sup>13</sup>**C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  152.97, 149.86, 146.48, 146.39, 146.03, 141.92, 139.19, 138.80, 136.31, 131.15, 128.06, 121.75, 120.30, 118.44, 118.24, 112.58, 112.27; **HRMS:** *m/z* calcd. for C<sub>23</sub>H<sub>15</sub>BrN<sub>4</sub>O<sub>3</sub> [M+H<sup>+</sup>]: 475.0400, found: 475.0376.



**4,5-Di(furan-2-yl)-2-phenyl-1H-imidazole (21):**<sup>[8]</sup> <sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.97 – 7.82 (m, 2H), 7.55 – 7.30 (m, 5H), 7.00 (d, J = 3.3 Hz, 2H), 6.53 (dd, J = 3.4, 1.8 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  194.50, 172.68, 141.64, 129.45, 129.09, 125.66, 120.16, 111.97, 107.94, 107.87; **MS (GC-MS)**: m/z 276 (M<sup>+</sup>).



**1-(Furan-2-yl)-2-(thiophen-2-yl)ethane-1,2-dione** (22):<sup>[9]</sup> 40 h; furan-2-carbaldehyde (0.25 mmol), thiophene-2-carbaldehyde (0.375 mmol); Yield: 72%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.07 (dd, J = 3.9, 1.2 Hz, 1H), 7.84 (dd, J = 4.9, 1.2 Hz, 1H), 7.78 (dd, J = 1.7, 0.7 Hz, 1H), 7.63 (dd, J = 3.7, 0.7 Hz, 1H), 7.21 (dd, J = 4.9, 3.9 Hz, 1H), 6.64 (dd, J = 3.7, 1.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  182.11, 177.55, 149.51, 138.92, 137.50, 137.33, 128.85, 124.73, 113.19, 100.15; MS (GC-MS): m/z 206 (M<sup>+</sup>).



**1-(Furan-2-yl)-2-(thiophen-3-yl)ethane-1,2-dione** (23): 40 h; furan-2-carbaldehyde (0.25 mmol), thiophene-3-carbaldehyde (0.375 mmol); Yield: 70%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.46 (dd, J = 2.9, 1.2 Hz, 1H), 7.77 (dd, J = 1.7, 0.7 Hz, 1H), 7.71 (dd, J = 5.2, 1.2 Hz, 1H), 7.53 (dd, J = 3.7, 0.7 Hz, 1H), 7.38 (dd, J = 5.1, 2.9 Hz, 1H), 6.63 (dd, J = 3.7, 1.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  183.96, 178.92, 149.90, 149.37, 137.83, 137.51, 127.81, 126.90, 124.24, 113.11; HRMS: *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>S [M+Na<sup>+</sup>]: 228.9930, found: 228.9932.



**1-(Furan-2-yl)-2-phenylethane-1,2-dione** (24):<sup>[9]</sup> 48 h; furan-2-carbaldehyde (0.25 mmol), benzaldehyde (0.375 mmol); Yield: 74%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 – 7.97 (m, 2H), 7.76 (dd, J = 1.7, 0.7 Hz, 1H), 7.72 – 7.60 (m, 1H), 7.57 – 7.47 (m, 2H), 7.39 (dd, J = 3.7, 0.7 Hz, 1H), 6.63 (dd, J = 3.6, 1.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  191.68, 180.56, 150.17, 149.31, 135.00, 132.81, 130.35, 129.08, 123.39, 113.11 MS (GC-MS): m/z 200 (M<sup>+</sup>).



