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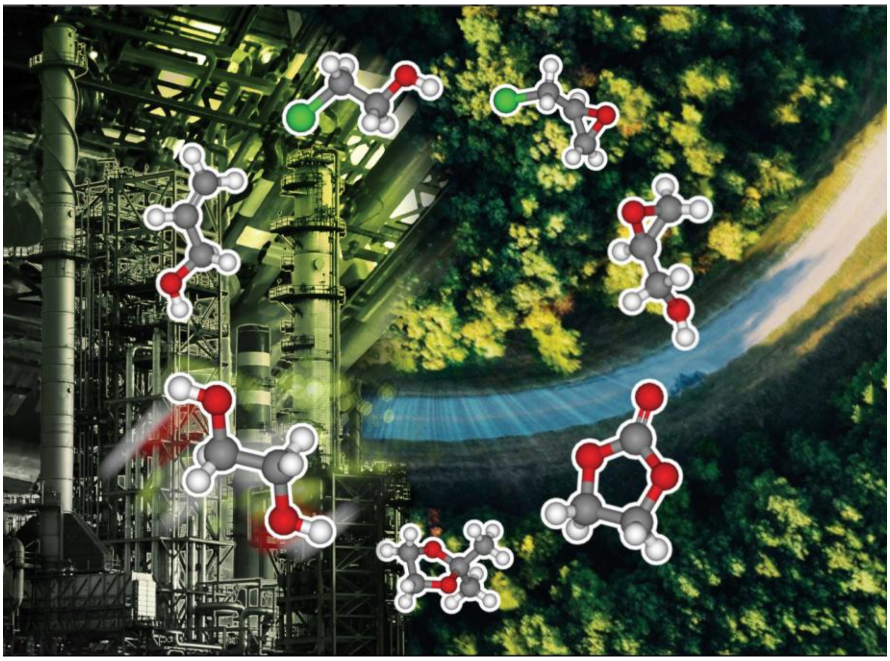
Thesis submitted in fulfillment of the requirements
for the degree of PhD of Sciences

NEW PERSPECTIVES TOWARD THE VALORIZATION OF BIO-BASED MOLECULES

SUPPORTING INFORMATIONS



FACULTY OF SCIENCES
Department of Chemistry
Academic Year 2024-2025

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1 PERSPECTIVES FOR THE UPGRADING OF BIO-BASED VICINAL DIOLS WITHIN THE DEVELOPING EUROPEAN BIOECONOMY

1.1 SELECTED PROCESSES FOR THE REACTION OF WILLIMASON'S OR DEHYDRATIVE EPOXIDATION

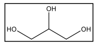
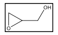
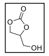
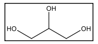
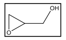
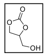
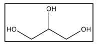
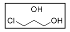
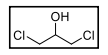
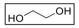
Entry	Polyol	Polyol (mol)	MM (g/mol) oximes	Mass (g)	Reagents & solvents	Solvent Density (g/mL)	Reagents & solvents n (mol)	Reagents & solvents equivalents	MM (g/mol) Reagents & solvents	Mass (g) Reagents & solvents	Derivatives	Product(s) yield (%)	**Mol of product(s)**	MM (g/mol) product(s)	Mass (g) product(s)	E-Factor	Atom economy	Ref.
1		0,25	92,08	23,02	Urea NH_4OAc ZnO		0,25 0,002 0,0005	1 0,008 0,002	60,06 77,08 81,38	15,02 0,15 0,04	 	58 5	0,15 0,01	74,08 118,09	10,74 1,48	2,13	48,69	119
2		0,022	92,08	2,00	Dimethyl carbonate [DABCO][DMC]		0,07 0,001	3,00 0,060	90,08 202,25	5,87 0,264	 	83 16	0,0180 0,0035	74,08 118,09	1,34 0,41	3,66	40,67	123
3		0,00011494	92,08	0,01	HCl 35% NaOH 4M Acetic acid (10 mol%)		0,0007 0,0010 0,0000	6,00 9 0,1	36,45 40,00 60,05	0,03 0,04 0,00	 	65 14	7,471E-05 1,609E-05	110,53 128,99	0,008 0,002	6,53	65,59	117
4		0,0027	62,07	0,17	Water Cs/SiO_2		1	1,00	18,015	18,02 0,10	 	14 17	0,1400 0,0005	44,05 44,05	6,17 0,02	1,95	70,97	118

Figure S1.1 Details of the sustainable assessment of selected processes toward the formation of epoxides.

1.2 SELECTED PROCESSES FOR THE FORMATION OF DHLORINATED DERIVATIVES AND EPICHLOROHYDRIN

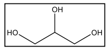
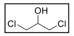
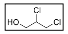
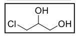
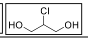
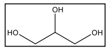
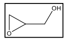
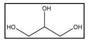
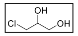
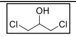
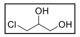
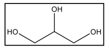
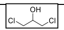
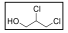
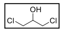
Entry	Polyol	Polyol (mol)	MM (g/mol) Polyol	Mass (g)	Reagents & solvents	Solvent Density (g/mL)	Reagents & solvents n (mol)	Reagents & solvents equivalents	MM (g/mol) Reagents & solvents	Mass (g) Reagents & solvents	derivatives	Product(s) yield (%)	**Mol of product(s)**	MM (g/mol) product(s)	Mass (g) product(s)	E-Factor	Atom economy	Ref.
1		0,54	92,08	50,00	HCl (100 mL/min) 14 h Adipic acid	1,528	3,52 0,0375	6,48 0,06906	36,45 146,14	128,35 5,48	   	88,96 1 3,7 2,7	0,48 0,01 0,00 0,00	128,98 128,98 110,54 110,54	62,30 0,70 0,00 0,00	1,92	78,18	133
2		0,00011494	92,08	0,01	HCl 35% (68µl/min) NaOH 4M Pimelic acid MTBE (320 µl/min)	 0,74	0,0007 0,0010 0,0000 0,0027	6,00 9 0,1 23,37	36,45 40,00 160,17 88,15	0,03 0,04 0,00 0,24	 	44 30	5,05752E-05 3,44831E-05	92,52 70,09	0,00 0,002	43,49	54,90	117
3	 	0,52 0,48	92,08 110,54 100,94 molar mass	47,88 53,0592 0,76 Sample mass (g)	Acetic acid TMSCl		0,05	0,05 2,7	60,05 108,64	0,03 2,40	 	96 4	0,4992 0,0208	128,98 110,54	64,39 2,30 Product mass (g) 0,89	2,59	61,54	135
4		1,63	92,08	150,00	Acyl chloride (2 mL/min)	1,104	2,25	1,38	78,49	176,64	  	92 4 4	1,50 0,07 0,07	128,98 128,98 110,54	193,30 8,40 7,20	0,56	51,79	137

Figure S1.2 Details of the sustainable assessment of selected processes of chlorination and intramolecular cyclization toward epichlorohydrin.

1.3 SELECTED PROCESSES FOR THE REACTION OF CARBONATION

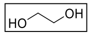
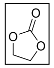
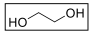
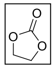
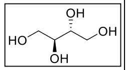
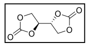
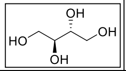
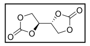
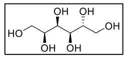
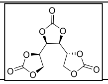
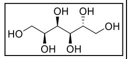
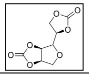
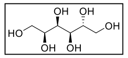
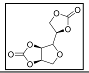
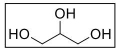
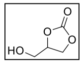
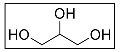
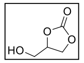
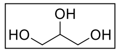
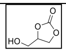
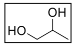
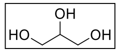
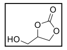
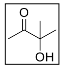
Entry	Polyol	Polyol (mol)	MM (g/mol) polyol	Mass (g)	Reagents & solvents	Solvent Density (g/mL)	Reagents & solvents n (mol)	Reagents & solvents equivalents	MM (g/mol) Reagents & solvents	Mass (g) Reagents & solvents	**1** derivatives	Product(s) yield (%)	**Mol of product(s)**	MM (g/mol) product(s)	Mass (g) product(s)	E-Factor	Atom economy	Ref.
1		0,00	62,07	0,12	DMC KF/Ca-Mg-Al HT		0,01 0,0001	3,00 0,05	90,08	0,54 0,00		98	0,00 0,01	88,06 32,04	0,17	2,85	57,88	192
2		1,00	62,07	62,07	DMC Barton's base		3,00 0,01	3,00 0,01	90,08 171,29	270,24 1,71		78	0,78 1,56	88,06 32,04	68,69	3,86	57,88	185
3		0,21	122,12	25,00	Diphenyl carbonate Zn(Oac)2.2H2O DMSO (45 ml)		0,43 0,0021 1,01	2,10 0,01 2,77	214,22 219,51 78,13	92,10 0,45 45,45		85	0,1785	174,11	31,08	4,24 2,78	31,62	84
4		0,02	122,12	2,00	DMC (41 mL) TBD	1,07	0,49 0,0008	29,70 0,05	90,08 139,20	43,87 0,11		90	0,01476	174,11	2,57	16,89	57,60	161
5		0,27	182,17	50,00	K_2CO_3 Diphenyl carbonate DMSO (70 mL)		0,00274 0,904 1,01	0,01 3,3 3,30	138,21 214,22 78,13	0,15 193,69 70,7		70	0,1918	260,15	49,90	5,30 3,89	31,54	164
6		0,66	182,17	120,02	MeOH DMC K_2CO_3	1,07	4,73 6,96 0,15	7,18 10 0,22	32,04 90,08 138,21	151,55 627,46 20,4034		40	0,2636	216,15	56,98	15,14 12,48	47,78	194
7		1,00	182,17	182,17	DMC TBD		6,96	3,35 0,05	90,08 139,20	4828,29 6,96		50	0,5	216,15	108,08	45,43	47,78	162
8		0,01	92,08	1,15	CO_2 (180 °C, 150 bar, 0.05 mL) 2-cyanopyridine		0,20 0,04	15,94 3,00	44,01 104,11	701,50 3,90		18,7	0,0023	118,09	0,28	2560,88 17,33 sans CO2	86,77	151
8		0,001	92,08	0,05	CO_2 (180 °C, 50 bar, 0.01 mL) Calcium carbide Zn(OTf)2 1,10-phenanthroline 1-methyl-2-pyrrolidinone (3 mL)	 1,03	0,0133 0,0025 0,0000 0,0001 0,0312	26,54 5,00 0,05 0,15 62,34	44,01 64,10 363,53 180,21 99,13	1168,15 0,16 0,01 0,01 3,09		92	0,0005	118,09	0,05	21564,55 60,10 21507,67	86,77	170
9		0,01	92,08	0,46	CO_2 (115 °C, 20 bar, 0.01 mL) Propylene oxide Amb-OH-910-I Mesitylene		0,01 0,02 0,0015	1,24 4 0,3	44,01 58,08 120,19	54,55 1,16 0,02 0,18	 	69 67	0,0035 0,0034	118,09 76,09	0,41 0,25	84,12 1,76 83,85	60,82	181
10		0,001	92,08	0,09	CO_2 (120 °C, 20 bar, 0.05 mL) Propargylic alcohol DBU DMF (2 mL)	 0,944	0,03 0,00 0,00 0,03	30,59 1,5 0,40 25,83	44,01 56,06 152,24 73,09	1346,43 0,13 0,06 1,89	 	97 63	0,0010 0,0006	118,09 102,13	0,11 0,06	11772,26 11,11 7527,16	61,46	22

Figure S1.3 Details of the sustainable assessment of selected processes of carbonatation.

1.4 SELECTED PROCESSES FOR THE REACTION OF KETALIZATION

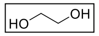
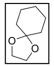
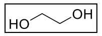
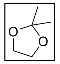
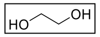
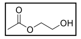
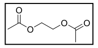
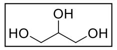
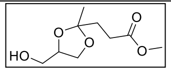
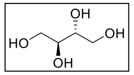
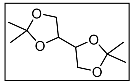
Entry	Polyol	Polyol (mol)	MM (g/mol) polyol	Mass (g)	Reagents & solvents	Solvent Density (g/mL)	Reagents & solvents n (mol)	Reagents & solvents equivalents	MM (g/mol) Reagents & solvents	Mass (g) Reagents & solvents	Derivatives	Product(s) yield (%)	**Mol of product(s)**	MM (g/mol) product(s)	Mass (g) product(s)	E-Factor	Atom economy	Ref.
1		0,01	62,07	0,47	Cyclohexanone Toluene $C_{73}H_{57}Br_2Cl_9Cu_2N_2P_4$	 0,867 	0,01 0,009 0,000015	1,00 1,20 0,0020	98,15 92,14 1692,15	0,74 0,83 0,03		93	0,01	142,2	0,99	1,07 0,24	88,75	273
2		0,001	62,07	0,06	Acetone UTL		0,01	5,00	58,08	0,29 0,00		99	0,00099	102,13	0,10	2,50	85,00	216
3		1,00	62,07	62,07	Isopropenyl acetate (1.2M) dans THF THF Amberlyst-15	 0,889 	1 10,23256136	1,00 10,23	100,12 72,11	100,12 737,87 0,8	  	29 63 2	0,29 0,63 0,02	102,13 104,11 146,14	29,62 65,59 2,92	8,18 0,66	62,97	228
4		0,15	92,08	13,80	Methyl levulinate H_2SO_4		0,0341 0,0003	0,23 0,002	130,14 98,08	4,44 0,01		97,2	0,033136364	204,22	6,77	1,70	91,90	209
5		0,002	122,12	0,24	Acetone Amberlyst-15 Benzene 20 ml	 0,876	0,01 0,00 0,22	3,000 0,047 112,12	58,08 314,40 78,13	0,35 0,01 17,52		54%	0,00108	202,25	0,22	81,96 1,75	84,88	198

Figure S1.4 Details of the sustainable assessment of selected processes of ketalization

2 DECIPHERING THE UNDERLYING COMPLEXITY OF APPARENTLY SIMPLE REACTIONS WITH ALCOHOLS

2.1 GENERAL INFORMATION

Conversions and yields for the dynamic covalent exchanges reactions toward orthoesters (DCE) were determined by Gas Chromatography (GC) coupled to mass spectrometer (Shimadzu GC-MS-QP2020 NX). The GC-MS is equipped with a 14% cyanopropylphenyl / 86% dimethyl polysiloxane (0.25 mm ID x 0.25 µm x 30 m) column while the program of temperature consisted in a plateau at 30 °C hold 5 min, a 5 °C min^{-1} ramp to 50 °C hold 8 min, a 30°C min^{-1} ramp to 120 °C hold 6 min, a 10 °C min^{-1} ramp to 175 °C and a 30°C min^{-1} ramp to 250 °C hold 2 min. A split ratio of 5 was used.

Yields for the dynamic covalent exchange reactions toward orthoersters were determined by ^{1}H NMR spectroscopy conducted on a high field Bruker Avance III HD 700 MHz spectrometer equipped with a 5 mm cooled probe(CryoProbe^{tm}) triple nuclei HCN (TCL) in CD_3CN. The chemical shifts were reported in ppm relative to the solvent residual peak. Octamethylcyclotetrasiloxane was used as internal standard. Preparation of the samples consisted in the prior weighing of the internal standard (6-8 mg), its further solvation in 580 CD_3CN and the final addition of 20 µl of reactional crude. Commercial references of ethylene glycol (**1**), triethylorthoformate (**2**) and ethyl formate (**13**) were used to perform peaks assignment on a ^{1}H NMR spectrum obtained from a typical reactional crude. Other compounds were identified based on reference spectra obtained from their isolation (**3** to **7** and **9**) or through careful structural analysis (**10** and **11**) reported in Section S12. Given that all signals arising from the ^{1}H spectrum were identified and assigned, a mass balance could be calculated for the determination of both the conversion as well and yields of all products.

A Spinsolve™ Ultra NMR (43 MHz) spectrometer from Magritek® equipped with a flow-through cell was used for the real-time monitoring of dynamic covalent exchanges (DCE) reaction. This experiment used a loop system, allowing the crude mixture to be pumped through a peristaltic pump (Magritek® - controlled by Spinsolve software) for analysis before being returned to the batch reactor. A ^{1}H-NMR spectrum (1D Extended) was recorded after each loop, consisting of 2 scans (50 s of repetition time, 90° of pulse angle).

2.2 REAGENTS AND SOLVENTS

The reagents and solvents are purchased from commercial sources; these compounds are used without purification (Table S2.1). All reagents were used as received, unless otherwise stated. Solvents were dried over 4 Å molecular sieve.

Table S2.1 Chemicals and suppliers.

Solvents	Purity (%)	CAS number	Supplier
Acetonitrile	>99%	64-17-5	VWR
Propylene carbonate	>99.8%	108-32-7	Sigma Aldrich
Dimethylformamide	>99.5%	68-12-2	VWR
Dimethyl sulfoxide	>99%	67-68-5	VWR
Ethyl acetate	>99.5%	141-78-6	VWR
D3-acetonitrile	>99.8%	2206-26-0	Eurisotop
Dichloromethane	>98%	75-09-2	VWR
Methanol	>98%	67-56-1	VWR
Chemicals	Purity (%)	CAS number	Supplier
Ethylene glycol (**1**)	99.8	107-21-1	VWR
Triethyl orthoformate (**2**)	>98%	122-51-0	Sigma Aldrich
Trimethyl orthoformate (**2.1**)	>98%	149-73-5	Sigma Aldrich
Triisopropyl orthoformate (**2.2**)	>98%	4447-60-3	Sigma-Aldrich
Formic acid (FA)	>96%	64-18-6	VWR International
Acetic acid (AA)	>99%	64-19-7	VWR International
Pimelic acid (PA)	>98%	111-16-0	Acros
Benzoic acid (Bz)	>99%	65-85-0	UCB
Succinic acid (SA)	>99%	110-15-6	Merck-Darmstadt
Oxalic acid (OA)	>98%	144-62-7	Sigma Aldrich
Trichloroacetic acid (TCA)	>98%	76-03-9	Baker
Trifluoroacetic acid (TFA)	>99%	76-05-1	Acros
Octamethylcyclotetrasiloxane	>98%	556-67-2	Sigma Aldrich

2.3 EXPERIMENTS

2.3.1 KINETIC STUDY USING 1:1 RATIO OF 1/2 WITH *IN-LINE* NMR MONITORING

A 0.73 M solution of ethylene glycol (**1**) and triethyl orthoformate (**2**) was prepared by dissolving **1** (1.10 g, 17 mmol, 1 equiv.) and **2** (2.60 g, 17 mmol, 1 equiv.) in 20 mL of dry acetonitrile. The medium was preheated to 60 °C for 15 min and magnetically stirred at 500 rpm prior to the addition of the catalyst. Then, 10 mol% of FA (0.078 g, 1.7 mmol, 0.1 equiv.) was added to the heated medium to trigger the reaction. The reaction was carried out over 1 h and monitored by in-line NMR as described in section 2.1.

2.3.2 Kinetic study using 1:1 ratio of 1/2 with off-line NMR

A 0.73 M solution of ethylene glycol (**1**) and triethyl orthoformate (**2**) was prepared by dissolving **1** (0.272 g, 4.38 mmol, 1 equiv.), **2** (0.650 g, 4.38 mmol, 1 equiv.) and internal standard octamethylcyclotetrasiloxane (0.050.g, 0.16 mmol) in 5 mL of dry acetonitrile. This solution was weighted and mixed in a round bottom flask, which had been preliminary dried under vacuum and then inerted with Argon. The reaction medium was preheated to 60 °C for 15 min and magnetically stirred at 500 rpm prior to the addition of the catalyst. A sample was collected before the addition of FA to ensure the reaction had not yet started. Then, 10 mol% of FA (0.020 g, 0.43 mmol, 0.1 equiv.) was added to the heated medium to trigger the reaction. The reaction was carried out over 3 h with regular aliquots of 30µL collected in Eppendorf tubes. Finaly, 20 µl of the crude was pipetted out and diluted with 580 µL of d$_3$-MeCN and transferred into NMR tubes for analysis. The same procedure was followed for the screening of catalysts using 5 or 10 mol% of catalyst according to the experiment and undried acetonitrile.

2.3.3 Kinetic study using 100:1 ratio of 1/2 with off-line NMR

The same procedure as described in section S2.3.1 was performed. A solution of ethylene glycol (**1**, 14.80M) and of triethyl orthoformate (0.1480 M) was prepared by dissolving **1** (6.218g, 0.1 mol, 100 equiv.), **2** (0.148 g, 1 mmol, 1 equiv.) and the internal standard octamethylcyclotetrasiloxane (0.013.g, 0.04 mmol) in 1 mL of dry acetonitrile. Then, 10 mol% of FA (0.005 g, 0.11 mmol, 0.1 equiv.) was added to the heated medium to trigger the reaction.

2.3.4 Kinetic study using 1:1 ratio of 1/2 in neat conditions with off-line NMR

The same procedure as described in section S2.3.1was performed. A solution of ethylene glycol (**1**, 4.5 M) and triethyl orthoformate (**2**, 4.5 M) was prepared by dissolving **1** (1.89 g, 4.5 mmol, 1 equiv.), **2** (4.52 g, 4.5 mmol, 1 equiv.) and the internal standard octamethylcyclotetrasiloxane (0.137 g, 0.46 mmol). Then, 10 mol% of FA (0.15 g, 0.45 mmol, 0.1 equiv.) was added to the heated medium to trigger the reaction.

2.3.5 Preparation of compound 3

In a 500 mL round-bottom flask, a solution of **1** and **2** was prepared dissolving **1** (3.12 g, 50 mmol, 1 equiv.) and **2** (39.30 g, 265 mmol, 5.3 equiv.) in 250 mL of acetonitrile. Then, 0.5 equivalent of formic acid (1.16 g, 25 mmol, 0.5 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and cooled down in an ice batch for 2 min to enable the complete consumption of **1**. The reaction medium was rapidly quenched with Na_2CO_3 and subsequently filtered to recover the neutralized solution The reaction effluent was then purified by a vacuum distillation to remove the unreacted **2**. ^{1}H NMR (400 MHz, CD_3CN) δ 5.16 (s, 1H), 3.67 – 3.54 (m, 4H), 3.51 (s, 1H), 1.17 (d, *J* = 7.1 Hz, 5H). ^{13}C NMR (101 MHz, CD_3CN) δ 118.26, 66.29, 61.93, 60.44.

2.3.6 KINETIC STUDY STARTING FROM SPECIES 3 AND AN EXCESS OF ETOH WITH OFF-LINE NMR

The same procedure as described in section S2.3.1 was performed. A solution 0.27 M of compound **3** was prepared by dissolving **3** (0.2190 g, 1.33 mmol, 1 equiv.) with EtOH (0.1983 g, 4.30 mmol, 3.2 equiv.) and internal standard octamethylcyclotetrasiloxane (0.0273 g, 0.09 mmol) in 4.3 mL of dry acetonitrile. Then, 52 mol% of FA (0.0326 g, 0.7 mmol, 0.52 equiv.) was added to the heated medium to trigger the reaction.

2.3.7 PREPARATION OF COMPOUND 4

In a 500 mL round-bottom flask, a solution of **1** and **2** was prepared dissolving **1** (1.60 g, 25.7 mmol, 1 equiv.) and **2** (38.50 g, 260 mmol, 10 equiv.) in 250 mL of acetonitrile. Then, 0.1 equivalent of formic acid (0.1183 g, 2.57 mmol, 0.1 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and heated at 60 °C over 2 hours. The reaction medium was rapidly quenched with Na_2CO_3 and subsequently filtered to recover the neutralized solution. The reaction effluent was then purified by a vacuum distillation to remove the remaining unreacted **2**. ^{1}H NMR (400 MHz, CD_3CN) δ 5.18 (s, 1H), 3.65 (s, 2H), 3.58 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ 117.31, 62.69, 59.50, 14.34.

2.3.8 KINETIC STUDY STARTING FROM SPECIES 4 AND AN EXCESS OF ETOH WITH OFF-LINE NMR

The same procedure as described in section S2.3.1 was performed. A solution 0.192 M of compound **4** by dissolving (0.4681 g, 1.75 mmol, 1 equiv.), EtOH (0.4784 g, 10.38 mmol, 5.9 equiv.) and the internal standard octamethylcyclotetrasiloxane (0.0369 g, 0.12 mmol) in 8 mL of dry acetonitrile. Then, 48 mol% of FA (0.0385 g, 0.83 mmol, 0.48 equiv.) was added to the heated medium to trigger the reaction.

2.3.9 PREPARATION OF COMPOUND 5

In a 50 mL round-bottom flask, a solution of **1** and **2** was prepared dissolving **1** (10.0 g, 161 mmol, 1 equiv.) and **2** (9.56 g, 64.5 mmol, 0.4 equiv.) in dry acetonitrile. Then, 0.004 equivalent of FA (0.03 g, 0.6 mmol, 0.004 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and cooled at 0 °C in an ice bath over 5 min. The reaction medium was rapidly quenched with Na_2CO_3 and subsequently filtered to recover the neutralized solution The reaction effluent was then purified by a silica column separation using a mixture of 7:3 acetonitrile/ethyl acetate as eluent. Finally, the column was flushed with a 9:1 dichloromethane/methanol effluent to recover a fraction mainly containing **5** (Section S12). ^{1}H NMR (400 MHz, CD_3CN) δ 5.21 (s, 1H), 3.70 – 3.53 (m, 7H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 112.81, 65.36, 60.99, 59.53, 14.34.

2.3.10 PREPARATION OF COMPOUND 6

In a 500 mL round-bottom flask, a solution of **1** and **2** was prepared dissolving **1** (15.52 g, 250 mmol, 1 equiv.) and **2** (37.09 g, 250 mmol, 1 equiv.) in 250 mL of acetonitrile. Then, 0.1 equivalent of formic acid (1.14 g, 24.7 mmol, 0.1 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and heated at 60 °C over 3 hours. The medium was then rapidly quenched with Na_2CO_3 and then, filtered to recover the neutralized solution. The reaction effluent was then purified by a vacuum distillation. ^{1}H NMR (400 MHz, CD_3CN) δ 5.79 (s, 1H), 4.07 – 3.85 (m, 4H), 3.55 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 114.96, 63.68, 14.45. CAS 4544-20-1.

2.3.11 PREPARATION OF COMPOUND 7

In a 50 mL round-bottom flask, a solution of **1** and **2** was prepared dissolving **1** (7.76 g, 125 mmol, 1 equiv.) and **2** (3.70 g, 25 mmol, 0.2 equiv.) in 25 mL of dry acetonitrile. Then, 0.02 equivalent of formic acid (0.115 g, 2.5 mmol, 0.02 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and heated at 70 °C overnight. The reaction medium was rapidly quenched with Na_2CO_3 and subsequently filtered to recover the neutralized solution The reaction effluent was then purified by a silica column separation using a mixture of 5:5 acetonitrile/ethyl acetate as eluent. ^{1}H NMR (400 MHz, CD_3CN) δ 5.81 (s, 1H), 4.09 – 3.84 (m, 4H), 3.63 – 3.48 (m, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 115.17, 65.60, 63.76, 60.94. CAS 30928-72-4.

2.3.12 PREPARATION OF COMPOUND 9

In a 50 mL round-bottom flask, a solution of **1** and **6** was prepared dissolving **1** (0.5 g, 8 mmol, 1 equiv.) and **6** (4.14 g, 35 mmol, 4.4 equiv.) in 25 mL of acetonitrile. Then, 0.2 equivalent of formic acid (0.08 g, 1.7 mmol, 0.2 equiv.) was added to the solution to trigger the reaction. The medium was magnetically stirred and heated at 70 °C overnight. The reaction medium was rapidly quenched with Na_2CO_3 and subsequently filtered to recover the neutralized solution The reaction effluent was then purified by a vacuum distillation to remove the excess of **6**. ^{1}H NMR (400 MHz, CD_3CN) δ 5.80 (s, 1H), 4.06 – 3.83 (m, 4H), 3.60 (s, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ 115.03, 63.77, 62.94. CAS 4544-19-8.

2.3.13 PREPARATION OF COMPOUND 14

The same procedure as described in section S2.3.11 was performed. ^{1}H NMR (400 MHz, CD_3CN) δ 8.10 (t, J = 0.8 Hz, 1H), 4.20 – 4.13 (m, 1H), 3.73 – 3.64 (m, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ 163.11,65.30, 59.65.

2.4 CHARACTERIZATION OF DYNAMIC COVALENT EXCHANGE PRODUCTS

2.4.1 STRUCTURAL CHARACTERIZATION OF A TYPICAL CRUDE OF DCE USING 700 MHZ NMR

2.4.1.1 ACYCLIC ORTHOESTERS IDENTIFIED BY NMR

Based on NMR analysis, we identified two separate regions within 5-6 ppm range, which allowed to characterize the product distribution. Specifically, compounds in the spectral window of 5 - 5.30 ppm were attributed to acyclic orthoesters while their cyclic counterparts were found between 5.70 and 6 ppm (Figure S2.1- acidic proton in blue).

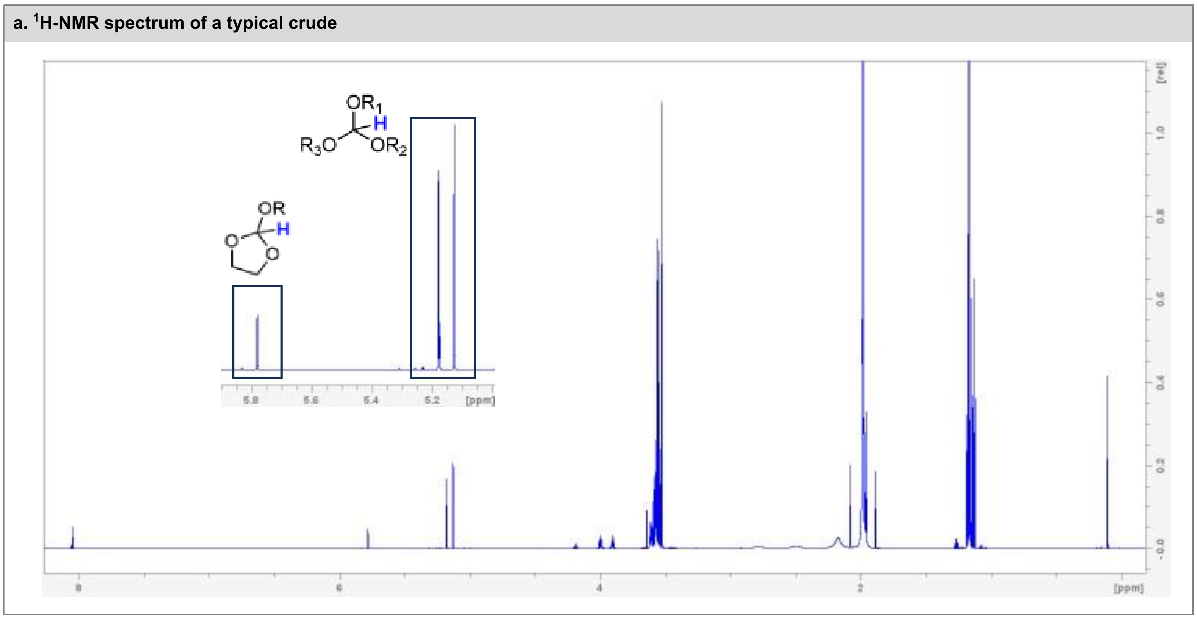
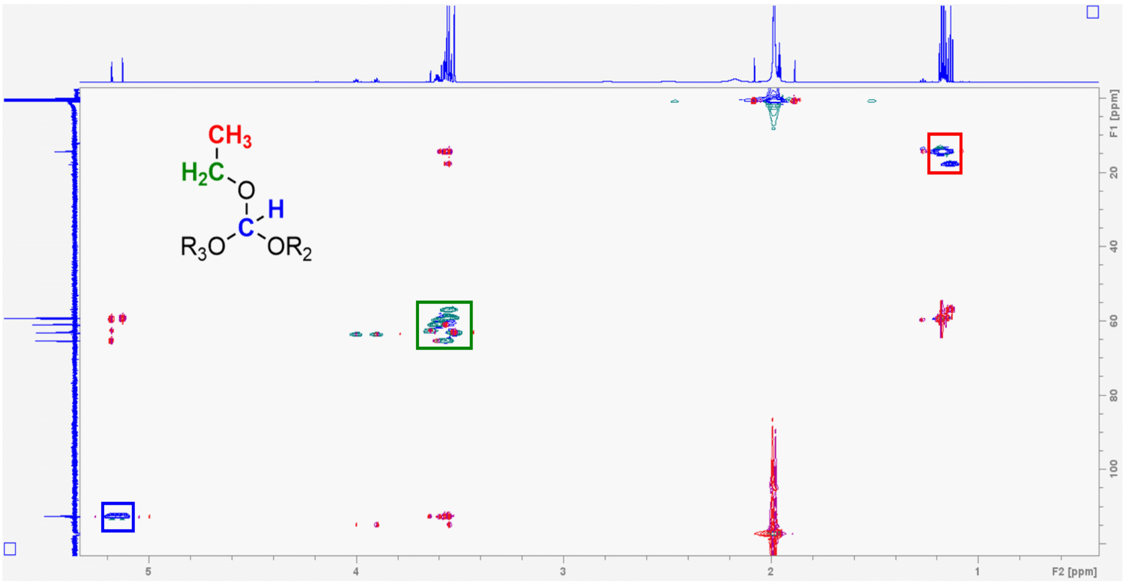


Figure S2.1 ^{1}H NMR of a typical crude of DCE (700 MHz – CD_3CN).

Focusing on the acyclic orthoester area, which includes **2** and various intermediates, 2D-HSQC and HMBC experiments were combined to assign their signals (Figure S2.1) and determine their structures.

The scaffold of the first acyclic product, species **3**, was elucidated by analyzing the correlations between the CH and CH_2 groups. Notably, the orthoformate proton at 5.18 ppm (Figure S2.2a – blue proton) exhibited correlations with two distinct types of CH_2 groups in the 2D-HMBC spectrum (2D-HMBC correlations highlighted in the green box). Examining the spectra of species **3** (Figure S2.2b), the first correlation appears to be similar to that of **2**, specifically with a methylene from an ethoxy moiety (Figure S2.2b1). The second corresponds to that with a hydroxy ethoxy group (-O-CH_2-CH_2-OH) (Figure S2.2b2).

a. Superimposition of 2D-HSQC and 2D-HMBC analyses of a typical crude of DCE and structure assignments



b. Superimposition of 2D-HSQC and 2D-HMBC analyses of the general structure of linear orthoester as well as specifically from product 3

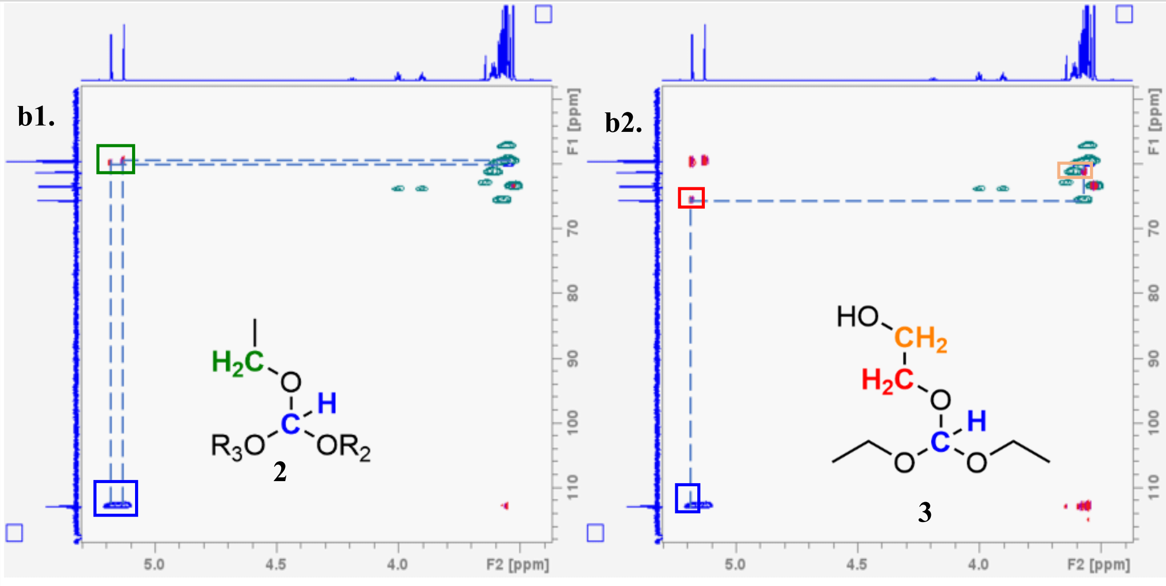
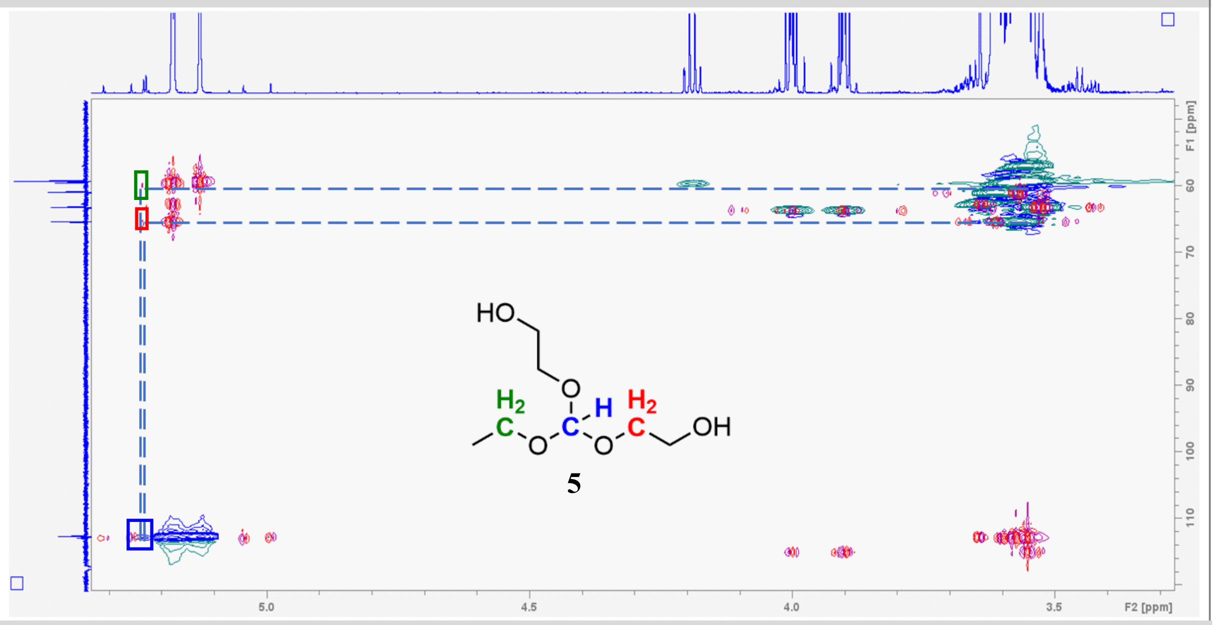


Figure S2.2 (a) Superimposition of the 2D-HSQC (blue-green signals) and HMBC (red) spectra obtained from a typical crude of DCE and corresponding assignments of the structural scaffold of acyclic orthoesters.; (b1) Superimposition of 2D-HSQC/HMBC correlations of **2** and (b2), the acyclic product **3**.

A similar pattern of CH/CH_2 correlations is observed for the proton at 5.234 ppm, which corresponds to the second acyclic molecule **5** (Figure S2.3a). Conversely, the intensity of the correlation between the orthoformate proton and the hydroxy ethoxy group is greater than with the ethoxy group. This suggests that **5** results from the exchange of two molecules of **1** with **2**. Additionally, a third compound **4** was identified. Unlike **3** and **5**, **4** does not show any correlation to an O-CH_2-CH_2-OH group (Figure S2.3b). Instead, its orthoformate proton (5.175 ppm) is correlated to a CH_2 whose proton signal appears as a singlet, with a constant CH to CH_2 proton integration ratio of 1:2. Furthermore, the correlation to the ethoxy group is more intense.

a. Superimposition of 2D-HSQC and 2D-HMBC analyses of a typical crude to identify 5



b. Superimposition of 2D-HSQC and 2D-HMBC analyses of a typical crude to identify 4

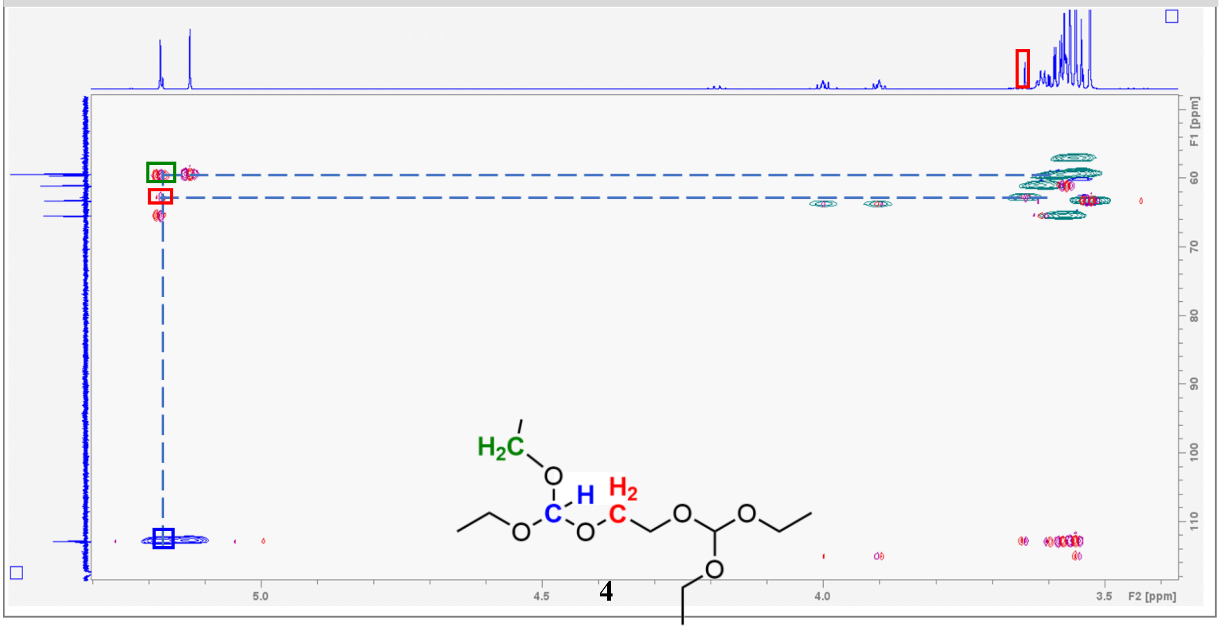
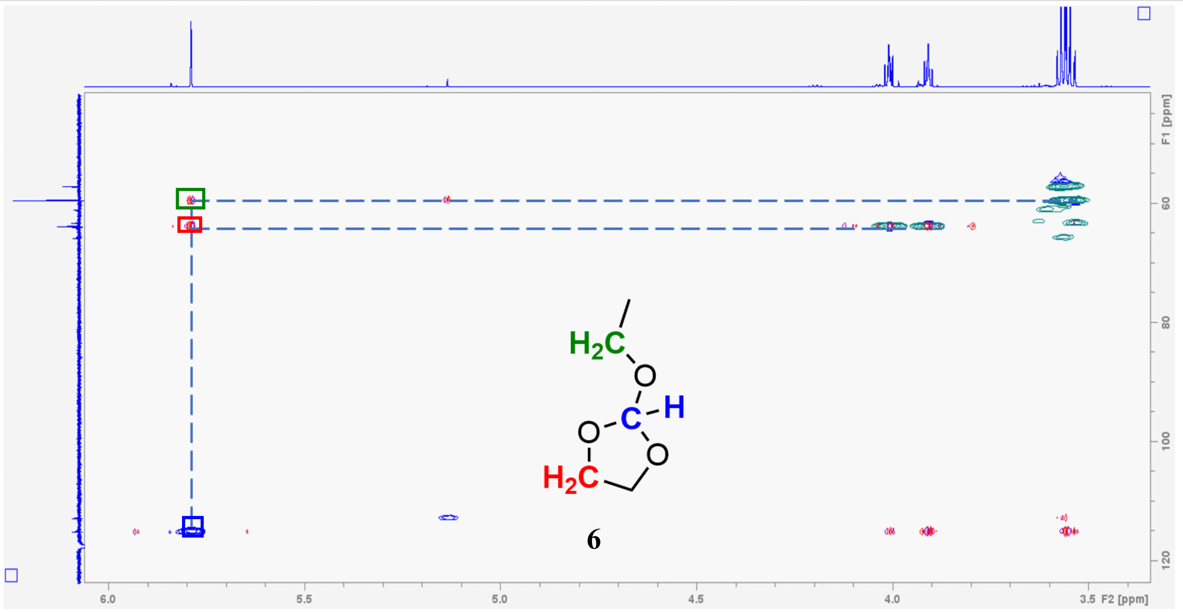


Figure S2.3 (a) Superimposition of the 2D-HSQC (blue-green signals) and HMBC (red) spectra obtained from a typical crude of DCE and corresponding assignments of the structural scaffold of acyclic orthoester **5;** and (b) **4**.

2.4.1.2 CYCLIC ORTHOESTERS IDENTIFIED BY NMR

Using the same approach for cyclic orthoesters, the structure of two products, **6** and **7**, was determined by NMR. Both compounds exhibited correlations with cyclic CH_2 groups (Figure S2.4a&b), with this correlation being the most intense for both. By increasing the intensity of the 2D-HMBC spectrum, an additional correlation to an ethoxy CH_2 then appears for **6** (Figure S2.4a), while **7** is correlated to an O-CH_2-CH_2-OH group (Figure S2.4b). Based on these findings, **6** and **7** are identified as dioxolanes substituted respectively by an ethoxy and an O-CH_2-CH_2-OH group.

a. Superimposition of 2D-HSQC and 2D-HMBC analyses for the identification of product 6



b. Superimposition of 2D-HSQC and 2D-HMBC analyses for the identification of product 7

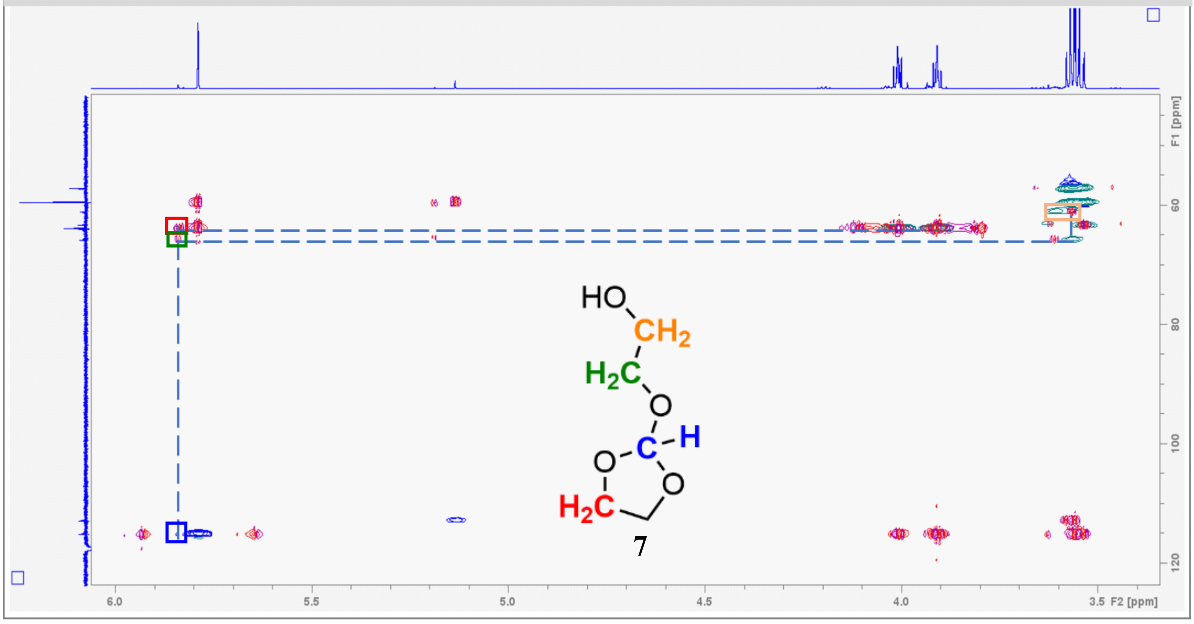


Figure S2.4 (a) Superimposition of the 2D-HSQC (blue-green signals) and HMBC (red) spectra and corresponding assignments of the structural scaffold of cyclic orthoester **6**; and (b) **7**.

Additionally, two formates were identified as hydrolysis products of **2** and **3**: ethyl formate **13**, with a formate proton signal at 8.06 ppm, and 2-hydroxyethyl formate **14**, with a formate proton signal at 8.12 ppm (Figure S2.5). These assignments were based on the reference spectra of ethyl formate **13** obtained commercially (Section S12).

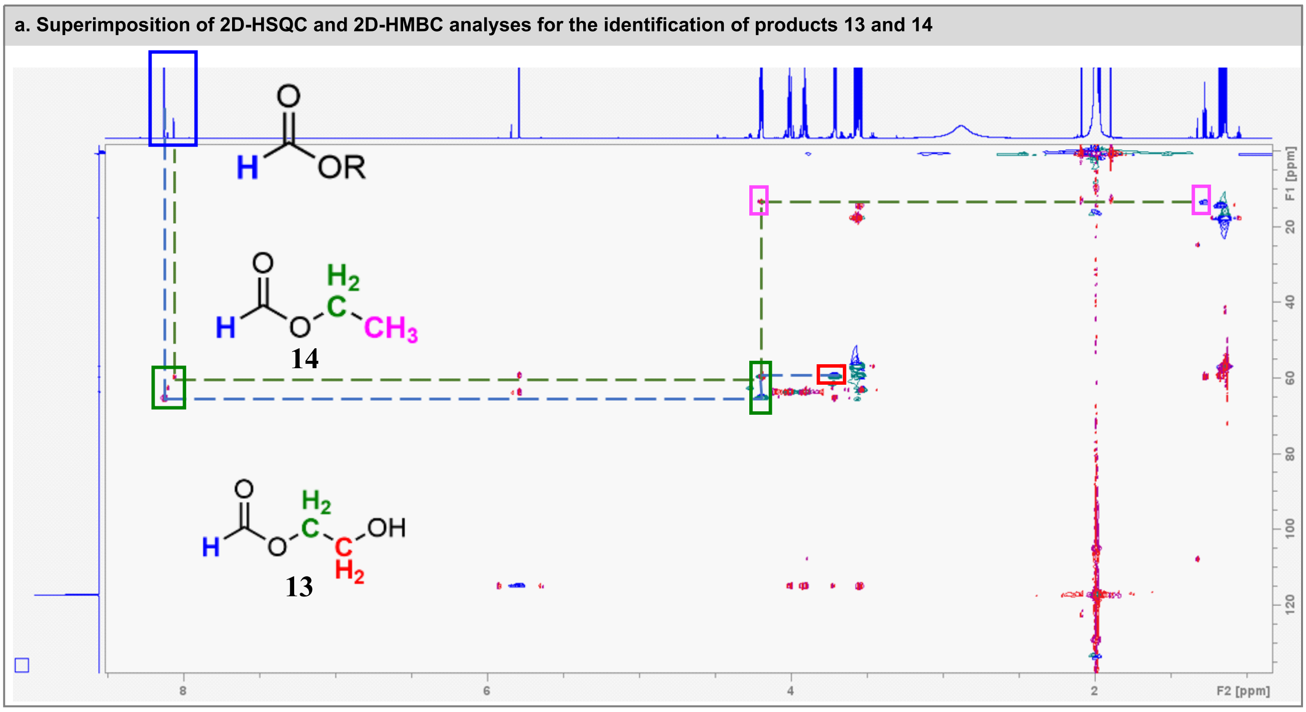

a. Superimposition of 2D-HSQC and 2D-HMBC analyses for the identification of products 13 and 14

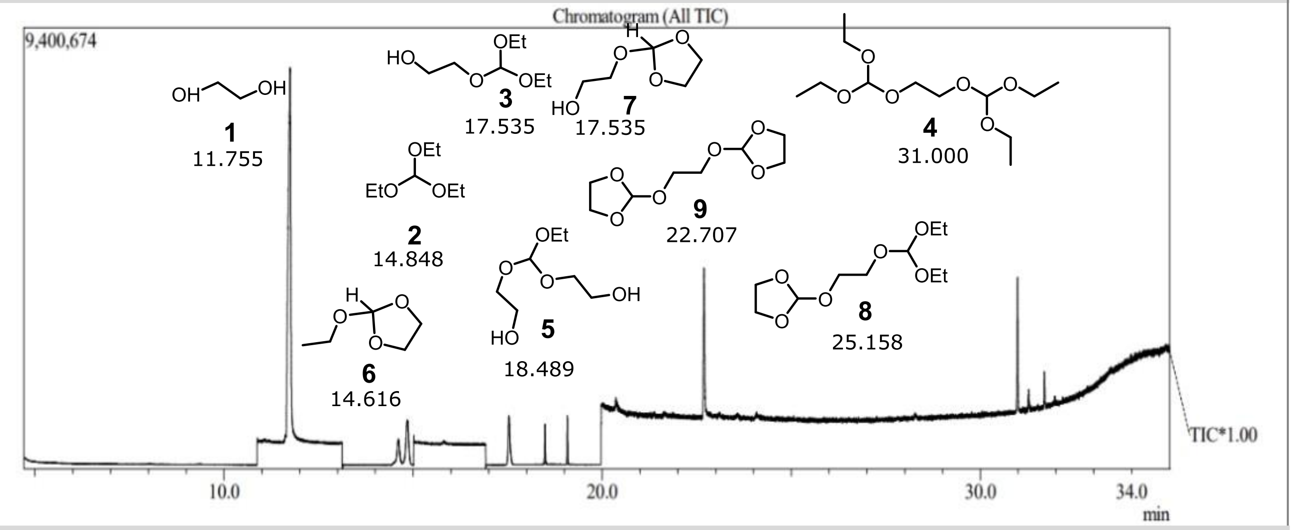
Figure S2.5 Superimposition of the 2D-HSQC (blue-green signals) and HMBC (red) spectra and corresponding assignments of the structural scaffold of side products **13** and **14**.

2.4.2 STRUCTURAL CHARACTERIZATION OF THE TYPICAL CRUDE OF DCE USING GC-MS

Following NMR characterization, GC-MS provided another layer of useful information to the understanding of the reaction. First, as it allowed to confirm the structures previously determined by NMR. Then, as it allowed to characterize the reaction crude more deeply based on fragmentation patterns. Indeed, from the total ion chromatogram (TIC) (Figure S2.6a), it can be seen that many more products are formed throughout the reaction, underlining its complexity. While some of these minor products could be identified first by GC-MS and then by NMR, others could solely be identified by GC-MS.