**1-(4-Ethoxyphenyl)-2-(furan-2-yl)ethane-1,2-dione** (25): 48 h; furan-2-carbaldehyde (0.25 mmol), 4-ethoxy benzaldehyde (0.375 mmol); **Yield:** 68%; <sup>1</sup>**H** NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 – 7.95 (m, 2H), 7.74 (dd, J = 1.6, 0.7 Hz, 1H), 7.37 (dd, J = 3.7, 0.7 Hz, 1H), 7.01 – 6.86 (m, 2H), 6.61 (dd, J = 3.7, 1.7 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 1.45 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  190.22, 181.09, 164.63, 150.33, 149.06, 132.86, 125.59, 123.19, 114.86, 112.99, 64.18, 14.74; **HRMS:** *m/z* calcd. for C<sub>14</sub>H<sub>12</sub>O<sub>4</sub> [M+H<sup>+</sup>]: 245.0808, found: 245.0806.



**1-(4-Fluorophenyl)-2-(p-tolyl)ethane-1,2-dione** (26): 48 h; 4-methyl benzaldehyde (0.25 mmol), 4-fluoro benzaldehyde (0.375 mmol); purified *via* GPC; **Yield:** 65%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.08 – 7.95 (m, 2H), 7.91 – 7.82 (m, 2H), 7.37 – 7.23 (m, 2H), 7.23 – 7.12 (m, 2H), 2.44 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  193.94, 168.89, 146.51, 132.93, 132.80, 130.64, 130.22, 129.94, 116.64, 116.35, 22.10; **HRMS:** *m/z* calcd. for C<sub>15</sub>H<sub>11</sub>FO<sub>2</sub> [M+H<sup>+</sup>]: 265.0635, found: 265.0636.



**1-(Furan-2-yl)-2-(p-tolyl)ethane-1,2-dione (27):** 36 h; furan-2-carbaldehyde (0.25 mmol), 4methyl benzaldehyde (0.375 mmol); **Yield:** 70%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.98 – 7.88 (m, 2H), 7.75 (dd, J = 1.7, 0.7 Hz, 1H), 7.37 (dd, J = 3.7, 0.7 Hz, 1H), 7.34 – 7.28 (m, 2H), 6.61 (dd, J = 3.7, 1.7 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  191.40, 180.87, 150.23, 149.17, 146.34, 130.46, 130.34, 129.81, 123.23, 113.04, 22.07; **HRMS:** *m/z* calcd. for C<sub>13</sub>H<sub>10</sub>O<sub>3</sub> [M+Na<sup>+</sup>]: 237.0522, found: 237.0525.



**1-(Furan-2-yl)-2-(5-methylfuran-2-yl)ethane-1,2-dione** (28): 36 h; furan-2-carbaldehyde (0.25 mmol), 5-methyl furan-2-carbaldehyde (0.375 mmol); purified *via* GPC; **Yield:** 80%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.76 (dd, J = 1.6, 0.8 Hz, 1H), 7.62 (dd, J = 3.7, 0.8 Hz, 1H), 7.55 (dd, J = 3.6, 0.8 Hz, 1H), 6.62 (dd, J = 3.7, 1.7 Hz, 1H), 6.27 (d, J = 2.7 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>): δ 177.56, 161.66, 149.79, 149.28, 148.62, 127.10, 124.58, 113.12, 110.40, 14.43; **HRMS:** *m/z* calcd. for C<sub>11</sub>H<sub>8</sub>O<sub>4</sub> [M+H<sup>+</sup>]: 205.0501, found: 205.0497.



**1-(5-(Hydroxymethyl)furan-2-yl)-2-(5-methylfuran-2-yl)ethane-1,2-dione** (29): 48 h; 5methyl furan-2-carbaldehyde (0.25 mmol), 5-(hydroxymethyl) furan-2-carbaldehyde (0.375 mmol); **Yield:** 64%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (d, J = 3.6 Hz, 1H), 7.54 (dd, J= 3.6, 0.6 Hz, 1H), 6.53 (d, J = 3.6 Hz, 1H), 6.27 (dd, J = 3.6, 0.9 Hz, 1H), 4.75 (s, 2H), 2.46 (s, 3H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  177.39, 176.27, 161.82, 161.69, 149.33, 148.62, 127.14, 125.86, 110.52, 110.42, 57.97, 14.43; **HRMS:** *m/z* calcd. for C<sub>12</sub>H<sub>10</sub>O<sub>5</sub> [M+H<sup>+</sup>]: 235.0601, found: 235.0601.