Mass spectra and fragmentation patterns are reported in Section 12. Generally, all the fragmentation patterns observed for the acyclic and cyclic orthoesters include the systematic loss of the orthoformate proton from the molecular ion, leading to an m/z loss of 1 per orthoester, i.e. molecular ion was not detected. Besides, the isomerization of alcohol functions of **3**, **5**, **7** into aldehydes was observed, leading to an additional m/z loss of 2 per alcohol function (Figure S2.6b). Noteworthy, compounds **10** and **11** could only be observed by NMR.

a. TIC chromatogram obtained from a typical crude of DCE and validation/identification of product distribution



b. Isomerization mechanism hypothesized of alcohol functions from 3, 5, 7 into aldehydes (loss of m/z = 2)

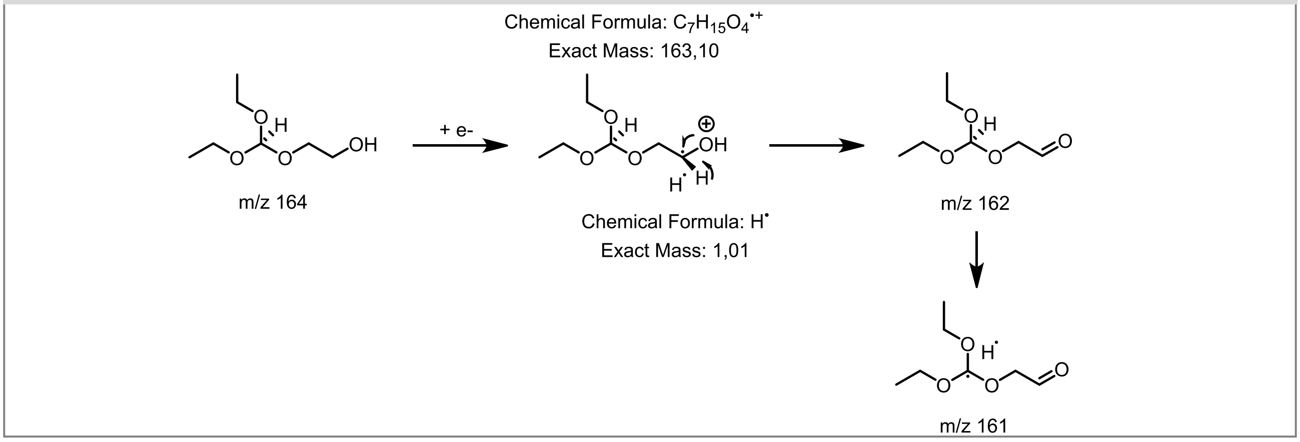


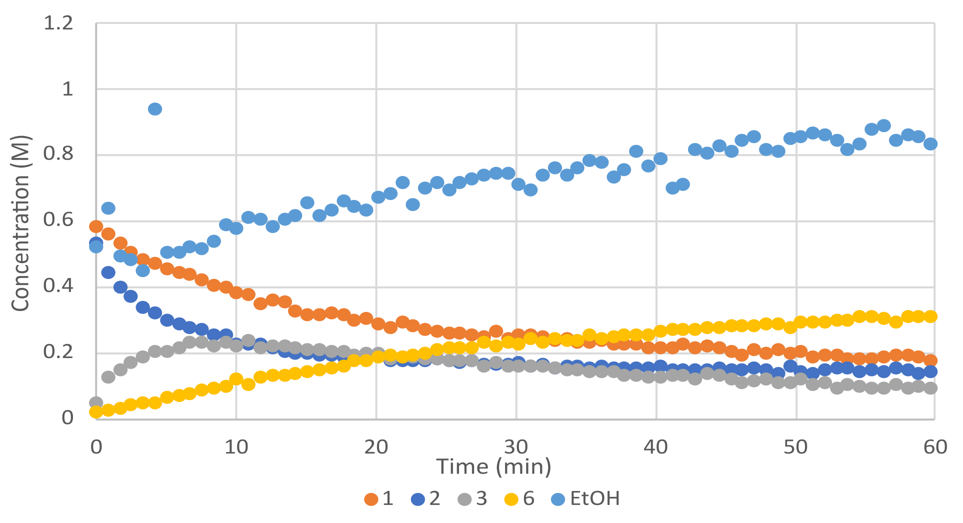
Figure S2.6 (a) TIC chromatogram obtained from a typical crude of DCE experiment and validation/identification of product distribution; (b) Hypothesized mechanism of alcohol isomerization into aldehydes.

2.5 PRELIMINARY EXPERIMENTS OF THE DCE REACTION USING IN-LINE NMR AND STABILITY ASSESSMENT OF SAMPLES OVER TIME

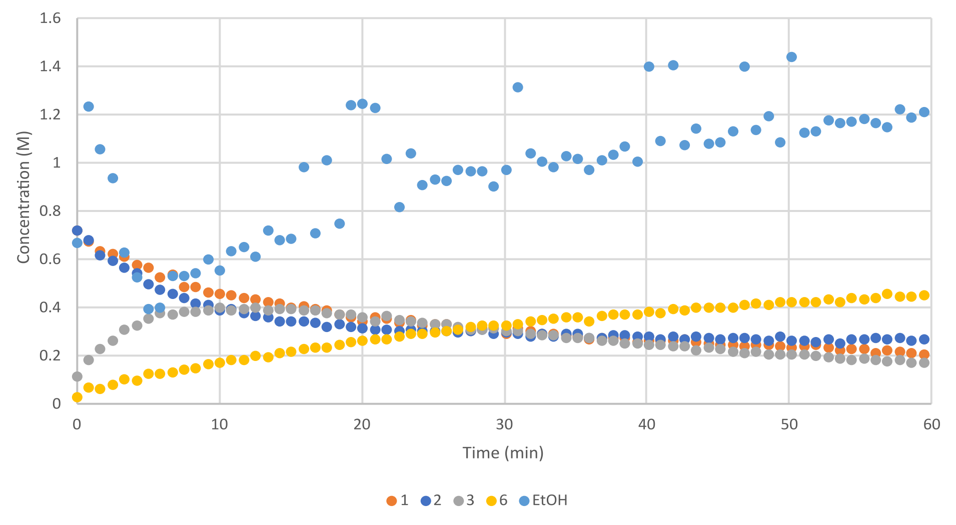
2.5.1 KINETIC STUDIES IN VARIOUS CONDITIONS OF TEMPERATURE AND CONCENTRATIONS

Preliminary experiments using stochiometric amount of **1** and **2** (described in section S2.5.1) were carried out at 0.58 and 0.72 M at 50°C as well as 0.72 M at 60 °C (Figure S2.7a&b). Higher temperatures were not considered due to the boiling point of acetonitrile, which is approximatively at 82 °C. Species quantification was based on the integration of **2** signal before the addition of the acidic catalyst. The results showed that increasing the temperature from 50 to 60 °C at 0.58 M enhanced the reaction kinetic. However, the formation of products such as **7** remains very low, preventing any accurate quantification with the 43 MHz NMR, and we decided to further increase the concentration of **1** and **2** to 0.72 M. These results are coherent and comparable to those obtained in the same conditions with an off-line high field NMR (700 MHz).

a. Kinetic study using 1:1 ratio of 1/2 (0.58 M) at 50 °C with 10 mol% of FA



b. Kinetic study using 1:1 ratio of 1/2 (0.72 M) at 50 °C with 10 mol% of FA



c. Kinetic study using 1:1 ratio of 1/2 (0.72 M) at 60 °C with 10 mol% of FA

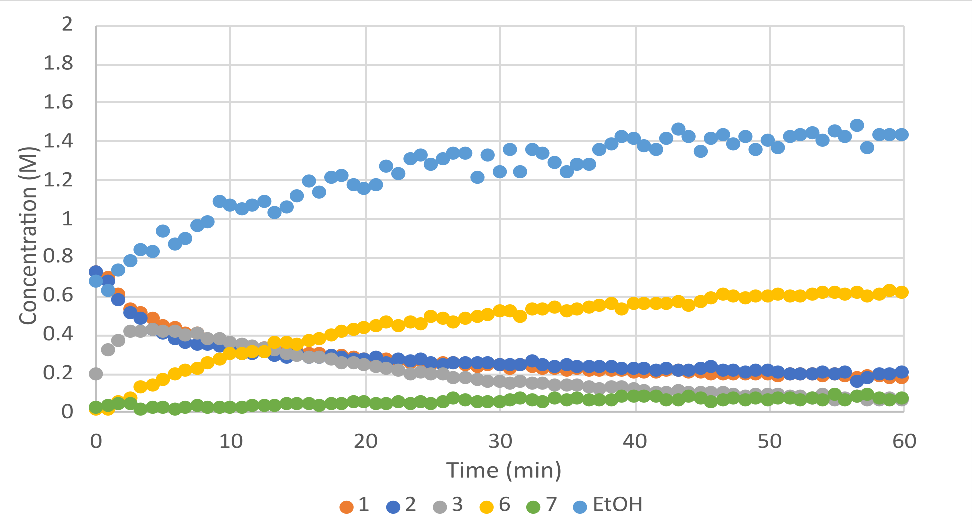


Figure S2.7 Kinetic studies using 1:1 ratio of **1**/**2** at 0.58 M at 50 °C (a), 0.72 M at 50 °C (b) and 0.72 M at 60 °C (c) monitored by 43 MHz ^{TM}Spinsolve NMR (^{1}H NMR).

2.5.2 STABILITY OF NMR SAMPLES OVER TIME

The ^{1}H-NMR analysis of the same crude sample was performed seven times at 15 mim intervals to evaluate the stability of the collected samples throughout the kinetic study. The spectral windows corresponding to acyclic and cyclic orthoesters were integrated, and the calculated ratios between the two regions were compared. The integration of cyclic orthoesters was systematically calibrated to 1. Variations ranging from 0.2567 to 0.2624 were observed across repetitions, except for the last one, which showed a ratio of 0.2533. This suggests that NMR samples prepared as described in Section S2.1 can be reliably analyzed within 1 hour and 30 min after collection before slow degradation begins.

2.6 PYTHON SCRIPT 1: TENSORIAL DECOMPOSITION OF ^{1}H-NMR RAW DATA TREATED WITH A FOURIER TRANSFORM

2.6.1 SELECTION OF NON-NEGATIVE TUCKER DECOMPOSITION

Our data posed two main constraints: the necessity for strictly positive factorized results to ensure realistic interpretation of NMR signal, and the three-dimensional nature of our data, which includes chemical shifts, intensity (from spectra) and, time (from kinetics). We considered a wide array of factorization methods to identify the most suitable algorithm. Classical methods like Principal Component Analysis (PCA) or Singular Value Decomposition (SVD) were quickly ruled out because their eigenvectors often contain negative values, creating artifacts like inverted signals in reconstructed ^{1}H spectra (physically impossible in 1H NMR data). Furthermore, these methods are inherently designed for 2D data structures and cannot efficiently capture the temporal dimension inherent in our dataset. Other methods, such as independent Component analysis (ICA), were also excluded because they assume statistical independency of components, which is unrealistic for NMR data. Non-Negative Matrix Factorization (NMF) was briefly considered but found inadequate for the handling of higher-dimensional data. Multivariate curve resolution (MCR) was also reviewed but require prior knowledge of either species concentration profiles or pure compound spectra present in the crude sample. Ultimately, we opted for tensor decomposition due to its ability to meet the requirement of non-negative factorization and handle higher-dimensional data. We considered two candidates: PARAFAC and Tucker decomposition. The later was chosen for its ability to handle complex patterns involving combinations of temporal, chemical shifts and intensity dimensions, which is crucial for capturing the dynamic nature of chemical reactions.

2.6.2 EXPLANATIONS OF THE SCRIPT OF NON-NEGATIVE TUCKER DECOMPOSITION

The Python script allows to perform a tensorial factorization of raw ^{1}H-NMR data using a non-negative tucker decomposition. This code was constructed as followed: (a) loading of data, (b) signal treatment, (c) transformation of data into tensors, (d) non-negative tucker analysis on the treated data and graphical output, (e) cross validation and graphical output, (f) operator decision according to the number of compounds (based rank) based on the graphical output,(g) and sensitivity analysis on the best rank as well as the precedent (best rank -1) and following rank (best rank +1). The script can be simply run by replying to the three dialog boxes generated during the whole code execution.

(a) Loading of data: a excel sheet must be provided following the required architecture: the first line contains the scale of time whereas the first column contains the chemical shifts. The first cell of the excel sheet must stay empty. Starting from that, every spectrum for a given time consists in a column. The loading of data is controlled by a dialog box that will open directly to the user explorer, allowing the user to select the proper excel file.

(b) Signal treatment: once the data are loaded, an automated treatment of data is performed, including a 2D medfilter and a Savitsky-Golay filter. Combination of both enables to improve the signal to noise ratio while maintaining the crucial spectral information such as signal width, height, proton coupling to name a few. This section eventually leads to the visualization of the treated data via a graphical output.

(c) Transformation of 2D matrix (NMR data) into a 3D tensor. This is performed by sequentially sampling the chemicals shifts in five matrices of same size, which allows to introduce a third dimension and use tensorial decomposition. As an illustration, chemical shifts at 1, 1.01, 1.02, 1.03 and 1.04 ppm are each going to be separated in a different matrix.

(d) Non-negative tucker analysis on the treated data and graphical output: a non-negative decomposition was selected to ensure the positive nature of NMR data but can also work for other spectral methods such as Raman or Infra-red spectroscopy. Data are then factorized according to 1 to 12 ranks, which corresponds in 1 to 12 species potentially present within the NMR kinetic data. Upstream to this decomposition, a non-negative matrix factorization (NMF) is implemented on the data. This 2D factorization is initialized by a NNDSVDAR (non-negative double singular value decomposition with alternating random initialization), using a coordinate descent (CD) solver, regularization strengths for αH and αW set at 0.1, a L1 ratio of 0.01 and Frobenius Norm as a cost function. This factorization gave the matrices of component and coefficient W and H respectively, which are subsequently used to initialize the two first factors (two first dimensions) of the non-negative tucker decomposition, fastening the computation time. The third factor is randomly generated due to NMF limitation to 2D matrixes. The tensor core is also randomly generated. Upon tensorial decomposition, a reconstructed tensor is calculated for every rank. Quantitative metrics are then calculated to evaluate the accuracy of the reconstructed tensor, comprising the relative error of reconstruction (rel_error) of a tensor X (dimensions IxJxK) and the explained variance relying on Frobenius norm ($\| \quad \|_F$):

$$\| X \|_F = \sqrt{\sum_{i=1}^{m} \sum_{j=1}^{n} | a_{i,j} |^2}$$

$$rel\_error = \frac{\| X - X_{approx} \|_F}{\| X \|_F}$$

$$explained\_variance = 1 - rel\_error$$

Where X corresponds to the original matrix and X_{approx} to the reconstructed matrix obtained from the non-negative Tucker algorithm

(e) Cross validation: a temporal cross validation is performed on the unfolded tensors at each rank. Tensor unfolding consists of converting a 3D tensor into a 2D matrix, generating the same dimension and shape of data initially introduced in point (a). The unfolded matrixes of each rank are then evaluated along the time dimension. Training starts with the first 5 times of the original data, and the models developed in point (d) are tested on the next point (the 6th). At each iteration, the Bayesian information criterion (BIC) and the Akaike information criterion (AIC) are calculated. The process is repeated for subsequent time points, from the 6th up to the last one. Finally, the mean BIC and AIC values are calculated for each rank. These statistical criteria help determine the best trade-off between model accuracy and complexity.

$$BIC = n * \ln\left(\frac{RSS}{n}\right) + k * \ln(n)$$

$$AIC = n * \ln\left(\frac{RSS}{n}\right) + 2 * k$$

RSS corresponds to residual sum of squares, n to the number of observations from the dataset and, k to the total number of parameters in the model.

(f) Operator decision: all these parameters are presented in a graphical output along the derivative of both the reconstruction error, the explained variance, the learning curves, the error derivative and training error evolution obtained for each rank (Figure S2.7). Based on these results, the user is asked to provide the best rank according to the quantitative metrics.

(g) Sensitivity analysis on the best rank and best rank±1: Once the best rank is determined, 10 repetitions of the non-negative Tucker decomposition are performed with 10 distinct NMF initializations. The relative error and explained variance are calculated for each tensor in every iteration. A second graphical output is then generated, displaying the variability of these two quantitative metrics for the best rank and best rank ±1. This provides insight into the variability of the results across different initializations and an assessment of the decomposition's robustness. Additionally, a hypothesis regarding the concentration profile is presented for each rank.

This tool provides preliminary statistical indicators to assist in the analysis of complex NMR kinetic data. It is designed to estimate a minimal number of compounds present in the mixture and guide targeted sampling for more advanced analyses. However, this tool does not replace a complete structural characterization. Its output should be considered as a working hypothesis to be validated, a guide to assist in optimizing subsequent reactions and a filter to narrow the search space. Efficiency of the tool is drastically demised for the identification of trace species as well as for compounds with multiple overlaps.

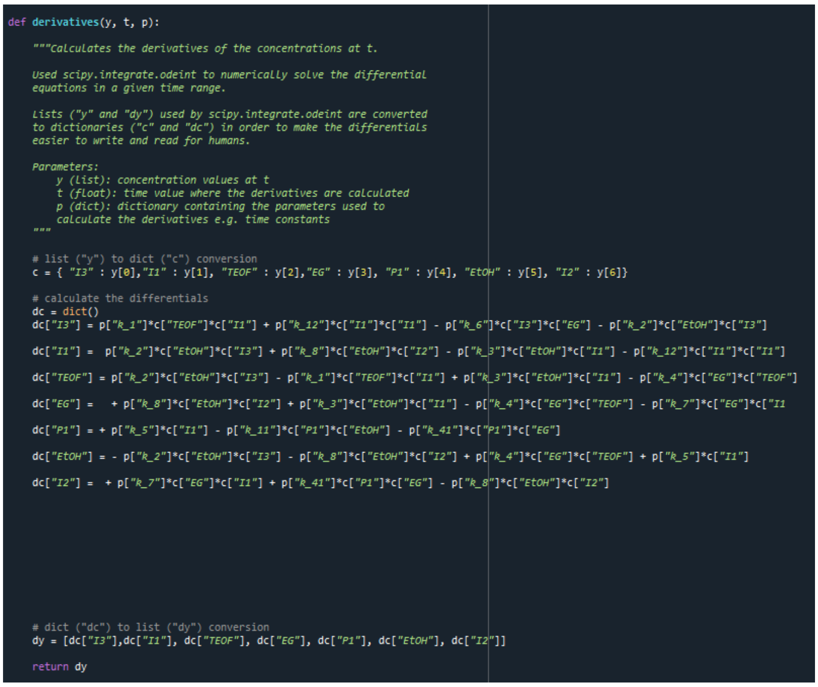
2.7 PYTHON SCRIPT 2: KINETIC MODELLING OF STOICHIOMETRIC AMOUNT OF 1 AND 2 USING 10 MOL% FA IN DRY ACETONITRILE

2.7.1 DESCRIPTION OF PYTHON SCRIPT 2

This script was inspired by the available '*Chemical Kinetics*' package, which utilizes the lmfit package to solve systems of differential equations.[1,2] It has been enhanced by incorporating quantitative metrics and quantile-quantile plots, enabling a more thorough evaluation of model accuracy, along with a user-friendly data loading process as presented in section S2.6. All figures generated by the script are saved in a folder selected by the user. This script can be easily utilized by following these steps: (a) loading the data, (b) formulating the differential equations, and (c) providing an initial approximation of the rate constants and concentrations.

(a) Loading of data: a CSV file must be provided following the required format: the first row contains the compound names, while the columns contain their respective concentrations. The first cell of the sheet must be labeled "t", and its column should contain the time data. Data loading is managed through a dialog box that automatically opens the user's file explorer, allowing them to select the appropriate Excel file. Immediately after, a second dialog box appears, prompting the user to choose a folder for saving the generated figures.

(b) Formulating the differential equations: this part is illustrated in the code provided with the supporting information (Figure S2.8).



```python
def derivatives(y, t, p):

    """Calculates the derivatives of the concentrations at t.

    Used scipy.integrate.odeint to numerically solve the differential
    equations in a given time range.

    Lists ("y" and "dy") used by scipy.integrate.odeint are converted
    to dictionaries ("c" and "dc") in order to make the differentials
    easier to write and read for humans.

    Parameters:
        y (list): concentration values at t
        t (float): time value where the derivatives are calculated
        p (dict): dictionary containing the parameters used to
        calculate the derivatives e.g. time constants
    """

    # list ("y") to dict ("c") conversion
    c = { "I3" : y[0],"I1" : y[1], "TEOF" : y[2],"EG" : y[3], "P1" : y[4], "EtOH" : y[5], "I2" : y[6]}

    # calculate the differentials
    dc = dict()
    dc["I3"] = p["k_1"]*c["TEOF"]*c["I1"] + p["k_12"]*c["I1"]*c["I1"] - p["k_6"]*c["I3"]*c["EG"] - p["k_2"]*c["EtOH"]*c["I3"]

    dc["I1"] =  p["k_2"]*c["EtOH"]*c["I3"] + p["k_8"]*c["EtOH"]*c["I2"] - p["k_3"]*c["EtOH"]*c["I1"] - p["k_12"]*c["I1"]*c["I1"]

    dc["TEOF"] = p["k_2"]*c["EtOH"]*c["I3"] - p["k_1"]*c["TEOF"]*c["I1"] + p["k_3"]*c["EtOH"]*c["I1"] - p["k_4"]*c["EG"]*c["TEOF"]

    dc["EG"] =   + p["k_8"]*c["EtOH"]*c["I2"] + p["k_3"]*c["EtOH"]*c["I1"] - p["k_4"]*c["EG"]*c["TEOF"] - p["k_7"]*c["EG"]*c["I1

    dc["P1"] = + p["k_5"]*c["I1"] - p["k_11"]*c["P1"]*c["EtOH"] - p["k_41"]*c["P1"]*c["EG"]

    dc["EtOH"] = - p["k_2"]*c["EtOH"]*c["I3"] - p["k_8"]*c["EtOH"]*c["I2"] + p["k_4"]*c["EG"]*c["TEOF"] + p["k_5"]*c["I1"]

    dc["I2"] =  + p["k_7"]*c["EG"]*c["I1"] + p["k_41"]*c["P1"]*c["EG"] - p["k_8"]*c["EtOH"]*c["I2"]









    # dict ("dc") to list ("dy") conversion
    dy = [dc["I3"],dc["I1"], dc["TEOF"], dc["EG"], dc["P1"], dc["EtOH"], dc["I2"]]

    return dy
```

Figure S2.8 Formulation of the differential equations in the Python script.

(c) Initialization of the rate constants and concentrations has to be done in the Python script (two distinct dictionaries): this part is illustrated in the script provided with the supporting information.

2.7.1.1 EVALUATION OF MODEL ACCURACY: COEFFICIENT OF DETERMINATION (R^2)

The calculation of R^2 is performed as the difference between 1 and the ratio of the sum of squared differences between the observed values (y_i) and the predicted values ($y_{i\ \mathrm{approx}}$) to the sum of squared differences between the observed values and their mean (y_{mean}).

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - y_{i_{approx}})^2}{\sum_{i=1}^{n} (y_i - y_{mean})^2}$$

The calculation of R^2 includes an interpolation function to match the number of experimental points with those of the theoretical fit (150 time points).

2.7.1.2 EVALUATION OF MODEL ACCURACY: ROOT MEANS SQUARE ERROR (RMSE) AND MEAN AVERAGE ERROR (MAE)

Calculation of RMSE and MAE are performed as follows:

$$RMSE = \sqrt{\frac{1}{n} * \sum_{i=1}^{n} (y_i - y_{i_{approx}})^2}$$

$$MAE = \frac{1}{n} * \sum_{i=1}^{n} |y_i - y_{mean}|$$

2.7.1.3 BAYESIAN CRITERION INFORMATION (BIC) AND AKAIKE INFORMATION CRITERION (AIC)

The calculation of BIC and AIC follows the approach outlined in Section 6d. Here, k represents the number of constants used in the system of differential equations, while n corresponds to the total number of experimental data points.

2.7.1.4 QUANTILE-QUANTILE PLOTS

Details about the calculations are described into the script provided with the supporting information.

2.7.2 CALCULATION OF EQUILIBRIUM CONSTANTS (*K*)

The equilibrium constants (*K*) have been calculated from the rate constants of reversible reactions. These reactions may exhibit different order dependencies in the forward and reverse directions. For instance, reversible reaction can display a two-order dependency towards a product and a one order dependency back to the reagents. In these cases, the calculated *K*' value possesses units reflecting the difference in reaction order between forward and reverse reactions. In this work, only rate constants and *K* of same unit or unitless are compared in order to facilitate the discussion. When *K*>> is indicated in a figure, it means that the reaction is considered irreversible under this set of experimental conditions.

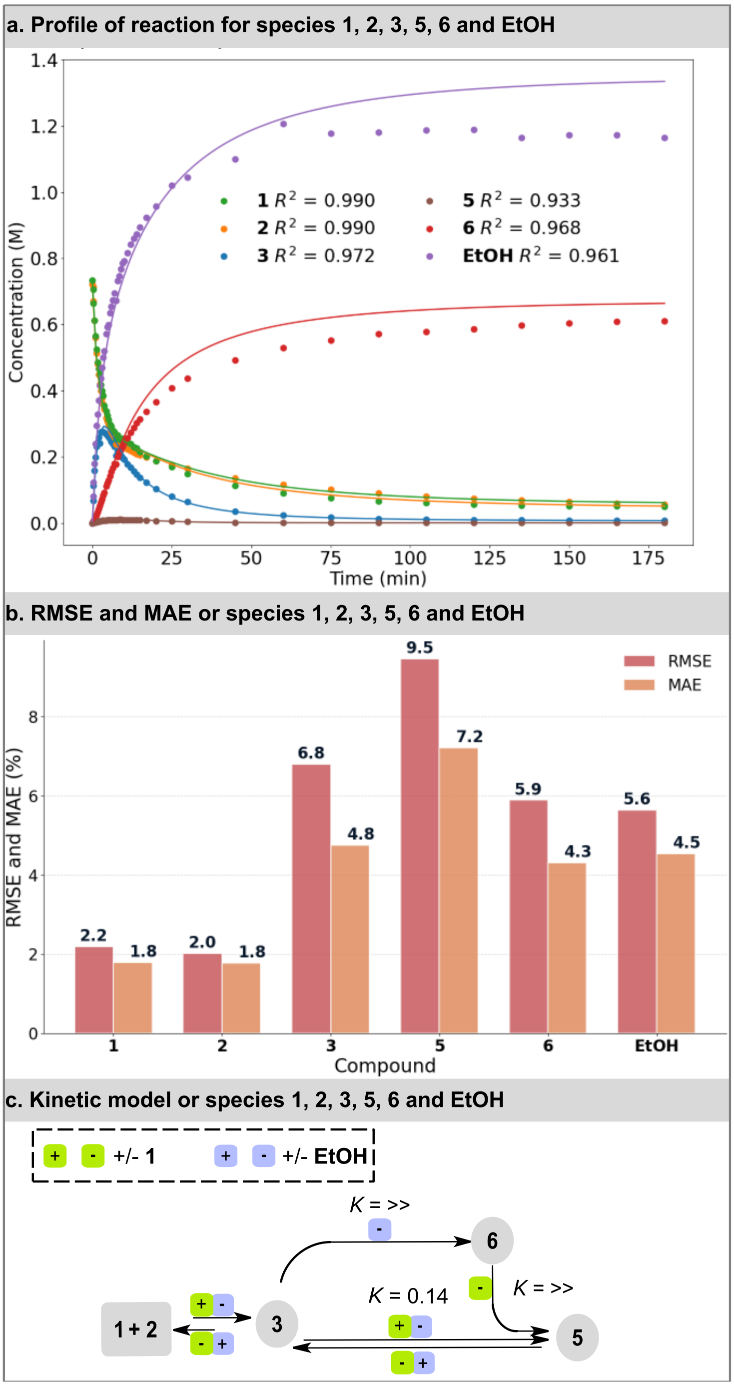
2.7.3 METHODOLOGY TO REFINE KINETIC MODELS AND WORKING HYPOTHESIS

As working hypothesis, the system of differential equations formulated for each product always includes the reversibility of each step. Once the model is obtained, neglectable contributions from either the reversible reaction or non-occurring reaction between species are removed.

2.7.4 DEVELOPMENT OF MODEL I INCLUDING SPECIES 1, 2, 3, 5, 6 AND ETOH

First modeling of the dynamic covalent exchanges toward orthoesters comprised reagents **1** and **2** as well as the first product of their reaction, intermediate **3**, as well as **5** and **6**.

2.7.4.1 MODEL I



a. Profile of reaction for species 1, 2, 3, 5, 6 and EtOH

b. RMSE and MAE or species 1, 2, 3, 5, 6 and EtOH

c. Kinetic model or species 1, 2, 3, 5, 6 and EtOH

Figure S2.9 (a) Profile of concentrations of the various species **1**, **2**, **3**, **5**, **6** and **EtOH** over time; (b) RMSE and MAE obtained from **model I**; and (c) the system obtained from kinetic modelling of NMR data with the theoretical **model I**.

2.7.4.2 Quantile-quantile plot of model I

a. Quantile-quantile plot for Model I

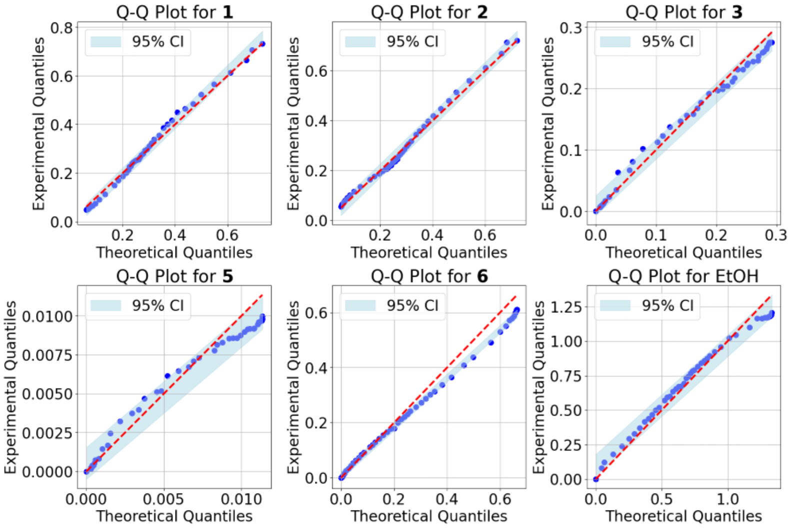
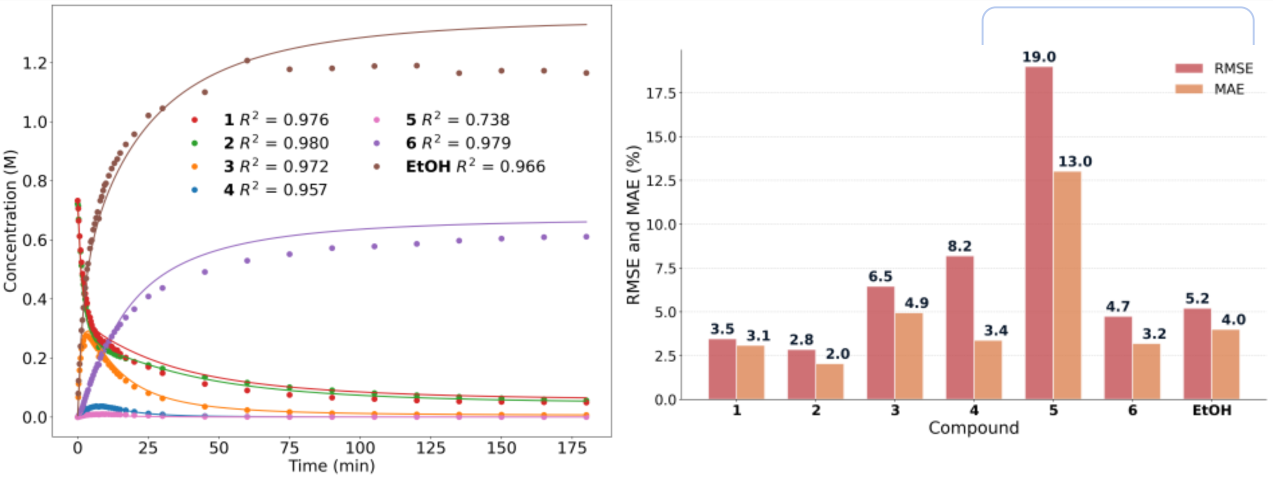


Figure S2.10 Quantile-quantile plot obtained from the species **1**, **2**, **3**, **5**, **6** and **EtOH** with **model I**.

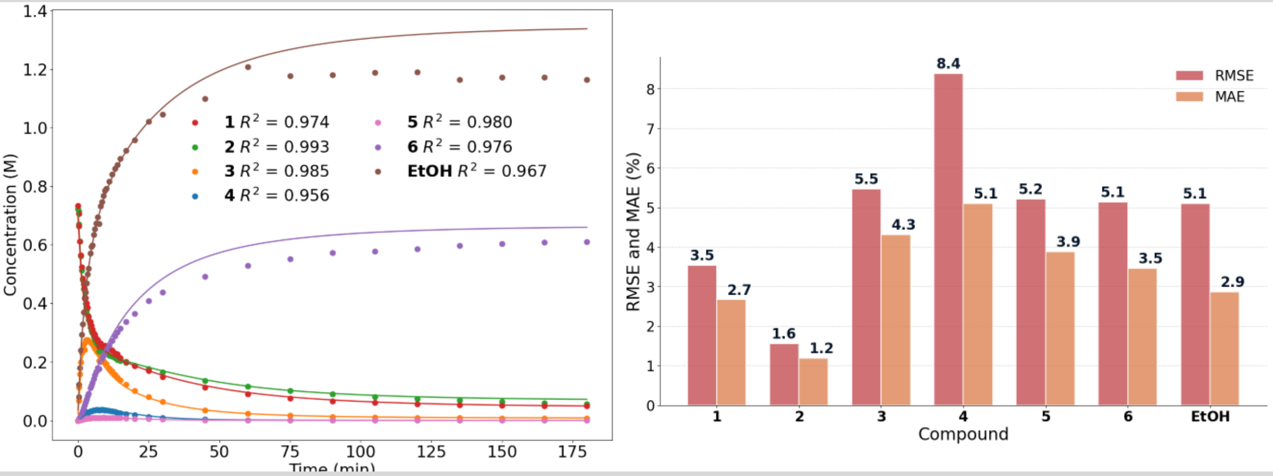
2.7.5 DEVELOPMENT OF MODEL II INCLUDING SPECIES 1, 2, 3, 4, 5, 6 AND ETOH

2.7.5.1 PROFILE OF CONCENTRATIONS AND COMPARISON OF RMSE AND MAE FOR MODEL II COMPRISING EITHER PATH (A) OR (B) OR BOTH (A&B)

a. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6 and EtOH including path (a)



b. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6 and EtOH including path (b)



c. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6 and EtOH including path (a&b)

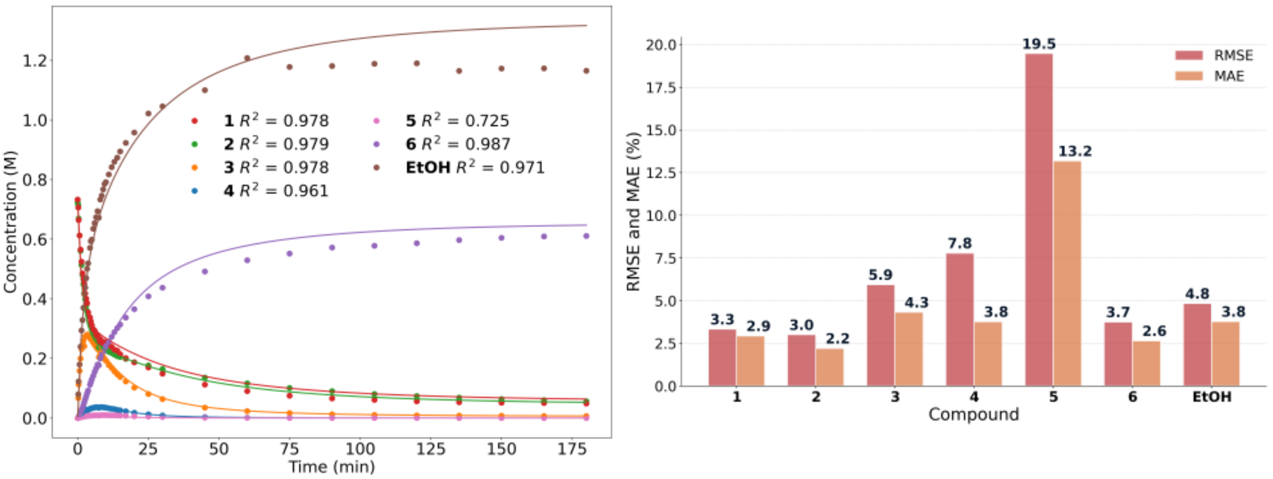


Figure S2.11 Profile of concentrations of the various species **1**, **2**, **3**, **5**, **6** and **EtOH** over time and RMSE and MAE obtained from **model II** including path (a), (b) or (a&b).

2.7.5.2 QUANTILE-QUANTILE PLOT FOR MODEL II INCLUDING PATH (A), (B) OR (A&B)

Despite the accurate description obtained thus far for each species, the Q-Q plot generated for each species including a 95% confidence intervale clearly indicates that **model II** is incomplete, with residuals of **1**, **2** and **5** that do not follow a normal distribution.

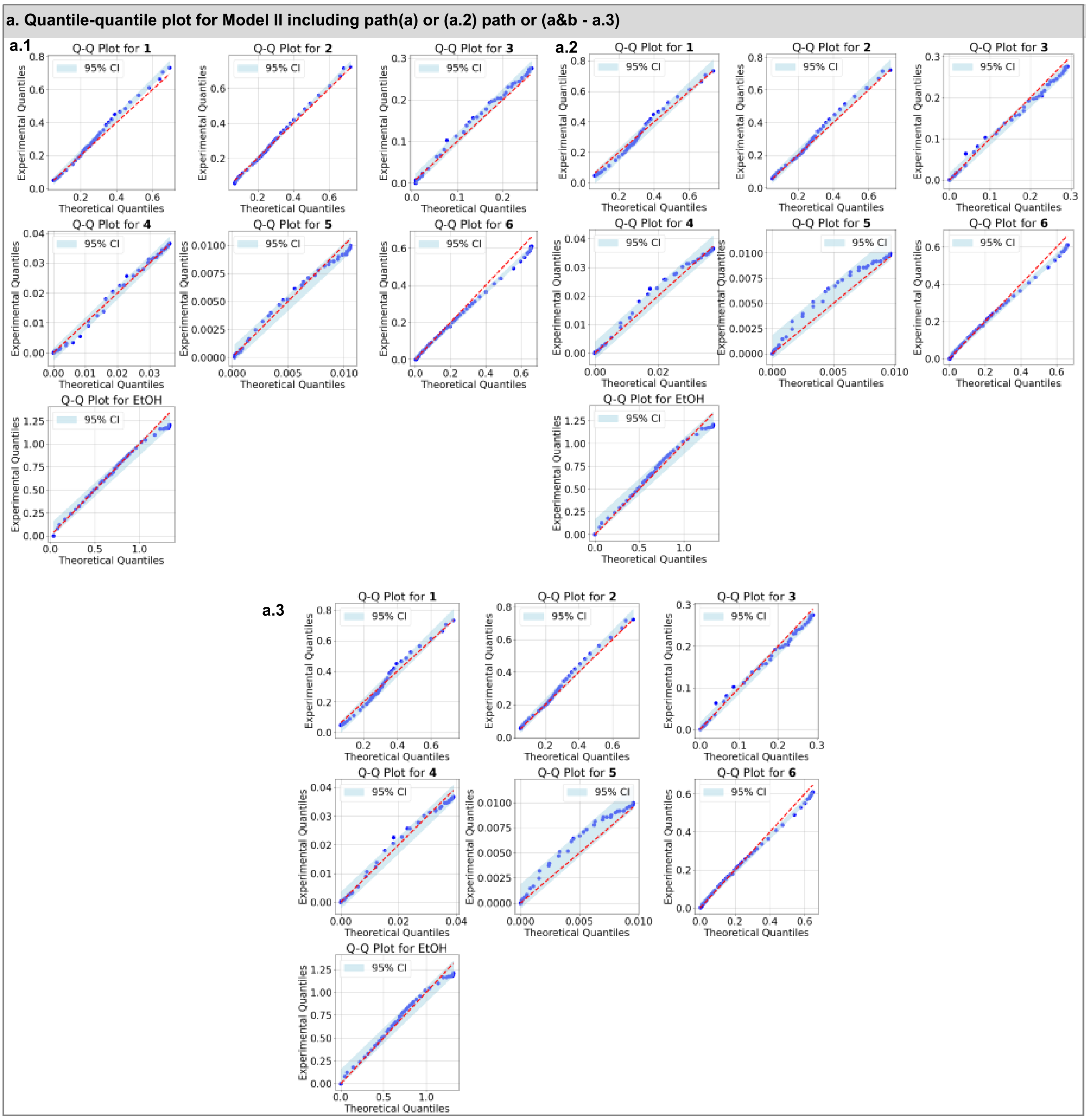


Figure S2.12 Quantile-quantile plots obtained from the species **1**, **2**, **3**, **4**, **5**, **6** and **EtOH** using **model II** including path (a – a.1), (b – a.2) or (a&b – a.3).

2.7.5.3 FINAL MODEL II OF 1 TO 6 INCLUDING PATH (B)

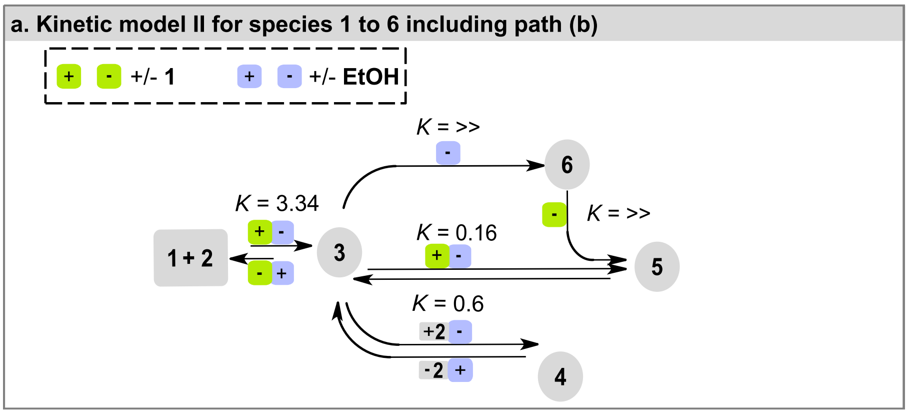


Figure S2.13 Reaction system obtained from kinetic modelling of NMR data with the theoretical **model II**.

2.7.6 DEVELOPMENT OF MODEL III INCLUDING SPECIES 1, 2, 3, 5, 6, 7 AND ETOH

2.7.6.1 MODEL III INCLUDING PATH (A), (B) OR (A&B)

Figure S2.14 displays the kinetics for model III including either the intramolecular cyclization of **5** into **7** (path a) or the substitution of **6** with **1** (path b). **Model III** is derived only from path a, providing a poor accuracy over the experimental data. By contrast, adjustment of **model III** with path b leads to a high improvement in model accuracy, especially for **5** and **7**, with RMSE values reduced from 34% and 24% to 5% and 3%, respectively.

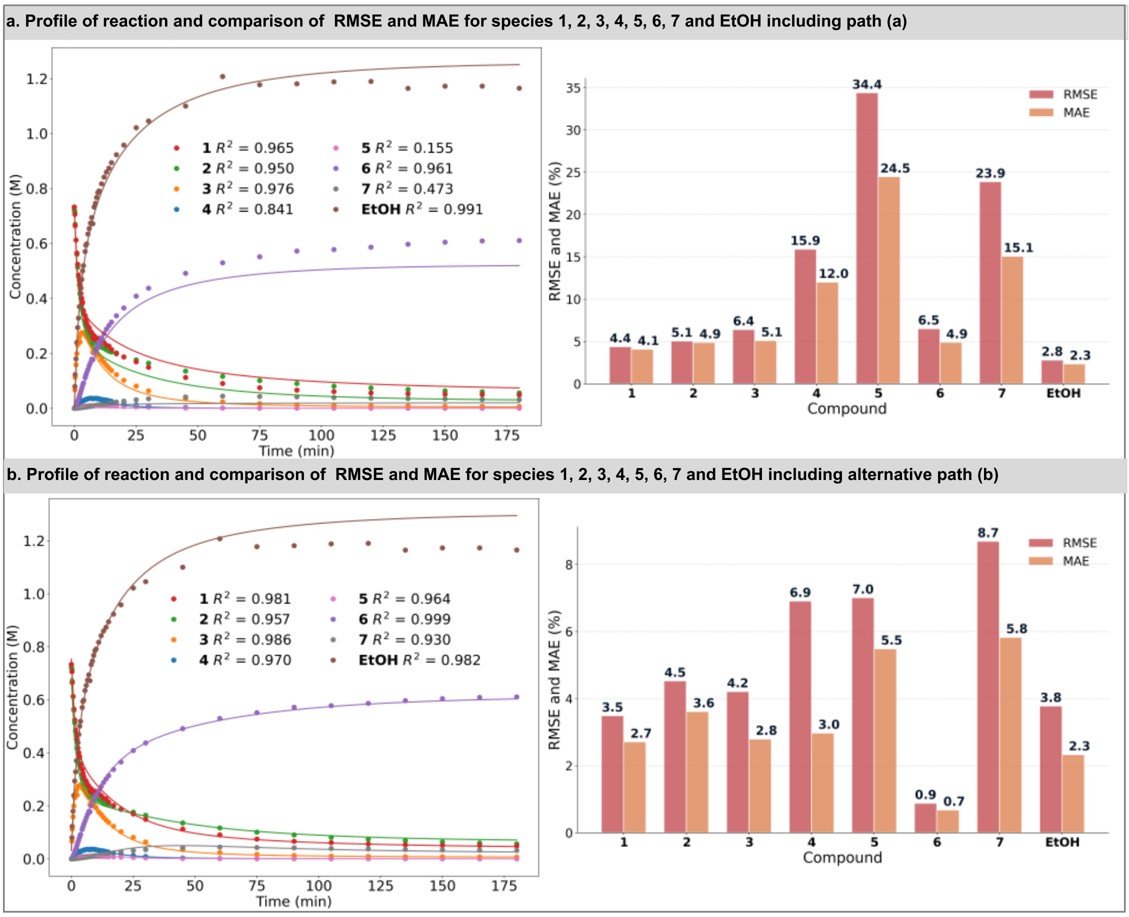


Figure S2.14 Profile of concentrations of the various species **1**, **2**, **3**, **5**, **6**, **7** and **EtOH** over time and RMSE and MAE obtained from **model III** including path (a), (b) or (a&b).

2.7.6.2 QUANTILE-QUANTILE PLOTS FOR MODEL III INCLUDING PATH (A) OR (B)

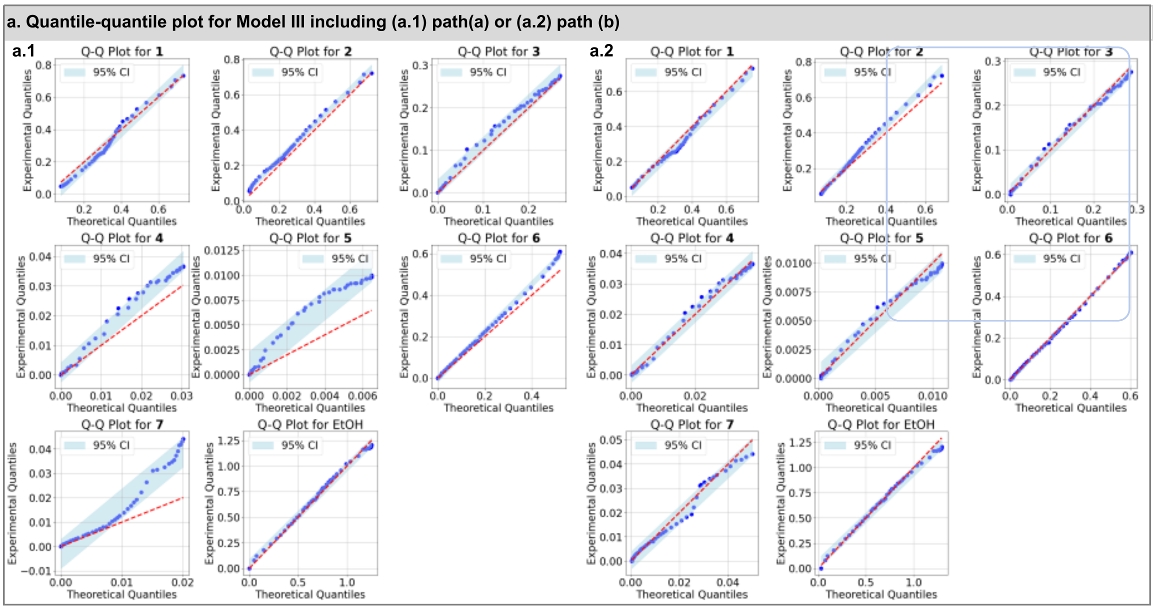


Figure S2.15 Quantile-quantile plots for model III including path (a) or (b).

2.7.6.3 MODEL III INCLUDING PATH (A&B) WITH/WITHOUT THE FORMATION OF 4 FROM 2 MOLECULES OF 3

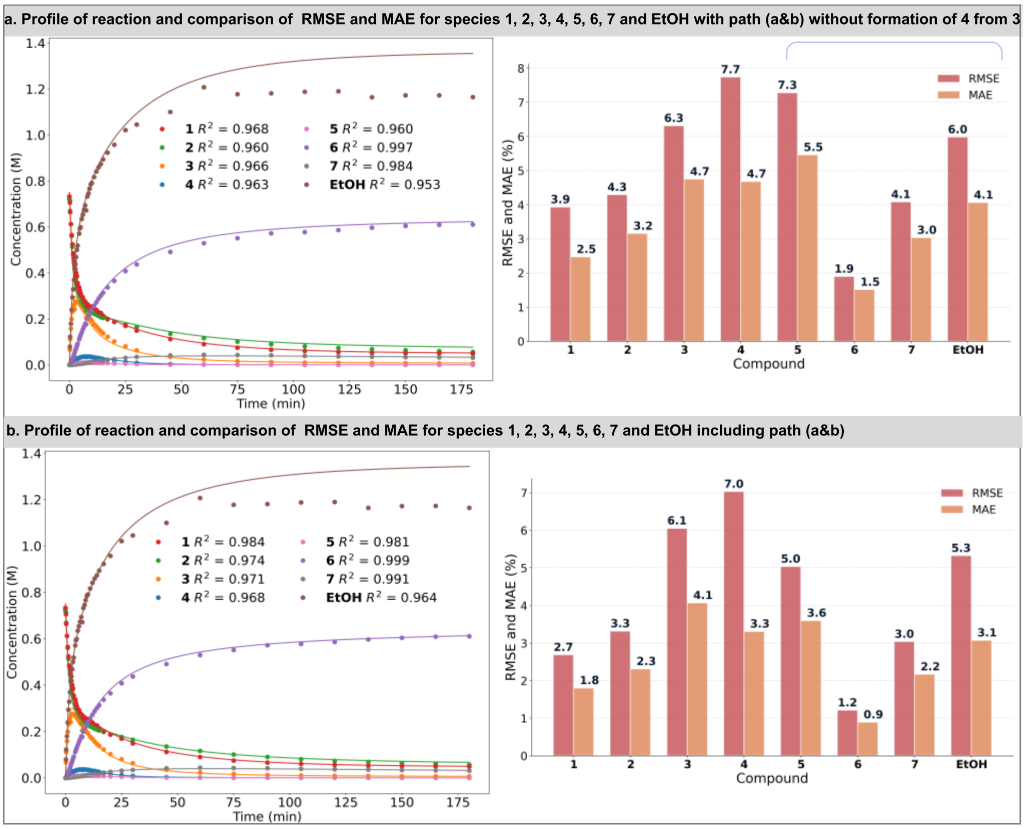


Figure S2.16 Profile of concentrations of the various species **1**, **2**, **3**, **5**, **6**, **7** and **EtOH** over time and RMSE and MAE obtained from **model III** including path (a&b) with/without formation of **4** from 2 molecules of **3**.

2.7.6.4 Quantile-quantile plot for model III including path (a&b) including the formation of 4 from 2 molecules of 3

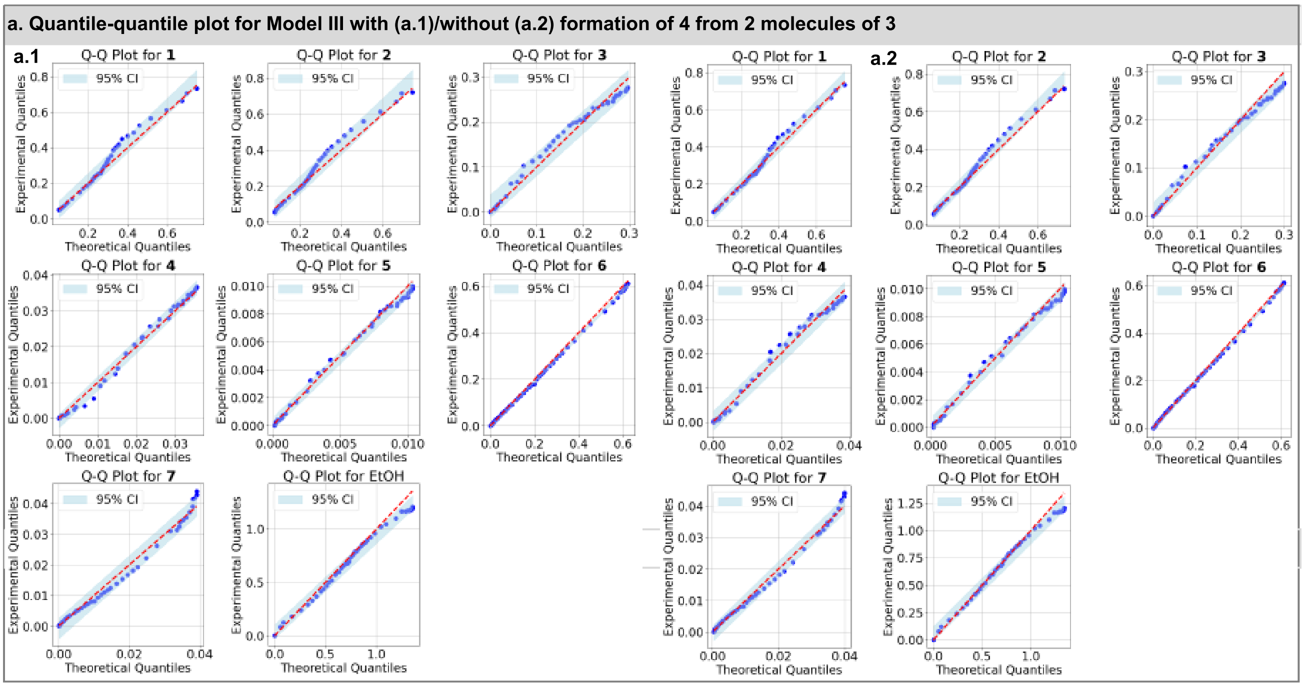


Figure S2.17 Quantile-quantile plots for **model III** including path (a) or (b).

2.7.6.5 Final model of 1 to 7 including path (a&b) including formation of 4 from 2 molecules of 3

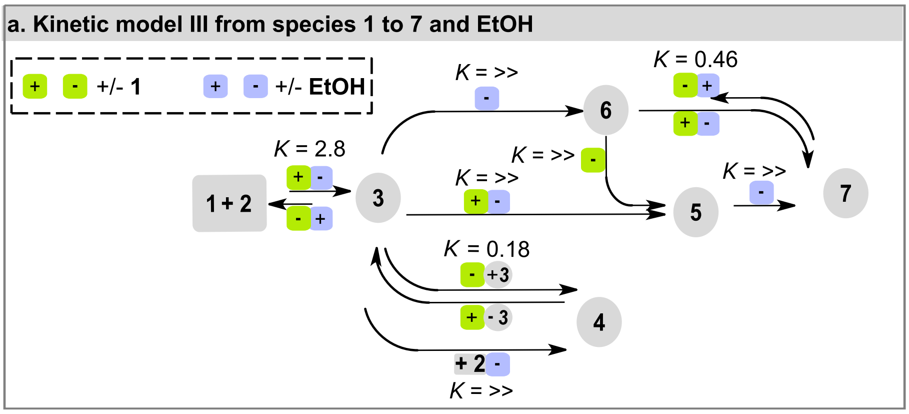


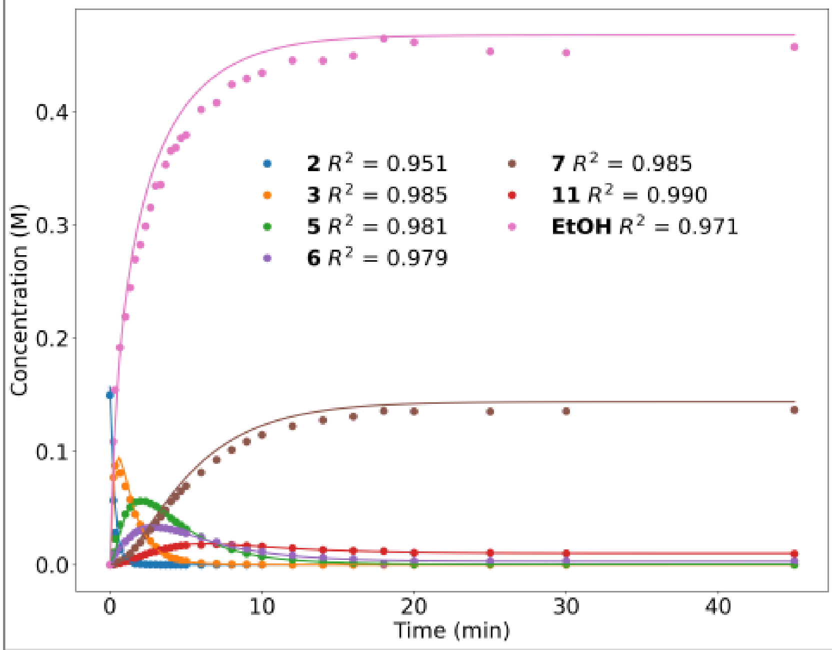
Figure S2.18 Reaction system obtained from kinetic modelling of NMR data with the theoretical **model III**.

2.7.7 Kinetic study using an excess of 100:1 ratio of 1/2 using off-line NMR

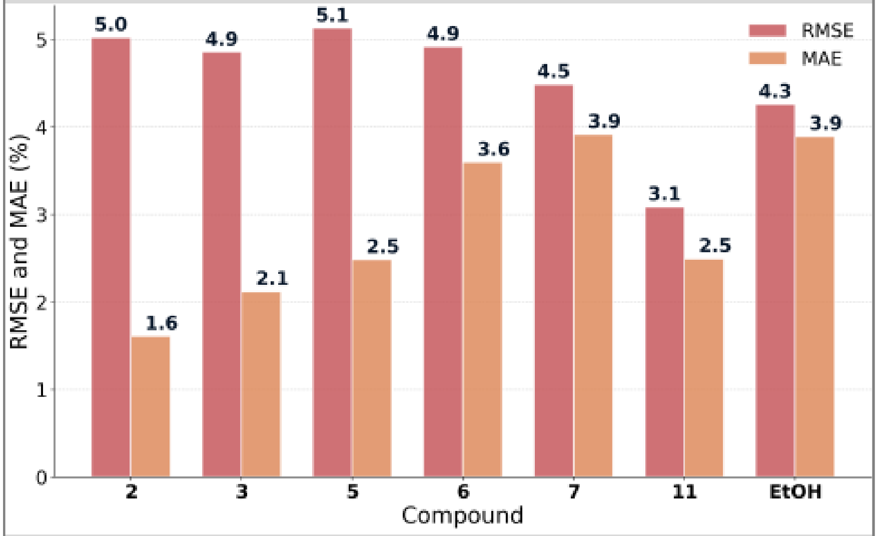
This kinetic study was performed to validate the occurrence of path b (Section S7.6). Using a large excess of **1** allowed to both shift the equilibrium toward the cyclic species **6** and **7**, and to ease kinetic modeling by considering pseudo first order conditions. The resulting kinetic model validated the hypothesis and competitive mechanisms toward **7**. Contrasting with **model III** in stochiometric amount, the rate constant toward the formation of **3** is very high, at 3.15 L mol^{-1}s^{-1}, logically attributed to the excess of **1**. However, reversible reactions driven by **EtOH** still occur, hampering the formation of thermodynamic products **7** and its tri-hydroxylated species **11** (characterization in Section 12).

2.7.7.1 MODEL USING A 1/100 RATIO OF 2/1

a. Profile of reaction for species 1, 2, 3, 5, 6, 7, 11 and EtOH



b. RMSE and MAE for species 1, 2, 3, 5, 6, 7, 11 and EtOH



c. Kinetic model for species 1, 2, 3, 5, 6, 7, 11 and EtOH

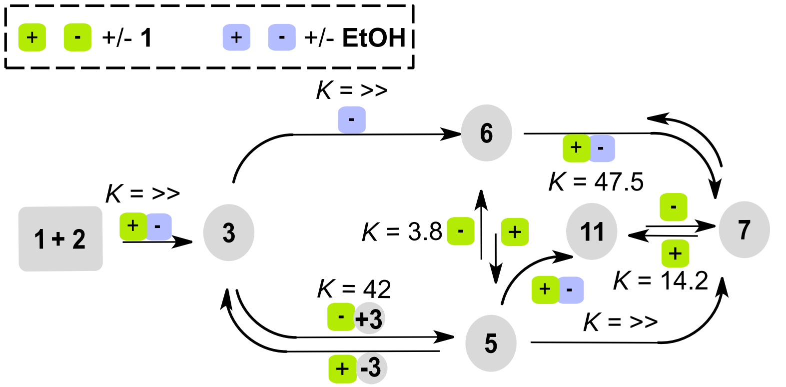


Figure S2.19 (a) Profile of concentrations of the various species **1**, **2**, **3**, **5**, **6**, **7** and **EtOH** over time; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.7.7.2 QUANTILE-QUANTILE PLOT

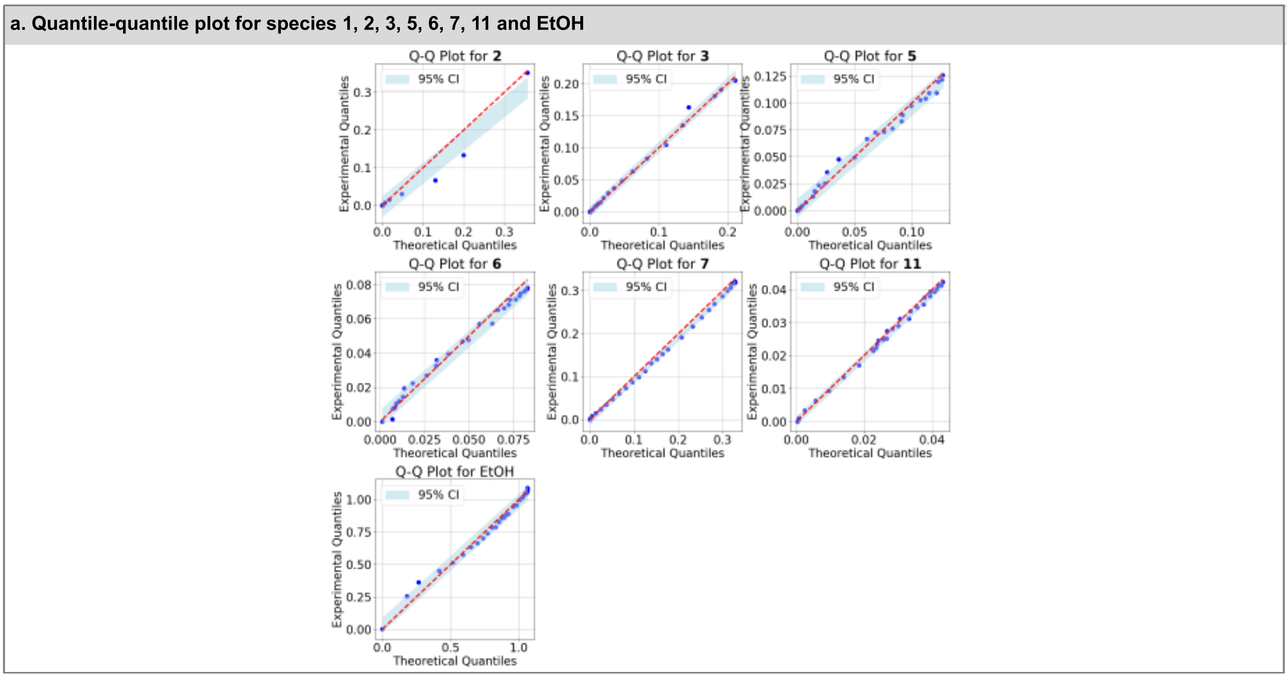


Figure S2.20 Quantile-quantile plots for model with 100:1 ratio of **1**/**2**.

2.7.7.3 SYSTEM OF DIFFERENTIAL EQUATIONS DESCRIBING THE KINETIC MODEL

This kinetic study was conducted with a large excess of **1**, allowing it to be considered constant throughout the reaction, achieving a pseudo-first-order reaction with respect to **1**.

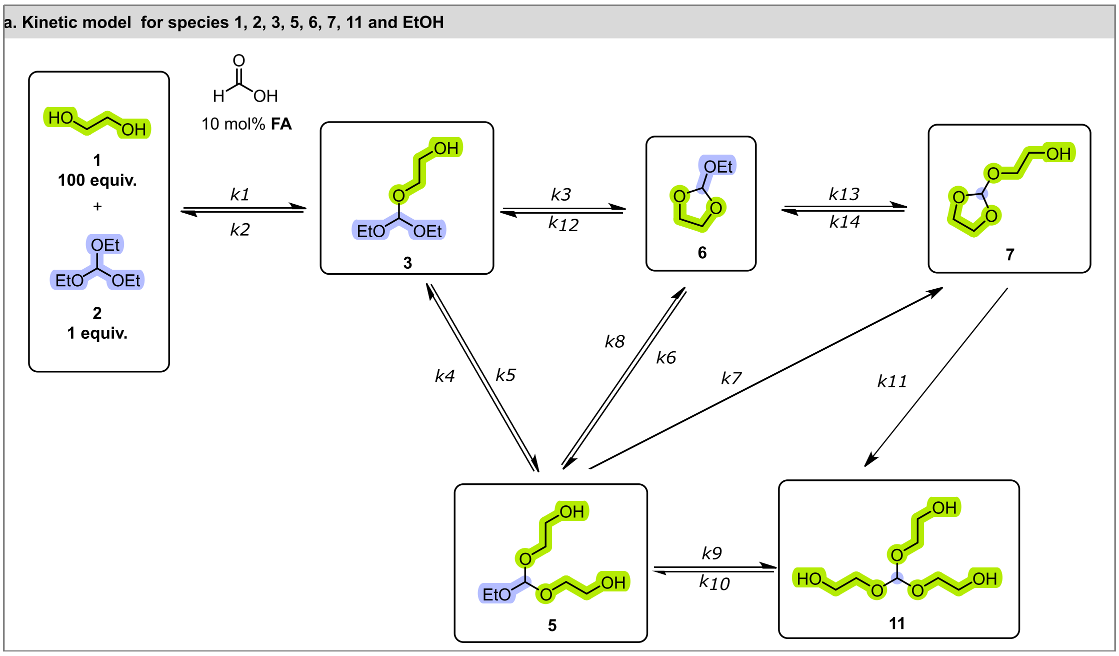


Figure S2.21 Representation of kinetic model including the rate constants.

$$\frac{dC[2]}{dt} = -\,k1 * [2] + k2 * [3] * [EtOH]$$

$$\frac{dC[3]}{dt} = \; k1 * [2] - k2 * [3] * [EtOH] - k3 * [3] - k4 * [3] + k5 * [3] - k4 * [5] * [EtOH]]$$

$$\frac{dC[5]}{dt} = \; k5 * [3] - k4 * [5] * [EtOH] + k6 * [6] - k7 * [5] - k8 * [5] + k10 * [11] * [EtOH] - k9 * [5]$$

$$\frac{dC[11]}{dt} = \; -k10 * [11] * [EtOH] + k9 * [5] + k11 * [7]$$

$$\frac{dC[6]}{dt} = \; -k12 * [6] * [EtOH] - k6 * [6] + k8 * [5] - k13 * [6] + k3 * [3] - k14 * [7] * [EtOH]$$

$$\frac{dC[7]}{dt} = k7 * [5] + k13 * [6] - k14 * [7] * [EtOH] - k11 * [7]$$

$$\frac{dC[EtOH]}{dt} = k1 * [2] - k2 * [3] * [EtOH] + k3 * [3] + k5 * [3] - k4 * [5] * [EtOH] + k7 * [5] - k12 * [6] * [EtOH] - k14 * [7] * [EtOH] + k13 * [6] + k9 * [5]$$

2.7.7.4 Model initialization and calculated concentrations and rate constants

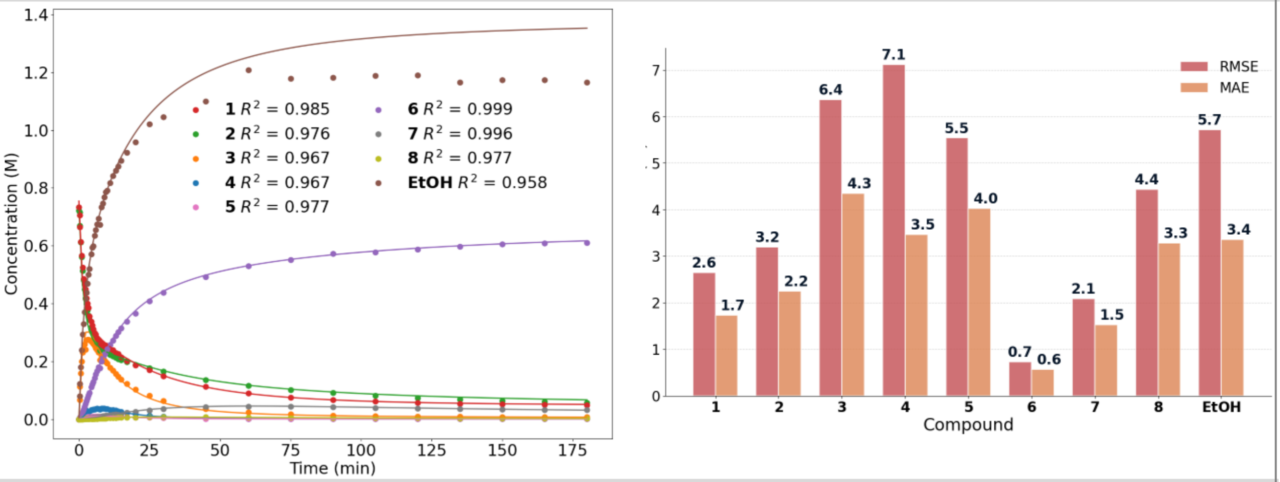
Table S2.2 Model initialization with calculated concentrations and rate constants for kinetic study using a 1:100 ratio of **2**/**1**.

Calculated rate constants		Model initialization		Optimized values of initialization		R²	RMSE	MAE
k_2	0.0458	c0_2	0.15	c0_2	0.156	0.95	0.00751	0.00239
k_1	3.23	c0_3	0	c0_3	0	0.985	0.00429	0.00185
k_3	0.292	c0_5	0	c0_5	6.92e-05	0.98	0.00294	0.00141
k_12	9.93e-06	c0_11	0	c0_11	0.000159	0.992	0.000493	0.000402
k_5	0.619	c0_6	0	c0_6	7.69e-05	0.979	0.00164	0.0012
k_4	0.0287	c0_7	0	c0_7	0.000262	0.988	0.00539	0.00467
k_7	0.137	c0_EtOH	0	c0_EtOH	9.99e-07	0.978	0.0175	0.0156
k_13	0.281							
k_8	0.0972							
k_6	0.0383							
k_14	0.0135							
k_9	0.122							
k_10	0.229							
k_11	0.0158							

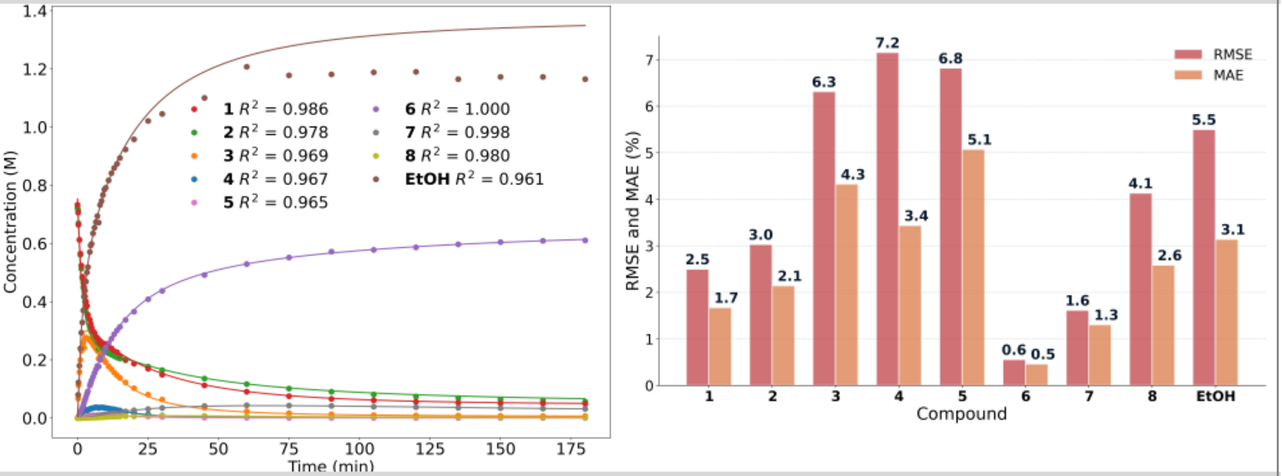
2.7.8 Development of model IV including species 1, 2, 3, 5, 6, 7, 8 and EtOH

2.7.8.1 Comparison of reaction profiles and their corresponding RMSE and MAE for path a.1, a.2 and b and their combinations

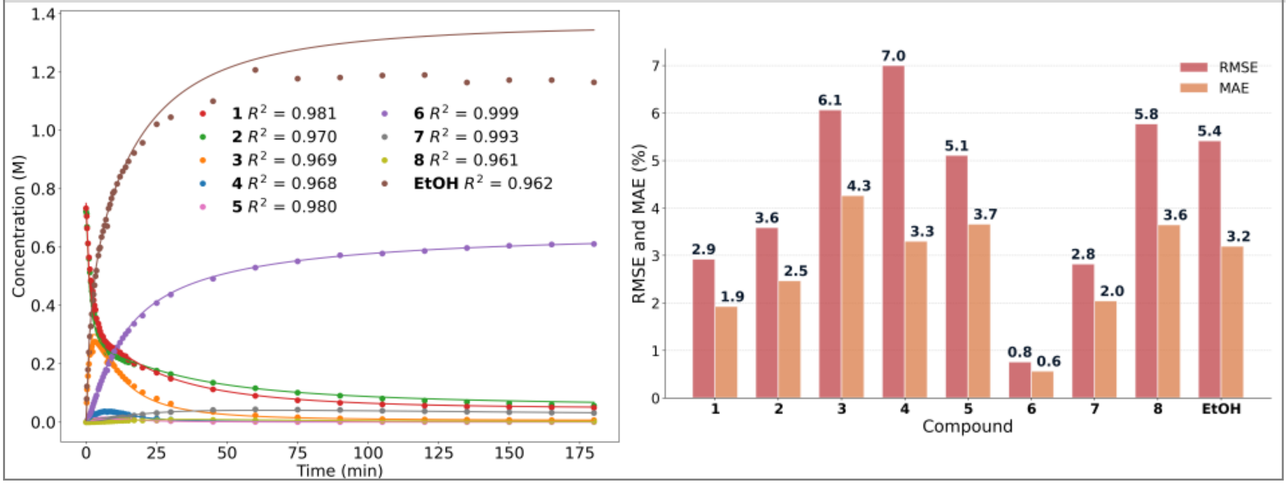
a. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7 ,8 and EtOH including path (a.1)



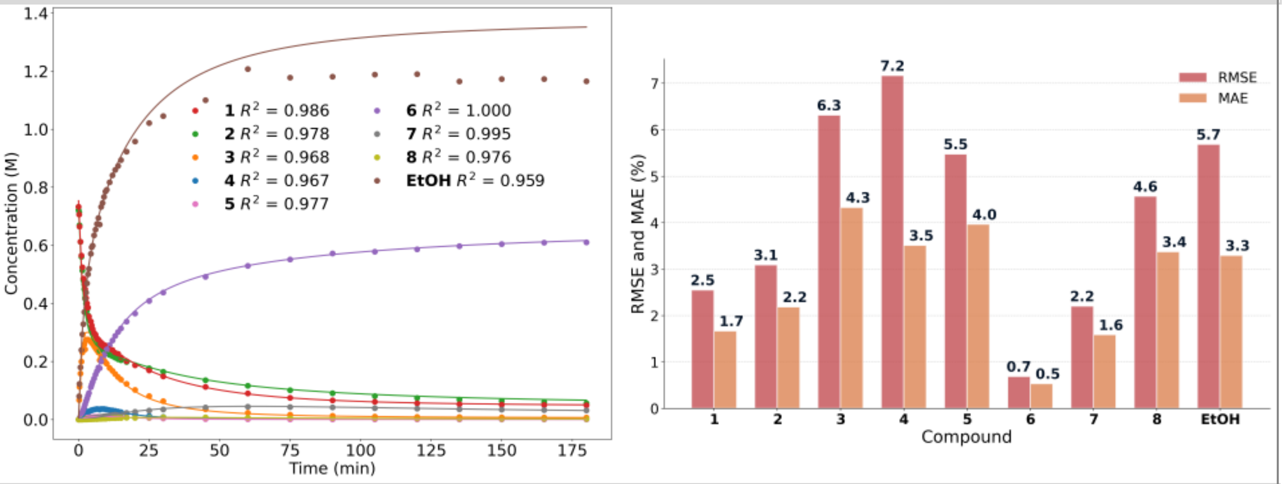
b. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7, 8 and EtOH including alternative path (a.2)



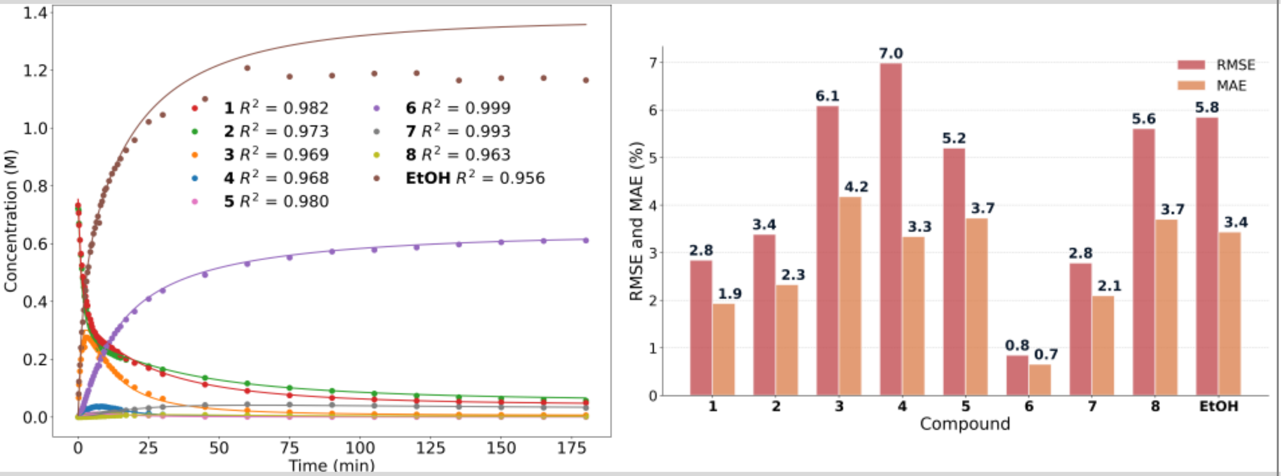
c. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7, 8 and EtOH including path (b)



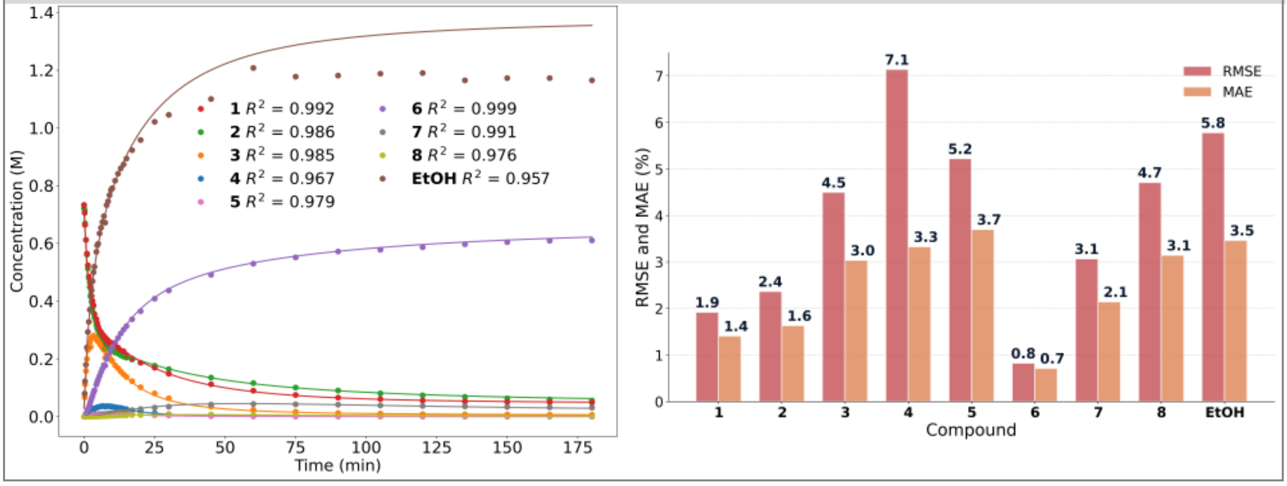
d. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7 ,8 and EtOH including path (a.1&b)



e. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7, 8 and EtOH including alternative path (a.2&b)



f. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7, 8 and EtOH including path (a.1&a.2)



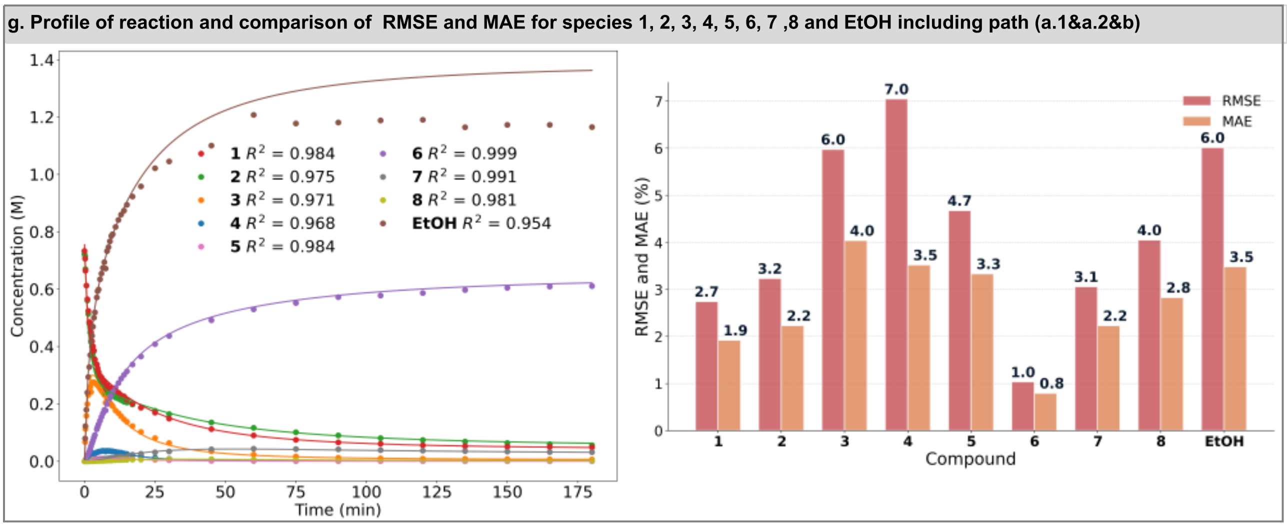
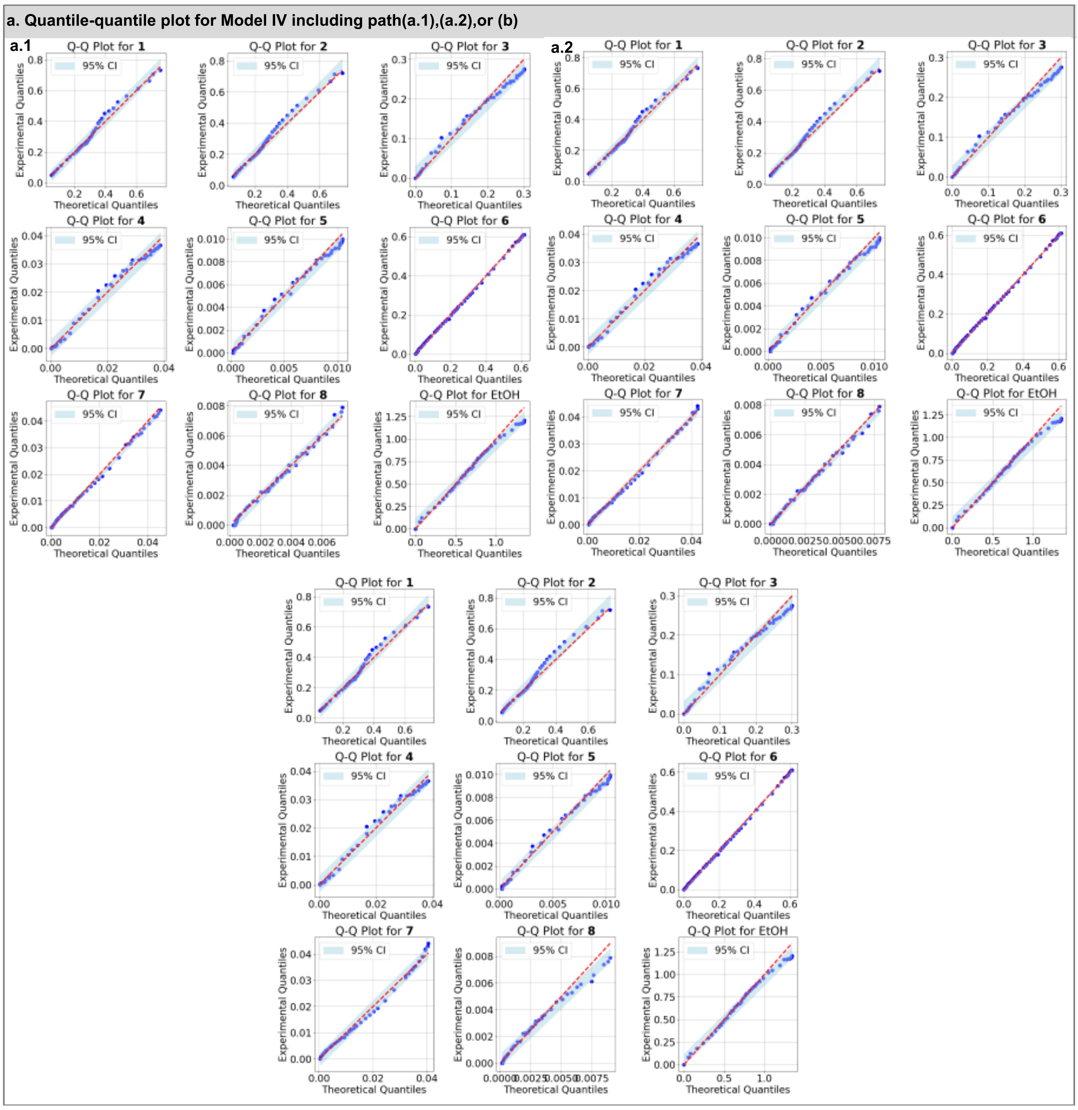
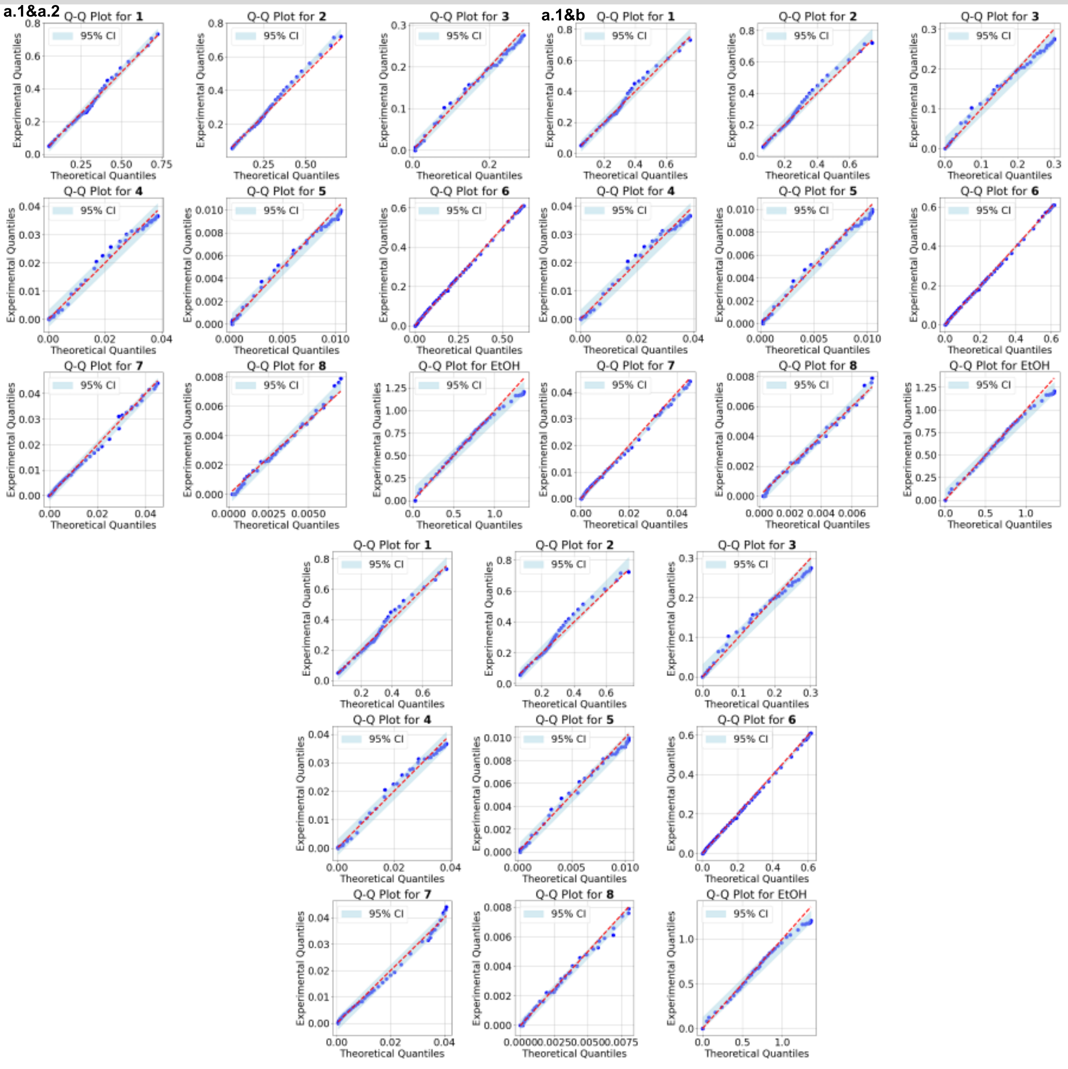

g. Profile of reaction and comparison of RMSE and MAE for species 1, 2, 3, 4, 5, 6, 7 ,8 and EtOH including path (a.1&a.2&b)

Figure S2.22 Profile of concentrations of the various species **1** to **8** and **EtOH** over time and RMSE and MAE obtained for paths (a.1), (a.2), (b), combination of (a.1&a.2), (a.1&b), (a.2&b), (a.1&a.2&b).

2.7.8.2 QUANTILE-QUANTILE PLOTS


a. Quantile-quantile plot for Model IV including path(a.1),(a.2),or (b)

b. Quantile-quantile plot for Model IV including path(a.1&a.2),(a.1&b)or (a.2&b)



c. Quantile-quantile plot for Model IV including path(a.1&a.2&b)

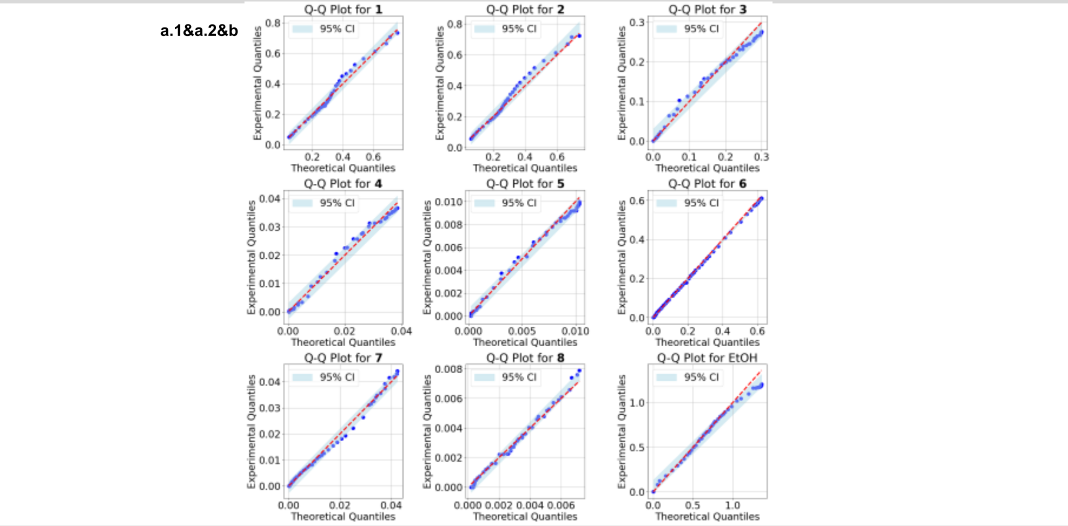


Figure S2.23 Quantile-quantile plots for paths (a.1), (a.2), (b), combination of (a.1&a.2), (a.1&b), (a.2&b), (a.1&a.2&b).

2.7.8.3 COMPARISON OF BIC AND AIC FOR THE NUMBER OF INTERCONNECTIONS BETWEEN SPECIES FOR THE VARIOUS MODELS

Path (a1&a2) was found to offer the best trade-off balance between model complexity and accuracy, as evidenced by the most negative value of BIC (Figure S2.24). AIC values give the same results, therefore supporting the occurrence of only path b. Further complexification of the model gave lower values of BIC and AIC compared to path b. These results suggest that **model IV** may not fully capture all reaction pathways, especially those involving compound **8**. The difficulty in incorporating compound **8** clearly highlights the challenge of modeling low-concentration species with minimal impact on the DCE system.

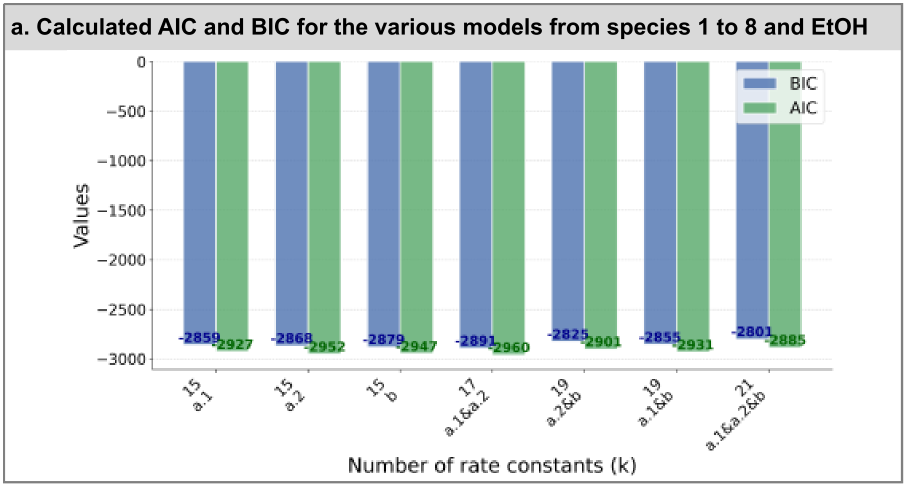

a. Calculated AIC and BIC for the various models from species 1 to 8 and EtOH

Figure S2.24 Calculated BIC and AIC values for paths (a.1), (a.2), (b), combination of (a.1&a.2), (a.1&b), (a.2&b), (a.1&a.2&b) including the number of rate constants as metric of model complexification.

2.7.8.4 FINAL MODEL OF 1 TO 8 AND ETOH INCLUDING PATH (B)

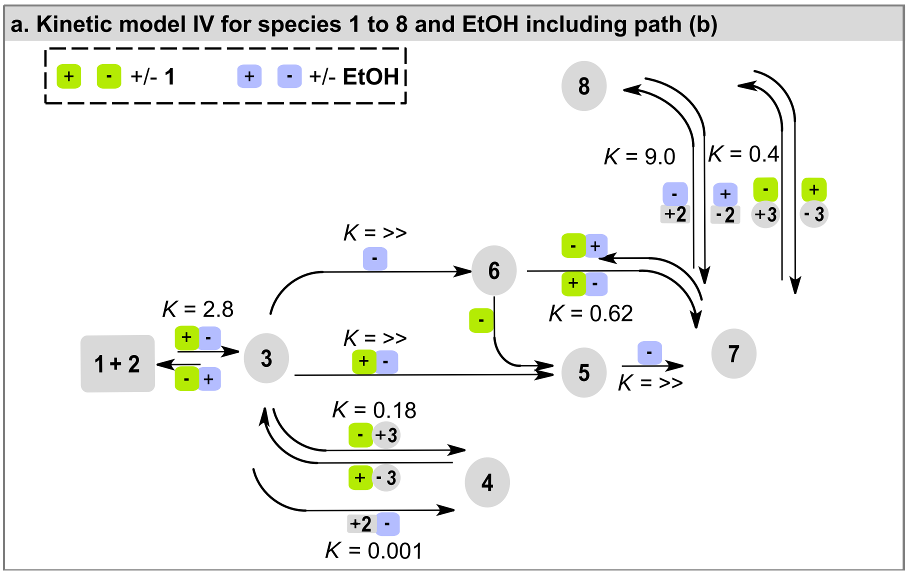

a. Kinetic model IV for species 1 to 8 and EtOH including path (b)

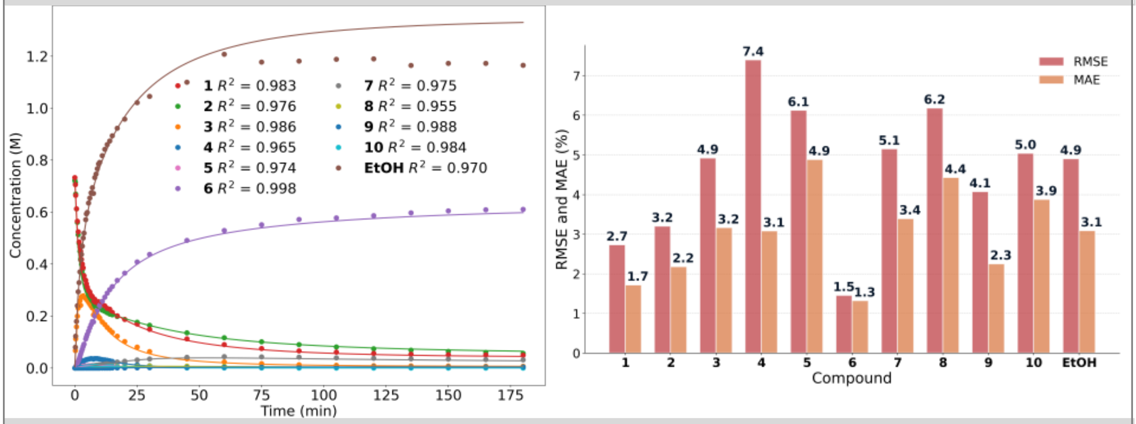
Figure S2.25 Representation of **model IV**.

2.7.9 Kinetic study of stochiometric amount of 1 and 2 using 10 mol% of FA in dry acetonitrile to form 3, 4, 5, 6, 7, 8 ,9 and 10

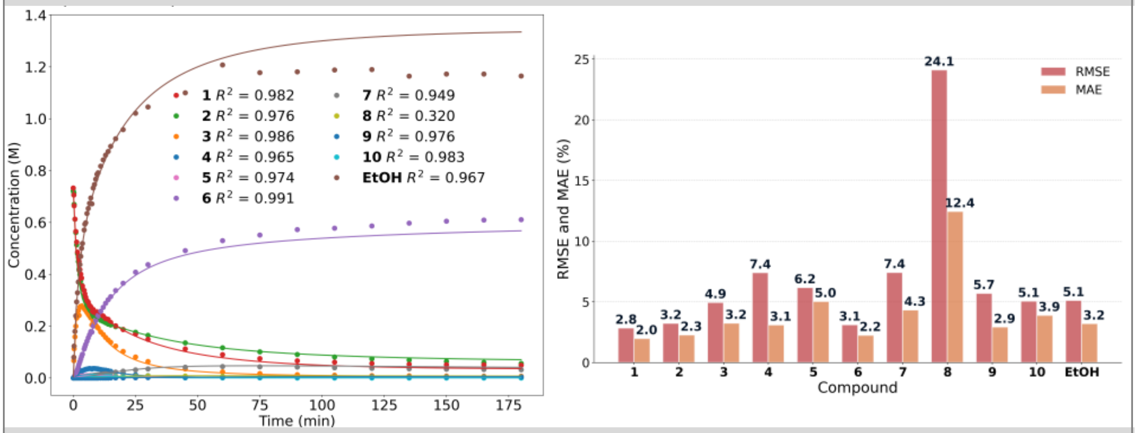
2.7.9.1 Comparison of reaction profiles and their corresponding RMSE and MAE for path a.1, a.2 and b and their combinations

Formation of **9** is hypothesized to occur via the nucleophilic substitution of **6** with **7** or with two molecules of **7**, whereas generation of **10** comes from the reaction of **5** with **2** or **3**. Due to the unconclusive results obtained for the formation of **8** in model **IV**, paths (a.1), (a.2) and (b) are all considered in **model V** (k = 21). Notably, the model featuring solely paths (a.1&a.2 – **model VI**, k = 22) exhibits a low accuracy for **8** with R^2 and MAE values of 0.33 and 24%. Interestingly, while path (b) provided the best fit for the 8-compound model (**model IV**), this is not the case for **model VIII**. Indeed, the addition of two more molecules to the system creates an even more interconnected network and reveals that contributions previously insignificant can become relevant in a more complex system.

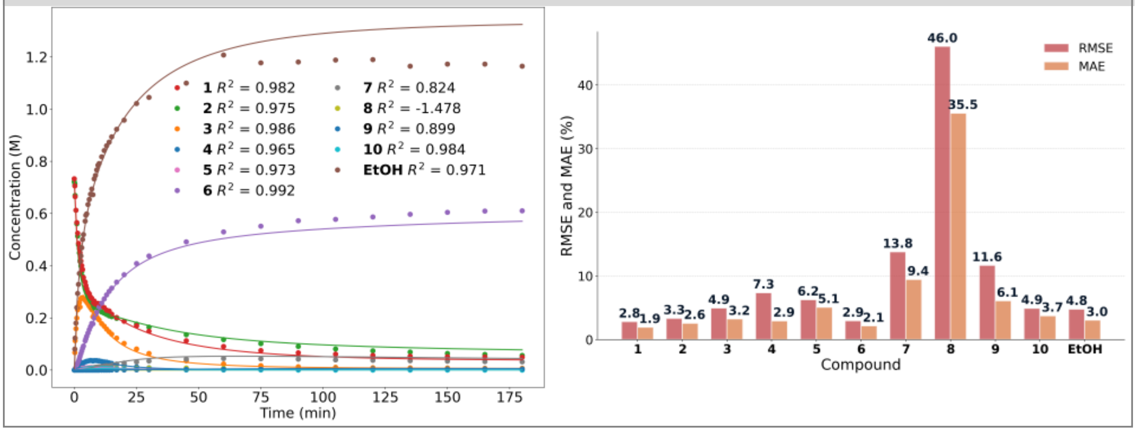
a. Profile of reaction and comparison of RMSE and MAE for species 1 to 10 and EtOH including path (a.1&a.2&b) - Model V



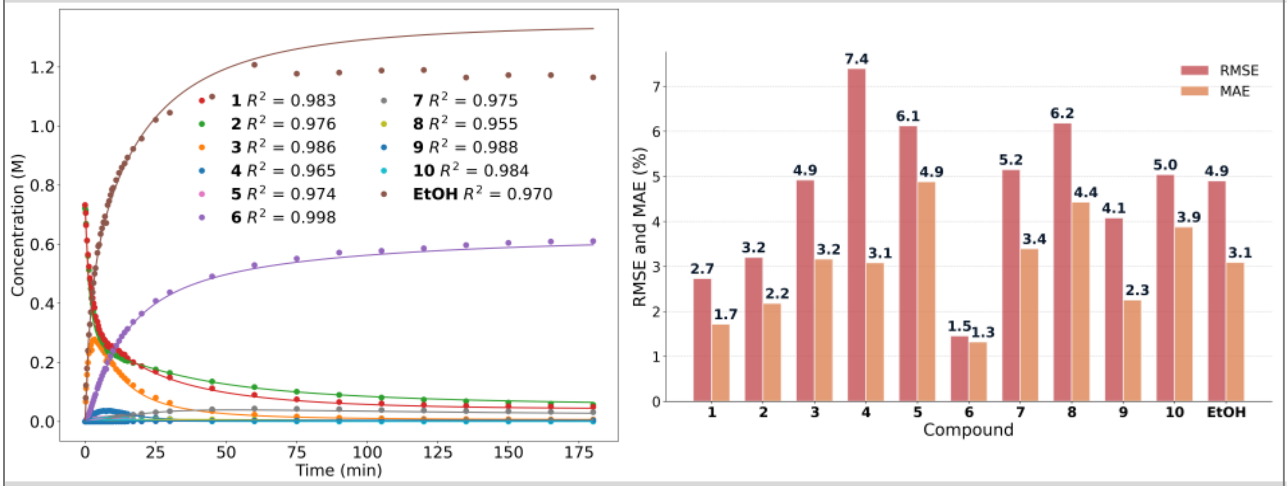
b. Profile of reaction and comparison of RMSE and MAE for species 1 to 10 and EtOH including path (a.1&a.2) - Model VI



c. Profile of reaction and comparison of RMSE and MAE for species 1 to 10 and EtOH including path (b) - Model VII



d. Profile of reaction and comparison of RMSE and MAE for species 1 to 10 and EtOH including Model VIII + formation of 9 from only 7



e. Profile of reaction and comparison of RMSE and MAE for species 1 to 10 and EtOH including Model V + formation of 9 from only 7

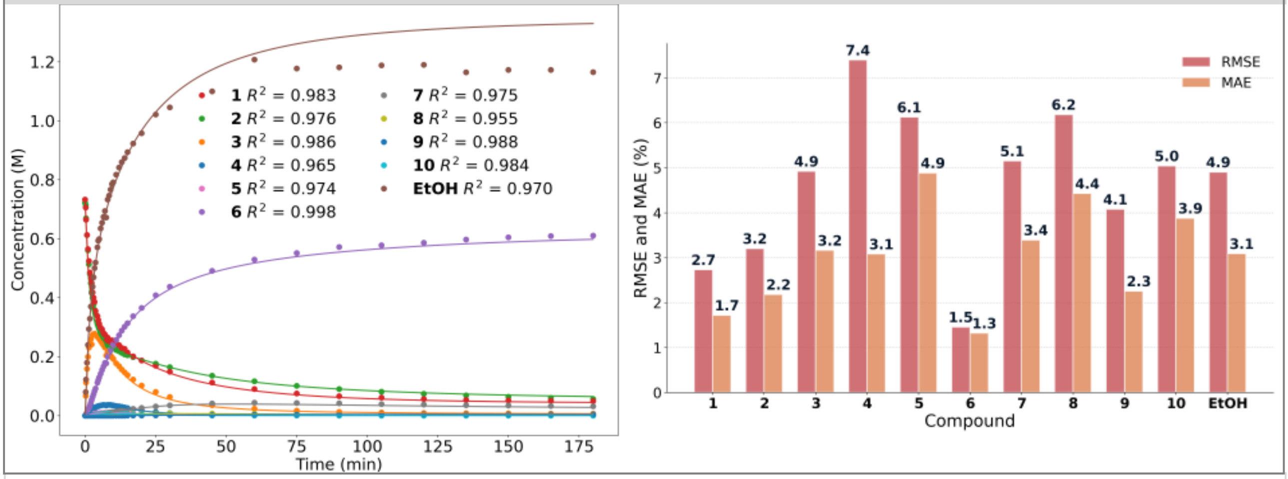


Figure S2.26 Profile of concentrations of the various species **1** to **10** and **EtOH** over time and RMSE and MAE obtained for **models V** to **X**.

Removal of unsignificant contribution from the **model IX** led to **model X**, therefore yielding exactly the same metrics of accuracy.

2.7.9.2 QUANTILE-QUANTILE PLOTS

a. Quantile-quantile plot for Model IV including path(a1&a2&b-a.1) or (a.1&a.2) or path (b - a.3)

b. Quantile-quantile plot for Model VIII (b.1), IX (b.2) and X (b.3)

Figure S2.27 Quantile-quantile plots for models **V** to **X**.