**1-(Furan-2-yl)-2-(furan-3-yl)ethane-1,2-dione (30):** 36 h; furan-2-carbaldehyde (0.25 mmol), furan-3-carbaldehyde (0.375 mmol); **Yield:** 76%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (dd, J = 1.4, 0.8 Hz, 1H), 7.82 – 7.73 (m, 1H), 7.72 – 7.64 (m, 1H), 7.49 (dd, J = 1.9, 1.4 Hz, 1H), 6.92 (dd, J = 2.0, 0.8 Hz, 1H), 6.63 (dd, J = 3.7, 1.7 Hz, 1H); <sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>):  $\delta$  184.08, 177.03, 152.03, 149.56, 149.45, 144.27, 124.94, 123.39, 113.17, 109.09; **HRMS:** *m/z* calcd. for C<sub>10</sub>H<sub>6</sub>O<sub>4</sub> [M+Na<sup>+</sup>]: 213.0158, found: 213.0166.



**1-(Pyridin-2-yl)-2-(thiophen-2-yl)ethane-1,2-dione (31):** 48 h; picolinaldehyde (0.25 mmol), thiophene-2-carbaldehyde (0.375 mmol); **Yield:** 62%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.75 – 8.68 (m, 1H), 8.24 – 8.15 (m, 1H), 8.01 – 7.88 (m, 1H), 7.83 (dd, J = 4.9, 1.1 Hz, 1H), 7.70 (dd, J = 3.9, 1.1 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.18 (dd, J = 4.9, 3.9 Hz, 1H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>): δ 192.76, 187.31, 151.59, 150.03, 140.25, 137.38, 136.38, 136.23, 128.78, 128.21, 123.93; **HRMS:** *m/z* calcd. for C<sub>11</sub>H<sub>7</sub>NO<sub>2</sub>S [M+H<sup>+</sup>]: 218.0270, found: 218.0278.



**1-(Benzofuran-2-yl)-2-(furan-2-yl)ethane-1,2-dione** (32): 48 h; furan-2-carbaldehyde (0.25 mmol), benzofuran-2-carbaldehyde (0.375 mmol); **Yield:** 75%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.99 (d, J = 1.0 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.71 – 7.59 (m, 2H), 7.59 – 7.49 (m, 1H), 7.41 – 7.27 (m, 1H), 6.66 (dd, J = 3.7, 1.7 Hz, 1H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  179.14, 176.87, 156.75, 149.71, 149.57, 149.35, 130.01, 127.17, 125.07, 124.54, 124.34, 120.88, 113.33, 112.81; **HRMS:** m/z calcd. for C<sub>14</sub>H<sub>8</sub>O<sub>4</sub> [M+H<sup>+</sup>]: 241.0495, found: 241.0505.



**1-(Furan-2-yl)-2-(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione** (33): 48 h; furan-2carbaldehyde (0.25 mmol), 5-(hydroxymethyl) furan-2-carbaldehyde (0.375 mmol); **Yield:** 71%; <sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (dd, J = 1.7, 0.8 Hz, 1H), 7.63 (dd, J = 3.7, 0.8 Hz, 1H), 7.60 (d, J = 3.7 Hz, 1H), 6.63 (dd, J = 3.7, 1.7 Hz, 1H), 6.55 (d, J = 3.7 Hz, 1H), 4.76 (s, 2H), 2.22 (s, 1H); <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  177.01, 176.81, 162.09, 149.61, 149.53, 149.15, 126.11, 124.85, 113.22, 110.59, 57.96; **HRMS:** *m*/*z* calcd. for C<sub>11</sub>H<sub>8</sub>O<sub>5</sub> [M+H<sup>+</sup>]: 221.0444, found: 221.0445.