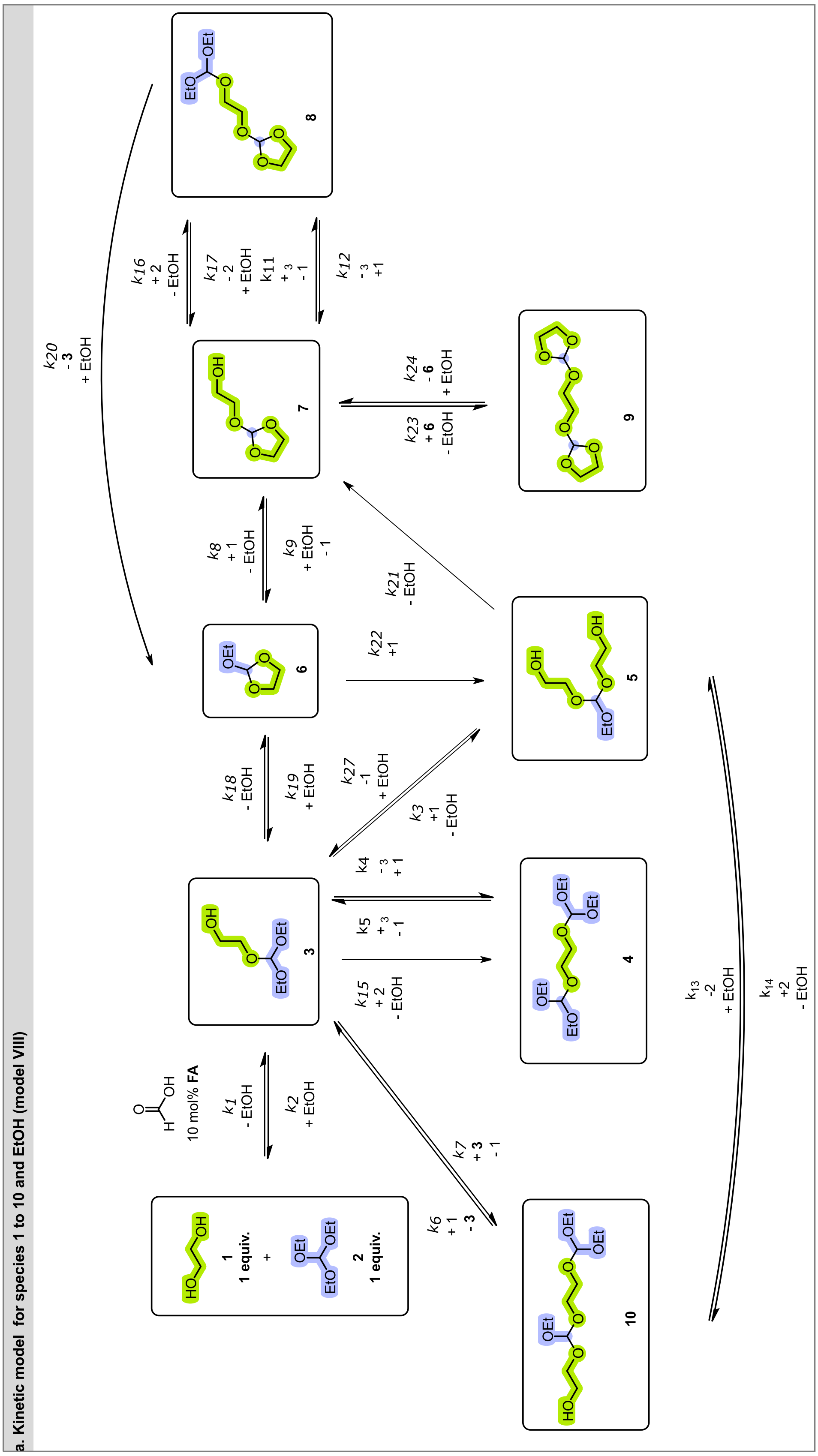


Figure S2.28 Representation of kinetic **model VIII** including the equilibrium constants.

$$\frac{d[C1]}{dt} = -k1*[1]*[2] + k2*[3]*[EtOH] - k3*[3]*[1] + k4*[3]*[3] - k5*[4]*[1] - k6*[10]*[1] + k7*[5]*[3] - k8*[6]*[1] + k9*[7]*[EtOH] + k11*[7]*[3] - k12*[8]*[1] + k27*[5]*[EtOH] + k25*[4]*[EtOH]$$

$$\frac{d[C2]}{dt} = -k1*[1]*[2] + k2*[3]*[EtOH] + k13*[10]*[EtOH] - k14*[5]*[2] + k15*[2]*[3] - k16*[2]*[7] + k17*[8]*[EtOH] + k25*[4]*[EtOH]$$

$$\frac{d[C3]}{dt} = k1*[1]*[2] - k2*[3]*[EtOH] - k5*[3]*[3] + k4*[4]*[1] - k15*[3]*[2] + k6*[10]*[1] - k7*[5]*[3] - k3*[3]*[1] - k11*[7]*[3] + k12*[8]*[1] - k18*[3] + k19*[6]*[EtOH] + k20*[8]*[EtOH] + k27*[5]*[EtOH]$$

$$\frac{d[C4]}{dt} = k4*[3]*[3] - k5*[4]*[1] + k15*[3]*[2] - k25*[4]*[EtOH]$$

$$\frac{d[C5]}{dt} = -k3*[3]*[1] + k13*[10]*[EtOH] - k14*[5]*[2] + k6*[10]*[1] - k7*[5]*[3] - k21*[5] + k22*[6]*[1]$$

$$\frac{d[C6]}{dt} = k18*[3] - k19*[6]*[EtOH] - k22*[6]*[1] - k8*[6]*[1] + k9*[7]*[EtOH] + k20*[8]*[EtOH] + k23*[6]*[7] - k24*[9]*[EtOH]$$

$$\frac{d[C7]}{dt} = -k23*[6]*[7] + k24*[9]*[EtOH] + k8*[6]*[1] - k9*[7]*[EtOH] - k11*[7]*[3] + k12*[8]*[1] - k16*[2]*[7] + k17*[8]*[EtOH] + k21*[5]$$

$$\frac{d[C8]}{dt} = k11*[7]*[3] - k12*[8]*[1] + k16*[2]*[7] - k17*[8]*[EtOH] - k20*[8]*[EtOH] - k27*[5]*[EtOH]$$

$$\frac{d[C9]}{dt} = k23*[6]*[7] - k24*[9]*[EtOH]$$

$$\frac{d[C10]}{dt} = -k13*[10]*[EtOH] + k14*[5]*[2] - k6*[10]*[1] + k7*[5]*[3] + k16*[2]*[7] - k17*[8]*[EtOH]$$

$$\frac{d[CEtOH]}{dt} = k23*[6]*[7] - k24*[9]*[EtOH] - k20*[8]*[EtOH] - k13*[10]*[EtOH] + k14*[5]*[2] + k1*[1]*[2] - k2*[3]*[EtOH] + k8*[6]*[1] - k9*[7]*[EtOH] + k18*[3] - k19*[6]*[EtOH] + k21*[5] + k16*[2]*[7] - k17*[8]*[EtOH] + k15*[2]*[3] + k3*[3]*[1] - k27*[5]*[EtOH] - k25*[4]*[EtOH]$$

2.7.9.4 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

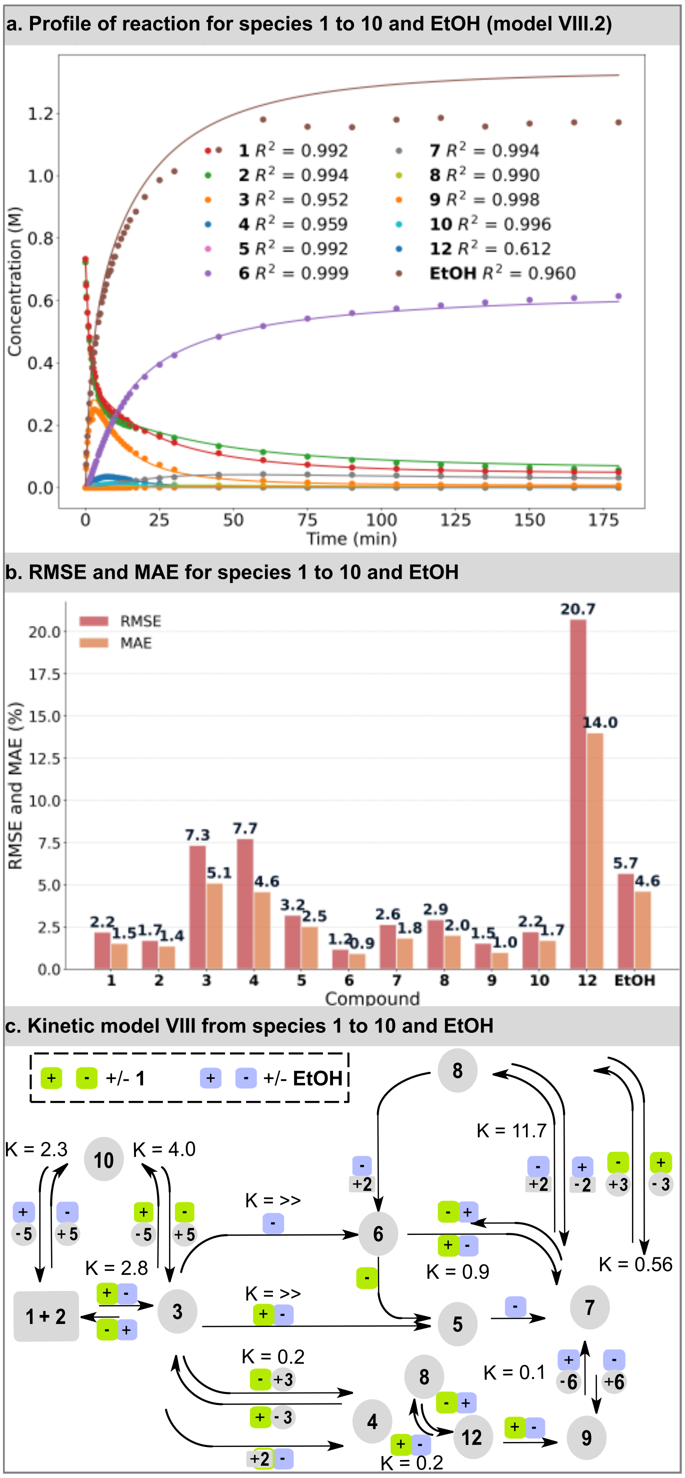
Table S2.3 Model initialization with calculated concentrations and rate constants for kinetic study using a 1:1 ratio of **2**/**1**.

Calculated rate constants		Model initialization		Optimized values of initialization		R²	RMSE	MAE
k_15	0.00947	c0_4	0	c0_4	0	0.965	0.002	0.001
k_2	0.213	c0_3	0	c0_3	0	0.986	0.013	0.008
k_1	0.609	c0_2	0.722	c0_2	0.722	0.976	0.023	0.015
k_18	0.101	c0_1	0.733	c0_1	0.733	0.983	0.02	0.012
k_6	0.974	c0_6	0	c0_6	0	0.998	0.008	0.008
k_3	0.0347	c0_EtOH	0	c0_EtOH	0	0.97	0.059	0.037
k_21	0.2	c0_5	0	c0_5	0	0.974	0.000	0.000487
k_19	0.000628	c0_7	0	c0_7	0	0.975	0.002	0.001
k_4	0.182	c0_8	0	c0_8	0	0.955	0.000	0.000
k_8	0.00667	c0_10	0	c0_10	0	0.984	0.001	0.000
k_7	0.524	c0_9	0	c0_9	0	0.988	0.001	0.001
k_6	0.227							
k_11	0.835							
k_12	2							
k_22	0.0011							
k_16	0.121							
k_17	0.00524							
k_13	0.157							
k_14	0.12							
k_23	0.00731							
k_9	0.00459							
k_24	0.0271							
k_20	0.0401							
K_27	0.00001							

2.7.10 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND 2 USING 10 MOL% OF FA IN DRY ACETONITRILE TO FORM 3, 4, 5, 6, 7, 8 ,9, 10 AND 12 (MODEL VIII.2)

To confirm that **model VIII** represented an optimal balance between data fit and model parsimony, **model VIII.2** was developed by integrating compound **12** (Section S7.X in Supporting information). Although the improvement of ΔAIC/BIC was higher to 10, the change in the slope at **model VIII** indicates an inflexion point where additional complexity yields proportionally smaller improvements in accuracy, of approximatively 20 % less, compared to previous complexification (**model I** to **VIII**).

2.7.10.1 KINETIC MODEL


a. Profile of reaction for species 1 to 10 and EtOH (model VIII.2)

b. RMSE and MAE for species 1 to 10 and EtOH

c. Kinetic model VIII from species 1 to 10 and EtOH

Figure S2.29 Representation of kinetic **model VIII.2** including the equilibrium constants.

Errors observant for product **12** due to the absence of signal assignment within the NMR kinetic.

2.7.10.2QUANTILE-QUANTILE PLOTS

a. Quantile-quantile plot for species 1, 2, 3, 5, 6, 7, 8, 9, 10, 12 and EtOH

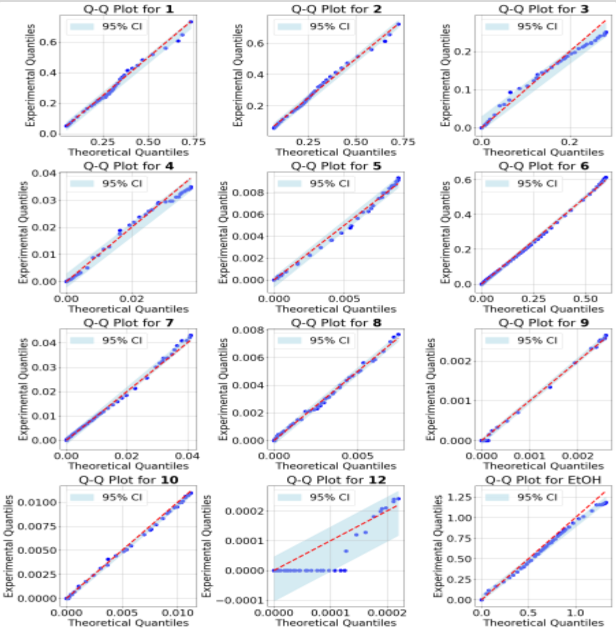


Figure S2.30 Quantile-quantile plots for model **VIII.2**.

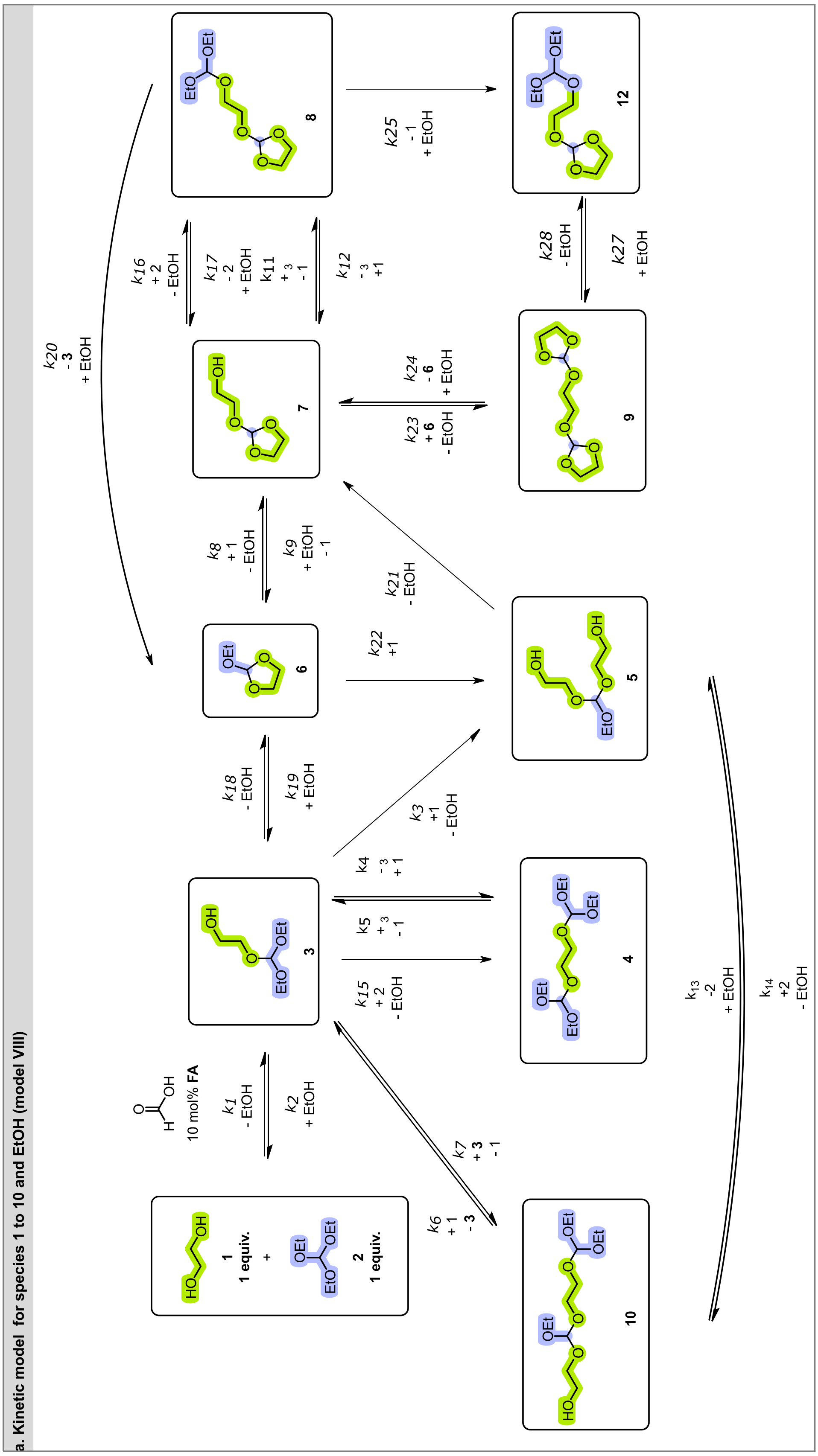


Figure S2.31 Representation of kinetic **model VIII.2** including the equilibrium constants.

2.7.11 KINETIC STUDY IN NEAT CONDITIONS

2.7.11.1 REACTION PROFILE AND THEIR CORRESPONDING RMSE AND MAE WITH ADDITION OF INTERCONNECTION BETWEEN 4+1 TO 10

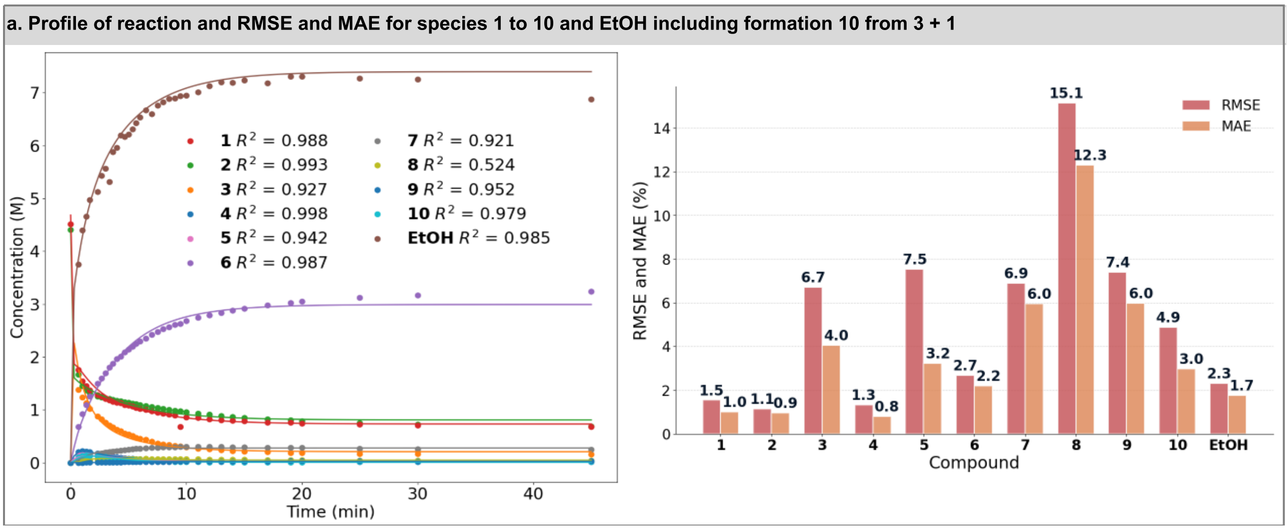

a. Profile of reaction and RMSE and MAE for species 1 to 10 and EtOH including formation 10 from 3 + 1

Figure S2.32 Alternative profile of concentration of species **1** to **10** and **EtOH** over time and RMSE and MAE under neat conditions.

2.7.11.2 QUANTILE-QUANTILE PLOTS

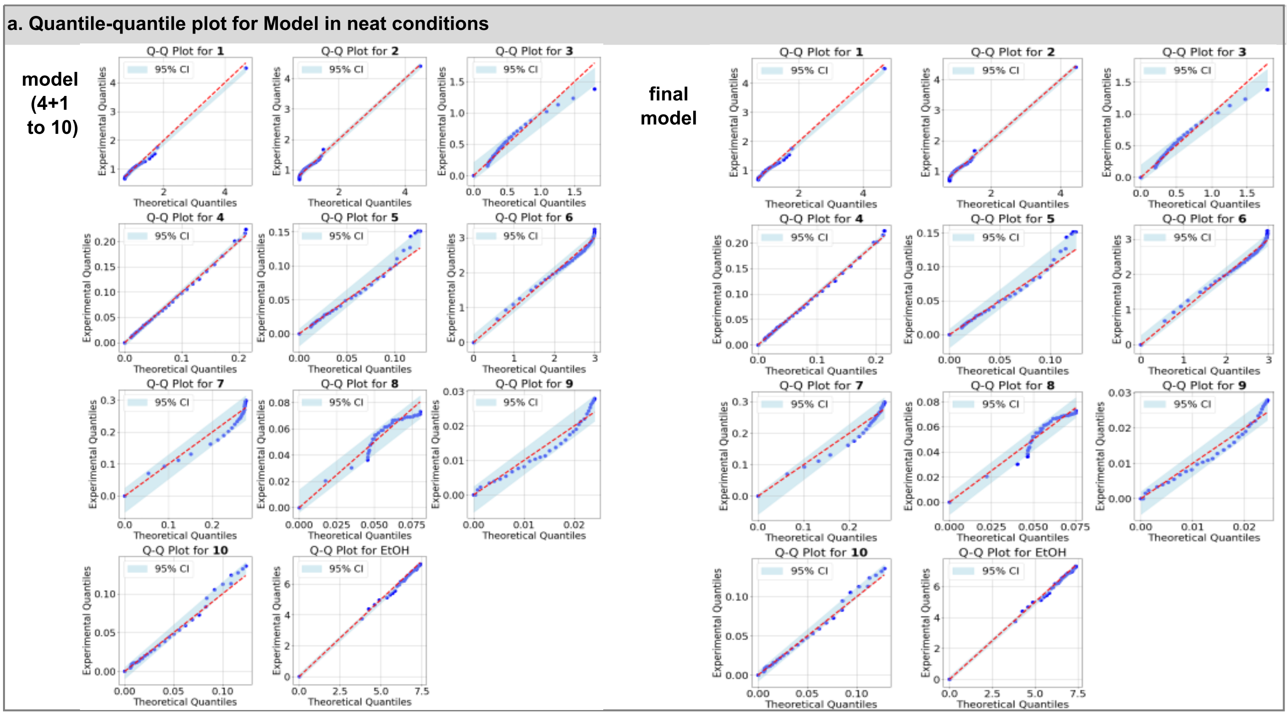
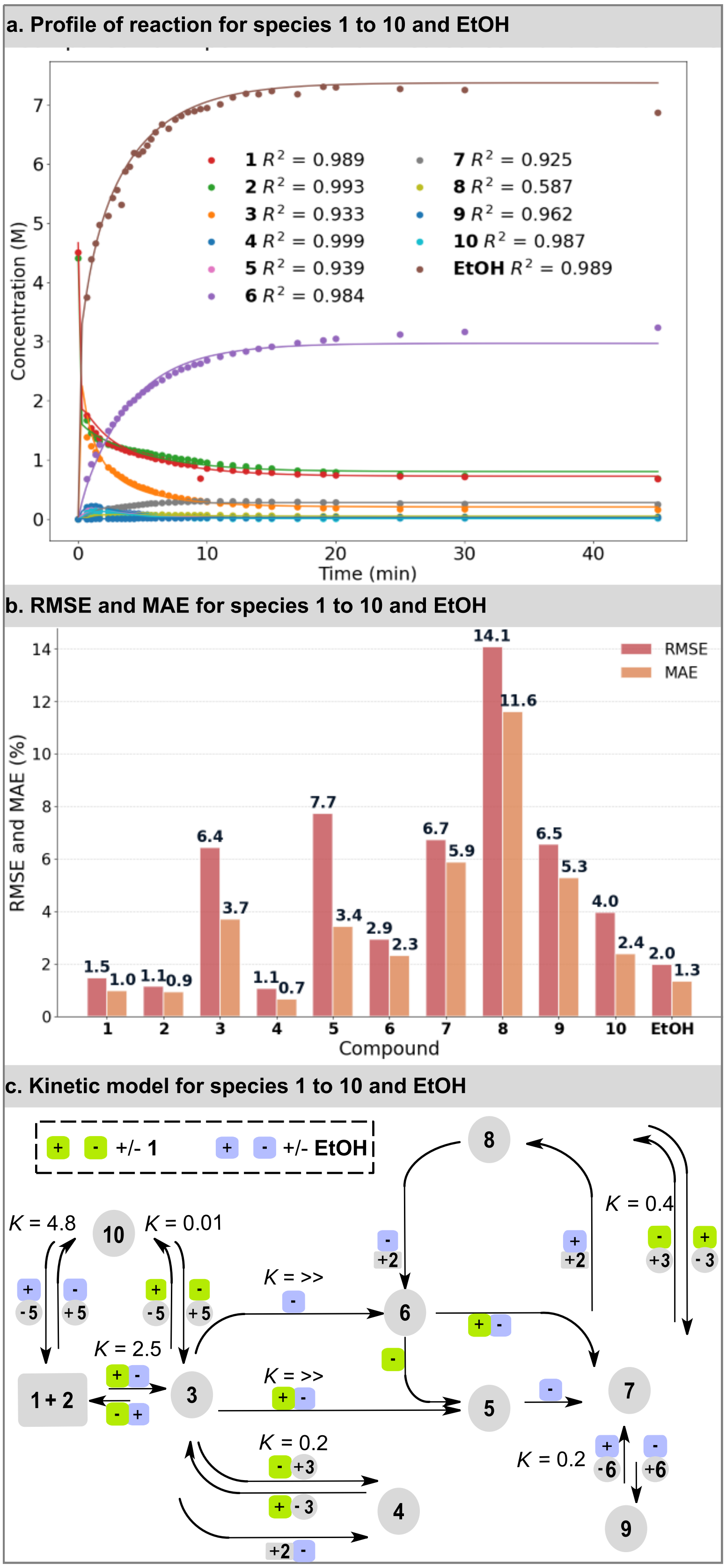

a. Quantile-quantile plot for Model in neat conditions

Figure S2.33. Quantile-quantile plots for **model** using neat conditions.

2.7.11.3 FINAL MODEL

This model is obtained from the treatment of the kinetic data with **model VIII**.



a. Profile of reaction for species 1 to 10 and EtOH

b. RMSE and MAE for species 1 to 10 and EtOH

c. Kinetic model for species 1 to 10 and EtOH

Figure S2.34 (a) Profile of concentrations of the various species **1** to **10** and **EtOH** over time; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.7.11.4 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

Table S2.4 Model initialization and calculated concentrations and rate constants for kinetic study using a 1:1 ratio of **2**/**1**.

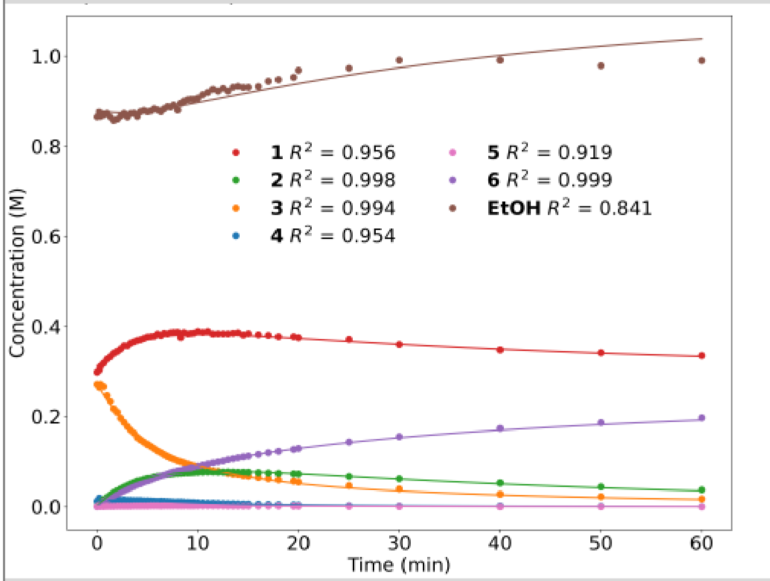
Calculated rate constants		Model initialization		Optimized values of initialization		R²	RMSE	MAE
k_15	0.00161	c0_4	0	c0_4	0	0.999	0.002	0.001
k_2	6.99	c0_3	0	c0_3	0	0.933	0.088	0.051
k_1	17.5	c0_2	4.51	c0_2	4.45	0.993	0.05	0.041
k_18	0.409	c0_1	4.51	c0_1	4.64	0.989	0.066	0.044
k_6	2.15	c0_6	0	c0_6	0	0.984	0.095	0.074
k_3	0.0886	c0_		c0_		0.989	0.144	0.098
k_21	1.16	EtOH	0	EtOH	0	0.939	0.011	0.005
k_19	0.00438	c0_5	0	c0_5	0	0.925	0.020	0.017
k_4	0.0806	c0_7	0	c0_7	0	0.587	0.010	0.008
k_8	0.134	c0_8	0	c0_8	0	0.987	0.005	0.003
k_7	0.444	c0_10	0	c0_10	0	0.962	0.001	0.001
k_11	0.00256	c0_9	0	c0_9	0			
	20.0058							
k_12	5							
k_22	0.0005							
k_16	1.37							
	0.00000							
k_17	1							
k_13	0.00589							
k_14	0.506							
k_23	0.0147							
k_9	0.00001							
k_24	0.0271							
k_20	0.0669							
K_20	0.884							
K_27	0.00001							

2.7.12 KINETIC STUDY STARTING FROM SPECIES 3 AND AN EXCESS OF ETOH

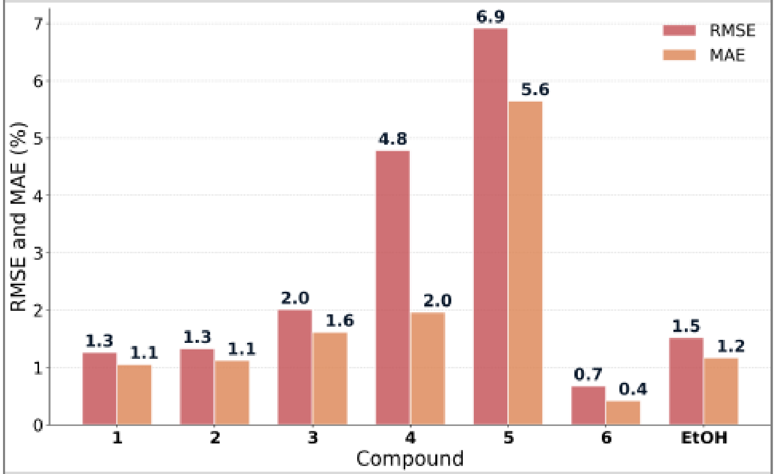
2.7.12.1 FINAL MODEL

Due to the low concentration of species **7**, **8**, **9** and **10**, it was not possible to determine an accurate model of the system. Furthermore, some minor overlapping signals were observed with the triplet of EtOH, resulting in biased integration. As a result, the **model** only describes the DCE system up to compound **6**. However, the remaining products were accurately described (R^2 = 0.91 – 0.99), highlighting the robustness of **model VIII** when applied to different systems starting with distinct reagents.

a. Profile of reaction for species 1 to 6 and EtOH



b. RMSE and MAE for species 1 to 6 and EtOH



c. Kinetic of model for species 1 to 6 and EtOH

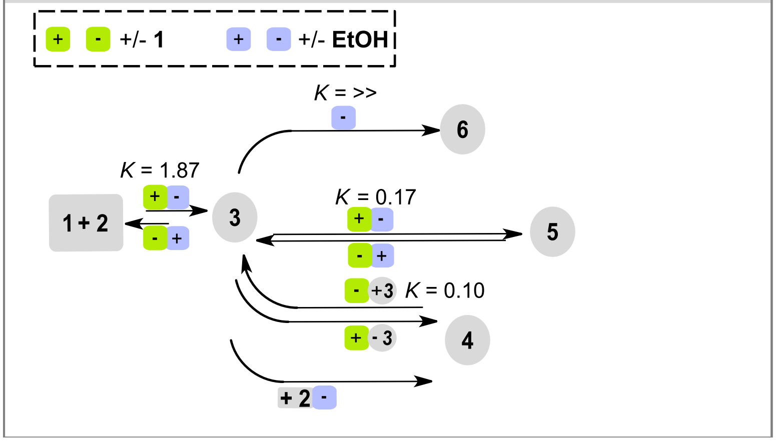


Figure S2.35 (a) Profile of concentrations of the various species **1** to **7** and **EtOH** over time; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.7.12.2 Quantile-quantile plot

a. Quantile-quantile plot for Model with 3 as reagent

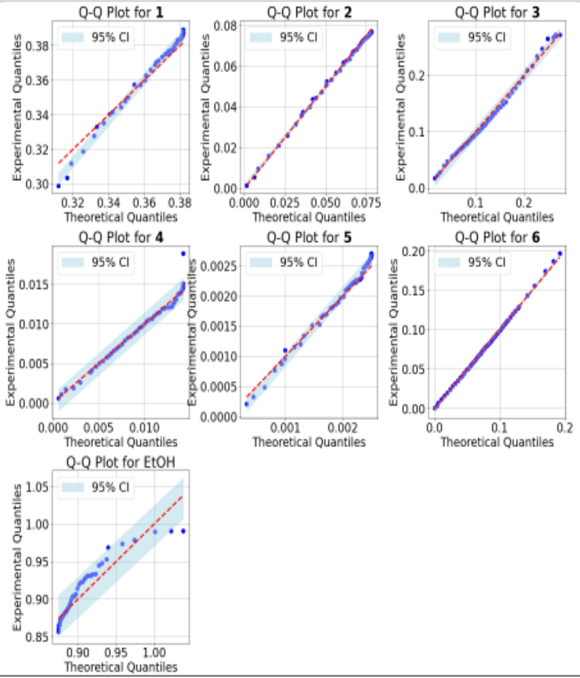


Figure S2.36 Quantile-quantile plots for **model** using **3** as reagent.

2.7.12.3 System of differential equations describing the kinetic model

a. Kinetic model for species 1 to 6 and EtOH

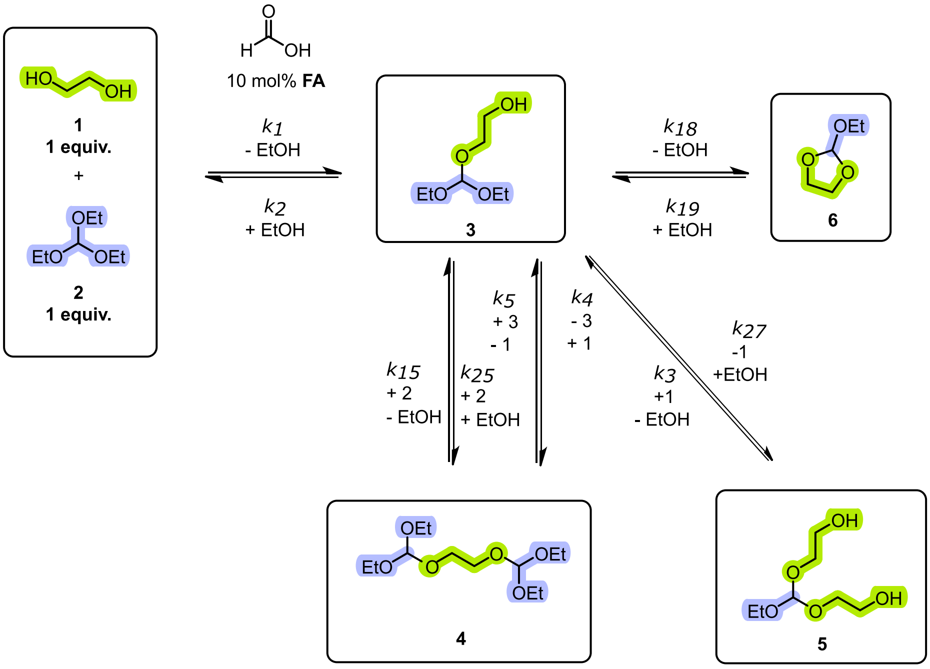


Figure S2.37 Representation of kinetic model starting from intermediate **3** including the rate constants.

$$\frac{d[C1]}{dt} = -\,k5 * [4] * [1] - k1 * [1] * [2] + \ k4 * [3] * [3] + k3 * [5] * [EtOH] - k27 - [3] * [1]$$

$$\frac{d[C2]}{dt} = -k1 * [1] * [2] + \ k15 * [4] * [EtOH] - \ k25 * [3] * [2]$$

$$\frac{d[C3]}{dt} = k1 * [1] * [2] - k2 * [3] * [EtOH] - k25 * [3] * [2] \ - k27 * [3] * [1] + k3 * [5] * [EtOH] - k18 * [3] \\ + k19 * [6] * [EtOH] + \ k15 * [4] * [EtOH] + \ k5 * [4] * [1] - k4 * [3] * [3]$$

$$\frac{d[C4]}{dt} = +k25 * [3] * [2] - \ k15 * [4] * [EtOH] + \ k5 * [3] * [3] - \ k4 * [4] * [1]$$

$$\frac{d[C5]}{dt} = -k27 * [3] * [1] - k3 * [5] * [EtOH]$$

$$\frac{d[C6]}{dt} = k18 * [3] - k19 * [6] * [EtOH]$$

$$\frac{d[CEtOH]}{dt} = \ k25 * [3] * [2] - \ k15 * [4] * [EtOH] + k1 * [1] * [2] + k18 * [3] - k19 * [6] * [EtOH] - k3 * [5] \\ * [EtOH] + k27 * [3] * [1]$$

2.7.12.4 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

Table S2.5 Model initialization and calculated concentrations and rate constants for kinetic study using a compound **3**.

Calculated rate constants		Model initialization		Optimized values of initialization		R^2	RMSE	MAE
k_25	0.238	c0_4	0.0131	c0_4	0	0.954	0.0009	0.00037
k_2	0.0941	c0_3	0.273	c0_3	0.272	0.994	0.00546	0.0044
k_1	0.174	c0_2	0.00147	c0_2	0	0.998	0.00102	0.00086
k_18	0.0576	c0_1	0.312	c0_1	0.299	0.956	0.0049	0.0041
k_5	0.867	c0_6	0.00066	c0_6	0	0.999	0.00133	0.00083
k_3	0.00793	c0_ EtOH	0.881	c0_ EtOH	0.865	0.841	0.0145	0.116
k_27	0.152					0.919	0.00019	0.00015
k_19	0.000351	c0_5	0.00078	c0_5	0			
k_4	0.0604							

2.7.13 KINETIC STUDY STARTING FROM SPECIES 4 AND AN EXCESS OF ETOH

2.7.13.1 FINAL MODEL

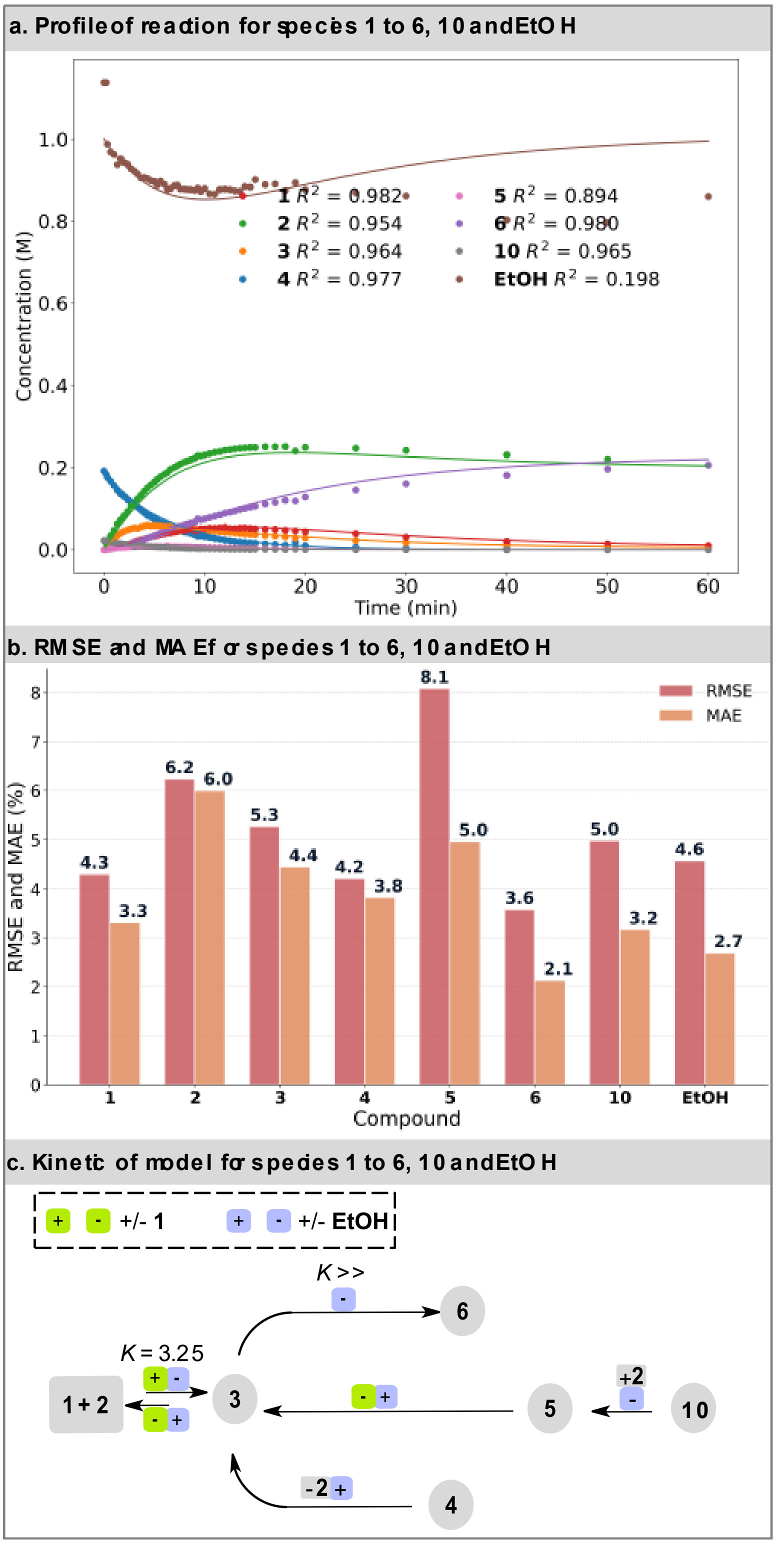


Figure S2.38 (a) Profile of concentrations of the various species **1** to **6**, **10** and **EtOH** over time; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.7.13.2 QUANTILE-QUANTILE PLOT

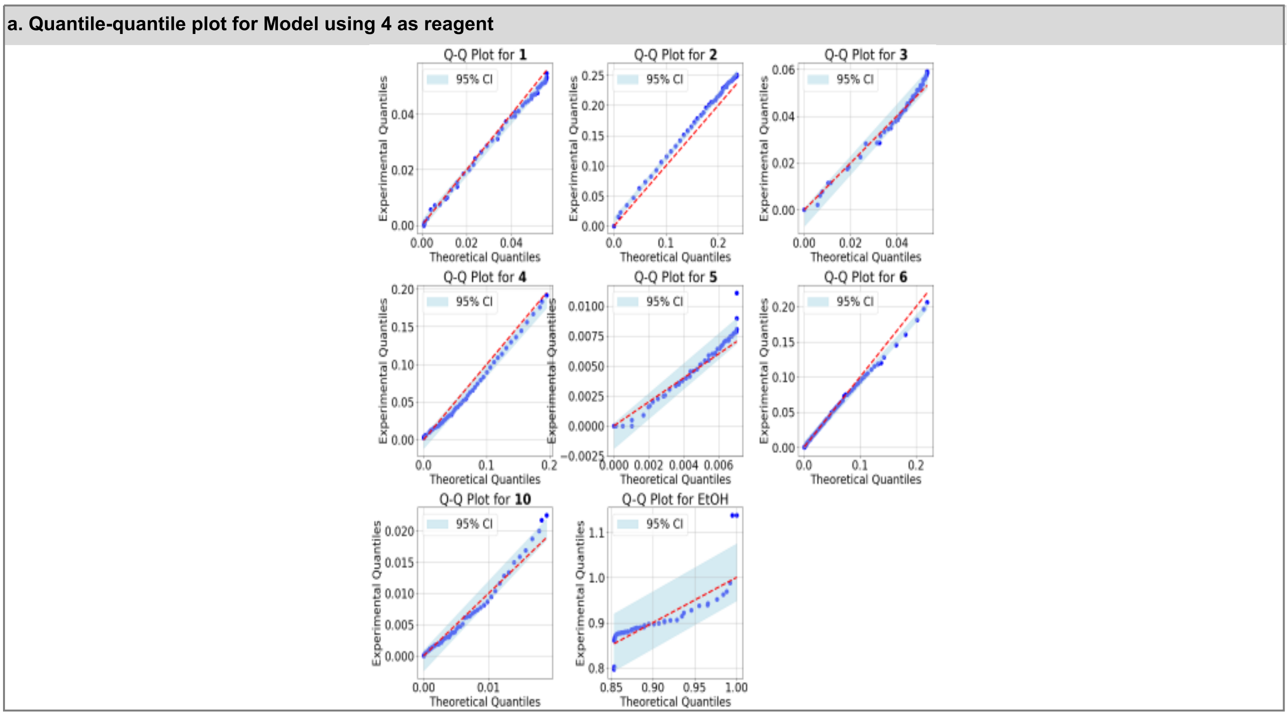


Figure S2.39 Quantile-quantile plots for **model** using 4 as a reagent.

2.7.13.3 System of differential equations describing the kinetic model

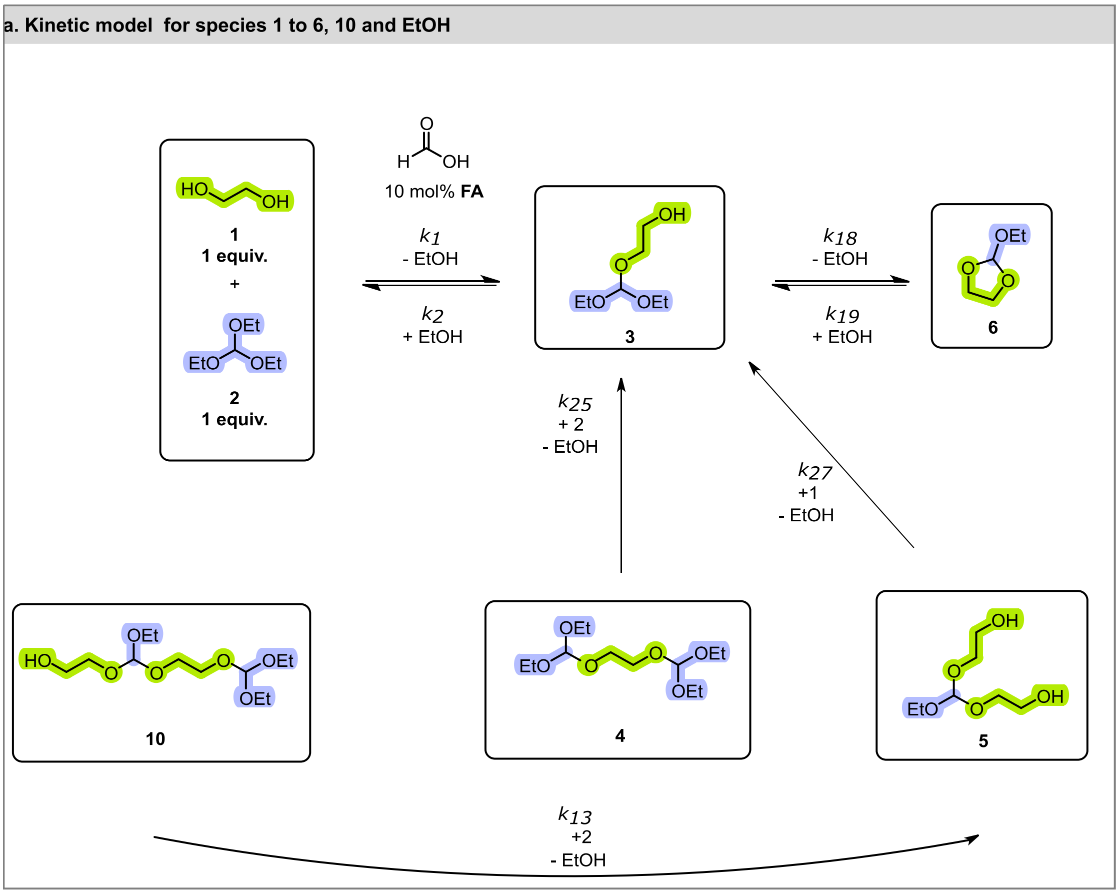


Figure S2.40 Representation of kinetic **model** using **4** as reagent including the rate constants.

$$\frac{d[C1]}{dt} - k1 * [1] * [2] + k2 * [3] * [EtOH] + \ k13 * [10] * [EtOH] + k27 * [5] * [EtOH]$$

$$\frac{d[C2]}{dt} = -k1 * [1] * [2] + k2 * [3] * [EtOH] + \ k25 * [4] * [EtOH] + k13\$[10] * [EtOH]$$

$$\frac{d[C3]}{dt} = k1 * [1] * [2] - k2 * [3] * [EtOH] \ + k27 * [5] * [EtOH] - k18 * [3] + k19 * [6] * [EtOH] + \ k25 * [4] * [EtOH]$$

$$\frac{d[C4]}{dt} = - k25 * [4] * [EtOH]$$

$$\frac{d[C5]}{dt} - k27 * [5] * [EtOH]$$

$$\frac{d[C6]}{dt} = k18 * [3] - k19 * [6] * [EtOH]$$

$$\frac{d[CEtOH]}{dt} = - k25 * [4] * [EtOH] + k1 * [1] * [2] - k2 * [3] * [EtOH] + k18 * [3] - k19 * [6] * [EtOH] - \ k13 * [10] * [EtOH] - k27 * [5] * [EtOH]$$

2.7.13.4 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

Table S2.6 Model initialization and calculated concentrations and rate constants for kinetic study using a compound **4**.

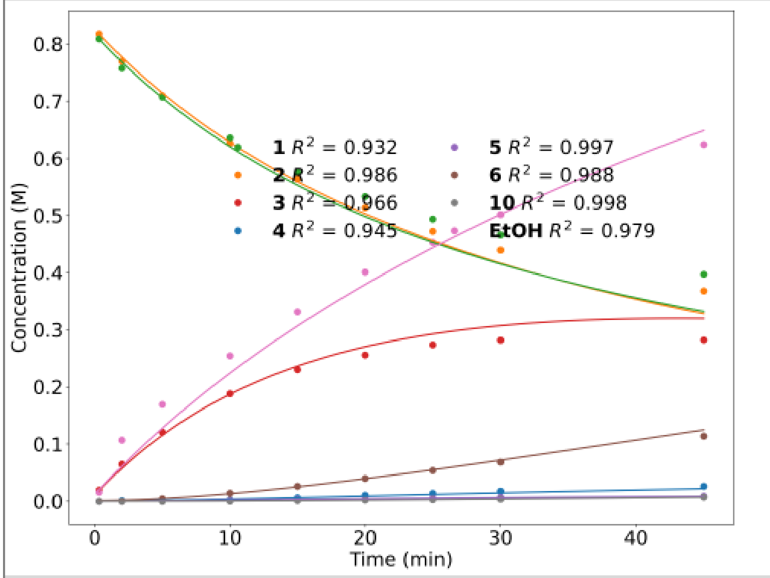
Calculated rate constants		Model initialization		Optimized values of initialization		R^2	RMSE	MAE
k_25	0.177	c0_4	0.195	c0_4	0.195	0.977	0.00808	0.00733
k_2	0.181	c0_3	0	c0_3	0	0.964	0.00312	0.00263
k_1	0.59		0.00076		0.00076	0.954	0.0156	0.0151
k_18	0.17	c0_2	7	c0_2	7	0.982	0.00235	0.00181
k_27	0.206	c0_1	1.03e-05	c0_1	1.03e-05	0.98	0.00736	0.00438
k_19	0.00215	c0_6	0.00072	c0_6	0.00072	0.198	0.052	0.0306
k_13	0.19	c0_ EtOH	1.15	c0_ EtOH	1.15	0.894	0.00089	0.00055
			0.00035		0.00035			0.00071
		c0_5	3	c0_5	3			
		c0_10	0.0197	c0_10	0.0197			

2.8 SOLVENT SCREENING

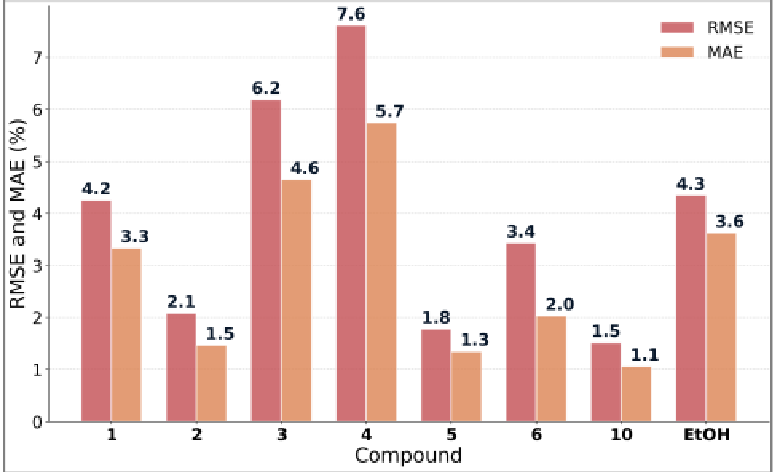
2.8.1 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND 2 USING 10 MOL% OF FA IN DRY DIMETHYL SULFOXIDE

2.8.1.1 FINAL MODEL

a. Profile of reaction for species 1 to 6, 10 and EtOH



b. RMSE and MAE for species 1 to 6, 10 and EtOH



c. Kinetic of model for species 1 to 6, 10 and EtOH

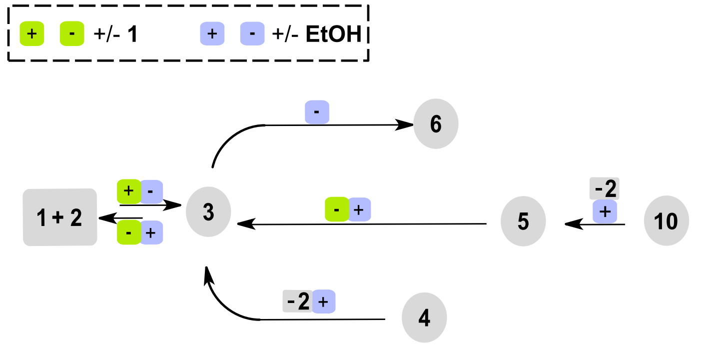


Figure S2.41 (a) Profile of concentrations of the various species **1** to **6**, **10** and **EtOH** over time using dimethyl sulfoxide (DMSO) as a solvent; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.8.1.2 QUANTILE-QUANTILE PLOT

a. Quantile-quantile plot for kinetic sudy using DMSO

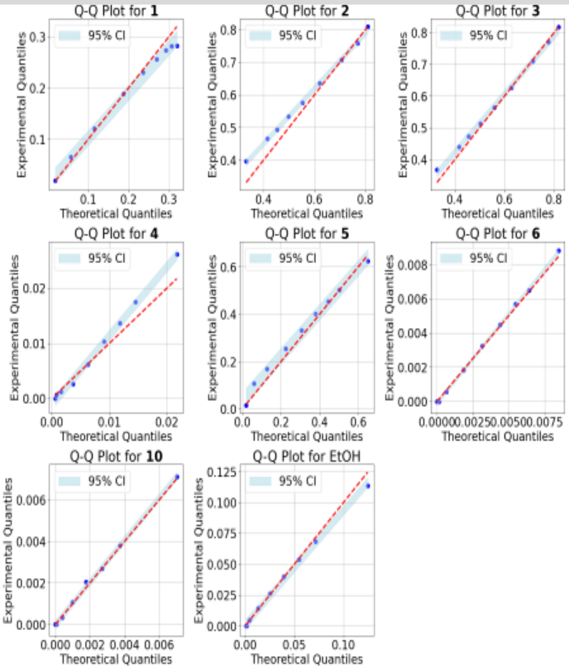


Figure S2.42 Quantile-quantile plots for kinetic study using dimethyl sulfoxide (DMSO) as a solvent.

2.8.1.3 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

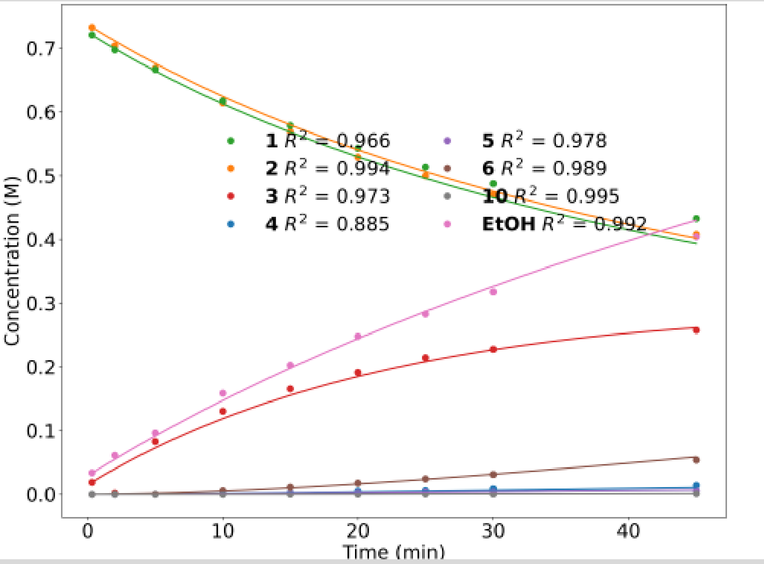
Table S2.7 Model initialization and calculated concentrations and rate constants for kinetic study using dimethyl sulfoxide as a solvent.

Calculated rate constants		Model initialization		Optimized values of initialization		R²	RMSE	MAE
k_15	0.00411	c0_4	0.000601	c0_4	0.000601	0.945	0.00199	0.0015
k_1	0.0379	c0_2	0.818	c0_2	0.818	0.986	0.017	0.012
k_18	0.0111	c0_1	0.809	c0_1	0.809	0.932	0.0344	0.027
k_3	0.00303	c0_3	0.0183	c0_3	0.0183	0.966	0.0174	0.0131
k_13	0.0791	c0_5	0	c0_5	0	0.997	0.00015	0.00011
		c0_6	0.000989	c0_6	0.000989	0.988	0.0039	0.00231
		c0_EtOH	0.0198	c0_EtOH	0.0198	0.979	0.0271	0.0226
		c0_10	0	c0_10	0		0.000108	7.54e-05

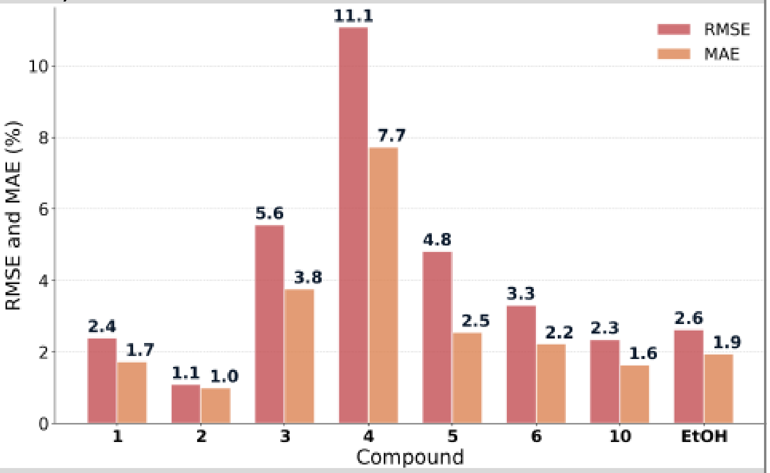
2.8.2 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND 2 USING 10 MOL% OF FA IN DRY DIMETHYLFORMAMIDE

2.8.2.1 FINAL MODEL

a. Profile of reaction for kinetic study in DMF (species 1 to 6, 10 and EtOH)



b. RMSE and MAE for kinetic study in DMF (species 1 to 6, 10 and EtOH)



c. Kinetic study in DMF (species 1 to 6, 10 and EtOH)

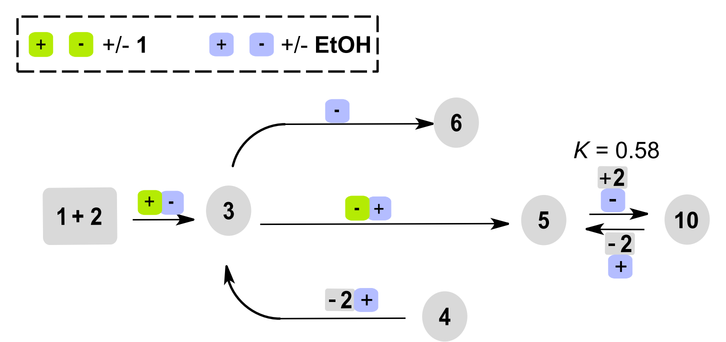


Figure S2.43 (a) Profile of concentrations of the various species **1** to **6**, **10** and **EtOH** over time using dimethylformamide (DMF) as a solvent; (b) RMSE and MAE obtained; and () the system obtained from kinetic modelling of NMR data with the theoretical model.

2.8.2.2 QUANTILE-QUANTILE PLOT

a. Quantile-quantile plot for kinetic study in DMF

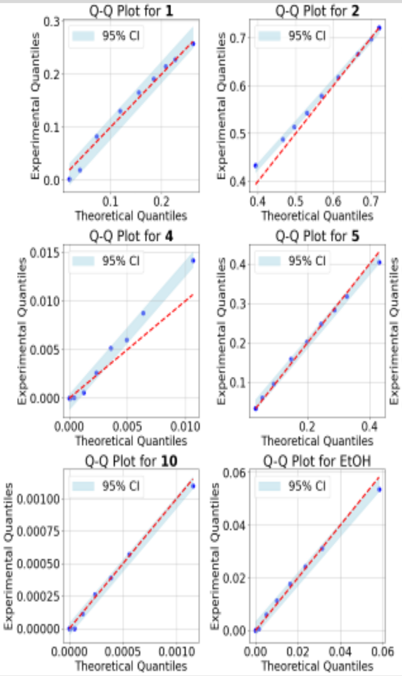


Figure S2.44 Quantile-quantile plots for kinetic study using dimethylformamide (DMF) as a solvent.

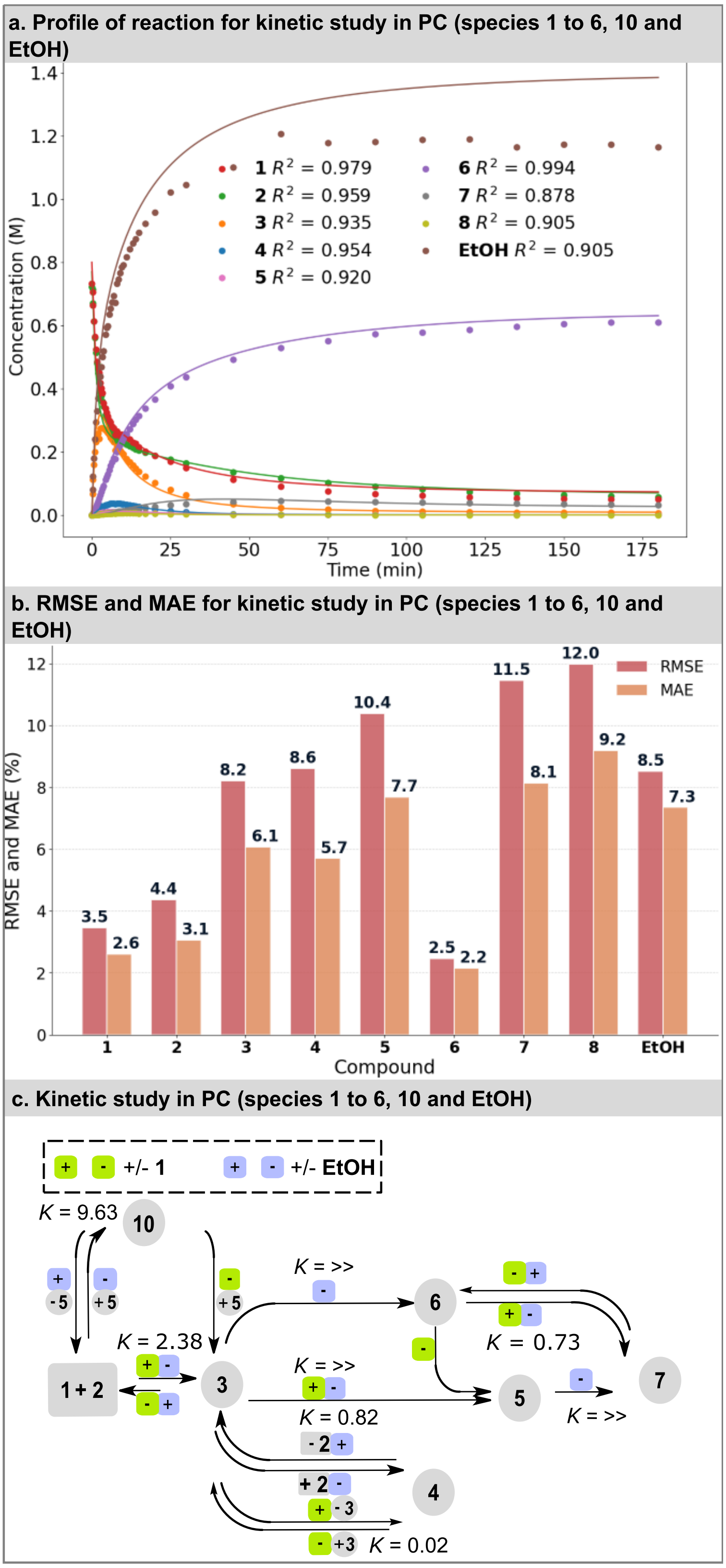
2.8.2.3 MODEL INITIALIZATION AND CALCULATED CONCENTRATIONS AND RATE CONSTANTS

Table S2.8 Model initialization with calculated concentrations and rate constants for kinetic study using dimethylformamide as a solvent.

Calculated rate constants		Model initialization		Optimized values of initialization		R²	RMSE	MAE
k_15	0.00265	c0_4	0	c0_4	0	0.885	0.00157	0.00109
k_1	0.0246	c0_2	0.733	c0_2	0.733	0.994	0.00796	0.00728
k_18	0.00727	c0_1	0.721	c0_1	0.721	0.966	0.0172	0.0125
k_3	0.00201	c0_3	0.0189	c0_3	0.0189	0.973	0.0143	0.00969
k_14	0.0372	c0_5	0	c0_5	0	0.978	0.00028	0.00015
k_13	0.0217	c0_6	0	c0_ 6	0	0.989	0.00177	0.00119
		c0_ EtOH	0.033	c0_EtO H	0.033	0.992	0.0106	0.00786
		c0_10	0	c0_10	0		2.57e-05	1.79e-05

2.8.3 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND 2 USING 10 MOL% OF FA IN DRY PROPYLENE CARBONATE

2.8.3.1 FINAL MODEL



a. Profile of reaction for kinetic study in PC (species 1 to 6, 10 and EtOH)

b. RMSE and MAE for kinetic study in PC (species 1 to 6, 10 and EtOH)

c. Kinetic study in PC (species 1 to 6, 10 and EtOH)

Figure S2.45 (a) Profile of concentrations of the various species **1** to **6**, **10** and **EtOH** over time using propylene carbonate (PC) as a solvent; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.8.3.2 QUANTILE-QUANTILE PLOT

a. Quantile-quantile plot for kinetic study in PC

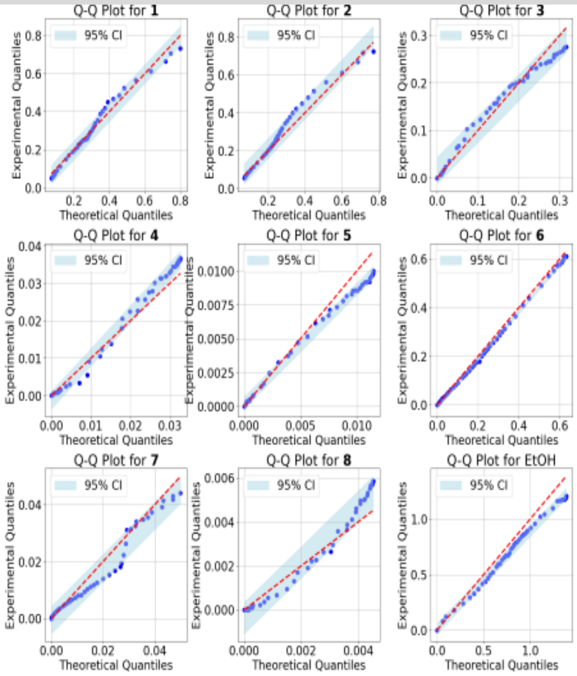


Figure S2.46 Quantile-quantile plots for kinetic study using propylene carbonate (PC) as a solvent.

2.8.3.3 MODEL INITIALIZATION AND CALCULATED CONCENTRATIONS AND RATE CONSTANTS

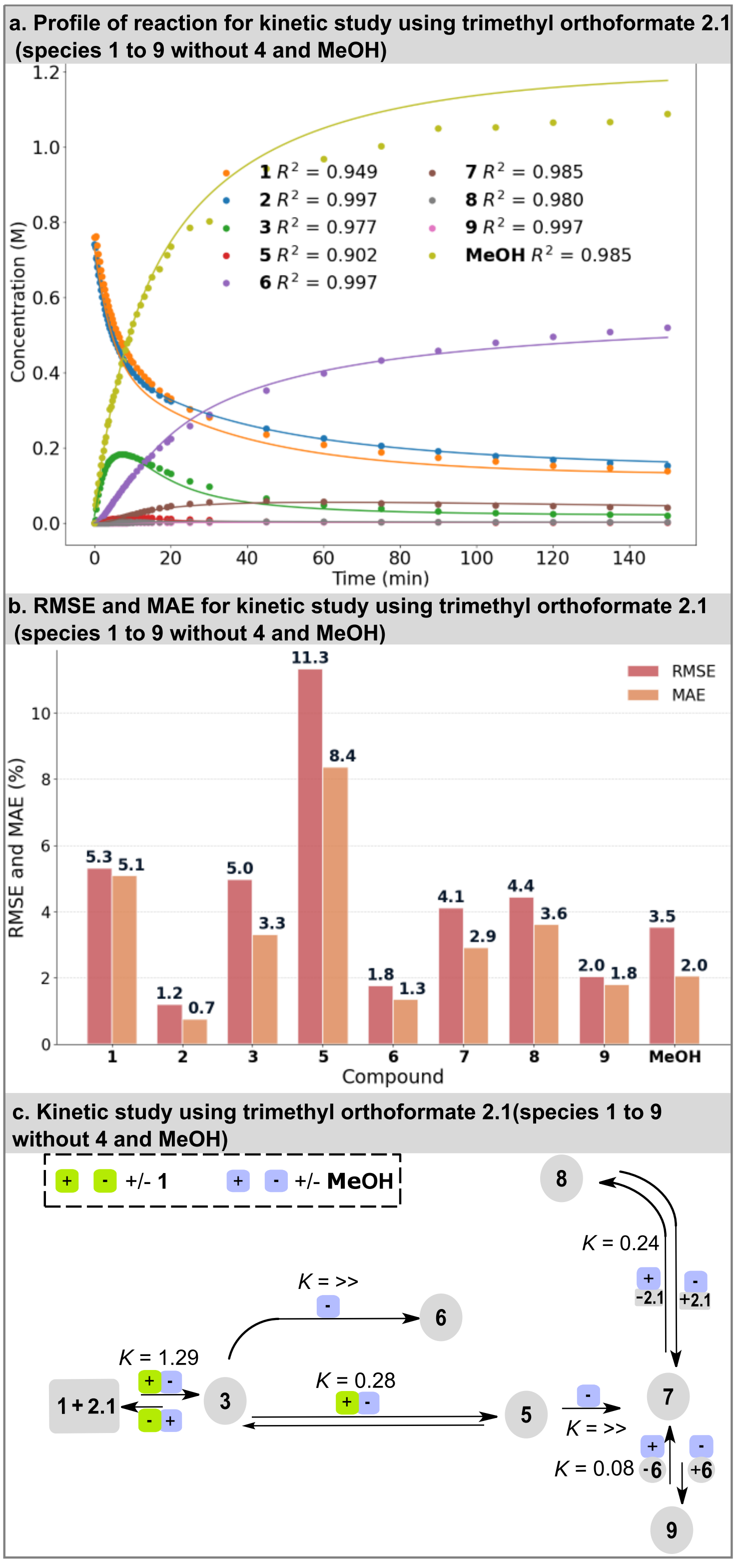
Table S2.9 Model initialization with calculated concentrations and rate constants for kinetic study using propylene carbonate as a solvent.

Calculated rate constants		Model initialization		Optimized values of initialization		R^2	RMSE	MAE
k_15	0.0818	c0_4	0	c0_4	0	0.954	0.00315	0.00209
k_25	0.0996	c0_3	0	c0_3	0	0.935	0.0226	0.0167
k_2	0.291	c0_2	0.77	c0_2	0.77	0.959	0.0315	0.022
k_1	0.695	c0_1	0.80	c0_1	0.80	0.979	0.0254	0.0191
k_18	0.107	c0_6	0	c0_6	0	0.994	0.015	0.0132
k_5	0.211	c0_		c0_		0.905	0.103	0.0887
k_3	0.0337	EtOH	0	EtOH	0	0.92	0.00104	0.00076
k_21	0.153	c0_5	0	c0_5	0	0.878	0.005	0.0035
k_19	0.00092	c0_7	0	c0_7	0	0.905	0.007	0.0005
k_4	0.00506	c0_10	0	c0_10	0			
k_8	0.015							
k_13	4.26							
k_14	0.442							
k_6	8.01							
k_7	0.037							
k_9	0.0204							

2.9 REAGENT SCREENING

2.9.1 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND TRIMETHYL ORTHOFORMATE 2.1 USING 10 MOL% OF FA IN DRY ACETONITRILE

2.9.1.1 FINAL MODEL



a. Profile of reaction for kinetic study using trimethyl orthoformate 2.1 (species 1 to 9 without 4 and MeOH)

b. RMSE and MAE for kinetic study using trimethyl orthoformate 2.1 (species 1 to 9 without 4 and MeOH)

c. Kinetic study using trimethyl orthoformate 2.1(species 1 to 9 without 4 and MeOH)

Figure S2.47 (a) Profile of concentrations of the various species **1**, **2.1**, **3**, **5**, **6**, **7**, **8**, **9** and **MeOH** over time using trimethyl orthoformate (**2.1**) as a solvent; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.9.1.2 QUANTILE-QUANTILE PLOT

a. Quantile-quantile plot for kinetic study using trimethyl orthoformate (2.1)

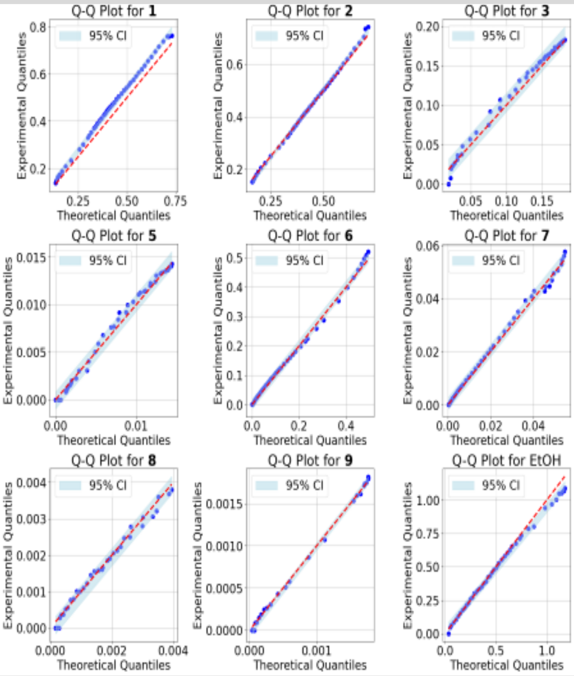


Figure S2.48 Quantile-quantile plots for kinetic study using trimethyl orthoformate (**2.1**) as a reagent.

2.9.1.3 SYSTEM OF DIFFERENTIAL EQUATIONS DESCRIBING THE KINETIC MODEL

a. Kinetic model for species 1 to 10 without 4 and MeOH when using trimethyl orthoformate 2.1

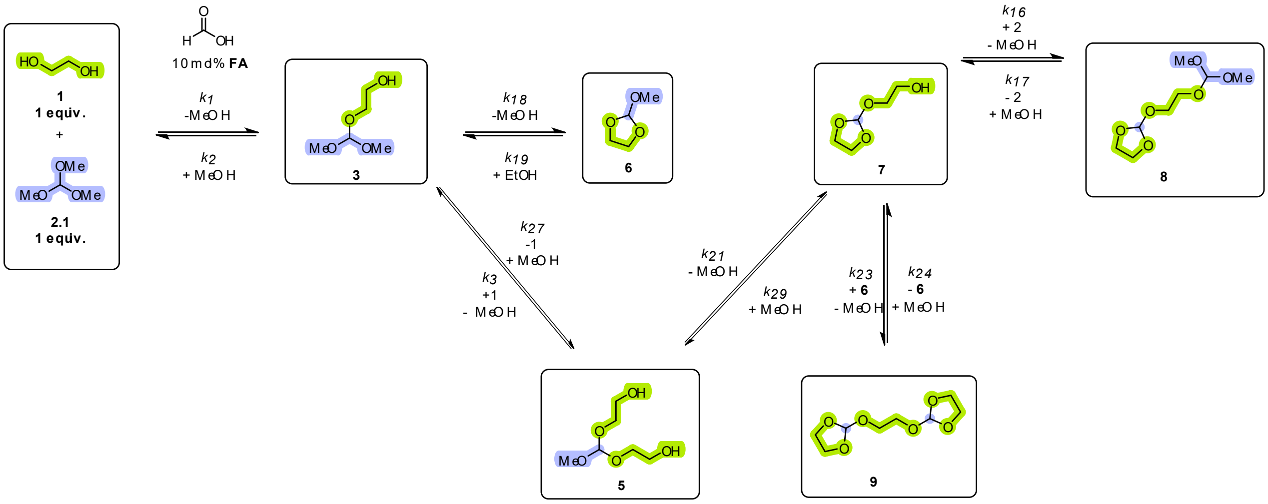


Figure S2.49 Representation of kinetic of reaction between **1** and trimethyl orthoformate (**2.1**), including the rate constants.

$$\frac{d[C1]}{dt} - k1 * [1] * [2] + k2 * [3] * [MeOH] + k3 * [3] * [1] + k27 * [5] * [MeOH]$$

$$\frac{d[C2]}{dt} = -k1 * [1] * [2] + k2 * [3] * [MeOH] + k16 * [2] * [7] - k17 * [8] * [MeOH]$$

$$\frac{d[C3]}{dt} = k1 * [1] * [2] - k2 * [3] * [MeOH] + k27 * [5] * [MeOH] - k3 * [3] * [1] - k18 * [3] + k19 * [6] * [MeOH]$$

$$\frac{d[C5]}{dt} = + k3 * [3] * [1] - k27 * [5] * [EtOH] - k21 * [5] + k29 * [7] * [MeOH]$$

$$\frac{d[C6]}{dt} = k18 * [3] - k19 * [6] * [MeOH]$$

$$\frac{d[C7]}{dt} = -k21 * [5] - k29 * [7] * [MeOH] - k16 * [2] * [7] + k17 * [8] * [MeOH] - k23 * [6] * [7] + k24 * [9] * [MeOH]$$

$$\frac{d[C8]}{dt} = k16 * [2] * [7] - k17 * [8] * [MeOH]$$

$$\frac{d[C9]}{dt} = k23 * [6] * [7] - k24 * [9] * [MeOH]$$

$$\frac{d[CMeOH]}{dt} = k1 * [1] * [2] - k2 * [3] * [MeOH] + k18 * [3] - k19 * [6] * [MeOH] + k3 * [3] * [1] + k27 * [5] * [MeOH] + k21 * [5] - k29 * [7] * [MeOH] + k16 * [2] * [7] - k17 * [8] * [MeOH] + k23 * [6] * [7] - k24 * [9] * [MeOH]$$

2.9.1.4 MODEL INITIALIZATION WITH CALCULATED CONCENTRATIONS AND RATE CONSTANTS

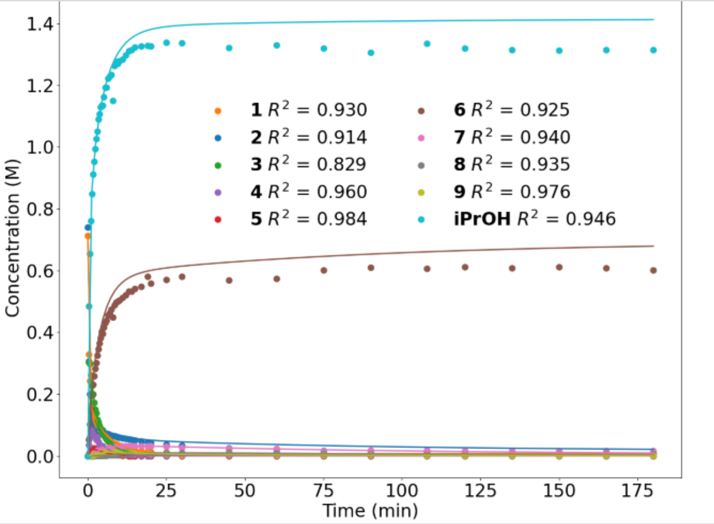
Table S2.10 Model initialization with calculated concentrations and rate constants for kinetic study using trimethyl orthoformate (**2.1.**).

Calculated rate constants		Model initialization		Optimized values of initialization		R^2	RMSE	MAE
k_2	0.107	c0_2	0.711	c0_2	0	0.997	0.00891	0.00553
k_1	0.138	c0_1	0.73	c0_1	0	0.949	0.0405	0.0387
k_18	0.0814	c0_3	0.0187	c0_3	0.77	0.977	0.00905	0.00604
k_19	0.0022	c0_5	0	c0_5	0.80	0.902	0.00162	0.0012
k_3	0.0613	c0_6	0	c0_6	0	0.997	0.00913	0.00698
k_27	0.216	c0_7	0.0002			0.985	0.00237	0.00168
k_21	0.224			c0_7	0	0.997	3.69e-05	3.26e-05
k_29	0.00792	c0_9	4.11e-05	c0_9	0			
k_16	0.046	c0_8	0.0001	c0_8	0			
k_17	0.188	c0_MeOH	0.0343	c0_MeOH				
k_23	0.0143							
k_24	0.173							

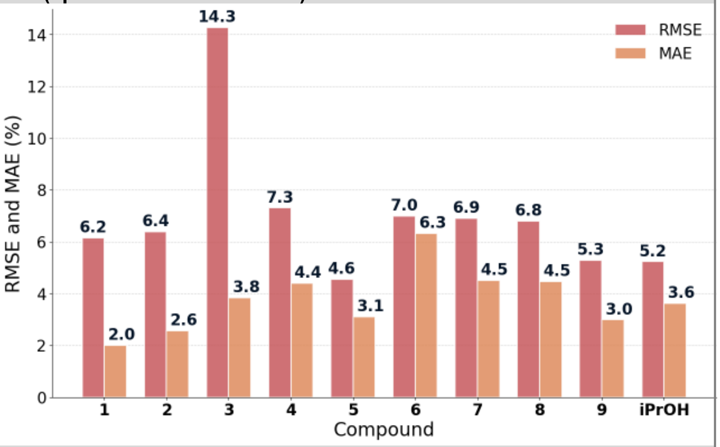
2.9.2 KINETIC STUDY OF STOCHIOMETRIC AMOUNT OF 1 AND TRIISOPROPYL ORTHOFORMATE (2.2) USING 10 MOL% OF FA IN DRY ACETONITRILE

2.9.2.1 FINAL MODEL

a. Profile of reaction for kinetic study using triisopropyl orthoformate 2.3 (species 1 to 9 and ^{i}PrOH)



b. RMSE and MAE for kinetic study using triisopropyl orthoformate 2.3 (species 1 to 9 and ^{i}PrOH)



c. Kinetic study using triisopropyl orthoformate 2.3 (species 1 to 9 and ^{i}PrOH)

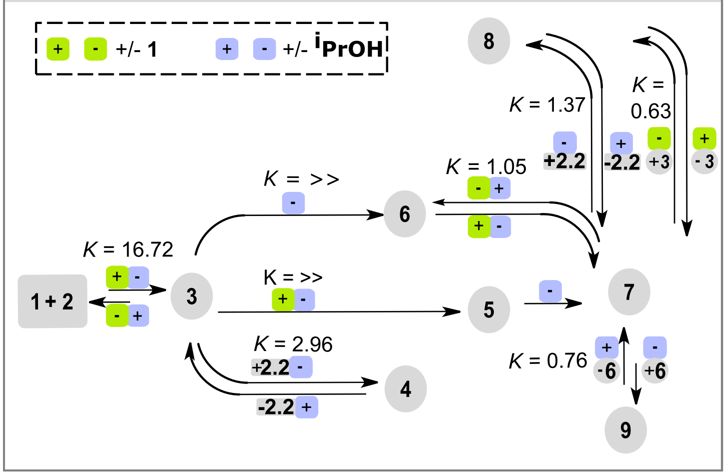


Figure S2.50 (a) Profile of concentrations of the various species **1**, **2.1**, **3**, **5**, **6**, **7**, **8**, **9** and **^{i}POH** over time using trimethyl orthoformate (**2.2**) as a solvent; (b) RMSE and MAE obtained; and (c) the system obtained from kinetic modelling of NMR data with the theoretical model.

2.9.2.2 Quantile-quantile plot

a. Quantile-quantile plot for kinetic study using triisopropyl orthoformate (2.2)

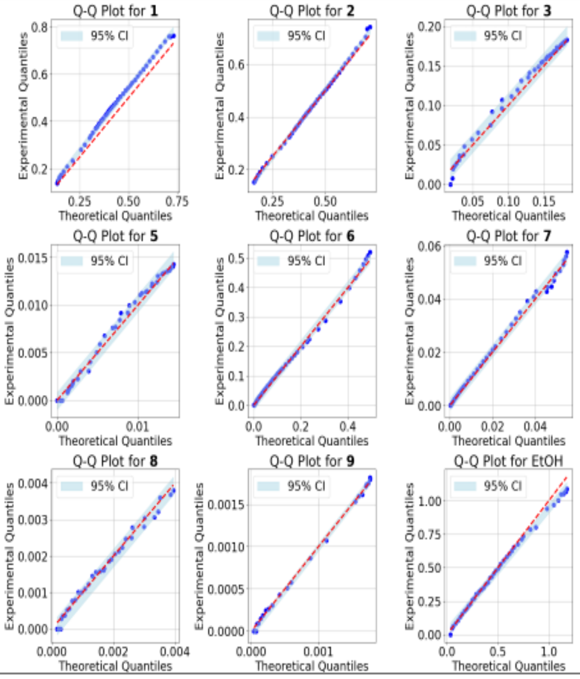


Figure S2.51 Quantile-quantile plots for kinetic study using triispropyl orthoformate (**2.2**) as a reagent

2.9.2.3 SYSTEM OF DIFFERENTIAL EQUATIONS DESCRIBING THE KINETIC MODEL

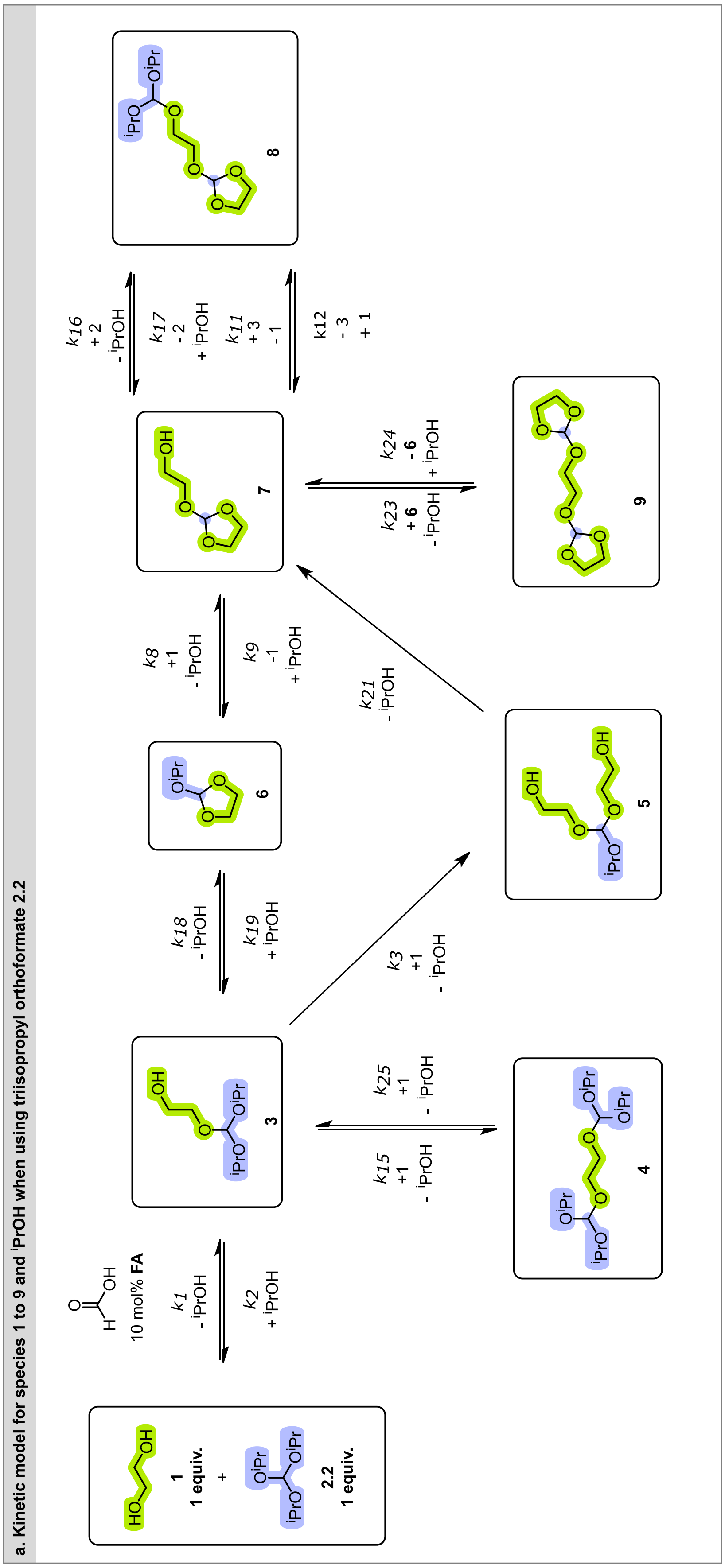


Figure S2.52 Representation of kinetic of reaction between **1** and triisopropyl orthoformate (**2.2**), including the rate constants.

2.9.2.4 MODEL INITIALIZATION AND CALCULATED CONCENTRATIONS AND RATE CONSTANTS

Table S2.11 Model initialization with calculated concentrations and rate constants for kinetic study using triisopropyl orthoformate (**2.2.**)

Calculated rate constants		Model initialization		Optimized values of initialization		R^2	RMSE	MAE
k_15	1.34	c0_2	0.72	c0_2	0.72	0.914	0.0472	0.0189
k_25	0.452	c0_1	0.72	c0_1	0.72	0.93	0.0438	0.0143
k_2	0.486	c0_3	0	c0_3	0	0.829	0.0433	0.0117
k_1	8.13	c0_5	0	c0_5	0	0.984	0.0011	0.000754
k_18	0.546	c0_4	0	c0_4	0	0.96	0.00642	0.00387
k_3	0.326	c0_6	0	c0_6	0	0.925	0.0427	0.0386
k_21	0.409	c0_7	0	c0_7	0	0.94	0.00224	0.00146
k_19	0.0009	c0_9	0	c0_9	0			
k_8	0.0114	c0_8	0	c0_8	0			
k_11	8.07	c0_iPOH	0	c0_iPOH	0			
k_12	12.7							
k_16	0.0989							
k_17	0.0719							
k_23	0.0715							
K_9	0.0109							
K_24	0.0938							

2.10 COMPUTATIONS

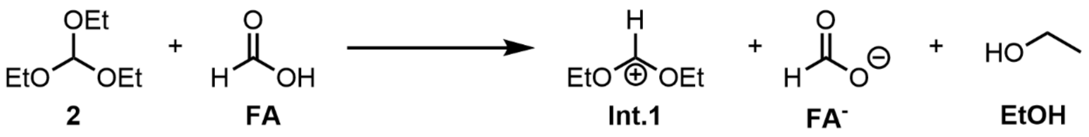
2.10.1 COMPUTATIONAL METHODS

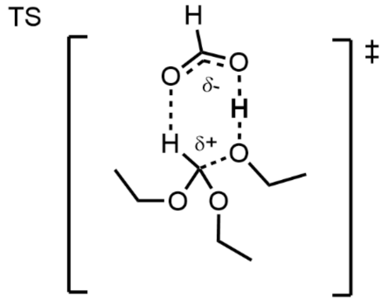
DFT computations were performed using the Gaussian 16 (Revision C.01)[3] software package. All stationary points were optimized and localized at the B3LYP-GD3BJ/6-31+G*(d) level of theory. The SMD method was used to model solvent effects using the built-in parameters for acetonitrile (MeCN, ε = 38.8). Stationary points were characterized by frequency calculations (local minima with only real frequencies and transition states with one imaginary frequency) and a systematic attempt to locate the lowest-energy conformers. transition states were further validated by intrinsic reaction coordinate (IRC) calculations.

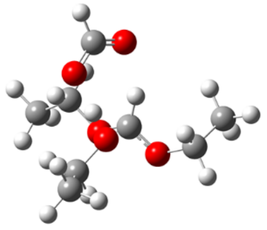
2.10.2 CARTESIAN COORDINATES AND ENERGIES FOR REPRESENTATIVE TRANSITION STATES

2.10.2.1 DCE MECHANISM FOR THE FORMATION OF 3, 4, 5, 6, 7, 10 AND 11

Table S2.12 Transition state: activation of **2** in carbocation int.**1**



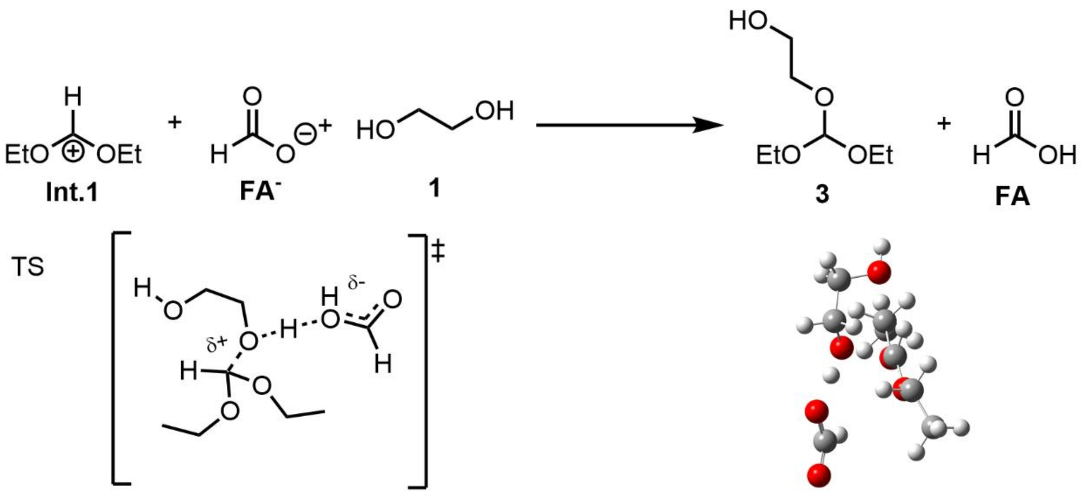




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.73600800 -0.49526400 -0.37547200 H -0.74122900 -0.56797700 0.71553800 O -1.79142200 -0.09024900 -1.02965900 O 0.01754200 -1.30046500 -1.07728100 O 0.28237700 1.14710500 -0.22163600 C -2.78948500 0.65377600 -0.24436200 H -3.30915000 1.25401200 -0.99178600 H -2.25370900 1.31627600 0.43889400 C -3.72106700 -0.29921000 0.47391700 H -3.18114000 -0.90959900 1.20668500 H -4.47947000 0.28452700 1.00911200 H -4.23024200 -0.96073900 -0.23539400 C 1.12679700 -1.95006300 -0.36038500 H 1.75867600 -1.16551800 0.06136800 H 0.69249900 -2.54366000 0.44786000 C 1.87050300 -2.80216300 -1.36059500 H 2.28236400 -2.19001700 -2.17019500 H 2.70104100 -3.30156700 -0.84881800 H 1.21733300 -3.57001600 -1.78933400 C 1.07294500 1.45279000 -1.38673000	H = -691.58975 Hartree G = -691.65602 Hartree

H 1.95990700 0.80823400 -1.40611500 H 0.45223100 1.21010300 -2.25449400 C 1.46225600 2.92200800 -1.39631600 H 2.03944400 3.14347500 -2.30283200 H 0.57083300 3.55972100 -1.38818300 H 2.08114400 3.17343700 -0.52723400 C 1.20382600 0.13353900 2.72423900 H 1.79849800 -0.02996000 3.64905300 O 0.08269800 -0.41590400 2.64489600 O 1.76087100 0.87656000 1.84863700 H 0.88584400 1.06039700 0.62044200	

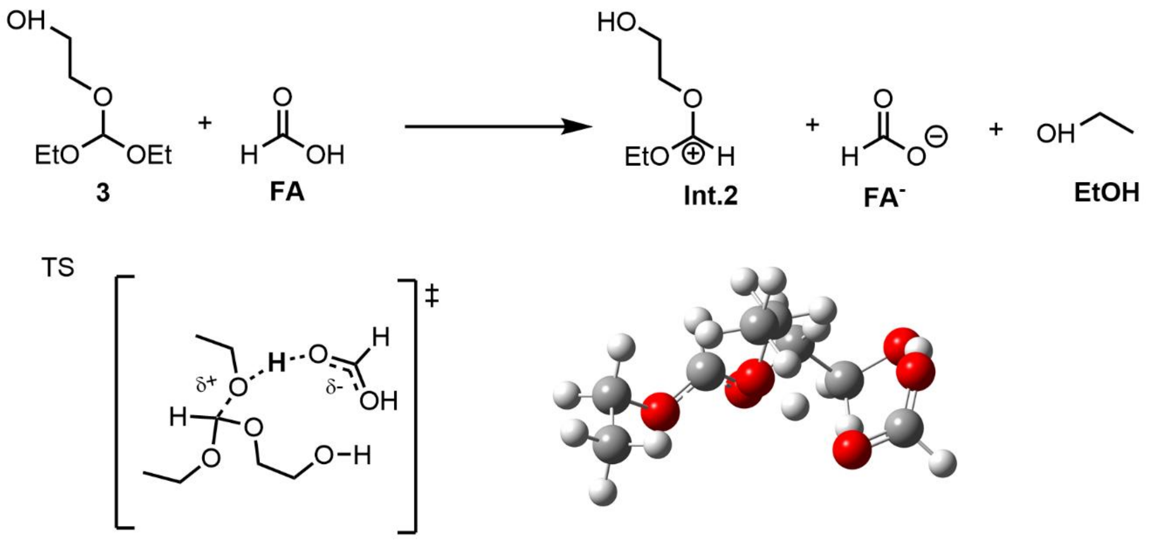
Table S2.13 Transition state: substitution of carbocation int.**1** by **1**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.48691100 0.42200100 0.76777300 H -1.14502500 -0.32406700 1.21298800 O -0.98759600 1.53003300 0.29651200 O -0.32582500 -0.64502700 -0.85354300 O 0.73813100 0.56631000 1.19358800 C -2.40701200 1.51097700 -0.08390800 H -2.97536500 1.11845600 0.76316800 H -2.50150500 0.83571500 -0.93631000 C -2.79928800 2.92793800 -0.42949200 H -2.20294000 3.30850300 -1.26588800 H -3.85441500 2.93838500 -0.72590700 H -2.67529900 3.59478500 0.43070300 C -0.66112200 -2.04464100 -0.78514800 H -0.27682200 -2.52342100 -1.69298000 H -0.17789000 -2.50940700 0.08364500 C -2.15571500 -2.24380400 -0.71866800 H -2.64773700 -1.67935900 -1.52131700 H -2.37127800 -3.31225400 -0.85559700 C 1.37619700 -0.59518600 1.82720000 H 0.63778600 -1.07778900 2.47422900 H 1.66747200 -1.27444100 1.02399400 C 2.57500200 -0.08811000 2.59310800 H 3.08315400 -0.94116400 3.05697000 H 3.28250200 0.41088100 1.92198800 H 2.27593500 0.60938500 3.38299300	H = -766.79962Hartree G = -766.86864Hartree

O -2.62043000 -1.80193200 0.56695400	
H -3.59222200 -1.83404200 0.57480900	
H 0.68759600 -0.56323500 -1.15686300	
C 2.66577800 0.57121200 -1.47323300	
H 1.99866000 1.43663800 -1.26229000	
O 3.87907900 0.79787700 -1.62986700	
O 2.08486900 -0.56924800 -1.53541000	

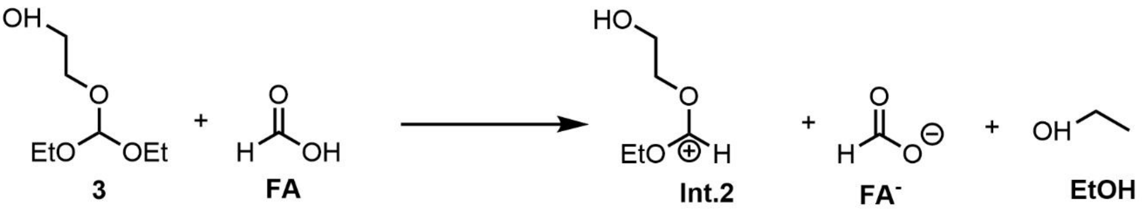
Table S2.14 Transition state: activation of **3** in carbocation int.**2** (first structure identified)

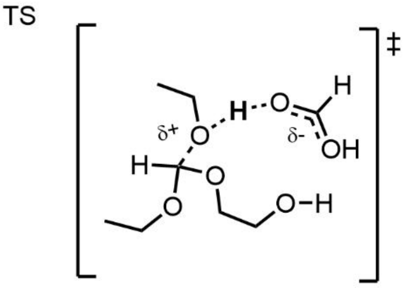


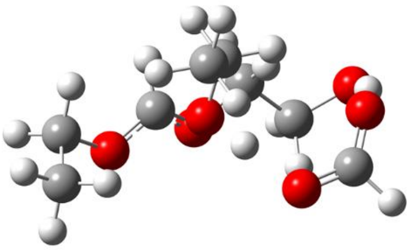
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H = -766.80181 Hartree
C -1.20429400 0.84285000 -0.50559600	G =-766.86834 Hartree
H -1.30718500 1.24424500 -1.51251600	
O -1.62426700 -0.36550200 -0.25702700	
O -1.29819000 1.74107900 0.43468100	
O 0.70285700 0.65763200 -0.69542000	
C -1.67950300 -1.30698500 -1.38535900	
H -0.66058400 -1.66491500 -1.54572000	
H -2.02737400 -0.75847200 -2.26582200	
C -2.61823300 -2.42479000 -0.99773900	
H -3.63112600 -2.04853500 -0.81783600	
H -2.65809200 -3.15020400 -1.81844000	
H -2.26228400 -2.94082400 -0.09955300	
C -1.40289200 1.36841500 1.85366500	
H -1.72285000 2.30487300 2.31244500	
H -2.18681400 0.61574300 1.96201200	
C -0.09500800 0.89915300 2.47127600	
H 0.73815500 1.48780200 2.06873800	
H -0.17350800 1.12427700 3.54595100	
C 1.23878600 1.30551600 -1.87117900	
H 2.23094700 0.87793400 -2.04876500	
H 0.60597200 1.06525100 -2.73652100	
C 1.32257700 2.80375600 -1.64998600	
H 1.76681000 3.27920200 -2.53279200	
H 0.33251700 3.24457700 -1.48998800	
H 1.94909000 3.03170300 -0.78007900	
O 0.11170100 -0.49229400 2.30450700	
H 0.97563000 -0.68219200 1.86388100	

H 1.02223200 -0.32633200 -0.68264000 C 2.40617100 -2.00629100 0.17249400 H 3.07318200 -2.88043500 0.02151200 O 2.47110100 -1.41457800 1.27725200 O 1.65300500 -1.71551600 -0.81015800	

Table S2.15 Transition state: activation of **3** in carbocation int.**2** (second geometry identified)



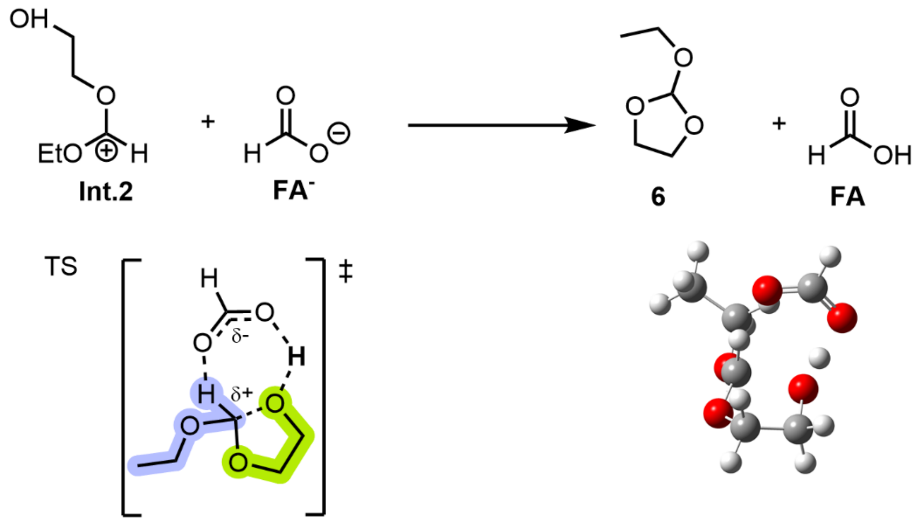




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.91574900 -1.21624800 -0.36319800 H -1.07702700 -1.05955100 -1.43088400 O -1.91009400 -1.56903300 0.39681900 O -0.81924100 0.68671600 -0.08410700 O 0.23257100 -1.68064200 0.05227100 C -3.26595800 -1.17665800 -0.02202600 H -3.80983600 -2.11770400 -0.12739700 H -3.20159500 -0.68508800 -0.99538700 C -3.87283400 -0.28240500 1.03532000 H -3.30064400 0.64339300 1.14227800 H -4.89720300 -0.03110200 0.73530800 H -3.91469100 -0.79369700 2.00325300 C -0.74673100 1.54060900 -1.24770200 H 0.28393200 1.89674400 -1.35234300 H -0.98350200 0.92348400 -2.12164400 C -1.72959500 2.69179500 -1.12349300 H -1.49894200 3.31042100 -0.24847800 H -1.67176100 3.32539600 -2.01765700 H -2.75615000 2.31976800 -1.02879300 C 1.39205600 -1.37966100 -0.78941900 H 1.34007300 -2.00996900 -1.68104100 H 1.34902400 -0.32501400 -1.06412800 C 2.64204700 -1.63969900 0.04590800 H 2.46292400 -1.30027700 1.07503200 H 2.88360800 -2.70596000 0.07335500 C 2.15030300 1.58545800 1.24180600 H 2.85734700 1.83943200 2.05923600 O 2.61245200 1.49534900 0.07767600 O 0.94348100 1.41848800 1.60477000 H -0.06927700 0.95421100 0.58864100	H = -766.80102 Hartree G -766.86789 Hartree

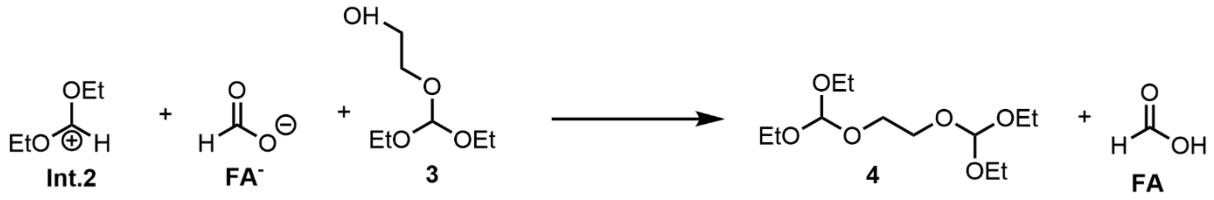
O 3.75374100 -0.96552900 -0.53200500 H 3.57920200 -0.00642300 -0.39592200	

Table S2.16 Transition state: intramolecular cyclization of int.**2** in **6**

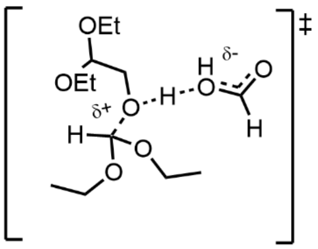


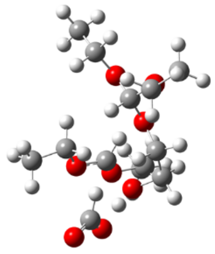
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.52938200 -0.76669500 0.20479700 H -0.30122800 0.19346900 0.67899100 O -0.06079800 -1.88406900 0.73881300 O -1.64232700 -0.92533700 -0.44882400 C -2.38446000 0.30866300 -0.77116500 H -1.65803000 1.07257000 -1.06035900 H -2.97757000 0.02896200 -1.64202300 C 1.38188000 -1.80432700 0.89044400 H 1.71288100 -2.77577200 1.25495000 H 1.62692300 -1.01763300 1.60955200 C -3.24428500 0.73504900 0.39832100 H -3.81636600 1.62453500 0.10888400 H -3.94984700 -0.05574800 0.67530600 H -2.63318400 0.99102400 1.27109300 C 1.87004000 -1.46674800 -0.52072100 H 2.86549600 -1.01406400 -0.49728900 H 1.87927900 -2.35548400 -1.15631600 O 0.90914400 -0.54561400 -1.05026900 H 1.25607300 0.46766700 -0.93802200 C 1.40105800 2.39567800 0.24604000 H 1.77703300 3.43613500 0.33035600 O 1.72554100 1.79884800 -0.84030400 O 0.72461800 1.93049900 1.18540700	H = -611.81983 Hartree G= -611.87285 Hartree