#### 9. Computational Details

#### **1. DFT calculations**

All DFT calculations were performed within the Turbomole 7.0<sup>[10]</sup> program package. The molecular structures were optimized using the B3LYP<sup>[11]</sup> functional combined with Grimme's dispersion correction with Becke-Johnson damping (D3(BJ))<sup>[12]</sup>, applying increased convergence criteria (10<sup>-8</sup> H in total energy and 10<sup>-4</sup> au in in the maximum norm of the Cartesian gradient) and a fine integration grid (m4 in Turbomole convention). Ahlrich's revised all electron basis sets were utilized throughout.<sup>[13]</sup> No symmetry restrains were imposed and the optimized structures were defined as minima (no negative eigenvalue) or transition states (one negative eigenvalue) by vibrational analyses at the D3(BJ)-B3LYP/def2-TZVP level of theory. Additionally, the nature of the located transition states was confirmed by displacement of the structures along the vibration mode that represents the reaction coordinate followed by full structure optimizations.

To account for solvent energies, the (free) energies have been evaluated by single point calculations in the optimized structures applying the same method (D3(BJ)-B3LYP) but a slightly larger basis set (def2-TZVPP) and the conductor-like screening model (COSMO)<sup>[14]</sup> ( $\varepsilon$  = 47 for DMSO). We find that the energy loss in the formation of charged species is largely compensated by the COSMO correction. The final energies were calculated by adding the single point energies

with the zero-point vibrational energy (ZPVE) or the free energy (G) that were obtained from the vibrational analyses at the D3(BJ)-B3LYP/def2-TZVP level.

Conformers of the different structures have been fully evaluated and the ones with the lowest single point energies chosen.

### 2. Alternative Pathways

#### a) Activation of DMSO by CO<sub>2</sub>

Nucleophilic attack of DMSO at  $CO_2$  does not occur if not accompanied by a proton shift from one methyl group of DMSO to  $CO_2$ . The transitions state for this reaction has been located but is rather high in energy (50.2 kcal/mol) compared to the energies of the path presented in the text. Scans of the possible reaction of DMSO with the  $CO_2$ –NHC adduct using a simplified model of the NHC catalyst were not productive (see **Figure S1**).



Figure S1. Evaluated pathways for the reaction between DMSO and CO<sub>2</sub>.

# b) DMSO as hydride acceptor

Frequently, DMSO has been suggested to act as a hydride acceptor. To evaluate this possibility, we have calculated the thermodynamic hydricities ( $\Delta G_{H-}$ ) for the theoretical reaction:

$$AH \rightarrow A^+ + H^-$$

as:  $\Delta G_{\text{H-}}(\text{AH}) = G(\text{A}^+) + G(\text{H}^-) - G(\text{AH})$ 

The energy of the hydride ion was obtained from its SCF energy using  $H = E_{SCF} + \frac{5}{2} \cdot RT$  (1.48 kcal·mol<sup>-1</sup> at 298.15 K) while the free energies for the rest were calculated as described above. This approach is rather crude but should be valid for a comparative study.

According to our results (Figure S2) hydride transfer to DMSO is uphill and therefore not expected to take place. On the other hand, for entropic reasons (release of  $CO_2$ ), the carboxylate

ester is indeed a better hydride donor than the hydroxyl compound (lines 1 and 2), possibly explaining the mediating effect of  $CO_2$ . However, the best hydride donor would be the deprotonated hydroxyl compound (line 3). All in all, even when we neglect that DMSO should not act as hydride acceptor, the calculated energies do poorly explain while oxidation only takes place in presence of  $CO_2$ .



Figure S2. Calculated thermodynamic hydricities of possible intermediates in the oxidation step.