Table S2.17 Transition state: substitution of int.**1** with **3** in **4**



TS

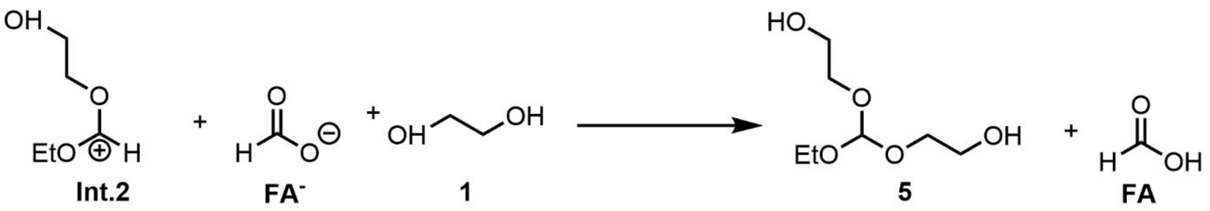


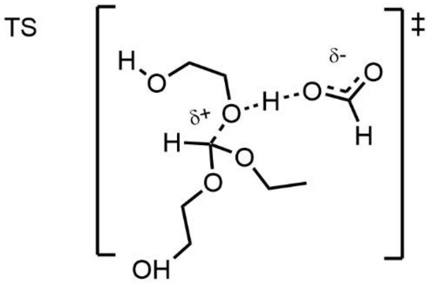


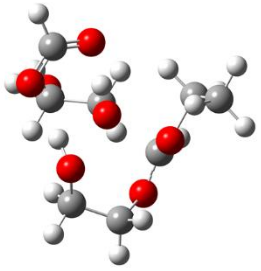
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.94457100 -0.92614700 -0.23186100 H -0.97524700 -1.30345700 0.09082400 O -2.04186000 -0.29357700 -1.37222700 O -3.03490300 -1.57668500 0.07831600 C -0.79519700 0.25429500 -1.92483200 H -0.13172800 -0.58715100 -2.13886400 H -0.34347500 0.88950500 -1.16253200 C -1.15343100 1.03734100 -3.16435600 H -1.82616800 1.86729800 -2.92388000 H -0.23506400 1.45142700 -3.59615000 H -1.62889100 0.39600400 -3.91445200 C -2.99849200 -2.36770500 1.31264700 H -1.99425300 -2.78934800 1.41875000 H -3.19306100 -1.67648500 2.13579900 C -4.05786200 -3.43986500 1.20680900 H -4.06290400 -4.02382300 2.13429700 H -5.05176200 -2.99905500 1.07293200 H -3.85188200 -4.11788000 0.37145600 H -2.09027300 1.46039800 0.66053000 C -1.51720700 3.46224800 -0.32100000 H -0.50369100 3.00434300 -0.33322000 O -1.64633400 4.59807400 -0.80858000 O -2.43988100 2.74870300 0.21241400 C 2.02829500 -0.32847800 0.17262900 H 1.96301100 0.57379300 -0.45750900 O 2.09069600 -1.47884300 -0.60314400 O 0.85881200 -0.49159700 0.92005600 O 3.14962200 -0.22867800 1.01463400 C 3.10755100 -1.43143900 -1.61848800 H 4.09404100 -1.35889400 -1.14429300 H 2.95498600 -0.53431300 -2.23601800 C 2.99942200 -2.69075700 -2.45466600 H 2.01608600 -2.76083100 -2.93398300 H 3.76586300 -2.67933700 -3.23857600 H 3.15219900 -3.58367500 -1.83729800 C 0.47652800 0.66479600 1.67432100 H 1.12070200 0.77236000 2.55642700	H = -1113.6819 Hartree G = -1113.7724 Hartree

H 0.57817500 1.56577300 1.05501500	
C -0.95678900 0.48079000 2.12661000	
H -1.06302500 -0.46492100 2.66648000	
H -1.22336700 1.29701600 2.80823600	
C 3.88427200 1.00859100 0.92949300	
H 4.22552200 1.16005800 -0.10317700	
H 3.22843300 1.84647100 1.19999700	
C 5.06201600 0.92065900 1.87839500	
H 5.64223900 1.84997700 1.83413400	
H 4.72203900 0.77501200 2.91042000	
H 5.72140900 0.08809600 1.60658200	
O -1.91329000 0.47456200 1.05651700	

Table S2.18 Transition state: substitution of int.2 with **1** in **5**



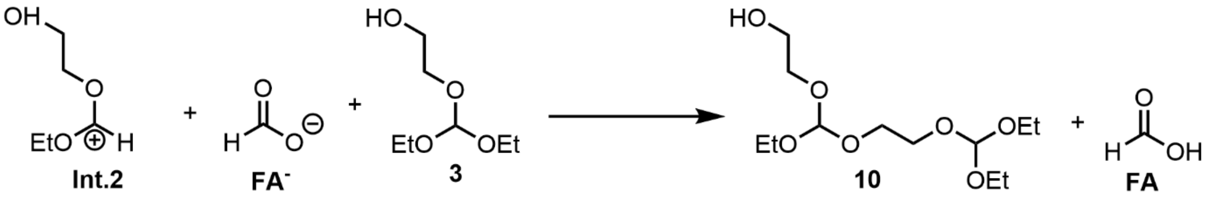




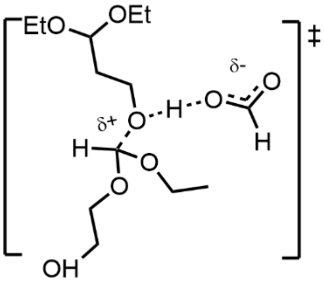
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -842.01323 Hartree
C 0.94873400 -0.98430000 -1.08133000	G = -842.08294 Hartree
H 0.64952600 -0.97426200 -2.12792000	
O 1.91102600 -0.20115600 -0.68324900	
O 0.81084200 -2.14654400 -0.50464400	
O -0.63290200 -0.09812200 -0.49443500	
C 2.16740100 1.01469200 -1.47134000	
H 1.43831000 1.75909600 -1.14448800	
H 2.00653000 0.77346700 -2.52649100	
C 3.58753600 1.44582700 -1.19179200	
H 4.30440000 0.68073000 -1.50892200	
H 3.79167800 2.36601700 -1.75122000	
H 3.73145100 1.65264300 -0.12582200	
C 1.32591100 -2.38958200 0.85258700	
H 1.27857300 -3.47713100 0.92243600	
H 2.36653000 -2.06113000 0.89589900	
C 0.49759900 -1.75776400 1.96264200	
H -0.56835900 -1.82134700 1.71471500	
H 0.67100600 -2.38271000 2.85103900	
C -1.79331300 -0.35169700 -1.29591200	
H -1.85389800 0.37123300 -2.11856500	
H -1.69020900 -1.35709000 -1.71691700	
C -3.03653800 -0.28278900 -0.42101500	
H -2.95008600 -1.00937900 0.39795400	

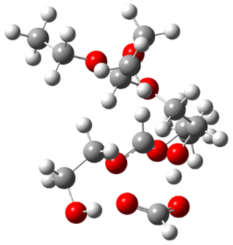
H -3.13978600 0.72112400 0.01115100	
O 0.89171100 -0.43191800 2.27092500	
H 0.17946900 0.22076500 2.07364700	
H -0.55145900 0.92549700 -0.28334900	
C -0.83880100 2.56741000 1.25036600	
H -1.08390600 3.61379000 1.52457200	
O -0.84533200 1.70904500 2.16177200	
O -0.57755500 2.37451600 0.01657500	
O -4.15333400 -0.59005200 -1.26372200	
H -4.96658900 -0.49824500 -0.73872600	

Table S2.19 Transition state: substitution of int.**2** with **3** in **10**



TS

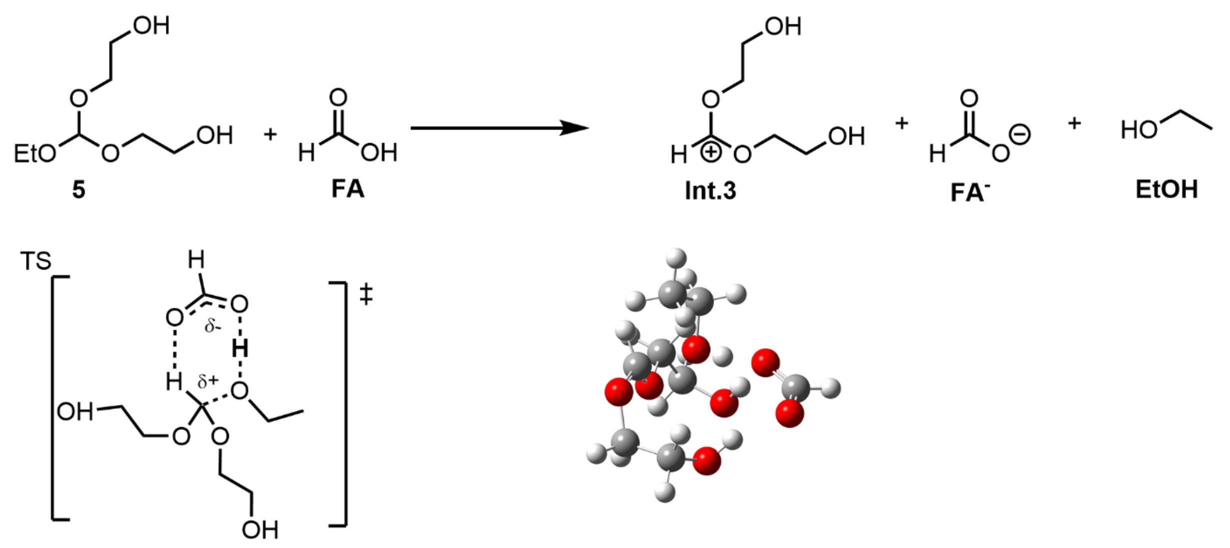




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1188.8997Hartree
C 2.03041800 -0.87510100 0.17758500	G = -1188.9905 Hartree
H 1.13860000 -1.44595500 -0.08273700	
O 2.00907100 -0.12566100 1.25501900	
O 3.21361100 -1.40574300 -0.02674700	
C 0.68860100 0.29443900 1.71996200	
H 0.08489900 -0.59691400 1.91120500	
H 0.23116000 0.89650200 0.93354500	
C 0.86323700 1.11083400 2.98037600	
H -0.14938000 1.30662300 3.36879000	
H 1.40662300 0.53482400 3.73691800	
C 3.33298000 -2.33276200 -1.15382500	
H 2.41931700 -2.93380200 -1.20367400	
H 3.42103900 -1.72772100 -2.05954400	
C 4.55931700 -3.18515400 -0.92252400	
H 4.67733800 -3.87138900 -1.76898100	
H 5.46072600 -2.56646200 -0.85319600	
H 4.46146800 -3.77797000 -0.00662500	
H 1.89616800 1.33183500 -1.02010500	
C 1.28751000 3.62991700 -0.52652700	
H 1.31316100 4.65669900 -0.94650100	
O 2.02947300 2.78876300 -1.12772400	
O 0.55006300 3.42951300 0.46697000	
C -2.07753400 -0.51538900 -0.20772400	
H -2.01259500 0.45848400 0.30461200	
O -2.14818600 -1.55876800 0.70626700	

O -0.90442000 -0.77458900 -0.92204100	
O -3.19371300 -0.51614400 -1.06281900	
C -3.17466600 -1.38317500 1.69772000	
H -4.15662500 -1.37647500 1.20894300	
H -3.03012100 -0.41307400 2.19516600	
C -3.07204600 -2.52300900 2.69118600	
H -2.09447100 -2.52504400 3.18712100	
H -3.84804500 -2.41445800 3.45806200	
H -3.21386100 -3.48906200 2.19272400	
C -0.54826200 0.25444200 -1.85160200	
H -1.19232000 0.20542800 -2.73854700	
H -0.66648100 1.24293900 -1.38767000	
C 0.88793400 0.03122900 -2.26903700	
H 1.04024600 -1.00266000 -2.58996700	
H 1.13634800 0.69412400 -3.10381100	
C -3.93566900 0.71924500 -1.11419500	
H -4.28437900 0.97771400 -0.10562400	
H -3.28135000 1.52684000 -1.46760100	
C -5.10680200 0.52523200 -2.05526300	
H -5.69154000 1.45104300 -2.11219300	
H -4.76010600 0.27351800 -3.06437300	
H -5.76421100 -0.27728500 -1.70081100	
O 1.84092900 0.29569000 -1.21834600	
O 1.58161300 2.31802000 2.77387200	
H 1.22075200 2.74854300 1.96247200	

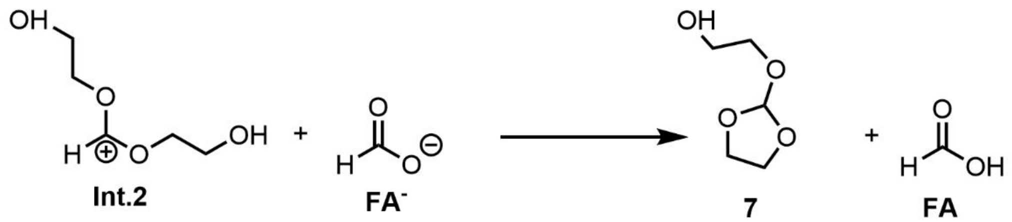
Table S2.20 Transition state: activation of **5** in carbocation int.**3**

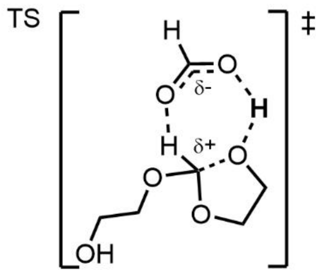


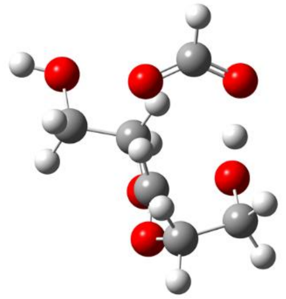
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -842.01746 Hartree
C -0.84405300 -1.35417900 -0.53732300	G = -842.0836 Hartree
H -1.13362400 -1.53133000 -1.57100100	
O 0.38626100 -1.59495100 -0.16981800	
O -1.80666300 -1.53156900 0.31790300	
O -0.86075100 0.56413300 -0.78170900	
C 1.37987600 -1.62049500 -1.25054400	
H 1.23748500 -0.72788000 -1.86496900	
H 1.19853100 -2.51557400 -1.85256500	
C 2.76310000 -1.66236700 -0.64461000	
H 2.86472300 -2.54494600 -0.00289900	

H 3.46045300 -1.78011600 -1.48896000 C -1.57730900 -1.53672500 1.77138700 H -2.46584400 -2.04971900 2.14153200 H -0.68687900 -2.12992500 1.98803400 C -1.47966800 -0.14472600 2.37574400 H -2.17948200 0.53141100 1.87023500 H -1.80962500 -0.24637000 3.41996700 C -1.36995600 1.00868200 -2.06126600 H -1.05989900 2.05173100 -2.18388000 H -0.90485800 0.41759000 -2.86116500 C -2.88054800 0.88049600 -2.08854000 H -3.26060800 1.25144900 -3.04786100 H -3.19854600 -0.16228600 -1.97866000 H -3.33387500 1.46978200 -1.28343600 O -0.15515300 0.35930100 2.36905800 H -0.07571400 1.18384400 1.83743600 H 0.07765100 0.95414400 -0.64116700 C 1.45474100 2.57739500 0.32438700 H 2.31159000 3.27988400 0.29725400 O 0.57086200 2.75820400 1.18783000 O 1.47834100 1.64572300 -0.55438600 O 3.09867000 -0.52559300 0.13790900 H 2.58889300 0.25785100 -0.16758500	

Table S2.21 Transition state: intramolecular cyclization of int.**3** in **7**



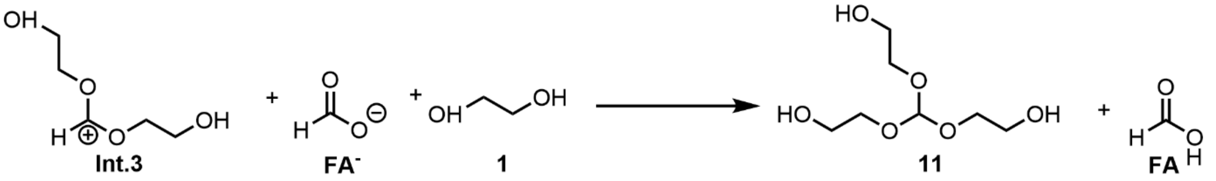




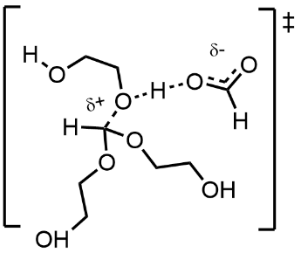
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.06522200 -0.91953400 0.20722900 H 0.03733100 0.08133200 0.65220700 O 0.81400700 -1.85979400 0.74717700 O -0.96139900 -1.37710600 -0.44959400 C -2.00290900 -0.40628100 -0.78552000 H -1.54081100 0.56092100 -0.99984000 H -2.46811000 -0.80054300 -1.68918700 C 2.18275000 -1.39234500 0.90945000 H 2.75405200 -2.23280900 1.30076000 H 2.19468300 -0.55398000 1.61129700 C -2.99220200 -0.32065000 0.36496900	H= -687.02806 Hartree G = -687.08555 Hartree

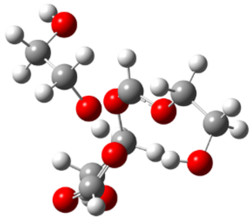
H -3.40927100 -1.31515300 0.57224700	
H -2.48620300 0.04465400 1.26913100	
C 2.58451100 -0.96642900 -0.50536200	
H 3.43032500 -0.27305800 -0.47995100	
H 2.83288000 -1.83493700 -1.11995800	
O 1.42933400 -0.33531900 -1.06772500	
H 1.49044600 0.72247400 -0.94884200	
C 1.08634000 2.63543000 0.25142200	
H 1.17313200 3.73744000 0.35028100	
O 1.58328700 2.15475600 -0.82513800	
O 0.53032200 2.00195700 1.17328800	
O -4.00886800 0.58868800 -0.05818700	
H -4.64417900 0.69705300 0.67016200	

Table S2.22 Transition state: substitution of int.**3** with **1** in **11**



TS



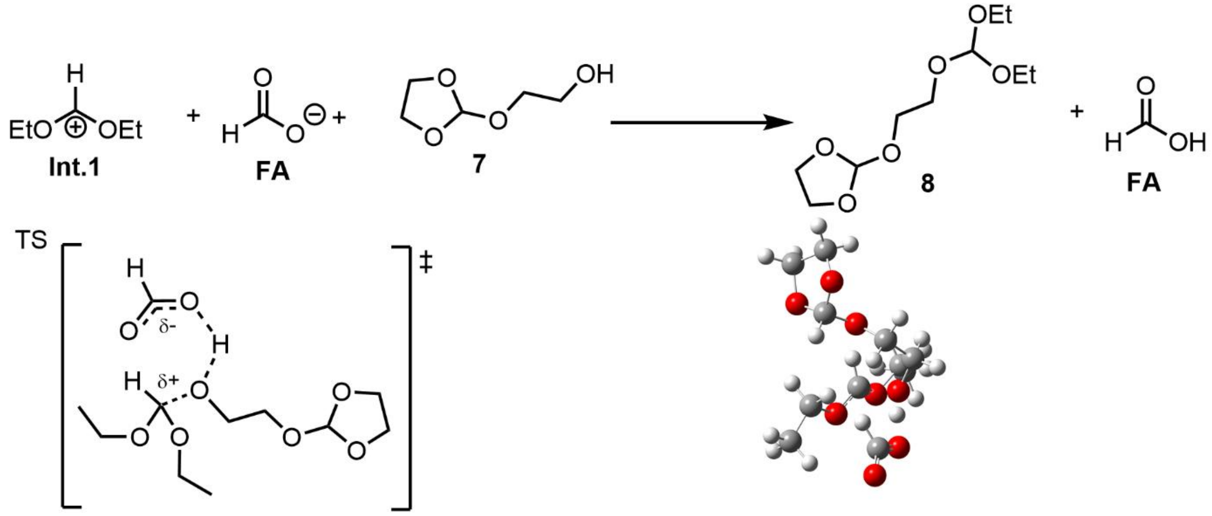


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -917.23056 Hartree
C -0.80614000 -1.08259700 0.63092600	G = -917.29952 Hartree
H -1.42926600 -1.75776900 0.05003500	
O 0.46336900 -1.37685900 0.82266700	
O -1.45591200 -0.51081600 1.61169700	
O -0.74952400 0.23148300 -0.66462900	
C 1.06641000 -2.25715900 -0.17837000	
H 0.82719800 -1.86834900 -1.17189300	
H 0.63109600 -3.25462900 -0.06309500	
C 2.56018900 -2.30768700 0.05055000	
H 2.77085500 -2.67918900 1.05990100	
H 2.95512600 -3.04390400 -0.66692900	
C -0.77606700 0.27380600 2.64716300	
H -1.47902900 0.21888900 3.48022700	
H 0.15872200 -0.21889900 2.92132000	
C -0.54398900 1.72729500 2.25871400	
H -1.38416000 2.09177000 1.65515900	
H -0.53867500 2.29565600 3.19917800	
C -1.54253100 0.04825500 -1.86157300	
H -1.27727100 0.86501000 -2.54024900	
H -1.28400700 -0.90622300 -2.33653600	
C -3.01881100 0.10921300 -1.55633200	
H -3.56062500 0.21778300 -2.50606000	
H -3.23484500 0.98114700 -0.92620000	
O 0.70335100 1.94339400 1.61707600	

H 0.60150400 2.18630000 0.67116600 H 0.23455800 0.41709700 -0.95778000 C 1.83696900 1.93884600 -1.55306800 H 2.74221500 2.24502800 -2.11257500 O 1.15499400 2.81846700 -0.99113100 O 1.59257600 0.67886900 -1.55295200 O 3.22321700 -1.05765700 -0.08899900 H 2.71015400 -0.46886300 -0.68651400 O -3.40614500 -1.10501700 -0.89729200 H -4.30714900 -0.99559300 -0.54870400	

2.10.2.2 DCE MECHANISM FOR THE FORMATION OF 8,9 AND 12

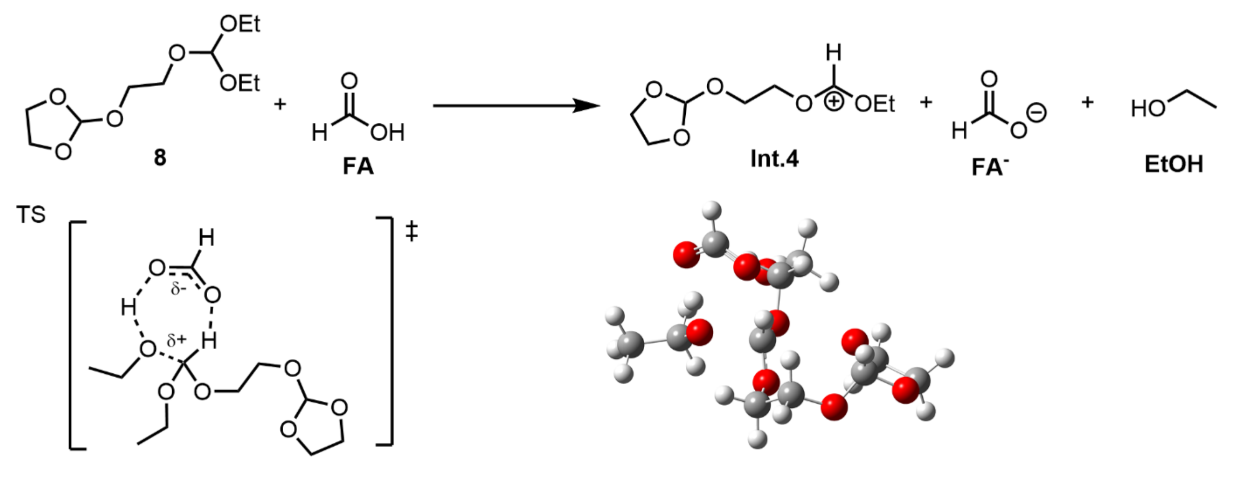
Table S2.23 Transition state: substitution of int.**1** with **7** in **8**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.04378200 1.24441200 0.58570400 H 0.03192800 1.24232600 0.41349700 O -1.55814600 0.43420500 1.47241400 O -1.72444900 2.35143100 0.45922300 C -0.73440600 -0.71911200 1.86191900 H 0.15769700 -0.33122600 2.36031000 H -0.44577300 -1.24489600 0.95126200 C -1.57027600 -1.58693900 2.77090800 H -2.46682600 -1.94646100 2.25527900 H -0.97421400 -2.45547700 3.07347500 H -1.86958600 -1.04200700 3.67284100 C -1.19425600 3.35028700 -0.47464000 H -0.10153100 3.32185200 -0.42224000 H -1.51997600 3.05088600 -1.47340400 C -1.74881200 4.69748600 -0.07404100 H -1.38344500 5.45284100 -0.77918100 H -2.84379900 4.69775500 -0.10685200 H -1.42119200 4.97629400 0.93336600 H -2.00176400 -0.51485700 -1.00725600 C -2.47586800 -2.74747800 -0.65558200 H -1.38193100 -2.80756400 -0.46382400 O -3.14415100 -3.78840200 -0.53248300 O -2.91596600 -1.59118400 -0.99293200	H= -1033.9133 Hartree G = -1033.9916 Hartree

O 1.51439100 -0.02592000 -0.60088800 C 0.79229600 -0.67885600 -1.65550000 H 1.45045000 -0.84169700 -2.51860100 H 0.42460300 -1.65413000 -1.30811900 C -0.35734800 0.21392700 -2.07203700 H 0.01251700 1.21557100 -2.31248600 H -0.82489200 -0.20349800 -2.97169600 O -1.37935200 0.35822400 -1.07586200 C 2.41893100 -0.86549500 0.08014200 H 1.92202900 -1.79556100 0.37568000 C 4.46334800 -0.10320500 -0.51973200 C 4.23629000 0.27062300 0.94243700 H 5.46675700 -0.47603500 -0.72953800 H 4.21806100 0.71904200 -1.20101400 H 4.89945600 -0.27623500 1.62052500 H 4.31416300 1.34403900 1.13028300 O 2.87474700 -0.15558700 1.19357000 O 3.53549700 -1.19337500 -0.70176300	

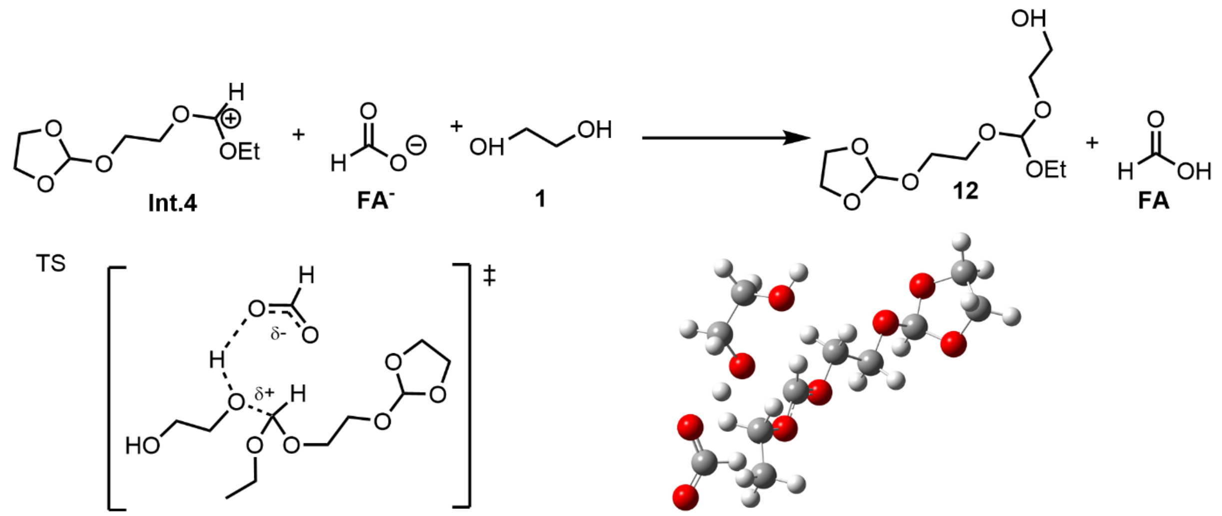
Table S2.24 Transition state: activation of **8** in int.**4**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.39311200 -0.20262600 -0.33428500 H -0.33139400 -0.62847000 0.66825400 O 0.26315900 -0.71420000 -1.34383600 O -0.60489900 1.07901600 -0.48288400 O -2.12301400 -1.02955900 -0.53435200 C 0.70061700 -2.10185200 -1.23302200 H 1.07379400 -2.32797500 -2.23212400 H -0.16847700 -2.72846900 -1.01503600 C 1.78146100 -2.31062100 -0.19050700 H 1.40873900 -2.11885400 0.82065000 H 2.07385200 -3.36678800 -0.24133500 C -1.11666100 1.79070900 0.68763700 H -2.09774900 1.38149000 0.94044000 H -0.42141600 1.63538800 1.51589700 C -1.20267300 3.25348500 0.34509600 H -1.42154900 3.79505900 1.27598300 H -0.23812100 3.60646900 -0.04307700 C -2.96502400 -0.38150300 -1.50953000 H -3.33083200 0.56775400 -1.10193200	H= -1109.1258 Hartree G = -1109.2068 Hartree

H -2.32719000 -0.16318400 -2.37122100 C -4.11550300 -1.29207600 -1.90537800 H -4.73087700 -0.79586600 -2.66630000 H -3.74082700 -2.23391000 -2.32246500 H -4.75481400 -1.51951300 -1.04447300 C -2.30258700 -1.04621400 2.70874400 H -2.69962300 -1.00781600 3.74622800 O -1.06826300 -1.18313700 2.55905600 O -3.18228500 -0.94090400 1.78968600 H -2.57036100 -1.01236200 0.40546100 O 2.93249600 -1.50593600 -0.46957300 C 3.25414600 -0.57694500 0.54491100 H 3.32184900 -1.08136800 1.51392900 C 4.21712500 1.35669300 -0.27188900 C 2.69389100 1.44082100 -0.32192700 H 4.65041000 2.05564900 0.45065400 H 4.68739200 1.49111100 -1.24882700 H 2.29470200 2.40418600 -0.00328000 H 2.29442900 1.17504100 -1.30552600 O 4.46942900 0.00801300 0.19380500 O 2.30422100 0.45292100 0.65419100 O -2.24316900 3.44680900 -0.61664100 H -2.26342600 4.38902500 -0.85661400	

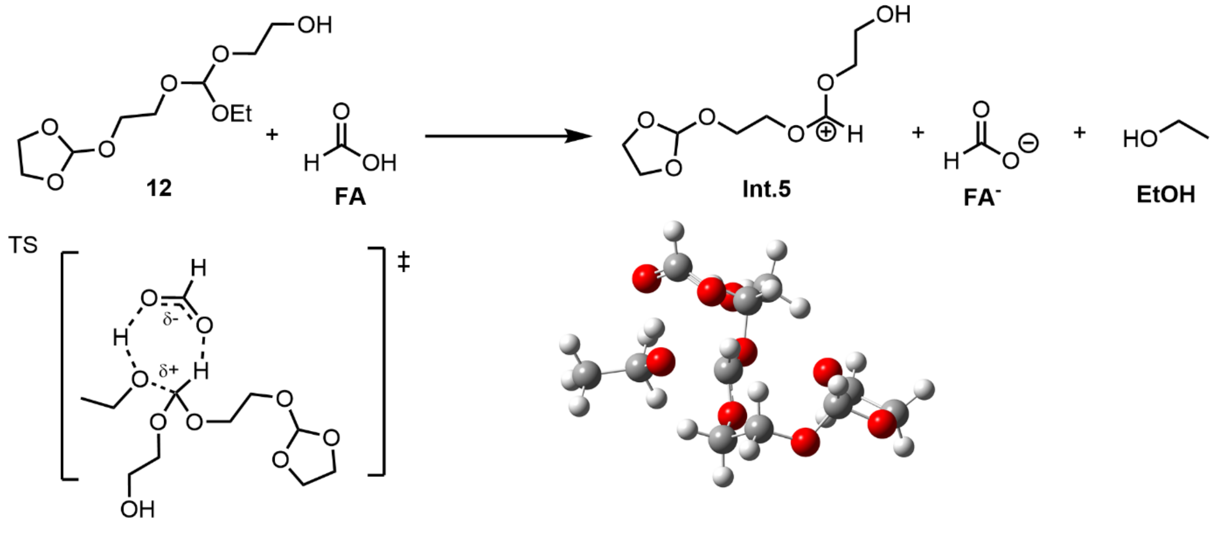
Table S2.25 Transition state: substitution of int.**4** with **1** in **12**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.38271100 0.02732500 0.84215100 H -1.26229800 1.01365900 1.28954300 O -0.34548400 -0.62048800 0.39705700 O -2.00253300 0.91478100 -0.85926800 O -2.36685500 -0.74748100 1.17439600 C 0.83893200 0.16871200 0.07782800 H 1.00942300 0.89551200 0.87479600 H 0.65287700 0.68123600 -0.86741400 C 1.98744300 -0.81555200 -0.03189500 H 1.78731300 -1.55282600 -0.82155600 H 2.13459000 -1.34368700 0.91771700 C -2.45440400 2.27985000 -0.80165500	H= -1109.12 Hartree G = -1109.2037 Hartree

H -2.92570700 2.52178700 -1.76161800 H -3.20272000 2.39978700 -0.00727300 C -1.29811600 3.22278900 -0.57400600 H -0.49502500 3.01520400 -1.29281800 H -1.65106000 4.25169600 -0.72572100 C -3.56100000 -0.11166200 1.75999700 H -3.22266100 0.67864400 2.43533900 H -4.12053000 0.31908500 0.92812600 C -4.34291600 -1.19060700 2.46905600 H -5.25099600 -0.74473100 2.89052500 H -4.63952700 -1.98001900 1.77018500 H -3.76166600 -1.63194700 3.28578400 O -0.82381100 3.05396400 0.77292100 H -0.01576600 3.58322100 0.88731800 H -2.79838900 0.32783900 -1.19711200 C -3.96448800 -1.68262000 -1.55422700 H -2.96042800 -2.10346100 -1.31857600 O -4.90227400 -2.48544000 -1.72124900 O -4.02248600 -0.40703200 -1.62987100 O 3.13475700 -0.03270100 -0.35978100 C 4.26923600 -0.80880600 -0.68598200 H 4.00850000 -1.55392400 -1.44531000 C 6.24305700 0.24332100 -0.11558600 C 5.66165100 -0.51868000 1.07337900 H 7.18356000 -0.19015200 -0.47012800 H 6.37446400 1.31008600 0.08043800 H 6.40528600 -1.07193600 1.64849700 H 5.07970500 0.12932000 1.73784600 O 4.79472000 -1.47602000 0.42894400 O 5.24533800 0.07056500 -1.15226600	

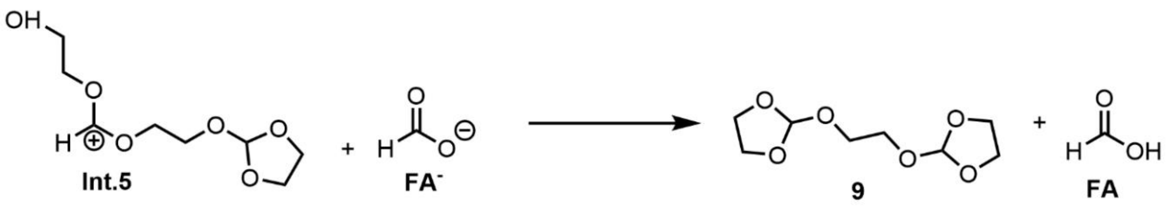
Table S2.26 Transition state: activation of **12** in int.**5**

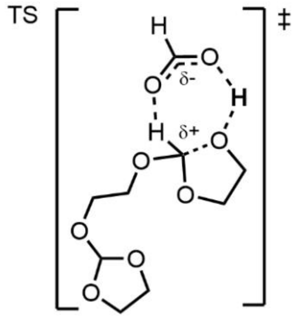


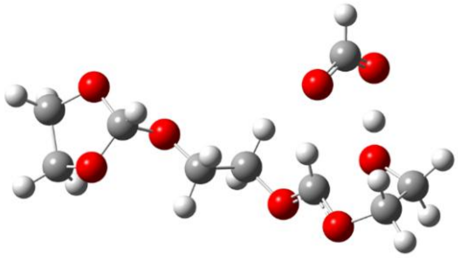
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.39311200 -0.20262600 -0.33428500 H -0.33139400 -0.62847000 0.66825400 O 0.26315900 -0.71420000 -1.34383600 O -0.60489900 1.07901600 -0.48288400 O -2.12301400 -1.02955900 -0.53435200	H= -1109.1258 Hartree G = -1109.2068 Hartree

C 0.70061700 -2.10185200 -1.23302200 H 1.07379400 -2.32797500 -2.23212400 H -0.16847700 -2.72846900 -1.01503600 C 1.78146100 -2.31062100 -0.19050700 H 1.40873900 -2.11885400 0.82065000 H 2.07385200 -3.36678800 -0.24133500 C -1.11666100 1.79070900 0.68763700 H -2.09774900 1.38149000 0.94044000 H -0.42141600 1.63538800 1.51589700 C -1.20267300 3.25348500 0.34509600 H -1.42154900 3.79505900 1.27598300 H -0.23812100 3.60646900 -0.04307700 C -2.96502400 -0.38150300 -1.50953000 H -3.33083200 0.56775400 -1.10193200 H -2.32719000 -0.16318400 -2.37122100 C -4.11550300 -1.29207600 -1.90537800 H -4.73087700 -0.79586600 -2.66630000 H -3.74082700 -2.23391000 -2.32246500 H -4.75481400 -1.51951300 -1.04447300 C -2.30258700 -1.04621400 2.70874400 H -2.69962300 -1.00781600 3.74622800 O -1.06826300 -1.18313700 2.55905600 O -3.18228500 -0.94090400 1.78968600 H -2.57036100 -1.01236200 0.40546100 O 2.93249600 -1.50593600 -0.46957300 C 3.25414600 -0.57694500 0.54491100 H 3.32184900 -1.08136800 1.51392900 C 4.21712500 1.35669300 -0.27188900 C 2.69389100 1.44082100 -0.32192700 H 4.65041000 2.05564900 0.45065400 H 4.68739200 1.49111100 -1.24882700 H 2.29470200 2.40418600 -0.00328000 H 2.29442900 1.17504100 -1.30552600 O 4.46942900 0.00801300 0.19380500 O 2.30422100 0.45292100 0.65419100 O -2.24316900 3.44680900 -0.61664100 H -2.26342600 4.38902500 -0.85661400	

Table S2.27 Transition state: intramolecular cyclization of int.**5** in **9**



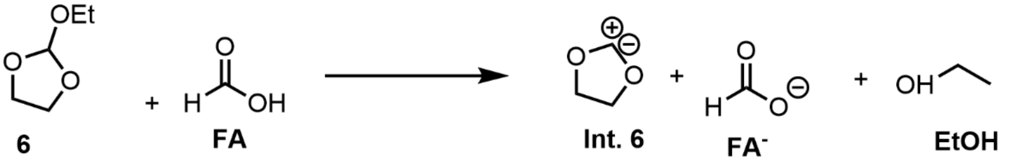


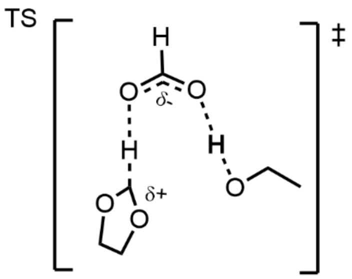


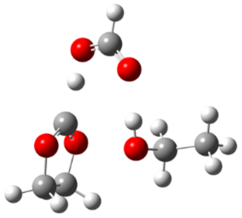
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.89698500 -0.95324100 0.13026900 H 1.72343100 0.03304100 0.57521300 O 2.69310700 -1.81599400 0.72893400 O 0.98468200 -1.51085100 -0.61367200 C -0.12362500 -0.65194000 -1.03054900 H 0.25508700 0.35186200 -1.23812600 H -0.49355000 -1.10456900 -1.95054000 C 3.98682500 -1.20982800 1.00715400 H 4.60896700 -1.99055300 1.44244200 H 3.85219300 -0.38286900 1.70990400 C -1.18391800 -0.64835600 0.05800400 H -1.50177400 -1.67365800 0.28200200 H -0.79027400 -0.19132400 0.97737500 C 4.45622900 -0.72871100 -0.36835800 H 5.22339200 0.04515300 -0.27203000 H 4.83837200 -1.56084700 -0.96433500 O 3.29189300 -0.20935200 -1.01957700 H 3.23504000 0.84760300 -0.88844600 C 2.54403100 2.67940900 0.29548700 H 2.51058100 3.78137700 0.42203100 O 3.17290700 2.27903100 -0.74430100 O 1.98167300 1.96862700 1.15510700 O -2.27100400 0.12044400 -0.45340200 C -3.25457900 0.41493600 0.51879100 H -2.78710000 0.86961800 1.39870000 C -5.36925000 0.53650600 -0.39666300 C -5.00098700 -0.90501100 -0.05069600 H -6.18604900 0.91964300 0.22304800 H -5.60553900 0.67721800 -1.45400100 H -5.80962700 -1.46554700 0.42006400 H -4.61745200 -1.45544500 -0.91662300 O -3.95473400 -0.72754900 0.92788900 O -4.16927000 1.28273100 -0.07439200	H= -954.14042 Hartree G = -954.20885 Hartree

2.10.2.3 DCE MECHANISM FOR THE FORMATION OF 7, 8, 12 AND 9 THROUGH THE SUBSTITUTION OF CARBOCATIONS OR CARBENE INTERMEDIATES

Table S2.28 Transition state: activation of **6** in int.**5**

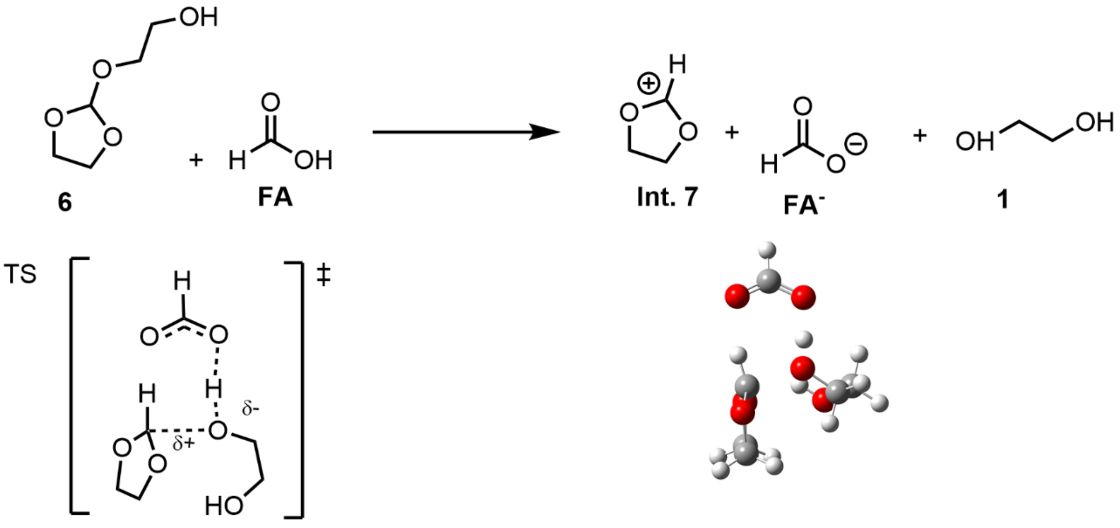






Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.06946300 -0.90483800 0.26247900 H 0.13992200 -1.77458400 0.48062600 O -1.53451400 -0.06048300 1.13669500 O 0.59451700 1.15616100 -0.76263900 C -2.63267700 0.75241000 0.55687700 H -2.30196300 1.78976700 0.58225300 H -3.50657800 0.60260000 1.18990000 C -2.76800800 0.17415200 -0.84504600 H -3.72094100 -0.31795800 -1.03668600 H -2.51856900 0.87258800 -1.64253100 O -1.72570700 -0.88224300 -0.86053700 H 1.18818700 0.37344000 -0.78669900 C 2.11412500 -2.10339400 0.04031000 H 2.94746300 -2.80667000 0.19677400 O 2.26784100 -1.09763900 -0.66059500 O 1.02499300 -2.46158900 0.65622400 C 0.98026700 1.96794700 0.34974400 H 1.02356000 1.35690200 1.26348900 H 0.17640200 2.70063500 0.48157000 C 2.31062800 2.67844800 0.12989600 H 2.54998100 3.31422700 0.99280700 H 3.12633500 1.95526700 0.00463700 H 2.26992400 3.31177300 -0.76487900	H= -611.80236 Hartree G = -611.86099 Hartree

Table S2.29 Transition state: activation of **7** in int.**7**

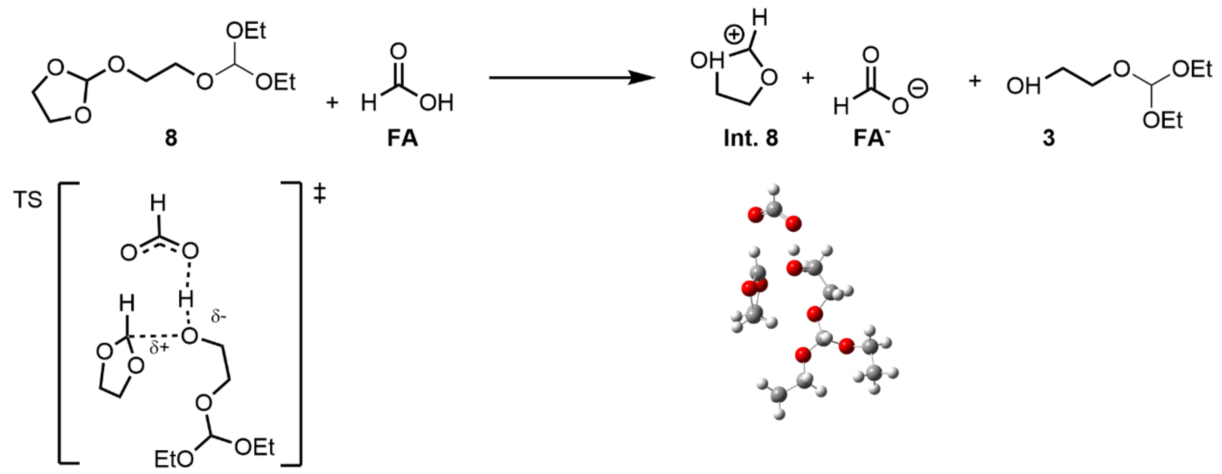


TS.1 int.7

Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.06946300 -0.90483800 0.26247900 H 0.13992200 -1.77458400 0.48062600 O -1.53451400 -0.06048300 1.13669500 O 0.59451700 1.15616100 -0.76263900 C -2.63267700 0.75241000 0.55687700 H -2.30196300 1.78976700 0.58225300 H -3.50657800 0.60260000 1.18990000	H= -611.80236 Hartree G = -611.86099 Hartree

C -2.76800800 0.17415200 -0.84504600 H -3.72094100 -0.31795800 -1.03668600 H -2.51856900 0.87258800 -1.64253100 O -1.72570700 -0.88224300 -0.86053700 H 1.18818700 0.37344000 -0.78669900 C 2.11412500 -2.10339400 0.04031000 H 2.94746300 -2.80667000 0.19677400 O 2.26784100 -1.09763900 -0.66059500 O 1.02499300 -2.46158900 0.65622400 C 0.98026700 1.96794700 0.34974400 H 1.02356000 1.35690200 1.26348900 H 0.17640200 2.70063500 0.48157000 C 2.31062800 2.67844800 0.12989600 H 2.54998100 3.31422700 0.99280700 H 3.12633500 1.95526700 0.00463700 H 2.26992400 3.31177300 -0.76487900	

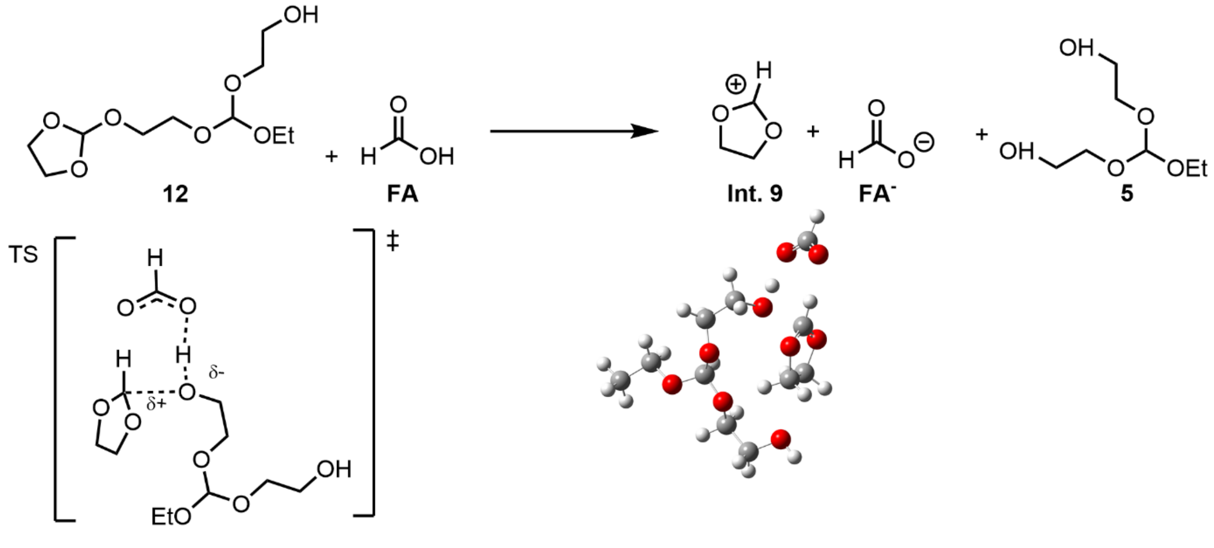
Table S2.30 Transition state: activation of **8** in int.**8**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -2.42076600 1.15146400 0.20642700 H -3.46778500 0.84883500 0.29138200 O -1.73244900 1.44408400 1.27913100 O -1.89797200 -0.70479900 -0.20837000 C -0.56813900 2.26294500 0.87555100 H 0.32397900 1.79435300 1.27942600 H -0.73688800 3.25704000 1.29152100 C -0.63777300 2.21038100 -0.64653900 H -0.52948800 3.17650300 -1.13594200 H 0.02965800 1.46556800 -1.07856700 O -2.02108500 1.75579900 -0.88419300 H -2.78837800 -1.12703800 -0.53690100 C -5.13154000 -1.14556100 -0.63529300 H -6.08882300 -1.61313800 -0.95050100 O -4.07989100 -1.76157400 -1.00960600 O -5.19250900 -0.08978600 0.03601900 C -1.34277900 -1.51182300 0.84193500 H -1.86933200 -2.47205400 0.87088000 H -1.48681000 -1.00616300 1.80406200 C 0.12897700 -1.74797800 0.58897500 H 0.27490200 -2.14305100 -0.42514900	H= -1033.9099 Hartree G = -1033.9882 Hartree

O 0.80454700 -0.49711200 0.73179200	
C 2.05169500 -0.42212200 0.10730700	
H 1.97187600 -0.71618500 -0.95238900	
H 0.51865900 -2.47716600 1.31169400	
O 2.39184700 0.91844900 0.23887000	
O 2.99879700 -1.23816200 0.75230000	
C 3.50787000 1.33727200 -0.56196000	
H 4.42223000 0.85360500 -0.19879500	
H 3.34193200 1.02380800 -1.60227500	
C 3.61046800 2.84645100 -0.46166800	
H 3.77156600 3.15909400 0.57669400	
H 4.45660800 3.20029800 -1.06244900	
H 2.69716700 3.32582000 -0.83328800	
C 3.45152100 -2.40085400 0.02708200	
H 3.71463900 -3.13102100 0.79814900	
H 2.62489900 -2.81778200 -0.56082200	
C 4.64852400 -2.09997300 -0.86084700	
H 4.99737800 -3.02704900 -1.33381700	
H 4.38981800 -1.38911400 -1.65351100	
H 5.47356100 -1.68157000 -0.27276500	

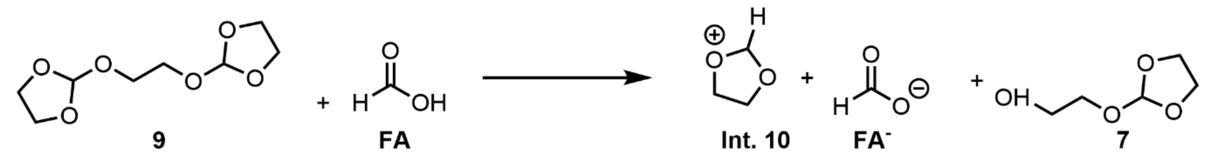
Table S2.31 Transition state: activation of **12** in int.**9**

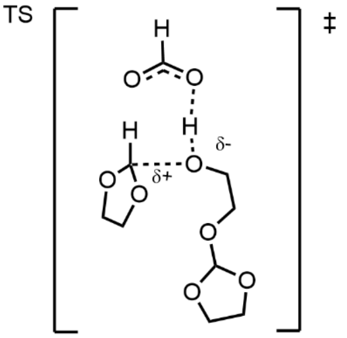


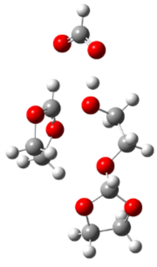
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1109.1233 Hartree
C 2.51449900 -1.01675400 0.42650000	G = -1109.2046 Hartree
H 3.48857200 -0.54266300 0.57749000	
O 1.74227700 -1.30249100 1.43035800	
O 1.74859000 0.79493100 -0.19304000	
C 0.64320900 -2.17307500 0.94065300	
H -0.29333300 -1.66694700 1.15346800	
H 0.73757100 -3.11302400 1.48324200	
C 0.93969300 -2.28165500 -0.55474400	
H 1.01213400 -3.29904300 -0.93001600	
H 0.27720100 -1.67779100 -1.17160300	
O 2.29150700 -1.68838600 -0.66497400	
H 2.57195600 1.17647500 -0.67271300	
C 4.93387300 1.39697600 -0.76546000	
H 5.86183100 1.84983400 -1.17807600	
O 3.85377400 1.76272000 -1.33140200	

O 5.05876200 0.59401200 0.18986700 C 1.34571900 1.71111800 0.83218100 H 1.96559400 2.61446900 0.78214300 H 1.49560200 1.24348700 1.81314400 C -0.10997600 2.09173000 0.66102500 H -0.28903500 2.41435300 -0.37044600 O -0.94661400 0.97371800 0.99311000 C -1.91757400 0.60168300 0.06117600 H -1.55238600 0.77128900 -0.96528500 H -0.35247100 2.92253800 1.33508100 O -2.13830400 -0.74661400 0.31194900 O -3.14098000 1.27098400 0.23905900 C -2.93064400 -1.41217000 -0.67833100 H -3.94325700 -0.99250500 -0.69671800 H -2.47390300 -1.27605500 -1.66912200 C -3.01195900 -2.87798200 -0.32915300 H -3.37608600 -2.99585400 0.70038400 H -3.73135200 -3.35241600 -1.01052300 C -3.22628400 2.58505400 -0.33695600 H -2.64462500 3.29298500 0.26725900 H -2.79839200 2.56617200 -1.34932600 C -4.68631700 2.99297000 -0.37619600 H -4.77834700 4.00039900 -0.79953400 H -5.26901000 2.30182000 -0.99632500 H -5.11542800 3.00427600 0.63262900 O -1.71542600 -3.47555400 -0.47298800 H -1.78695800 -4.41572400 -0.23483000	

Table S2.32 Transition state: activation of **9** in int.**10**





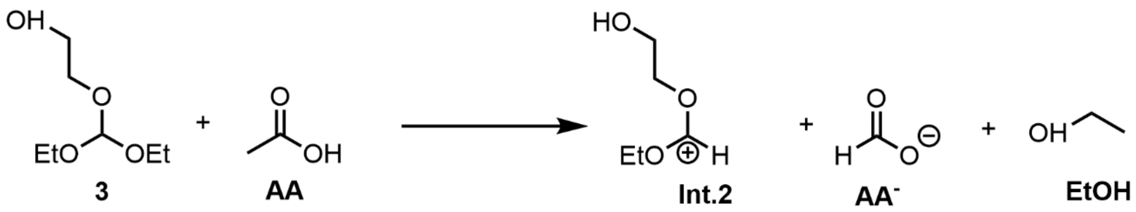
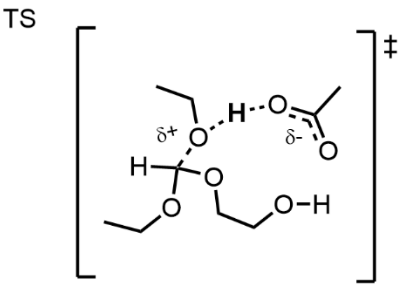
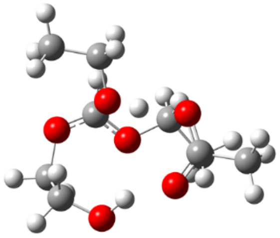


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.80662800 1.20511300 0.29566200 H -2.82668000 0.93201700 0.58100100 O -0.89460100 1.40108900 1.20983700 O -1.46823500 -0.66757100 -0.30811200 C 0.21325300 2.17223200 0.60389900 H 1.13265700 1.62304800 0.78495100 H 0.21132200 3.14546200 1.09571600 C -0.18238500 2.22129200 -0.86869600	H= -954.14259 Hartree G = -954.21109 Hartree

H -0.12686000 3.21206900 -1.31586900 H 0.33239700 1.47779000 -1.47633500 O -1.60774200 1.84264300 -0.82784600 H -2.42595500 -1.02584200 -0.47121100 C -4.74810400 -0.91875200 -0.09427100 H -5.77747300 -1.31385800 -0.23175400 O -3.83399500 -1.56572400 -0.70208800 O -4.60727200 0.09668100 0.62663200 C -0.77575800 -1.54379700 0.59250300 H -1.34412300 -2.47452400 0.69874500 H -0.70263900 -1.06775600 1.57768200 C 0.60489600 -1.85673500 0.06225500 H 0.53926800 -2.25211100 -0.96063700 O 1.37063400 -0.64694700 0.06739300 C 2.53486200 -0.69107900 -0.71557000 H 2.31011900 -1.07784900 -1.71540700 C 4.17993800 0.71512500 0.09708600 C 4.21223200 -0.64009700 0.80090000 H 5.06827800 0.88664500 -0.51917700 H 4.03623500 1.55288200 0.78395400 H 5.21801700 -1.03422700 0.95244400 H 3.66758100 -0.62621000 1.75142300 H 1.08147900 -2.61069400 0.70242000 O 3.03092900 0.61664600 -0.77913300 O 3.53684800 -1.49265000 -0.14675100	

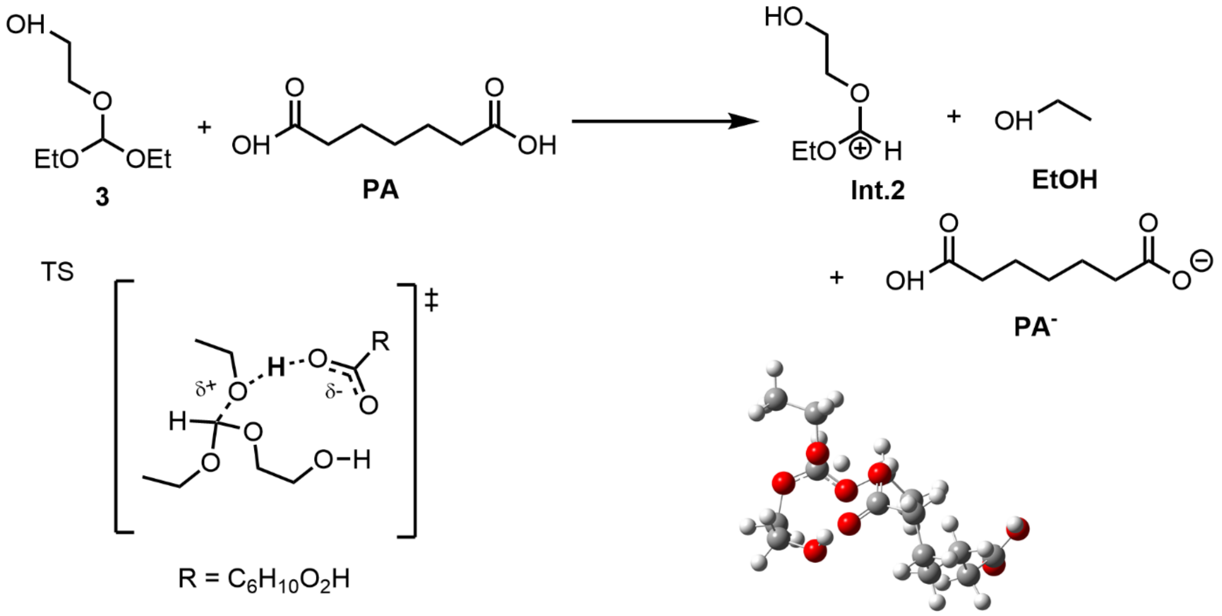
2.10.2.4 COMPUTATIONS FOR THE SCREENING OF CATALYSTS

It should be noted that the calculations of this section use a transition state with a slightly higher $\Delta G^{\ddagger}$ (14.5 kcal mol^{-1}) than the one identified later in the study (13.5 kcal mol^{-1}). This minor difference did not significantly affect our study as we were comparing the same transition state in presence of different acids.