### 3. Calculated Structures



**Figure S3.** Structures of the transition states of (a) the direct subtitution of  $HCO_3^-$  by DMSO and (b) the proton shift to the sulfonium ylide

 $CO_2$ 

3

Energy = -188.5873351766

- C 0.0263438 0.0000000 -0.0000019
- O -1.1336183 -0.0000000 0.0000010
- O 1.1862745 -0.0000000 0.0000010

# DMSO

10

Energy = -553.1643118688

- S -2.4490823 0.8662338 0.7785258
- C -4.0711733 0.8491649 -0.0413156
- Н -4.5684120 -0.1046256 0.1385877
- Н -4.6509970 1.6592503 0.3980458
- Н -3.9315131 1.0270240 -1.1078957
- C -1.7127882 -0.4680965 -0.2120012

- Н -0.6774732 -0.5619199 0.1116910
- Н -2.2455428 -1.4022814 -0.0308038
- Н -1.7500047 -0.1898030 -1.2654936
- O -1.7749958 2.1273696 0.3638801

#### $H_2O$

3

Energy = -76.42649010690

0	-0.0123480	0.0000000	0.0000000
Η	0.5724125	-0.7651042	0.0000000
Н	0.5724124	0.7651043	0.0000000

# HCO<sub>3</sub>-

# 5

Energy = -264.4578056723

C -1.7856041 1.1151180 -0.0000032

O -1.0866106 2.1302468 0.0000026

- O -1.0293467 -0.1224951 -0.0000027
- Н -1.7319142 -0.7838111 0.0000194
- O -3.0219248 0.9394914 0.0000012

## DMS

## 9

Energy = -477.9618981180

- S -2.4458118 0.8794646 0.7211457
- C -4.0915630 0.8692625 -0.0363943

- Н -4.5919425 -0.0864035 0.1258530
- Н -4.6711673 1.6567829 0.4439215
- H -4.0325182 1.0764765 -1.1057791
- C -1.6847998 -0.4753365 -0.2104033
- Н -0.6640110 -0.5825795 0.1547148
- Н -2.2187426 -1.4123503 -0.0462765
- Н -1.6564305 -0.2503700 -1.2774413

# C<sub>5</sub>H<sub>3</sub>O-CHOH-CO-C<sub>5</sub>H<sub>3</sub>O





Energy = -686.6472290993

С	-3.5627286	1.4418544	0.0846460
С	-2.3303366	1.6779968	0.6041957
С	-1.9787988	3.0125146	0.2294400
С	-3.0224789	3.4920387	-0.4914487
0	-3.9972178	2.5520470	-0.5933501
Η	-1.7443205	0.9780212	1.1711225
Η	-1.0678443	3.5370115	0.4640894
Η	-3.2170870	4.4294059	-0.9821674
С	-4.5338766	0.3251008	0.1321351
Η	-5.1123468	0.3455763	-0.7985103
С	-3.8919758	-1.0673861	0.2666069
С	-4.8176034	-2.2010200	0.1766515

- C -4.6125426 -3.5454167 0.2860313
- O -6.1485171 -1.9641562 -0.0835770
- C -5.8735492 -4.1717038 0.0860097
- Н -3.6629137 -4.0120833 0.4838894
- C -6.7661607 -3.1688635 -0.1327366
- Н -6.0907304 -5.2262986 0.1002239
- Н -7.8237312 -3.1515500 -0.3312922
- O -2.7117145 -1.2634642 0.4598144
- O -5.4201529 0.5121666 1.2507841
- Н -6.2212278 0.0010812 1.0823372

## C<sub>5</sub>H<sub>3</sub>O-CHOCO<sub>2</sub>H-CO-C<sub>5</sub>H<sub>3</sub>O



2	5
4	-

Energy = -875.2325822909

- C -3.7646459 1.5567458 0.1894496
- C -3.8998356 2.6050503 1.0380098
- C -2.7081161 3.3870625 0.8977008
- C -1.9404192 2.7502075 -0.0192377
- O -2.5746537 1.6300841 -0.4680145
- Н -4.7392212 2.7939574 1.6846394
- Н -2.4626168 4.2991925 1.4149297
- Н -0.9741590 2.9473109 -0.4479545

- C -4.6118833 0.3816054 -0.1280993
- Н -4.5476729 0.1574850 -1.1953161
- C -4.2283392 -0.8851761 0.6693456
- C -4.9666478 -2.1005883 0.3485190
- C -4.9266625 -3.3543366 0.8912482
- O -5.8777542 -2.0758805 -0.6771399
- C -5.8602562 -4.1411667 0.1658915
- Н -4.2967478 -3.6560332 1.7104344
- C -6.4040577 -3.3153012 -0.7716097
- Н -6.0975719 -5.1807473 0.3155399
- Н -7.1407345 -3.4590838 -1.5428944
- O -3.3508392 -0.8757818 1.5028991
- O -5.9798695 0.6637982 0.2159701
- C -6.7843830 1.0156469 -0.7937895
- O -8.0013861 1.2542201 -0.2816925
- Н -8.5663203 1.5123335 -1.0235829
- O -6.4890887 1.1032454 -1.9542838

#### C<sub>5</sub>H<sub>3</sub>O-CH-CO-C<sub>5</sub>H<sub>3</sub>O (Cation)



20

Energy = -610.5530923279

- C -3.5777722 1.3602478 -0.1066753
- C -2.2516178 1.5431222 0.3808411

- C -1.9062948 2.8544977 0.1400058
- C -3.0149119 3.4366465 -0.4814903
- O -4.0038711 2.5870007 -0.6374956
- H -1.6764341 0.7580150 0.8438136
- Н -0.9801024 3.3533469 0.3722629
- Н -3.1812778 4.4418432 -0.8420070
- C -4.4281272 0.3143304 -0.1494409
- Н -5.4014624 0.4764878 -0.5941544
- C -4.0571280 -1.0284822 0.3928608
- C -5.0862476 -2.0284488 0.2549006
- C -6.3672495 -2.0236071 -0.2781399
- O -4.8060082 -3.2742573 0.7300755
- C -6.8774453 -3.3238571 -0.1153228
- Н -6.8801469 -1.1917384 -0.7306012
- C -5.8847983 -4.0406040 0.5032522
- Н -7.8447848 -3.6927809 -0.4104171
- Н -5.8155939 -5.0657231 0.8275217
- O -2.9660116 -1.2201759 0.9004654

#### Transition State: C<sub>5</sub>H<sub>3</sub>O-CHOCO<sub>2</sub>H-CO-C<sub>5</sub>H<sub>3</sub>O + DMSO (direct path)



Energy = -1428.357579410

35

- C -0.3081428 -1.1121805 1.1560740
- C -1.5795172 -1.5386227 1.4167308
- C -0.2144711 -2.2545751 3.0218971

2.6332307

-1.5182136 -2.2744295

С

- 0 0.5364922 -1.5652895 2.1341174
- Н -2.4449904 -1.3190010 0.8179672
- Н -2.3354124 -2.7398985 3.1575855
- Н 0.3100487 -2.6594661 3.8696321
- C 0.2972494 -0.3136068 0.1180327
- H 1.2211865 0.1833528 0.4023081
- C -0.6271195 0.4008210 -0.8476709
- C -0.2549546 1.7120349 -1.3011982
- C 0.7759168 2.5634945 -0.9914691
- O -1.0352360 2.2687488 -2.2892960
- C 0.6208813 3.6964745 -1.8271772
- Н 1.5166219 2.3889253 -0.2210569
- C -0.4907031 3.4632542 -2.5841956
- Н 1.2410666 4.5763576 -1.8547206
- Н -0.9950768 4.0371640 -3.3431008
- O -1.5792819 -0.2201462 -1.3134630
- O -0.1537882 1.5080918 1.8043190
- C 0.9977417 1.7825272 2.1958302
- O 1.0695933 2.3920353 3.4387124
- H 2.0132024 2.5394821 3.5847445
- O 2.0892597 1.5786823 1.6084418
- S 0.0474646 -2.5536732 -1.4859563