Table S2.33 Transition state: activation of **3** in int.**2** using AA	
  	
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.38591800 0.24722600 -1.11575600 H 1.61075300 -0.53283000 -1.83772800 O 0.31872900 0.96283400 -1.22707900	H= -806.10096 Hartree G = -806.17237 Hartree

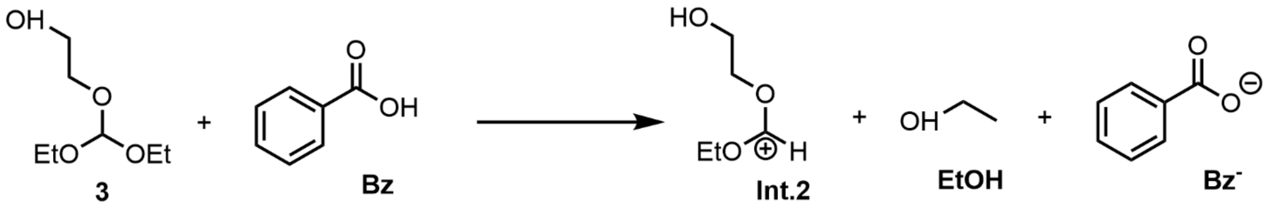
O 2.39737600 0.70285200 -0.45831500	
O 0.76079600 -1.27051100 0.20959400	
C -0.72801100 0.47835600 -2.15750300	
H -1.05317000 -0.49460900 -1.78747000	
H -0.25983000 0.38194500 -3.14034800	
C -1.84300900 1.49421500 -2.14111800	
H -1.49554100 2.47210100 -2.49159700	
H -2.63680700 1.14809100 -2.81288900	
H -2.26035100 1.59878900 -1.13531400	
C 2.28194000 1.88021100 0.42751100	
H 3.33002900 2.10555700 0.62486500	
H 1.82353400 2.69344400 -0.13900500	
C 1.53112000 1.61303500 1.73083700	
H 1.66009800 0.56341300 2.02265000	
H 2.02344900 2.23338100 2.49039600	
C 1.24884700 -2.57106400 -0.16035400	
H 0.66558500 -3.32227300 0.38629900	
H 1.08091300 -2.73788700 -1.23535100	
C 2.72441400 -2.69365000 0.17600100	
H 3.07768800 -3.70198600 -0.07211100	
H 3.32695300 -1.97420000 -0.38933400	
H 2.89296800 -2.52063600 1.24548300	
O 0.17041200 1.99804200 1.70944500	
H -0.43616700 1.24770700 1.49529800	
H -0.26314300 -1.31665900 0.24415000	
C -2.46560500 -0.61924800 0.80094400	
O -1.95505100 0.34609000 1.42950200	
O -1.80571800 -1.53403900 0.20232800	
C -3.98429900 -0.70975700 0.70846400	
H -4.46971500 -0.04156200 1.42511700	
H -4.29549100 -0.42113800 -0.30429300	
H -4.32201200 -1.73874200 0.87321500	

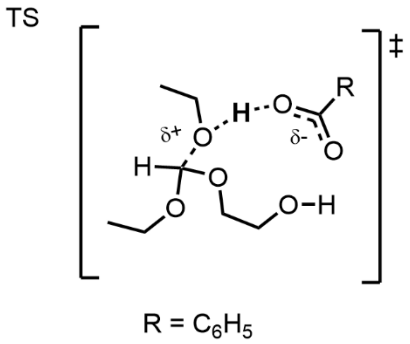
Table S2.34 Transition state: activation of **3** in int.**2** using PA

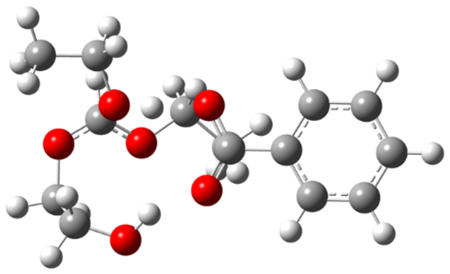


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -2.55171000 -1.64242300 -0.12686600 H -2.95948000 -1.98093000 -1.07520400 O -1.28765100 -1.73025800 0.11105600 O -3.39243200 -1.60731000 0.85172700 O -2.75942900 0.32129600 -0.84987300 C -0.37773800 -1.86245900 -1.04711500 H -0.27589200 -0.85932200 -1.46347000 H -0.85293900 -2.53361400 -1.76778500 C 0.93407000 -2.39651600 -0.52730300 H 0.82022100 -3.39918300 -0.10142500 H 1.64254500 -2.45195600 -1.36106500 H 1.34913100 -1.72906200 0.23308700 C -2.97187700 -1.32297800 2.23854500 H -3.84617400 -1.64220800 2.80616200 H -2.11653600 -1.95792100 2.47840600 C -2.66940900 0.14531000 2.50089900 H -3.34645100 0.77396500 1.91004100 H -2.90363300 0.31044400 3.56354000 C -3.43944600 0.37785400 -2.11421000 H -3.21373800 1.34361800 -2.58259300 H -3.05436600 -0.41149300 -2.77791700 C -4.93506500 0.21959400 -1.90533800 H -5.45464500 0.27750000 -2.86961900 H -5.17453400 -0.74729400 -1.44786200 H -5.32040900 1.01371800 -1.25497100 O -1.31107300 0.46858500 2.27414500 H -1.20884800 1.19437500 1.60744600 H -1.84102600 0.76277300 -0.95679700 C -0.04469100 2.25106000 -0.43117400 O -0.63599100 2.52059900 0.65149300 O -0.45723400 1.40192800 -1.28964900 C 1.24652600 3.00074100 -0.76424800 H 1.72049700 2.51905700 -1.62521000 H 0.96054400 4.01295300 -1.08450700 C 2.22759900 3.11129000 0.41219200 H 1.77065700 3.71688800 1.20374100 C 2.66165200 1.76699000 1.01328600 H 1.79632700 1.27328600 1.47485600 H 3.37869300 1.96165600 1.82312200 C 3.29897400 0.79998900 0.00688600 H 2.53941000 0.46090800 -0.70775100 H 4.06836600 1.34137100 -0.56465100 C 3.91728400 -0.40992800 0.71917500 H 3.20225200 -0.84868900 1.42238900 H 4.78164500 -0.08789200 1.31790500 C 4.40808500 -1.54680600 -0.15395300 H 3.11840400 3.65572000 0.06838700 O 4.53664700 -2.69174200 0.23745300 O 4.75503300 -1.25887900 -1.43175400 H 4.61148900 -0.31273500 -1.62968800	H= -1151.8352 Hartree G = -1151.924 Hartree

Table S2.35 Transition state: activation of **3** in int.**2** using Bz



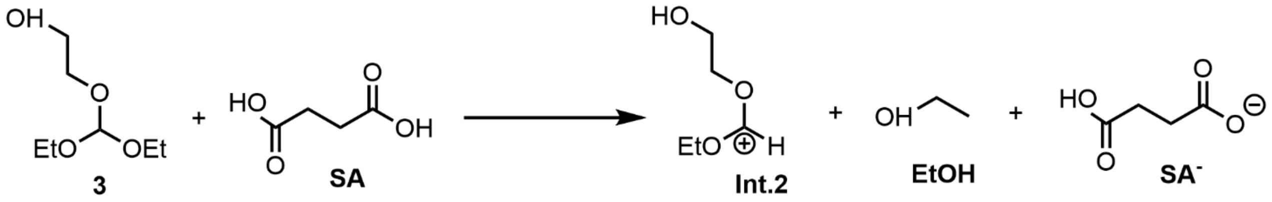




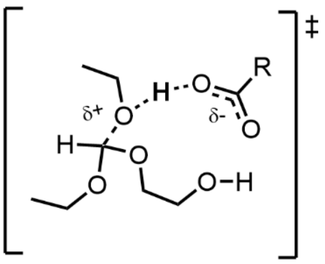
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.65999500 -0.09633200 -1.04231500 H 2.86234400 -1.00142700 -1.61049100 O 1.69007600 0.69010900 -1.38808600 O 3.68166100 0.39562800 -0.41660600 O 1.82765200 -1.21633300 0.43165500 C 0.69150800 0.14789500 -2.33577400 H 0.24138600 -0.72635100 -1.86381000 H 1.23472900 -0.14063100 -3.23936800 C -0.31977300 1.23788600 -2.59155300 H 0.15062900 2.11709500 -3.04503600 H -1.07677500 0.85394200 -3.28488100 H -0.81862000 1.53483200 -1.66435000 C 3.63593700 1.72698600 0.21624700 H 4.69102400 1.90373800 0.42667100 H 3.27628300 2.44916500 -0.51981300 C 2.81462200 1.78539800 1.50319500 H 2.83435700 0.80706200 1.99925600 H 3.33060900 2.50045000 2.15585100 C 2.21813000 -2.60194700 0.36937900 H 1.50241200 -3.17657100 0.96873200 H 2.14571100 -2.95659400 -0.66940100 C 3.62824600 -2.77569500 0.90301200 H 3.89826900 -3.83861200 0.88908000 H 4.35824900 -2.23096800 0.29462800 H 3.69837500 -2.41336300 1.93530200 O 1.49661300 2.27274100 1.33637100 H 0.83684800 1.55307200 1.19211200 H 0.79953700 -1.17261600 0.37699700 C -1.32814000 -0.20237900 0.61982100 O -0.77170100 0.79956800 1.13950000 O -0.72685900 -1.26223800 0.23975200 C -2.82791100 -0.16326700 0.41955600 C -3.56241500 0.96841600 0.80253100 C -3.50102800 -1.25106800 -0.15563400	H= -997.81688 Hartree G = -997.89401 Hartree

C -4.94566400 1.01317400 0.61438500 H -3.03823400 1.80873400 1.24638000 C -4.88448700 -1.20902400 -0.34474700 H -2.93075000 -2.12535200 -0.45208400 C -5.61033100 -0.07622400 0.03994000 H -5.50501000 1.89582900 0.91435600 H -5.39618000 -2.05777000 -0.79164700 H -6.68687000 -0.04238400 -0.10745100	

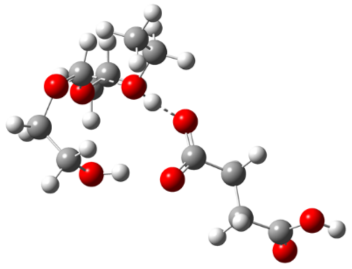
Table S2.36 Transition state: activation of 3 in int.**2** using SA



TS



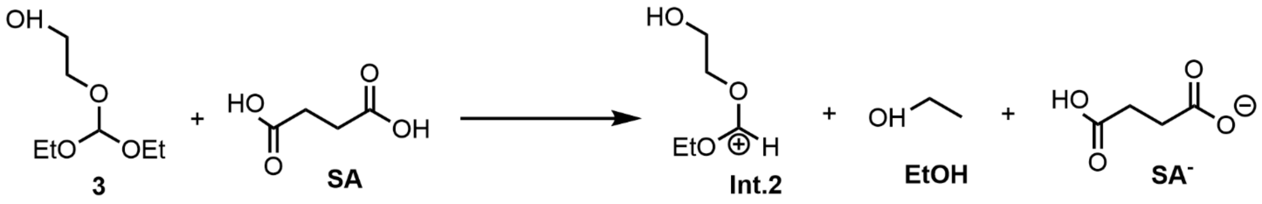
$R = C_3H_4OH$



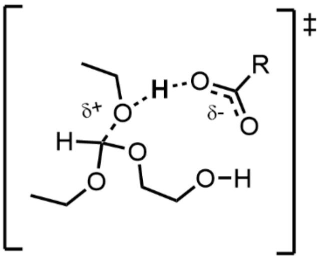
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 3.15769600 0.14770600 -0.37756900 H 3.57864500 -0.24892800 -1.29849500 O 2.59905500 1.31834800 -0.37755200 O 3.73235000 -0.27942300 0.70550600 O 1.62537800 -1.11498900 -0.52693100 C 2.07396600 1.82234800 -1.65806900 H 1.07156900 1.40235500 -1.76155000 H 2.72159500 1.45132500 -2.45805300 C 2.05896600 3.33055100 -1.58262800 H 3.06998200 3.73312500 -1.45729900 H 1.64263100 3.72350800 -2.51732500 H 1.42986000 3.67535000 -0.75495000 C 3.41452100 0.28680000 2.02787600 H 4.22613000 -0.10353500 2.64284900 H 3.48344500 1.37500600 1.96729000 C 2.06924500 -0.15574800 2.58161900 H 1.88766800 -1.20467900 2.31796500 H 2.16475600 -0.09890400 3.67705300 C 1.79897100 -2.10363000 -1.56120200 H 0.81193600 -2.52264500 -1.78601100 H 2.17292400 -1.61682700 -2.47355200 C 2.75298200 -3.18695100 -1.09258100 H 2.85782200 -3.94938700 -1.87402400 H 3.74808900 -2.78110000 -0.87869000 H 2.37327300 -3.66959700 -0.18456100	H= -1033.9654 Hartree G = -1034.0483 Hartree

O 1.01130400 0.68573800 2.16217600	
H 0.28387200 0.17086400 1.73082200	
H 0.72522000 -0.63452400 -0.67839800	
C -1.51000900 -0.18388700 -0.09750700	
O -1.23303500 -0.41831800 1.10720200	
O -0.65706700 -0.07440900 -1.04110000	
C -2.97329800 -0.02138700 -0.51736600	
H -3.06119000 0.91757400 -1.07709000	
H -3.20400500 -0.82728800 -1.22485000	
C -3.96377400 -0.03906000 0.65855500	
H -3.74605200 0.78000000 1.34724000	
H -3.87623400 -0.98474600 1.20064000	
C -5.37540100 0.12827100 0.16484100	
O -5.89126200 -1.02388700 -0.32507300	
H -6.79223700 -0.83853300 -0.66328800	
O -6.01083500 1.16962700 0.16183100	

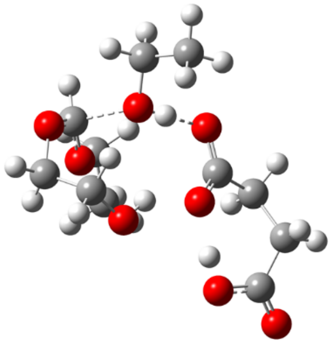
Table S2.37 Transition state: activation of **3** in int.**2** using SA (intramolecular stabilization of the carboxylate with the COOH)



TS



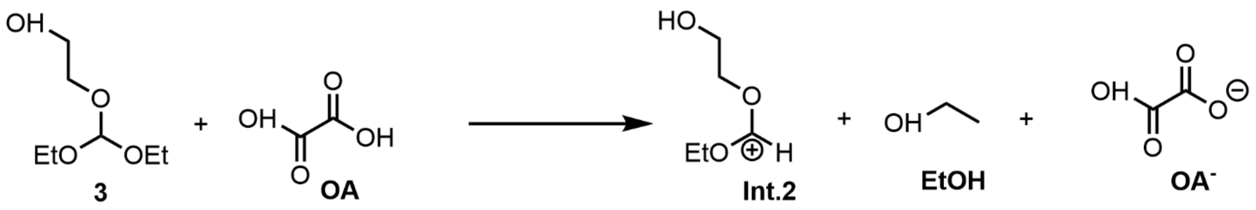
R = C_3H_4OH

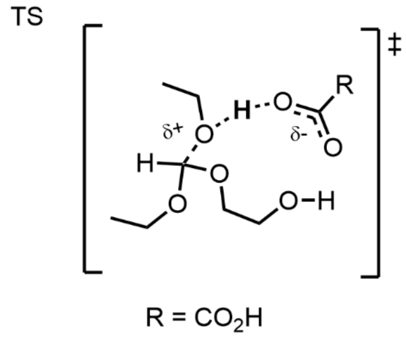


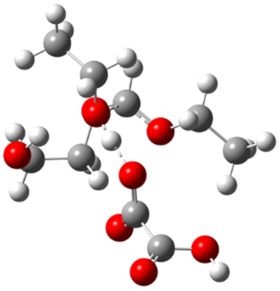
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1033.9786 Hartree
C -2.57470200 -0.58974500 -0.91491700	G = -1034.0583 Hartree
H -3.02641200 -0.06227100 -1.75208500	
O -1.49728100 -1.29692800 -1.10168600	
O -3.42325300 -0.96693700 -0.00147700	
O -1.89131400 1.02736600 -0.09437900	
C -0.75341800 -1.06101500 -2.35588100	
H -0.51406300 0.00256900 -2.40326800	
H -1.42047100 -1.33411600 -3.17793700	
C 0.48584000 -1.92120600 -2.30984100	
H 0.22750700 -2.98415700 -2.25212200	
H 1.06170800 -1.75450500 -3.22721400	
H 1.11390000 -1.65990100 -1.45317200	
C -3.00792100 -1.84898900 1.10258900	
H -3.96867000 -2.16921800 1.50745100	
H -2.47570000 -2.70632900 0.68538800	
C -2.19136300 -1.14931800 2.18351000	

H -2.55135300 -0.12076500 2.31204000 H -2.39607900 -1.69365800 3.11291100 C -2.80113900 2.14435000 -0.19651400 H -2.78761900 2.52809800 -1.22446100 H -3.79774000 1.74496000 0.01244900 C -2.43286200 3.22734400 0.80313300 H -3.14884200 4.05502400 0.72637000 H -2.46167000 2.83708800 1.82671300 H -1.43006300 3.62316500 0.60688700 O -0.78608200 -1.20158400 2.00693300 H -0.45651300 -0.51574700 1.38874000 H -0.96505400 1.30080400 -0.45364900 C 1.32010500 1.09074600 -0.36135100 O 1.08437800 0.33976800 0.63892500 O 0.41816000 1.71037400 -0.99759800 C 2.75513600 1.23531700 -0.85811700 H 2.89693600 0.49031300 -1.65396900 C 3.86376700 1.09624000 0.20525000 H 4.78681800 1.53052800 -0.18493000 C 4.19710500 -0.32325800 0.64178400 H 2.84681100 2.21518900 -1.33485800 H 3.58756900 1.66731300 1.10194700 O 5.33795500 -0.76822900 0.62704000 O 3.18329500 -1.07407200 1.07441500 H 2.30884400 -0.55523600 0.98151800	

Table S2.38 Transition state: activation of **3** in int.**2** using OA



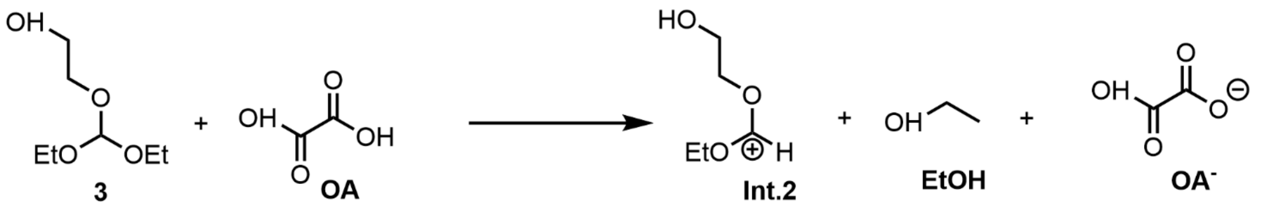




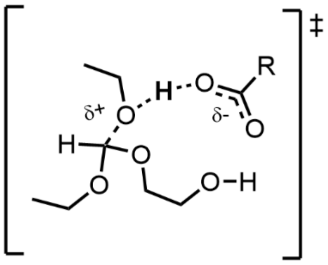
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.60344800 1.17223100 -0.41546300 H -2.14615300 1.91010700 0.17426600 O -0.43777500 1.50728000 -0.92013000 O -2.38179800 0.41366500 -1.14898100 O -1.18648700 0.05758400 0.99265700 C 0.32201400 2.54235900 -0.20503500 H 0.66373700 2.10907700 0.73690800 H -0.35864200 3.37616500 -0.00649200	H= -955.37332 Hartree G = -955.44716 Hartree

C 1.48024500 2.93980700 -1.08863400 H 1.12852800 3.34917500 -2.04186300 H 2.06685500 3.71045600 -0.57560000 H 2.13375200 2.08360900 -1.28399000 C -1.79082500 -0.67798400 -1.94436700 H -1.95887600 -0.42322800 -2.99321700 H -0.72153000 -0.74760800 -1.73289500 C -2.52315900 -1.94518600 -1.56277200 H -3.60621800 -1.79171100 -1.67612100 H -2.21710300 -2.73647300 -2.25607100 C -1.62110300 0.53483900 2.30026600 H -1.01491900 0.00348600 3.03956300 H -1.39772200 1.60527200 2.37161500 C -3.09805700 0.25588500 2.48893100 H -3.41077800 0.62231900 3.47385700 H -3.70288900 0.76418900 1.72976000 H -3.30429800 -0.81920500 2.44032600 O -2.21834700 -2.39484000 -0.24257500 H -2.02114400 -1.61822100 0.31602800 H -0.13873300 -0.12298000 1.00715200 C 1.89262100 -0.83401800 0.15811100 O 1.42023000 -1.30225000 -0.88743800 O 1.28747200 -0.30845000 1.15068600 C 3.41376500 -0.91643300 0.33179700 O 3.99515200 -1.85665900 0.84131100 O 4.04204500 0.16469500 -0.16731700 H 5.00986500 0.04838700 -0.04593700	

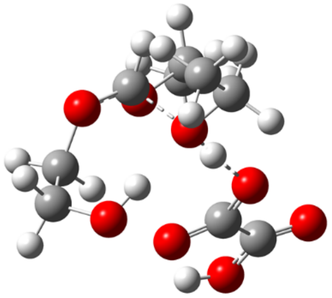
Table S2.39 Transition state: activation of **3** in int.**2** using OA (intramolecular stabilization of the carboxylate with the COOH)



TS



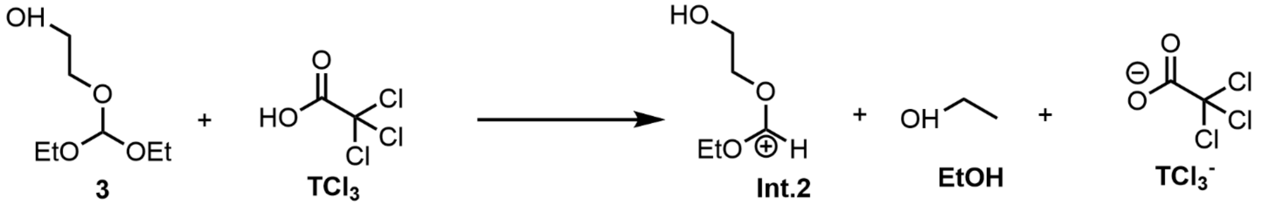
R = CO_2H



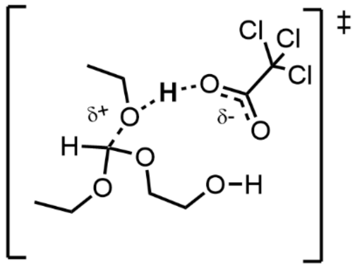
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.47976800 0.86240500 -0.93325200 H -1.99503500 1.81455600 -0.81694400 O -0.26230500 0.86978900 -1.43383300 O -2.27435700 -0.11477100 -1.30635900 O -1.24798000 0.52752000 0.83975700	H= -955.37825 Hartree G = -955.44914 Hartree

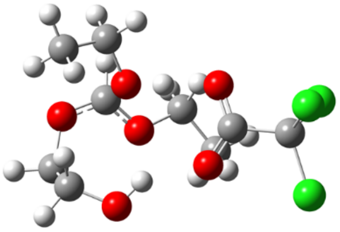
C 0.52274100 2.09737300 -1.24362800 H 0.73003000 2.19865900 -0.17658300 H -0.08965100 2.93784600 -1.58478600 C 1.79304300 1.95042300 -2.04717700 H 1.57430200 1.82462000 -3.11312900 H 2.39555000 2.85714400 -1.92117300 H 2.38312000 1.09549800 -1.70073700 C -1.72675700 -1.47356600 -1.46277600 H -1.81010500 -1.72135900 -2.52346300 H -0.68090800 -1.48664200 -1.14873300 C -2.57950100 -2.39277700 -0.61692000 H -3.63828700 -2.26118200 -0.88337300 H -2.29672300 -3.42628700 -0.84473500 C -1.73229600 1.58192100 1.72787300 H -1.24296100 1.41696900 2.69166100 H -1.40393200 2.54796000 1.32879500 C -3.24011700 1.50313500 1.84567100 H -3.58967300 2.29911600 2.51355000 H -3.72698700 1.63763800 0.87349400 H -3.55183600 0.53985900 2.26456600 O -2.38882700 -2.20225200 0.78542500 H -2.20161200 -1.25853700 0.94978400 H -0.22379000 0.34135700 1.03274500 C 1.83701800 -0.64044400 0.67787200 O 1.40210200 -1.59979600 0.00626700 O 1.19419800 0.22961600 1.33263300 C 3.39208300 -0.50564200 0.69010600 O 4.02563400 0.34844800 1.27145500 O 3.97873700 -1.46425000 -0.04174000 H 3.23220500 -2.00860800 -0.39638900	

Table S2.40 Transition state: activation of **3** in int.**2** using TCl_3



TS

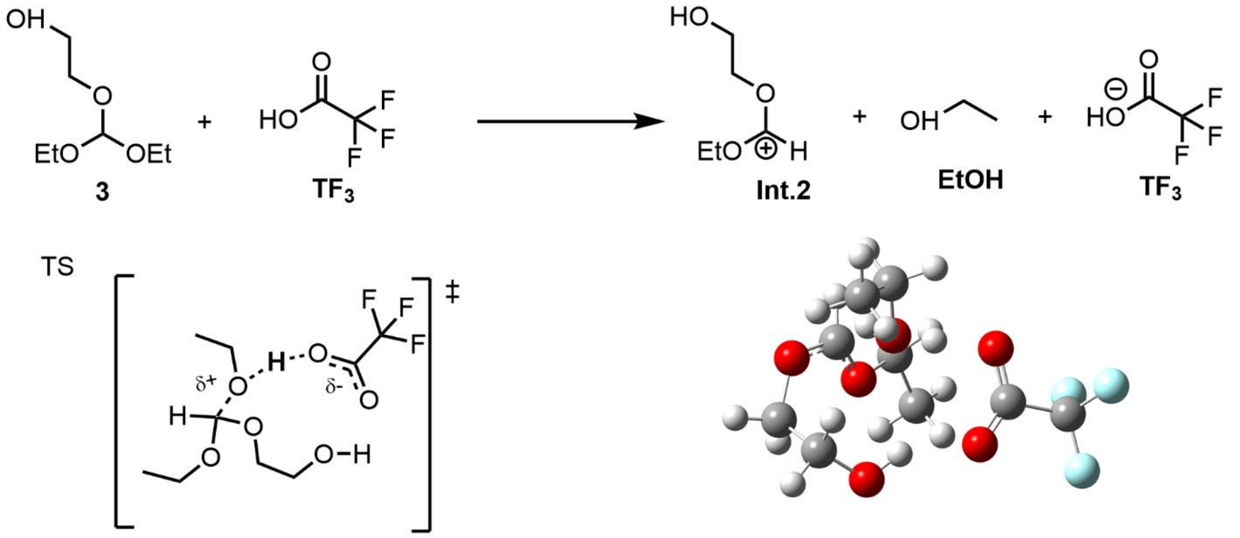




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.69347600 0.58745500 -0.99638200 H 2.81422500 0.37930100 -2.05856700 O 1.82944500 1.49829300 -0.62203400	H= -2184.9058 Hartree G = -2184.9842 Hartree

O 3.80575900 0.47655600 -0.31389600 O 1.84039600 -1.00805600 -0.60253600 C 0.83685800 1.92506300 -1.62658700 H 0.29206800 1.03939500 -1.95815300 H 1.39340200 2.35702700 -2.46286100 C -0.07036900 2.93197300 -0.96207800 H 0.49571900 3.80373300 -0.61622800 H -0.81400400 3.27002400 -1.69219700 H -0.59776900 2.48912800 -0.11176400 C 3.89738600 0.96376900 1.07027000 H 4.97278900 0.92562500 1.24890700 H 3.55506200 2.00061000 1.10072400 C 3.16904700 0.10718000 2.10166500 H 3.21445600 -0.94913200 1.81179900 H 3.73160300 0.22062900 3.03577800 C 2.33149300 -2.17206300 -1.32311800 H 1.45710900 -2.77112500 -1.59487300 H 2.80972700 -1.82881800 -2.24852800 C 3.29700800 -2.95991300 -0.46007700 H 3.64374100 -3.83931100 -1.01669200 H 4.17029400 -2.35764300 -0.19048400 H 2.80750300 -3.30329700 0.45810200 O 1.84408200 0.51940800 2.39924400 H 1.18573200 0.16073700 1.76920200 H 0.81935200 -0.93269900 -0.70949400 C -1.20091800 -0.41989600 0.22453100 O -0.65079100 -0.16523900 1.30290400 O -0.70021600 -0.85833500 -0.84737400 C -2.77244100 -0.21953400 0.14844400 Cl -3.39978200 0.75016500 1.51998200 Cl -3.23478100 0.59572800 -1.38974500 Cl -3.52953400 -1.86527000 0.20181300	

Table S2.41 Transition state: activation of **3** in int.**2** using TF_3

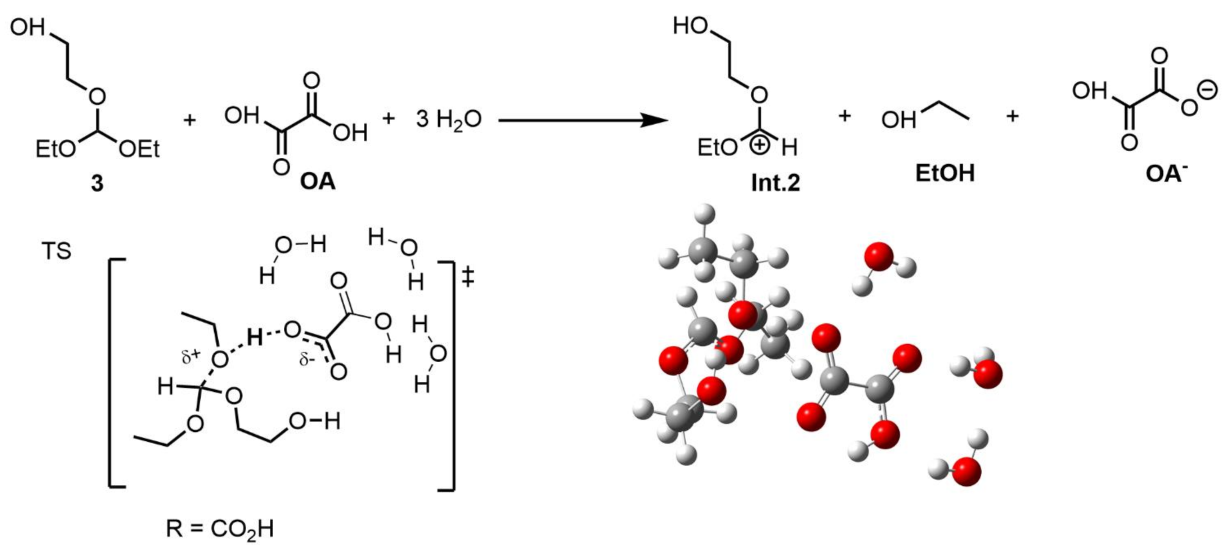


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.06009500 0.61456400 -1.03526200 H 2.16857000 0.39571000 -2.09655000	H= -1103.8624 Hartree G = -1103.9386 Hartree

O 1.16627300 1.49627800 -0.65825700 O 3.19173700 0.56617600 -0.37656300 O 1.28844000 -1.00225200 -0.59875500 C 0.13369800 1.85801700 -1.64730300 H -0.38417400 0.94401100 -1.94331500 H 0.65118500 2.28945300 -2.50858200 C -0.79763400 2.84463200 -0.98540900 H -0.26221500 3.75181500 -0.68490200 H -1.57856700 3.12443900 -1.70150000 H -1.27735600 2.40562000 -0.10512500 C 3.29386200 1.08644200 0.99453600 H 4.37379100 1.09790400 1.14787200 H 2.90814400 2.10827800 1.01162100 C 2.62754600 0.22221400 2.06109100 H 2.70883600 -0.83707300 1.79026100 H 3.20860800 0.37686000 2.97777300 C 1.81839500 -2.15862400 -1.30506800 H 0.96462400 -2.78927100 -1.57040400 H 2.28555700 -1.80948100 -2.23369300 C 2.80906800 -2.90338400 -0.43237000 H 3.18297900 -3.77894100 -0.97735000 H 3.66315100 -2.27013700 -0.17239000 H 2.33157900 -3.24950000 0.49109000 O 1.29490800 0.58619400 2.38622500 H 0.63545900 0.19274300 1.77830000 H 0.26252400 -0.97645800 -0.67925400 C -1.75966500 -0.53263400 0.30711500 O -1.19785600 -0.21019200 1.36385800 O -1.26681000 -0.97799000 -0.76904100 C -3.30933800 -0.36976000 0.24134100 F -3.84932400 0.07663300 1.39519500 F -3.66441200 0.51343400 -0.73004400 F -3.92097600 -1.54678900 -0.05355100	

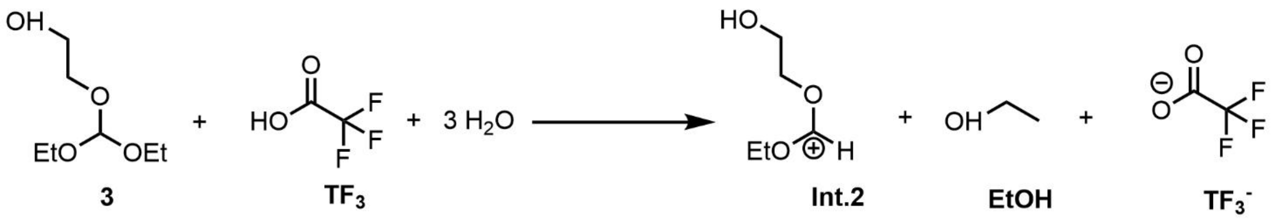
2.10.2.5 COMPUTATIONS FOR THE CATALYST SCREENING WITH 3 MOLECULES OF WATER

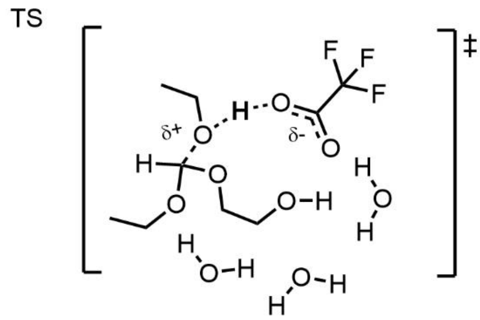
Table S2.42 Transition state: activation of **3** in int.**2** using OA and **3** molecules of water (intramolecular stabilization of the carboxylate with the COOH)

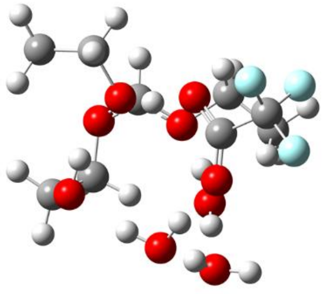


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.49310900 0.17023900 1.20706600 H 3.01229800 1.04997400 1.58713300 O 1.29848600 -0.10310600 1.70651300 O 3.30185300 -0.85502700 1.02150900 O 2.18758500 0.75322100 -0.42702400 C 0.52629600 1.03547200 2.21902700 H 0.26314500 1.67430700 1.37337500 H 1.16954400 1.58799300 2.91092700 C -0.70167900 0.48144000 2.90224300 H -0.42703200 -0.17163200 3.73767100 H -1.29282400 1.31671700 3.29450500 H -1.32696300 -0.08159900 2.20134300 C 2.75427000 -2.12539800 0.52150600 H 2.85627600 -2.85075800 1.33239700 H 1.70242000 -1.99765500 0.25860600 C 3.58625200 -2.52388600 -0.67713200 H 4.65082200 -2.53148400 -0.40224800 H 3.30181000 -3.53906300 -0.97245400 C 2.61817200 2.13135500 -0.69726900 H 2.04313100 2.45526900 -1.56807200 H 2.34049700 2.74978800 0.16202200 C 4.10690900 2.15625700 -0.96534100 H 4.41003600 3.18666700 -1.18472600 H 4.68008300 1.81219800 -0.09750600 H 4.36055800 1.53146000 -1.82902700 O 3.36506000 -1.68561100 -1.81246800 H 3.29038500 -0.76373400 -1.50648900 H 1.17463700 0.65134000 -0.64690600 C -0.91687100 -0.43973200 -0.74923500 O -0.46372200 -1.59625000 -0.69487100 O -0.30107700 0.65585300 -0.91293900 C -2.45996200 -0.33783800 -0.57708300 O -3.10002400 0.69626000 -0.60394300 O -3.02637600 -1.53047700 -0.38355600 H -2.28266100 -2.18597800 -0.40892000 O -5.89404400 0.86040100 -0.23875500 H -6.07175500 1.37439400 0.56803500 H -4.91843100 0.87453500 -0.35231900 O -6.02262400 -1.94043900 0.06666200 H -5.06747500 -2.07720000 -0.05190800 H -6.11897500 -0.96484900 -0.01020700 O -1.39129100 3.26012000 -0.93694600 H -2.35220700 3.15889500 -0.84004000 H -1.06690900 2.33340800 -0.93134200	H= -1184.6235 Hartree G = -1184.7175 Hartree

Table S2.43 Transition state: activation of **3** in int.**2** using TF₃ and **3** molecules of water (intramolecular stabilization of the carboxylate with the COOH)





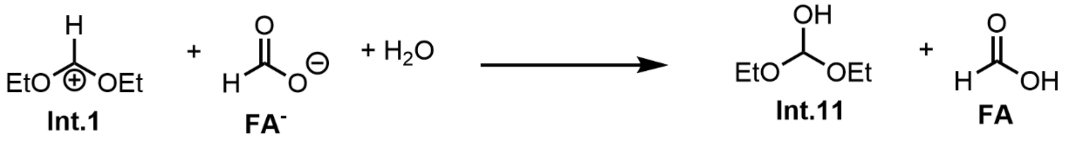


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1333.1167 Hartree
C -1.67190200 0.69828600 -1.28267600	G = -1333.2101 Hartree
H -1.56308900 1.30693700 -2.17988800	
O -1.05705400 -0.47804700 -1.26089300	
O -2.90567500 0.73884800 -0.80698900	
O -0.73775100 1.68200400 -0.18788400	
C 0.02867100 -0.65280800 -2.24634500	
H 0.70101300 0.20315600 -2.16778900	
H -0.43971500 -0.66566700 -3.23469700	
C 0.73582400 -1.94862400 -1.92919400	
H 0.06582700 -2.80702900 -2.03893300	
H 1.56871700 -2.07055300 -2.63090900	
H 1.13864500 -1.94242500 -0.91226100	
C -3.32877800 -0.14258000 0.28493000	
H -4.32584600 -0.47757000 -0.00696300	
H -2.66064700 -1.00005400 0.34924900	
C -3.39842100 0.61953400 1.59179400	
H -3.95277300 1.55644400 1.45747000	
H -3.93702300 -0.00124700 2.31378800	
C -0.64305400 3.10791400 -0.55859900	
H 0.14629300 3.51180500 0.07902000	
H -0.31971100 3.15723000 -1.60299300	
C -1.96055600 3.81522000 -0.33145400	
H -1.81941400 4.87839100 -0.55857500	
H -2.75208500 3.43177800 -0.98132100	
H -2.28342100 3.73075800 0.71191400	
O -2.11246500 0.88008600 2.16996500	
H -1.58882500 1.39526600 1.52467300	
H 0.24965200 1.31586500 -0.09797200	
C 2.30820600 0.20219000 0.56496600	
O 1.91091900 -0.57550200 1.44234100	
O 1.68685900 1.07412700 -0.10778100	
C 3.81698300 0.12479500 0.17658100	
O -1.36893400 -3.58057800 1.03044700	
H -1.07001200 -2.77461100 1.53199200	

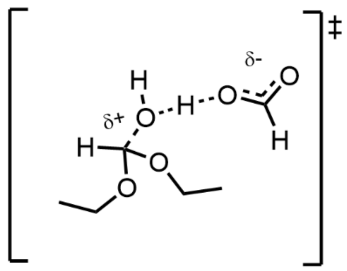
H -0.56309500 -4.10331100 0.87947300	
O -0.52965200 -1.40933500 2.45059000	
H 0.31891000 -1.08324600 2.07215200	
H -1.13478900 -0.63411700 2.41145000	
O -2.70758500 -3.21640000 -1.38744600	
H -2.39074400 -2.37147800 -1.74436200	
H -2.22106500 -3.31872500 -0.53506900	
F 3.95936800 -0.25993800 -1.11919400	
F 4.51413800 -0.75021600 0.92904200	
F 4.42450000 1.33206800 0.30145600	

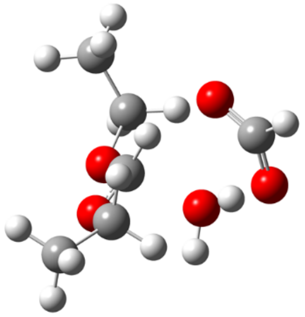
2.10.2.6 COMPUTATIONS FOR THE MECHANISM OF HYDROLYSIS

Table S2.44 Transition state: substitution of int.**1** with H_2O in int.**11**



TS

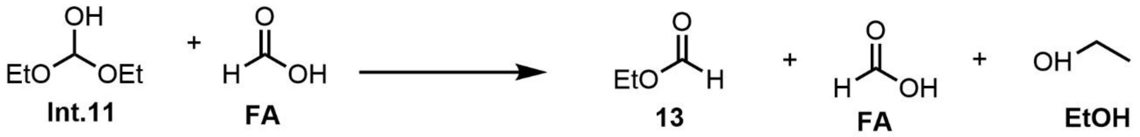


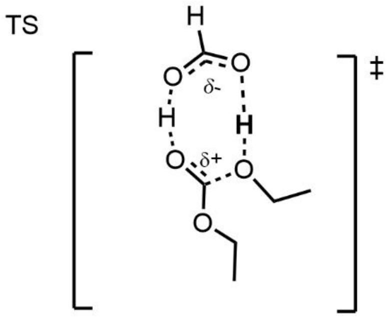


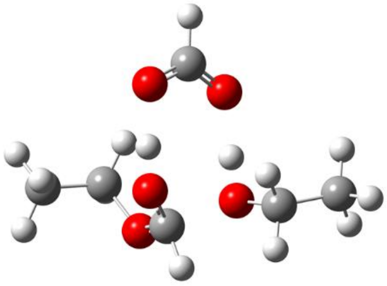
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -613.01626 Hartree
C -0.54300800 0.54554200 0.22038800	G = -613.07493 Hartree
H -0.36212000 -0.24474700 -0.51186900	
O -1.76694500 0.84757600 0.57736800	
O 0.25873800 1.58509500 0.25272800	
O 0.03269800 -0.57663800 1.60776000	
C -2.77963400 -0.18710600 0.32147400	
H -3.57766700 0.05339900 1.02461500	
H -2.34926500 -1.15567300 0.58716500	
C -3.25204300 -0.13407800 -1.11650600	
H -2.43737000 -0.35634200 -1.81512000	
H -4.03666800 -0.88689400 -1.25837400	
H -3.66908900 0.85004100 -1.35672400	
C 1.61156200 1.39314800 -0.28703700	
H 2.18528100 0.83878900 0.46023700	
H 1.53306500 0.79771500 -1.19986500	
C 2.19587300 2.76182800 -0.54622100	
H 2.24104500 3.35249600 0.37529200	
H 3.21598500 2.64278100 -0.92899600	
H 1.60771600 3.30737800 -1.29211300	
C 1.65753700 -2.33835900 -0.53323500	
H 2.43421200 -3.00133500 -0.96735500	
O 0.75370600 -1.91197500 -1.27989400	
O 1.80269700 -2.09479400 0.71658700	
H 0.80578300 -1.23111500 1.23332300	

H 0.42021300 -0.00645100 2.30020900	

Table S2.45 Transition state: Elimination of EtOH from int.**11** in **13**

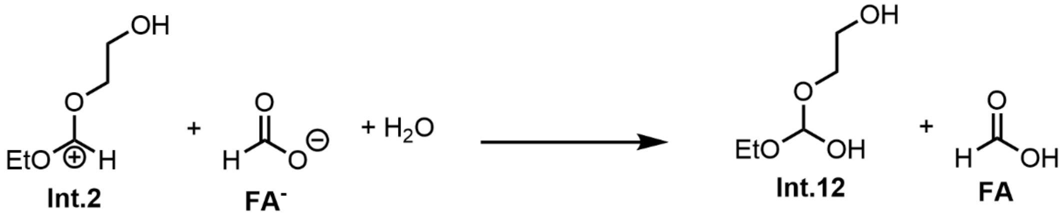




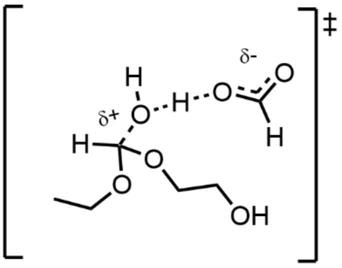


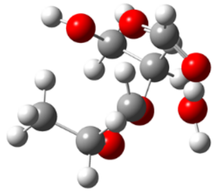
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -613.02495 Hartree
C -0.31468400 -1.29645900 0.47385800	G = -613.08115 Hartree
H 0.09798600 -2.25007900 0.79437400	
O -1.17616100 -1.46813100 -0.52507300	
O 1.15657200 -0.73605000 -0.37682700	
O -0.50884300 -0.43250000 1.44187300	
C -2.10709100 -0.40943700 -0.92141300	
H -2.30027400 -0.62574300 -1.97343400	
H -1.61113900 0.55909900 -0.85637000	
C -3.38286600 -0.46168400 -0.10373000	
H -3.20027500 -0.23981200 0.95202700	
H -4.08297100 0.28556300 -0.49665900	
H -3.85340100 -1.44805400 -0.18265500	
C 2.34853300 -0.79259600 0.46211100	
H 2.25087300 -0.05114000 1.26158800	
H 2.35447700 -1.79232000 0.90412300	
C 3.58407300 -0.55282000 -0.38324000	
H 3.56803000 0.44396600 -0.83796700	
H 4.47340300 -0.62161700 0.25486300	
H 3.66730100 -1.30347700 -1.17685200	
C 0.08301300 2.44634600 -0.07684300	
H 0.09210300 3.53988600 -0.22835400	
O -0.62658600 2.01752900 0.88198600	
O 0.76888100 1.75283900 -0.87886900	
H 0.98133200 0.25635400 -0.61641400	
H -0.61421900 0.57776000 1.15255300	

Table S2.46 Transition state: substitution of int.**2** with H_2O in int.**11**



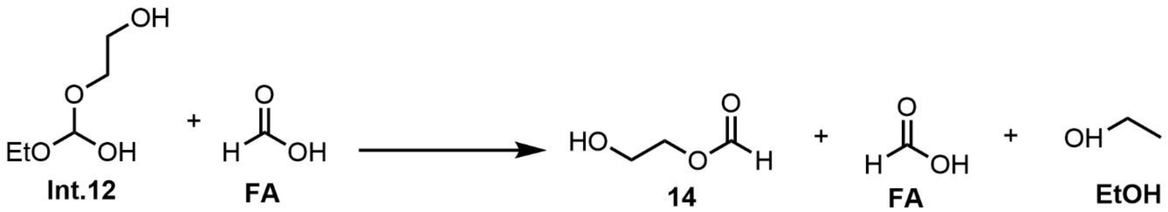
TS

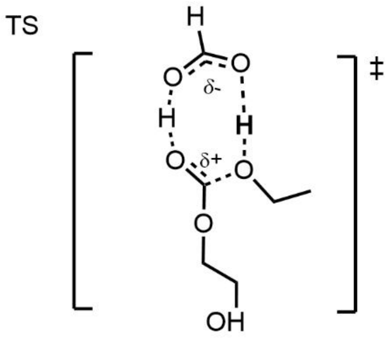


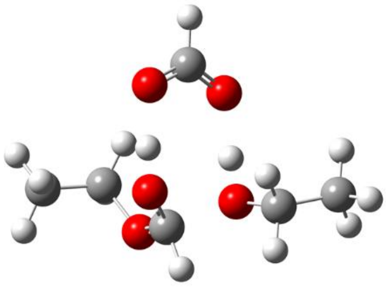


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.34910900 0.30290800 -0.68164900 H 0.04750200 -0.09127300 0.28894000 O 1.55731000 0.07363200 -1.14155500 O -0.12255900 1.45988200 -1.08721500 O -0.66965700 -0.98154200 -1.57434500 C 2.28297300 -1.04437200 -0.54679600 H 2.84817500 -1.49324700 -1.36494600 H 1.56766000 -1.77240400 -0.15524400 C 3.21262700 -0.53754300 0.52852300 H 3.82824800 -1.38177500 0.86980400 H 3.87480400 0.23624200 0.11862600 C -1.33472800 1.94712700 -0.41005200 H -1.76437400 2.64645300 -1.12803200 H -2.01792500 1.10563900 -0.27735600 C -0.98398400 2.61843800 0.90056200 H -0.30300300 3.46126900 0.73935200 H -1.90467100 2.99872700 1.35906200 H -0.52188500 1.91339800 1.59928000 C -2.55446000 -1.39671400 0.99688200 H -3.43680400 -1.67598900 1.60890100 O -1.54269300 -0.95378700 1.57335500 O -2.70462700 -1.57238000 -0.26522100 H -1.55863600 -1.23022400 -1.00388600 H -0.95438300 -0.57041100 -2.41371800 O 2.41506900 -0.01342700 1.59441100 H 3.00332500 0.41551600 2.23894800	H= -688.22803 Hartree G = -688.28821 Hartree