- C -0.1490329 -2.2135733 -3.2385859
- Н -0.6532220 -3.0672727 -3.6923114
- Н -0.7779669 -1.3286221 -3.3038243
- Н 0.8280575 -2.0449447 -3.6881718
- C 1.2050192 -3.9261115 -1.5592826
- Н 1.4665511 -4.1657749 -0.5303943
- Н 0.7027519 -4.7739100 -2.0254560
- Н 2.0903900 -3.6320442 -2.1203411
- O 0.9982408 -1.4142629 -0.9915672

### C<sub>5</sub>H<sub>3</sub>O-CHOS(CH<sub>3</sub>)<sub>2</sub>-CO-C<sub>5</sub>H<sub>3</sub>O (Cation)



30

Energy = -1163.774049383

- C 0.4765297 -1.1596670 0.2234005
- C -0.8093322 -1.4746190 0.5520373
- C -0.7361077 -2.3618565 1.6658390
- C 0.5860408 -2.5210363 1.9359672
- O 1.3404783 -1.7994390 1.0682122
- Н -1.6991929 -1.1098556 0.0659945
- H -1.5574430 -2.8100801 2.1983431
- Н 1.1271415 -3.0804478 2.6792383
- C 1.0725539 -0.3299380 -0.8332080

- Н 2.0091603 0.1121704 -0.4995553
- C 0.0919074 0.7346700 -1.3402062
- C -0.0427383 1.9325590 -0.5684347
- C -0.8620174 3.0280030 -0.6894017
- O 0.7665628 2.0851665 0.5326477
- C -0.5429341 3.8898185 0.3841526
- Н -1.5983200 3.1772428 -1.4612137
- C 0.4487825 3.2685899 1.0904136
- Н -0.9831544 4.8460841 0.6098269
- Н 1.0023232 3.5413775 1.9727963
- O -0.5451692 0.5024450 -2.3583327
- S 0.3955503 -1.9946869 -2.7578039
- C 0.5863879 -1.4376909 -4.4476154
- Н 0.0288754 -2.1334995 -5.0758116
- Н 0.1509809 -0.4440465 -4.4987368
- Н 1.6426812 -1.4329924 -4.7101819
- C 1.2528331 -3.5679672 -2.8247498
- Н 1.2768061 -3.9592647 -1.8093462
- Н 0.6712181 -4.2325531 -3.4645963
- Н 2.2602862 -3.4293091 -3.2129682
- O 1.5242139 -1.1332693 -1.9978640

# C<sub>5</sub>H<sub>3</sub>O-CHOSC<sub>2</sub>H<sub>5</sub>-CO-C<sub>5</sub>H<sub>3</sub>O



29

Energy = -1163.350717425

С	-3.8419755	1.5920023	0.1259946
С	-4.0492241	2.7864124	0.7330911
С	-2.8152480	3.5084553	0.6341317
С	-1.9524125	2.6974805	-0.0244566
0	-2.5648700	1.5230296	-0.3487438
Η	-4.9661575	3.1035019	1.1980936
Η	-2.6046309	4.4966631	1.0074055
Η	-0.9258950	2.7941051	-0.3303145
С	-4.7098829	0.4057574	-0.1073578
Η	-4.5511755	0.0549462	-1.1445705
С	-4.3902146	-0.7747585	0.8257611
С	-5.0436003	-2.0503646	0.5168554
С	-5.0479843	-3.2350197	1.1951985
0	-5.7747527	-2.1839213	-0.6373907
С	-5.8229352	-4.1459033	0.4255300
Η	-4.5472263	-3.4132567	2.1312073
С	-6.2339076	-3.4566622	-0.6733333
Η	-6.0429008	-5.1752623	0.6529089
Н	-6.8241935	-3.7241878	-1.5326869

- O -3.6578968 -0.6751703 1.7850428
- O -6.0631582 0.6909818 0.1079180
- S -6.9159631 1.2901590 -1.4300001
- C -6.3831223 0.6178916 -2.7969452
- Н -6.5056486 -0.4337226 -3.0135469
- Н -5.7053668 1.2141985 -3.3884605
- C -8.3451541 0.3094636 -0.9472454
- Н -8.5671127 0.5363291 0.0919932
- Н -9.1742499 0.5876482 -1.5941750
- Н -8.0946511 -0.7434633 -1.0526266

# Transition State: C5H3O-CHOSC2H5-CO-C5H3O



29

Energy = -1163.341237827

- C 0.9169516 1.6934720 0.0482809
- C 1.0129424 2.7481824 0.8975257
- C 1.7096063 3.7800517 0.1889107
- C 1.9836053 3.2770650 -1.0400099
- O 1.5001105 2.0074828 -1.1466638
- Н 0.6440262 2.7709989 1.9082973
- Н 1.9762756 4.7583938 0.5524920
- Н 2.4882147 3.6653534 -1.9069545
- C 0.2901135 0.3443538 0.1778475
- Н -0.2856453 0.2061966 -0.8743819
- C 1.2968554 -0.8165417 0.1914411
- C 0.7555880 -2.1768259 0.1061639
- C 1.3719944 -3.3858078 0.2560592
- O -0.5676376 -2.3762010 -0.1962344
- C 0.3794895 -4.3821083 0.0430560
- Н 2.4132923 -3.5235705 0.4913784
- C -0.7735921 -3.7126472 -0.2290786
- Н 0.5025826 -5.4510312 0.0868314
- Н -1.7762432 -4.0323175 -0.4545464
- O 2.4905488 -0.6360986 0.3037305
- O -0.6088533 0.2319914 1.1438576
- S -2.5434424 0.2346782 0.0384649
- C -1.8806793 0.3092170 -1.4646289
- Н -1.9078424 -0.5968044 -2.0513297
- Н -1.7259782 1.2536261 -1.9657994
- C -2.7675713 1.9604370 0.5184631
- Н -1.9379664 2.5492742 0.1364448
- Н -3.7227871 2.3232157 0.1423128
- Н -2.7491606 1.9819047 1.6053582

## C<sub>5</sub>H<sub>3</sub>O-CO-CO-C<sub>5</sub>H<sub>3</sub>O



20

Energy = -685.4509262878

С	-3.7180294	-0.7257678	-0.1985809	
С	-2.3898780	-0.7842034	0.1436874	
С	-1.9675661	0.5512833	0.3655576	
С	-3.0631418	1.3322656	0.1434718	
0	-4.1280759	0.5829932	-0.1958401	
Η	-1.8026093	-1.6824468	0.2052912	
Η	-0.9850659	0.8899494	0.6473505	
Η	-3.2280838	2.3952703	0.1872927	
С	-4.7309278	-1.7188036	-0.5151174	
С	-4.2666769	-3.1910991	-0.5156883	
С	-5.2791751	-4.1841592	-0.1979931	
С	-6.6074777	-4.1257213	0.1436438	
0	-4.8691348	-5.4929447	-0.1950771	
С	-7.0299513	-5.4611904	0.3651832	
Η	-7.1947641	-3.2274902	0.2047811	
С	-5.9342716	-6.2421931	0.1437244	
Η	-8.0126489	-5.7998200	0.6462986	
Η	-5.7693401	-7.3051879	0.1878246	
0	-5.8815936	-1.4289744	-0.7822435	
0	-3.1164793	-3.4808052	-0.7850502	

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(2)



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in Acetone- $d_6$ .







<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.





<sup>13</sup>C NMR spectrum in DMSO-d<sub>6</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.





<sup>13</sup>C spectrum in CDCl<sub>3</sub>.







<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.







<sup>13</sup>C spectrum in Benzene- $d_6$ .

(20)



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



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<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



<sup>13</sup>C spectrum in CDCl<sub>3</sub>.





<sup>13</sup>C spectrum in CDCl<sub>3</sub>.



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