Table S2.47 Transition state: Elimination of EtOH from int.**12** in **14**

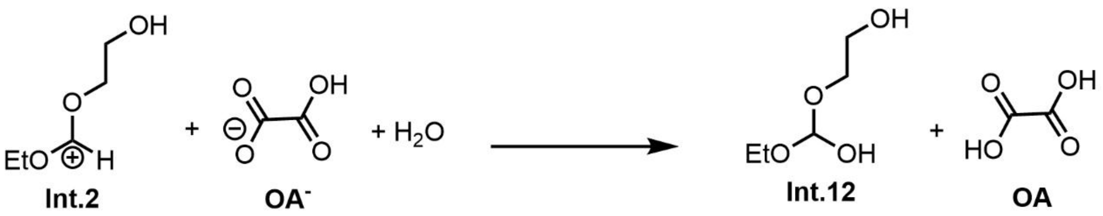




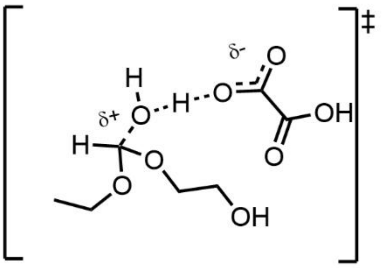


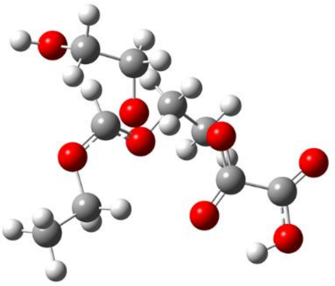
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.13154100 -1.14820400 0.55005800 H 0.14642600 -2.14030700 0.89862400 O -1.03570000 -1.23297700 -0.42469600 O 1.38031600 -0.83616300 -0.35846500 O -0.17384800 -0.23128200 1.48436600 C -1.77606200 -0.06205200 -0.87621000 H -2.05470400 -0.30932100 -1.90228300 H -1.12777200 0.81422700 -0.89378100 C -3.01003000 0.20281300 -0.04395300 H -2.75395800 0.31695900 1.01561300 H -3.44244500 1.14947800 -0.39920700 C 2.57683300 -1.05223400 0.44850800 H 2.62154500 -0.27994000 1.22306300 H 2.44166600 -2.02617200 0.92551600 C 3.80528700 -1.03508100 -0.43961800 H 3.93212900 -0.06150100 -0.92612800 H 4.69350900 -1.22756800 0.17423700 H 3.74139000 -1.81113100 -1.21029500 C 0.77791200 2.48300900 -0.11901900 H 0.94127900 3.55981600 -0.29815800 O 0.02869900 2.18453100 0.86032900 O 1.34213600 1.67748400 -0.90984100 H 1.34768200 0.16413600 -0.61728200 H -0.14233000 0.78171600 1.16428500 O -3.92889700 -0.87886700 -0.22857300 H -4.70045100 -0.72169800 0.34223800	H= -688.23606 Hartree G = -688.2961 Hartree

Table S2.48 Transition state: substitution of int.**2** with H_2O in int.**11** using OA water (intramolecular stabilization of the carboxylate with the COOH)



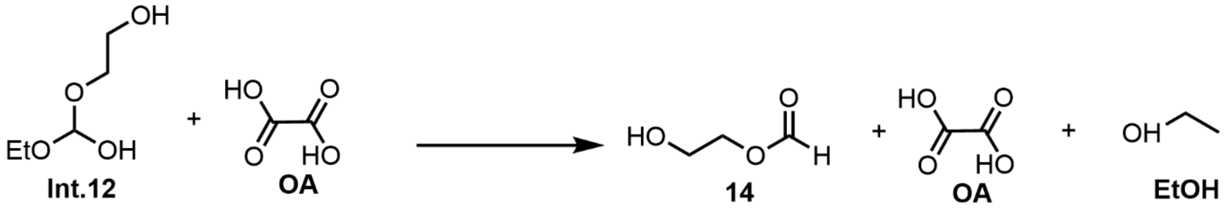
TS

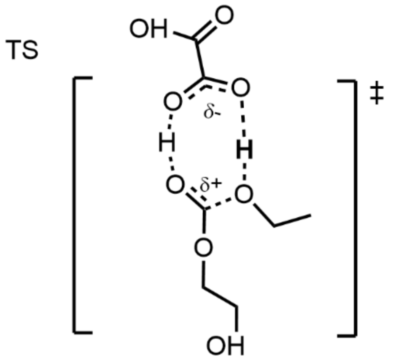


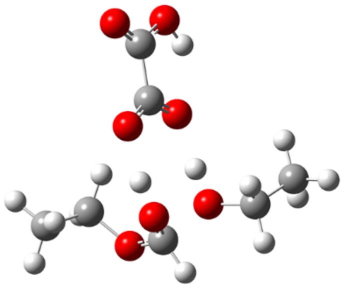


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -955.3771 Hartree
C -1.51954200 0.16774900 0.87169500	G = -955.45176 Hartree
H -2.26095200 -0.55890500 1.19624300	
O -0.34580000 0.20003500 1.48350000	
O -2.04128300 1.33474700 0.56324500	
O -1.17558100 -0.57492100 -0.71434500	
C 0.12801600 -1.05303200 2.07325000	
H 0.29324500 -1.76839500 1.26483600	
H -0.65424700 -1.42553100 2.74245800	
C 1.41227000 -0.74397300 2.80692600	
H 1.24447200 -0.01526000 3.60757100	
H 1.79909600 -1.66712800 3.25323100	
H 2.16913900 -0.35021300 2.11977100	
C -1.12559600 2.44139200 0.25334400	
H -0.70324000 2.79555400 1.19761900	
H -0.32074500 2.05814800 -0.37819100	
C -1.93953000 3.51120900 -0.43784600	
H -2.75873200 3.86147500 0.20034200	
H -1.28848800 4.36477500 -0.66027600	
C -1.81456000 -1.84775100 -1.00094800	
H -1.28846000 -2.27324800 -1.86021500	
H -1.69603600 -2.51845900 -0.14232600	
C -3.27126100 -1.65891400 -1.34353700	
H -3.64693300 -2.60383100 -1.76019900	
H -3.37845500 -0.87267200 -2.10167400	
H -0.13965600 -0.68275400 -0.83947000	
C 2.06693400 0.00508900 -0.93058700	
O 1.79020900 1.21178000 -1.10955900	
O 1.30027000 -0.99781100 -0.95898600	
C 3.57185300 -0.27728100 -0.62547600	
O 4.06629700 -1.36780700 -0.43822700	
O 4.29129100 0.85419900 -0.58811200	
H 3.64113700 1.57621100 -0.77677600	
H -2.35722400 3.14061500 -1.38054000	
O -3.98651500 -1.31676300 -0.14905400	
H -4.89654200 -1.07497600 -0.39102800	

Table S2.49 Transition state:Elimination of EtOH from int.**12** in **14** using OA (intramolecular stabilization of the carboxylate with the COOH)

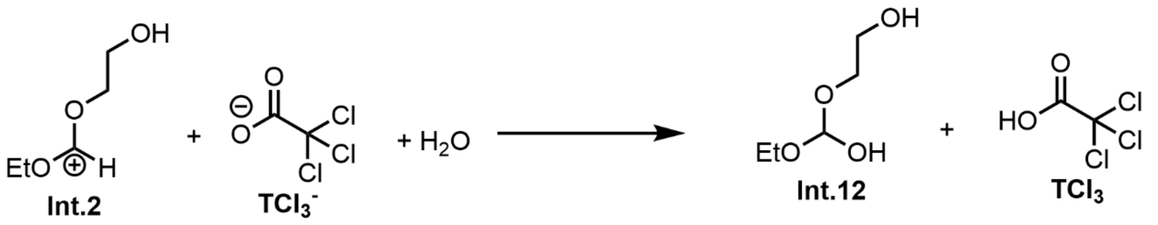




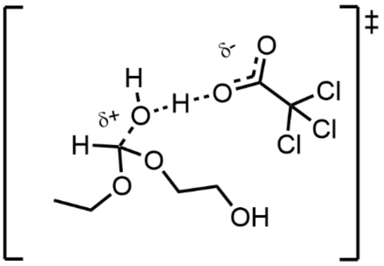


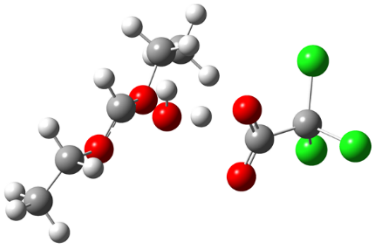
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.13154100 -1.14820400 0.55005800 H 0.14642600 -2.14030700 0.89862400 O -1.03570000 -1.23297700 -0.42469600 O 1.38031600 -0.83616300 -0.35846500 O -0.17384800 -0.23128200 1.48436600 C -1.77606200 -0.06205200 -0.87621000 H -2.05470400 -0.30932100 -1.90228300 H -1.12777200 0.81422700 -0.89378100 C -3.01003000 0.20281300 -0.04395300 H -2.75395800 0.31695900 1.01561300 H -3.44244500 1.14947800 -0.39920700 C 2.57683300 -1.05223400 0.44850800 H 2.62154500 -0.27994000 1.22306300 H 2.44166600 -2.02617200 0.92551600 C 3.80528700 -1.03508100 -0.43961800 H 3.93212900 -0.06150100 -0.92612800 H 4.69350900 -1.22756800 0.17423700 H 3.74139000 -1.81113100 -1.21029500 C 0.77791200 2.48300900 -0.11901900 H 0.94127900 3.55981600 -0.29815800 O 0.02869900 2.18453100 0.86032900 O 1.34213600 1.67748400 -0.90984100 H 1.34768200 0.16413600 -0.61728200 H -0.14233000 0.78171600 1.16428500 O -3.92889700 -0.87886700 -0.22857300 H -4.70045100 -0.72169800 0.34223800	H= -688.23606 Hartree G = -688.2961 Hartree

Table S2.50 Transition state: substitution of int.**2** with H_2O in int.**11** using TCl_3



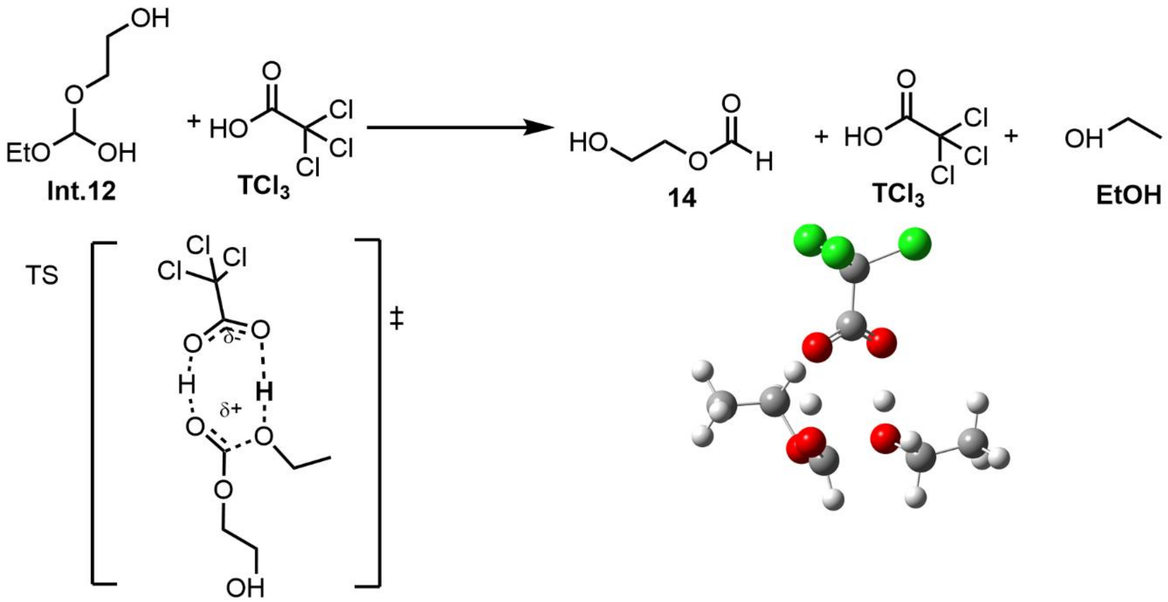
TS





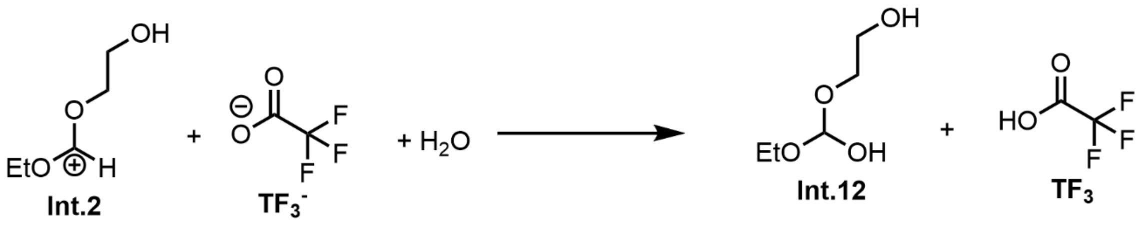
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.88525700 0.55874300 -0.34098100 H 3.40813600 1.10479800 -1.12925600 O 1.94735900 1.18727100 0.33417200 O 3.58862400 -0.24411700 0.42785700 O 2.02782100 -0.56618600 -1.44350600 C 1.26613200 2.28813300 -0.35251300 H 0.72285900 1.86931000 -1.20294700 H 2.02968300 2.98704300 -0.70831300 C 0.32881700 2.92407200 0.64693300 H 0.88206000 3.34614700 1.49301500 H -0.22245100 3.73240300 0.15370300 H -0.39441800 2.19352800 1.02304800 H 0.97280200 -0.56278600 -1.25807200 C -0.95682500 -0.73214700 -0.03012300 O -0.46482900 -1.31947100 0.93153200 O -0.44366200 -0.42988400 -1.15040900 C -2.49252700 -0.33373000 0.07333300 C 4.74877400 -0.88577900 -0.19326700 H 4.37274900 -1.66056200 -0.86636700 H 5.28698900 -0.12819000 -0.77247500 C 5.60125700 -1.46266000 0.91315800 H 5.04082100 -2.20088800 1.49714600 H 6.46837600 -1.96311800 0.46722300 H 5.96265400 -0.67598400 1.58445300 H 2.14637800 -0.27241400 -2.36970000 Cl -3.00835500 -0.13017800 1.78066300 Cl -3.43460000 -1.69693400 -0.66763000 Cl -2.86318900 1.18417200 -0.81937700	H= -2031.1167 Hartree G = -2031.1887 Hartree

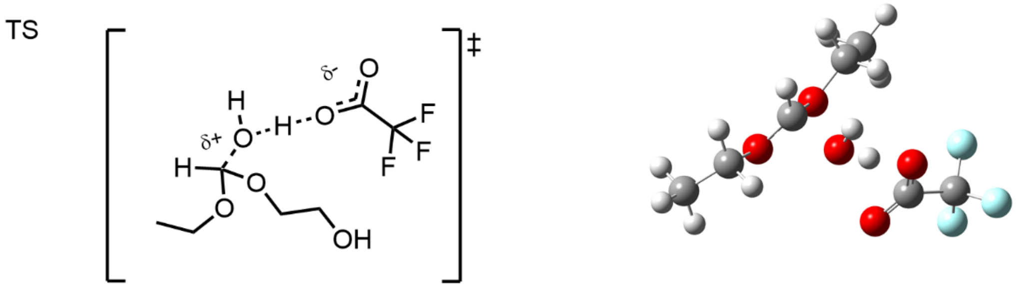
Table S2.51 Transition state: Elimination of EtOH from int.**12** in **14** using TCl$_3$



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -2031.1234 Hartree
C 3.09798900 -0.34391700 0.38303000	G = -2031.1941 Hartree
H 4.09140900 0.03674900 0.60453000	
O 3.12898400 -1.21133800 -0.61848600	
O 2.49653500 1.14179800 -0.40133200	
O 2.34047500 -0.50510200 1.45046800	
C 2.00032700 -2.10271700 -0.90881300	
H 2.11598900 -2.31103600 -1.97328200	
H 1.06301100 -1.56493500 -0.76737600	
C 2.07136300 -3.37263000 -0.08481100	
H 1.95218000 -3.17649800 0.98490800	
H 1.26169900 -4.03990500 -0.40379500	
H 3.02515200 -3.88640700 -0.24732200	
C 2.65275300 2.33519600 0.43238400	
H 2.01431800 2.22884800 1.31445100	
H 3.69959900 2.33584500 0.74446000	
C 2.30728400 3.57020200 -0.37454300	
H 1.26075700 3.55535900 -0.69869400	
H 2.45624700 4.45692800 0.25315100	
H 2.95207300 3.65616500 -1.25581200	
C -0.68132800 0.11591100 0.16954200	
O -0.21575400 -0.58163600 1.09994200	
O -0.07109900 0.79494200 -0.68560900	
H 1.49960200 0.99746600 -0.56174900	
H 1.33985000 -0.61941000 1.26713100	
C -2.24926700 0.05537600 0.00819300	
Cl -2.59735700 -1.43255500 -0.96645000	
Cl -3.06357000 -0.07435900 1.60141700	
Cl -2.88964600 1.48791400 -0.85675300	

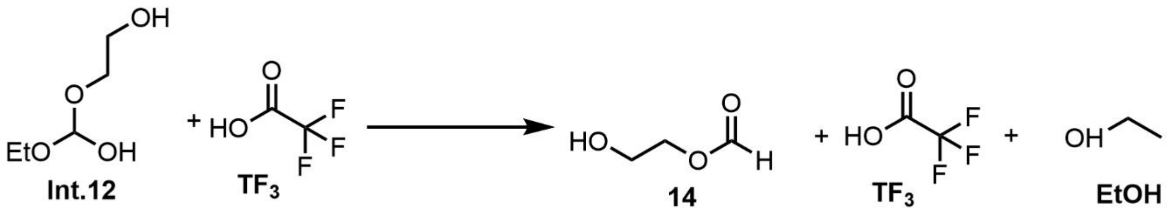
able S2.52 Transition state: substitution of int.**2** with H_2O in int.**11** using TF_3

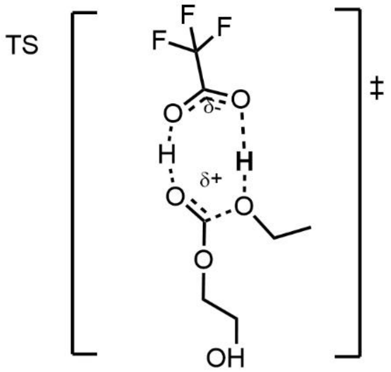


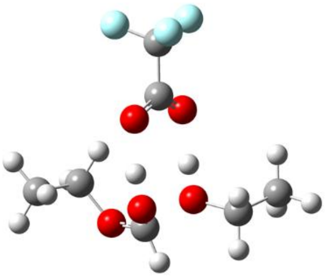


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -2.23631200 0.64076900 0.29571100 H -2.83189000 1.21548400 1.00822600 O -1.30571700 1.26876100 -0.38923400 O -2.84189000 -0.27783600 -0.42228000 O -1.36439100 -0.31968200 1.55048700 C -0.72210300 2.45880900 0.23596300 H -0.18076900 2.13701800 1.12943400 H -1.54200700 3.12519200 0.52155500 C 0.20305500 3.09156600 -0.77654500 H -0.34472600 3.39838400 -1.67422700 H 0.66242500 3.98062400 -0.32982400 H 1.00062900 2.39820100 -1.06317700 H -0.32110300 -0.36144000 1.32427800 C 1.56522600 -0.87603600 0.09967400 O 1.01779800 -1.63807100 -0.69923400 O 1.09951700 -0.28457300 1.12483600 C 3.07483600 -0.54532400 -0.12572300 C -3.99290600 -0.93630100 0.19995500 H -3.60610700 -1.61418400 0.96492700 H -4.61048100 -0.16567700 0.67272100 C -4.74048200 -1.67444000 -0.88617600 H -4.10031000 -2.42417400 -1.36387900 H -5.59788300 -2.18929500 -0.43786700 H -5.11231700 -0.98299900 -1.65019000 H -1.44320900 0.12802100 2.41738600 F 3.82803800 -0.89768500 0.95058800 F 3.26663000 0.78713500 -0.31995400 F 3.60281200 -1.17703000 -1.19653600	H= -950.07353 Hartree G = -950.14236 Hartree

Table S2.53 Transition state: Transition state: Elimination of EtOH from int.**12** in **14** using TF$_3$

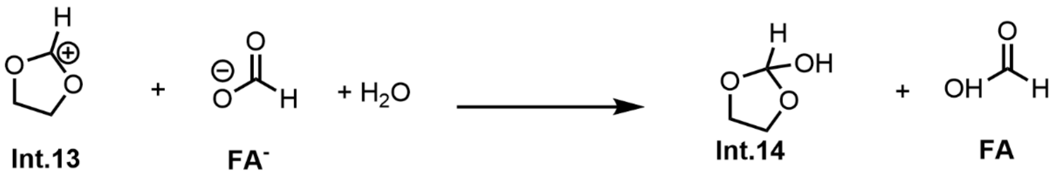


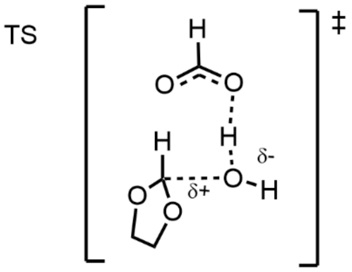


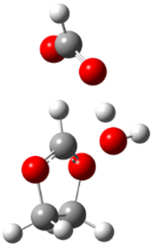


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.49370700 -0.35520300 0.42619300 H 3.46729100 0.03778000 0.70600100 O 2.59759200 -1.21999900 -0.57357400 O 1.91132000 1.11486800 -0.37848800 O 1.68509200 -0.53941100 1.45354700 C 1.48694700 -2.09963300 -0.95256400 H 1.66844400 -2.28879500 -2.01149000 H 0.54430500 -1.55955400 -0.85981200 C 1.50056500 -3.38560000 -0.15050500 H 1.32016900 -3.20974800 0.91419100 H 0.70741100 -4.04124300 -0.52947800 H 2.45925100 -3.90286600 -0.26639200 C 2.09827500 2.32684800 0.42357200 H 1.45451900 2.26201900 1.30574600 H 3.14391600 2.30774300 0.73861300 C 1.79068600 3.54695700 -0.42008300 H 0.74494500 3.55455400 -0.74681800 H 1.96543100 4.44679600 0.18173000 H 2.43977400 3.58733900 -1.30147000 C -1.29539900 0.08235000 0.11072900 O -0.85600600 -0.70116500 0.98694300 O -0.66878000 0.83236200 -0.67244800 H 0.91065600 0.99044000 -0.53497800 H 0.70152700 -0.69143200 1.22142300 C -2.84580400 0.07501500 -0.02768700 F -3.26884500 -1.12135400 -0.51338000 F -3.44990400 0.25481000 1.17111400 F -3.30961000 1.02980300 -0.85807200	H= -950.08002 Hartree G = -950.14626 Hartree

Table S2.54 Transition state: Transition state: substitution of int.**13** with H_2O in int.**14**



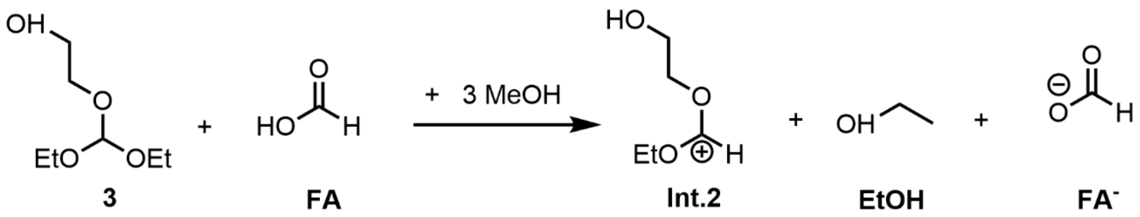


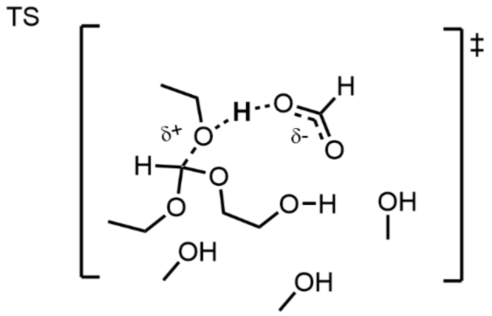


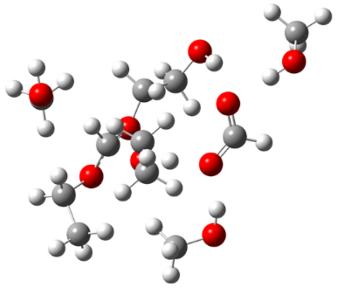
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.57339200 -0.47545700 0.15779600 H 0.37312100 -0.99575500 0.31993400 O -1.53311700 -0.54235300 1.04437600 O 0.24041400 1.27332500 0.57191800 C -2.78353800 -0.07972500 0.40997700 H -3.14564200 0.77628900 0.97767700 H -3.48435500 -0.91280400 0.46353500 C -2.33903400 0.27117700 -1.01299900 H -2.91019400 -0.22770000 -1.79385900 H -2.27387600 1.34395700 -1.19633000 O -0.96952600 -0.26874700 -1.06927500 H 1.23429200 1.16038100 0.25783000 C 3.02700500 -0.26293900 -0.19344800 H 4.07902500 -0.42981600 -0.50840400 O 2.64426200 0.95417300 -0.21370000 O 2.35147600 -1.26394100 0.13750800 H 0.27330300 1.34745800 1.54504600	H= -533.24244 Hartree G = -533.29094 Hartree

2.10.2.7 COMPUTATIONS FOR THE SCREENING OF SOLVENTS AND REAGENTS

Table S2.55 Transition state: activation of **3** in int.**2** in acetonitrile (SMD) with **3** molecules of methanol



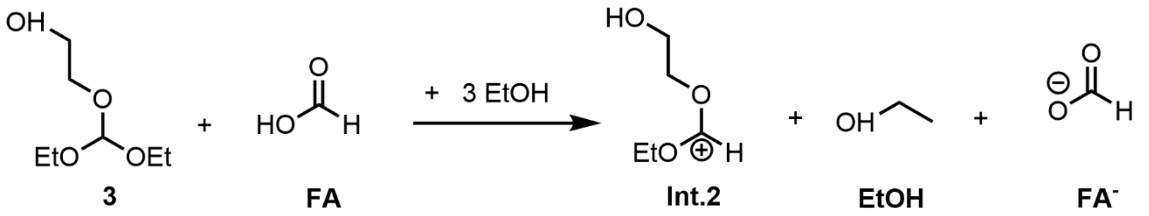


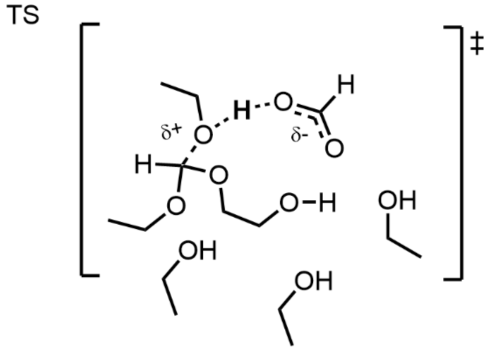


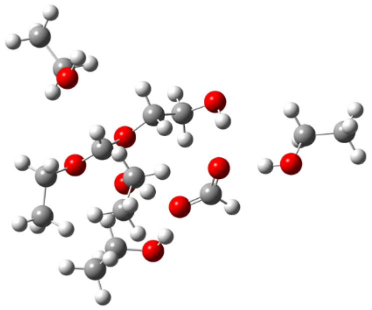
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1113.8615 Hartree
C -1.63839500 0.60389200 0.15820600	G = -1113.9672 Hartree
H -1.76558000 1.14025100 1.09691000	
O -2.70545500 0.09773700 -0.41766200	
O -0.80612400 -0.79454400 0.87143500	
O -0.79911400 1.09975800 -0.73492400	
C -3.79828300 -0.32801900 0.45949200	
H -4.67461200 0.21972200 0.10526400	
H -3.57387900 -0.01368000 1.48249800	
C -3.99084100 -1.82595600 0.35332000	
H -3.10901500 -2.36488200 0.70959300	
H -4.85109100 -2.11433600 0.96954300	
H -4.19564900 -2.12210500 -0.68120100	
C -0.39944700 -0.72135000 2.26935300	
H 0.66783700 -0.48164300 2.29943400	
H -0.95579700 0.10618600 2.71753800	
C -0.70872700 -2.03238900 2.96459400	
H -0.16746500 -2.86252200 2.49705300	
H -0.39719900 -1.96726200 4.01443900	
H -1.78224000 -2.24784800 2.93342500	
C 0.33162600 1.83107900 -0.18578600	
H -0.02430000 2.79753700 0.18178800	
H 0.75864900 1.25592600 0.63831500	
C 1.36811400 1.97178900 -1.29573900	
H 1.40649800 1.03999700 -1.87516300	
H 1.10967600 2.78796300 -1.97585400	
C 2.34475600 -1.23448300 -0.37018100	
H 3.09752800 -1.71520600 -1.02206100	
O 2.73031500 -0.35201700 0.43638600	
O 1.14881400 -1.64315800 -0.51757200	
H 0.00454900 -1.09190700 0.28953600	
O 2.64122300 2.28061300 -0.73502500	
H 2.92527400 1.47683200 -0.25420900	
C -1.38992100 -3.11809200 -1.99995700	

H -2.02034200 -3.67652100 -2.69962300	
H -1.54146100 -3.52809500 -0.99114800	
H -1.70918100 -2.06712400 -2.00311300	
C 5.97494500 0.77758200 0.21937100	
H 5.58529000 1.71617300 0.64173200	
H 7.06391000 0.77591900 0.33234200	
H 5.73739800 0.74966400 -0.85450100	
C -2.97872200 3.65395800 -0.76334100	
H -3.38031400 2.79259000 -1.30166600	
H -3.67028500 4.49903400 -0.87822600	
H -2.00578900 3.92237300 -1.19499800	
O -0.03731200 -3.26167700 -2.43015700	
H 0.51319500 -2.73106900 -1.81275200	
O 5.46910500 -0.36462900 0.90492800	
H 4.49457800 -0.38925400 0.76433700	
O -2.85653500 3.26345900 0.61042100	
H -2.51013400 4.02089000 1.11213400	

Table S2.56 Transition state: activation of **3** in int.**2** in acetonitrile (SMD) with **3** molecules of ethanol



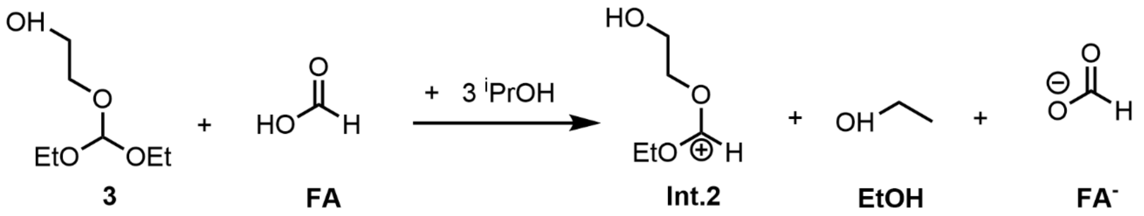


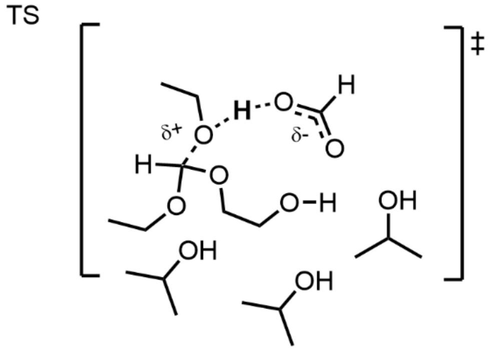


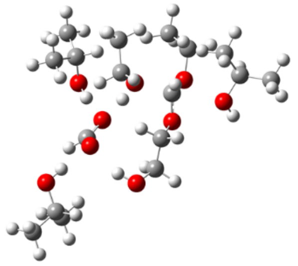
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1231.7495Hartree
C -1.70078100 0.48396300 0.29393500	G = -1231.8654 Hartree
H -1.79095900 1.18587100 1.12086800	
O -2.77683500 -0.15667600 -0.10014900	
O -0.76395200 -0.73076100 1.21372000	
O -0.93765900 0.82215700 -0.72999800	
C -3.78486900 -0.45449900 0.92063500	
H -4.70278800 0.01535500 0.55988200	
H -3.48843400 0.02055300 1.85955800	
C -3.93742300 -1.95366900 1.06252600	
H -3.01066900 -2.41405000 1.41549100	
H -4.73115400 -2.15964600 1.79077700	
H -4.22113000 -2.40940700 0.10794900	
C -0.29530200 -0.37864200 2.54722200	
H 0.77881100 -0.17949500 2.48460300	
H -0.80348100 0.54777200 2.83019000	

C	-0.61298200	-1.49845600	3.51829900
H	-0.11720100	-2.42893700	3.21964400
H	-0.25550500	-1.22380600	4.51846200
H	-1.69274100	-1.67520400	3.57216500
C	0.20073800	1.66858500	-0.40524200
H	-0.16228400	2.68130900	-0.20980900
H	0.69287200	1.27266000	0.48527000
C	1.16495000	1.61166300	-1.58498800
H	1.21317000	0.58279800	-1.96487000
H	0.83147000	2.26188200	-2.39835600
C	2.32872000	-1.29470700	-0.11458700
H	3.06576500	-1.85643600	-0.71816200
O	2.71530000	-0.26472700	0.49173300
O	1.14860200	-1.77037500	-0.10582000
H	0.02614000	-1.10995900	0.65356100
O	2.45173100	2.07121500	-1.18035800
H	2.79936400	1.39275900	-0.56644200
C	-1.43216700	-3.43628800	-1.40115500
H	-1.54254600	-3.72739600	-0.34545000
H	-1.73358500	-2.38253700	-1.48523600
C	5.92045700	0.88223100	-0.14213600
H	5.45708700	1.85707300	0.07712800
H	5.61693200	0.59225600	-1.16009700
C	-3.20065900	3.41999200	-0.77124800
H	-3.67230700	2.49500500	-1.11490800
H	-2.25494900	3.53975200	-1.31786400
O	-0.07043900	-3.59454000	-1.81439000
H	0.47223400	-2.99514600	-1.25582000
O	5.47931000	-0.09765200	0.80183600
H	4.50144900	-0.17778700	0.71729100
O	-2.93125000	3.20685100	0.62660100
H	-2.47955600	3.99755800	0.97046600
C	-4.11266500	4.61241500	-1.01592500
H	-3.64497600	5.54309600	-0.66863800
H	-4.31539200	4.71699500	-2.08961700
H	-5.06852600	4.48690400	-0.49333800
C	7.43220000	0.99957900	-0.06421300
H	7.79332700	1.74955800	-0.77877500
H	7.74712600	1.30339300	0.94185600
H	7.90960700	0.04058800	-0.30082000
C	-2.31917400	-4.30440900	-2.27520500
H	-2.03845400	-5.36141700	-2.18798900
H	-3.36871300	-4.20199900	-1.97304300
H	-2.23471300	-4.01040200	-3.32884100

Table S2.57 Transition state: activation of **3** in int.**2** in acetonitrile (SMD) with **3** molecules of isopropanol



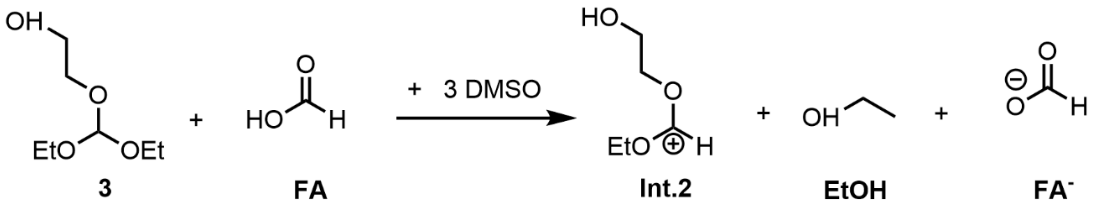


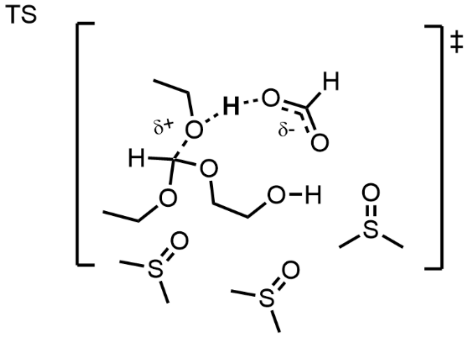


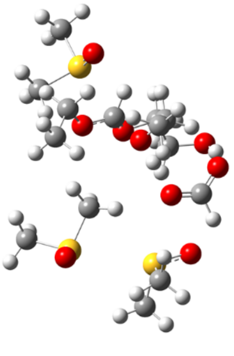
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.94290700 -0.36962700 -0.45664900 H 2.35255700 -0.71664700 0.49099200 O 2.71636400 0.31453300 -1.26831600 O 0.86005200 0.85534500 0.27894800 O 1.14204800 -1.17653500 -1.12828600 C 3.74991800 1.15913900 -0.66392800 H 4.68055500 0.85370000 -1.14664400 H 3.81233400 0.92982600 0.40208800 C 3.43611400 2.61747500 -0.92147000 H 2.49199200 2.90925700 -0.45361500 H 4.24119700 3.23186100 -0.50045400 H 3.37768000 2.81888100 -1.99683300 C 0.70625700 0.84670300 1.72941400 H -0.36048200 0.97342600 1.93146200 H 1.00762900 -0.13858600 2.10158200 C 1.53389100 1.94928200 2.35707000 H 1.23083000 2.93128900 1.98135100 H 1.38503000 1.93265200 3.44371000 H 2.60150000 1.80838600 2.15761400 C 0.31646800 -2.06500800 -0.32299300 H 0.95242100 -2.85503700 0.08475400 H -0.13161100 -1.49150600 0.48998800 C -0.78996600 -2.60104400 -1.22521000 H -1.14518300 -1.79364400 -1.87883200 H -0.42764300 -3.41976300 -1.85318600 C -2.48240000 0.46294300 -0.35643500 H -3.43574000 0.87405800 -0.73619100 O -2.52920400 -0.48942200 0.45994200 O -1.43011200 1.02295800 -0.80372300 H -0.07303800 0.83360900 -0.17716800 O -1.85194400 -3.11830600 -0.42863000 H -2.26494300 -2.33938200 -0.00238100 C -0.66087700 4.24535300 -0.16681700	H= -1349.6396 Hartree G = -1349.759 Hartree

H	0.28012200	3.68755100	-0.04921800
C	-5.61954000	-2.10874800	0.31752100
H	-4.95190800	-2.98245300	0.39354900
C	5.02842400	-2.28563400	0.20104300
H	5.19656500	-1.47070500	-0.51788000
O	-1.33914400	3.76030100	-1.33760900
H	-1.44807100	2.78919400	-1.23342300
O	-5.14981100	-1.08783000	1.21136000
H	-4.22372700	-0.86295900	0.96107300
O	3.68133000	-2.77947000	0.02289900
H	3.60850400	-3.14167000	-0.87761400
C	-7.00970500	-2.51531900	0.78667300
H	-7.40651300	-3.32412100	0.16175200
H	-6.98213800	-2.86426200	1.82579800
H	-7.69863500	-1.66268000	0.72633400
C	-0.33213400	5.71189600	-0.40695200
H	-1.25237200	6.29538000	-0.54069700
H	0.21794600	6.12736800	0.44574400
H	0.28530100	5.82894900	-1.30545900
C	5.10202500	-1.72794300	1.61374400
H	6.09031700	-1.29123600	1.79728800
H	4.34919000	-0.94657600	1.76599900
H	4.93216800	-2.52344700	2.35022200
C	-5.62137900	-1.62085900	-1.13147700
H	-4.61356300	-1.33409900	-1.45385800
H	-5.97764600	-2.41163800	-1.80413600
H	-6.28016600	-0.74958000	-1.24071600
C	-1.51149600	4.04201800	1.08708900
H	-1.75077700	2.98239500	1.23356900
H	-0.97926700	4.39546000	1.97911700
H	-2.45362600	4.59928300	1.00312700
C	6.05025700	-3.38948300	-0.05120800
H	5.95491900	-3.78636400	-1.07025600
H	7.06972800	-3.00109100	0.06401900
H	5.90935400	-4.21453400	0.65827400

Table S2.58 Transition state: activation of **3** in int.**2** in acetonitrile (SMD) with **3** molecules of dimethyl sulfoxide



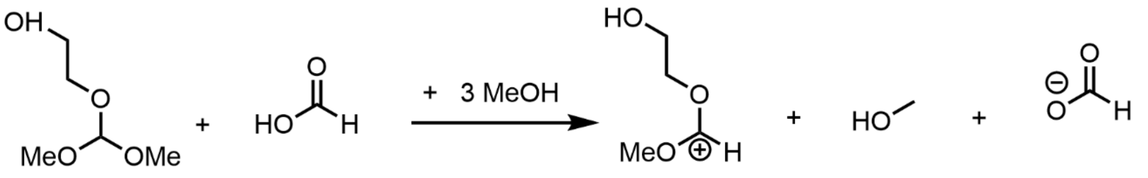




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.94182100 -0.34265200 0.70996500 H 2.77924900 -0.99562500 0.94436500 O 2.00259100 0.91847900 1.05361600 O 0.85240900 -1.09063100 1.98752600 O 1.30591400 -0.51388100 -0.42894900 C 2.81856900 1.25774200 2.22145700 H 3.63691100 1.87071900 1.83635400 H 3.23035700 0.33868000 2.64589300 C 1.96064300 2.00991300 3.21484500 H 1.13078100 1.38949200 3.56649300 H 2.57768800 2.29165200 4.07638800 H 1.55616600 2.92500100 2.76856000 C 1.36629000 -2.22490100 2.72865200 H 0.79494600 -3.11010900 2.43087500 H 2.40764200 -2.37484400 2.42313200 C 1.27280300 -1.96497500 4.22078400 H 0.23199100 -1.80680400 4.52556000 H 1.66514700 -2.83018200 4.76988900 H 1.85862700 -1.08249100 4.50154300 C 1.30998500 -1.87779400 -0.94319800 H 2.29307300 -2.07823300 -1.37708900 H 1.11655900 -2.56242100 -0.11563100 C 0.18236000 -1.98663800 -1.96306700 H -0.69593600 -1.44573900 -1.58778900 H 0.47298200 -1.54684700 -2.92160300 C -1.83930700 -2.71287500 0.79000100 H -2.92284300 -2.87535700 0.63513500 O -1.05152000 -3.61727300 0.42661400 O -1.53205300 -1.60071000 1.33451500 H -0.12091800 -1.30823500 1.64473000 O -0.12058900 -3.35785600 -2.19880400 H -0.52154900 -3.68487000 -1.36317100 C 5.63953500 0.69530000 -2.92909600 H 5.42017300 1.25525100 -3.84388000 H 6.33292900 1.24968700 -2.28904600 H 6.05537800 -0.28323500 -3.18428000 C 3.71171800 2.14975400 -1.64966600 H 2.79281200 2.17062700 -1.06075800 H 4.54173800 2.58045500 -1.08093500 H 3.56437300 2.68854000 -2.59124800 S 4.08586300 0.40675100 -2.02394800 O 4.47938500 -0.25670600 -0.69071600 C -1.14559700 1.58733500 0.06518100 H -0.94215300 1.48742300 -1.00455300 H -0.26271500 1.95113600 0.59533400 H -1.46391500 0.62662700 0.47545300 C -1.63525200 4.23906300 -0.35052100 H -2.30435600 5.09610300 -0.23417400 H -0.71427600 4.39263000 0.22074200 H -1.41321300 4.08320600 -1.41124000 S -2.50413200 2.77305100 0.29564400 O -2.65378400 2.98306200 1.81409400 C -5.48449600 0.63653500 -2.00517400 H -6.37676600 0.05548000 -1.75141400 H -5.55175700 1.65076200 -1.59927900 H -5.35476500 0.67942800 -3.09011500 C -4.58228700 -0.23980100 0.41748900	H= -2426.2413 Hartree G = -2426.3665 Hartree

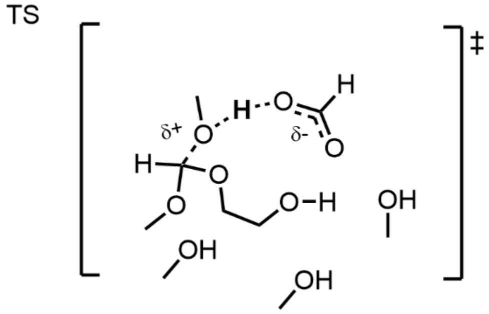
H -3.76788800 -0.64487700 1.02243400	
H -4.82998400 0.77179500 0.75151900	
H -5.46486200 -0.88550100 0.46890200	
S -4.01059700 -0.18348200 -1.31359400	
O -4.03116100 -1.63154500 -1.83447600	

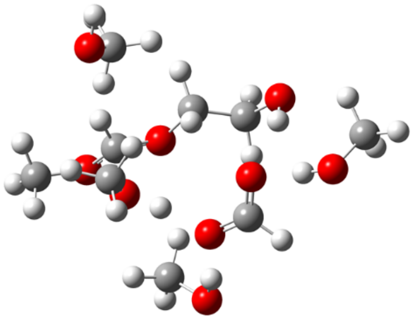
Table S2.59 Transition state: activation of **3** derived from trimethyl orthoformate **(2.1)** in int.**2** in acetonitrile (SMD) with **3** molecules of methanol



3 dervied from 2.1 **FA** **Int.2** **MeOH** **FA$^-$**

TS

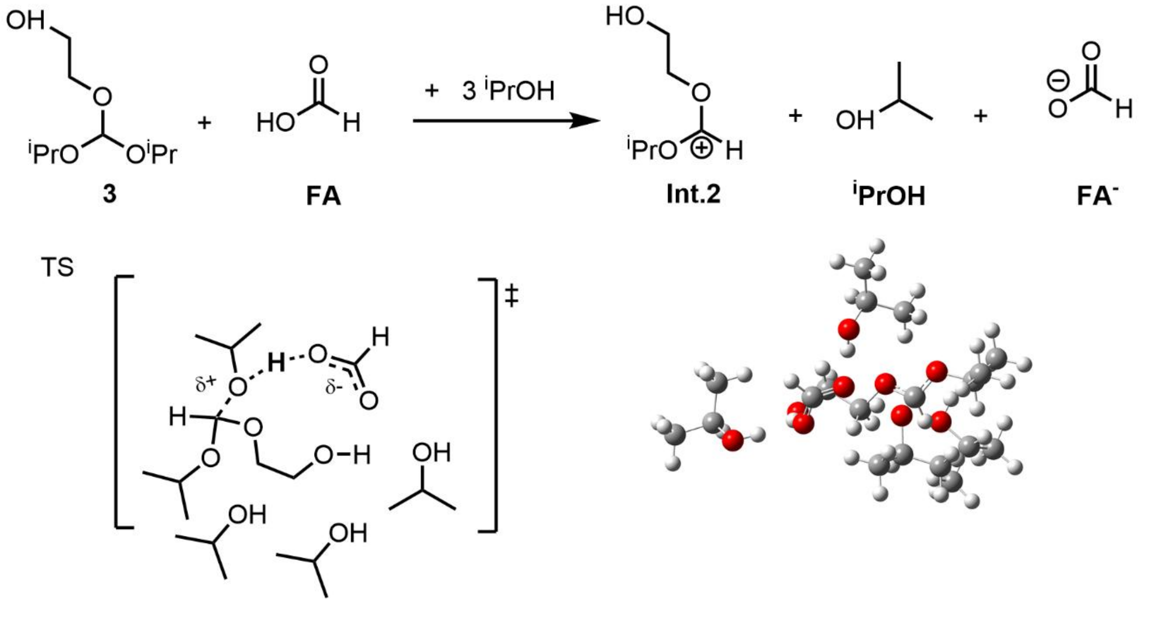




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1035.2687 Hartree
C 1.94231800 -0.12996100 0.47684500	G = -1035.3685 Hartree
H 2.03294800 -0.82250100 1.31262900	
O 3.00047500 0.56440200 0.12281600	
O 0.92290000 1.06488000 1.37331200	
O 1.22040200 -0.48717900 -0.56338700	
C 3.90644300 0.92751800 1.19354400	
H 4.83887500 1.20846000 0.70480600	
H 4.06624900 0.07444300 1.85859200	
C 0.59659200 0.70425300 2.73387500	
H 0.03384000 -0.23342900 2.76803300	
H 1.53273000 0.60356500 3.28586400	
C 0.15178300 -1.43842100 -0.28776100	
H 0.60109600 -2.41853700 -0.10913500	
H -0.39359300 -1.11001900 0.59909400	
C -0.78479700 -1.43381300 -1.48981100	
H -0.93971400 -0.40073400 -1.82769000	
H -0.36268400 -2.00629500 -2.32019300	
C -2.28838400 1.22395300 0.10858100	
H -3.08370800 1.72356000 -0.47541400	
O -2.55794900 0.13529300 0.67370000	
O -1.16776300 1.82619200 0.13705300	
H 0.05271000 1.29659800 0.85493400	
O -2.01975800 -2.05213700 -1.13842700	
H -2.44897100 -1.45395400 -0.49361400	
C 1.16347500 3.15087300 -1.83919100	
H 1.66543900 3.75914600 -2.59867400	
H 1.70286500 3.26737800 -0.88810400	

H 1.21604300 2.09659500 -2.14476400 C -5.55535200 -1.41127800 0.01238400 H -5.01274000 -2.33937500 0.24782500 H -6.62909100 -1.61968800 0.05928600 H -5.30543200 -1.10836000 -1.01535900 C 3.52279700 -2.79495400 -1.13643900 H 3.81251800 -1.79636200 -1.47083200 H 4.32424500 -3.50123900 -1.39005400 H 2.60218200 -3.09192000 -1.65568200 O -0.18385000 3.60895100 -1.74488600 H -0.63928600 3.03583300 -1.08872600 O -5.27557200 -0.37834400 0.95334100 H -4.31583900 -0.16746900 0.88625900 O 3.32667600 -2.71616500 0.28104300 H 3.10021700 -3.60340700 0.60711300 H 3.49326400 1.77672400 1.74223800 H 0.00210600 1.51483100 3.16288800	

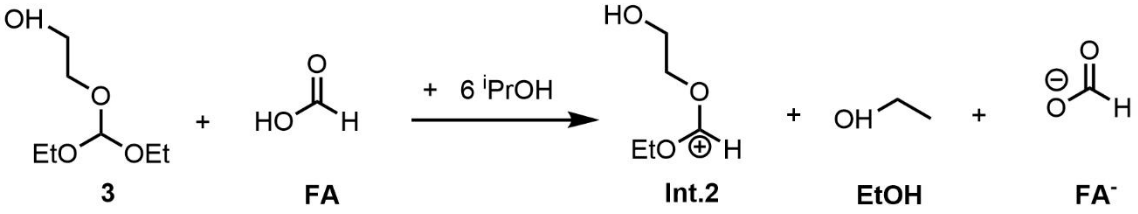
Table S2.60 Transition state: activation of 3 derived from triisopropyl orthoformate (**2.2**) in int.**2** in acetonitrile (SMD) with **3** molecules of isopropanol

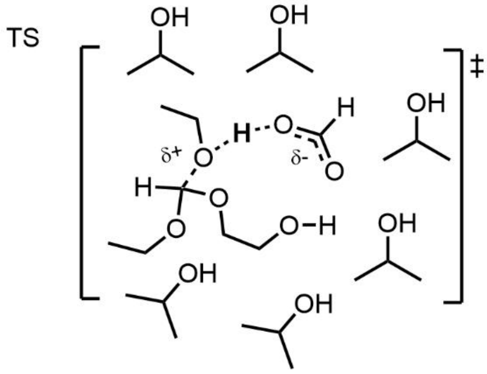


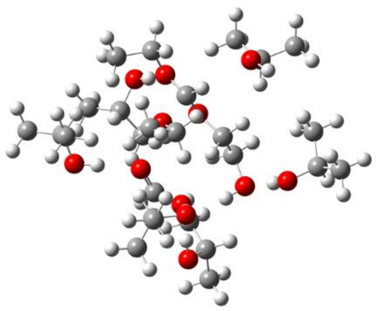
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.70342800 -0.03540600 -0.30389700 H 2.25905600 -0.88636400 0.08310300 O 2.37494100 1.04302600 -0.65627300 O 0.87911700 0.37984700 1.18110400 O 0.73989500 -0.28454900 -1.18493800 C 3.67530800 1.30556100 -0.01203000 H 3.92899000 0.42833500 0.58761400 C 3.52860600 2.53231500 0.87089100 H 2.75005100 2.38539200 1.62396000 H 4.47836400 2.72273900 1.38389100 H 3.27830200 3.41281500 0.26894200 C 0.96971300 -0.57547600 2.30869100 H 0.84946800 -1.57949400 1.88848800 C 2.33940500 -0.43738700 2.94925900	H= -1428.2321 Hartree G = -1428.3559 Hartree

H	2.49270900	0.58132900	3.32127200
H	3.14680200	-0.68782100	2.25609700
C	0.01331400	-1.52733400	-0.99825600
H	0.69927900	-2.36351400	-1.15964700
H	-0.38231800	-1.55902400	0.01789300
C	-1.15330900	-1.52104000	-1.98040000
H	-1.56500700	-0.50483200	-2.04403300
H	-0.83341400	-1.82571300	-2.98071900
C	-2.56559600	0.45115100	0.57104000
H	-3.49455300	1.01546800	0.36692600
O	-2.65085700	-0.79162900	0.73416300
O	-1.50305100	1.14865100	0.62426300
H	-0.10899800	0.60939500	0.95674900
O	-2.14841000	-2.44929900	-1.55681300
H	-2.52598000	-2.07420600	-0.73536300
C	-1.13834200	4.31575200	-0.81531300
H	-1.42893200	3.70477700	-1.68573300
C	-5.79697000	-1.98527400	-0.21242100
H	-5.15669200	-2.78459000	-0.62003900
C	4.45921600	-2.57149200	-0.45710700
H	4.77469800	-1.61217100	-0.02090800
O	-1.89952200	3.88798200	0.32426100
H	-1.74104400	2.92422600	0.45084200
O	-5.29745900	-1.60513100	1.07886900
H	-4.36231600	-1.31387800	0.97147800
O	3.42342100	-2.30998400	-1.43146900
H	3.80445800	-1.76308100	-2.14113500
C	-7.19961500	-2.54136300	-0.00925300
H	-7.61949000	-2.88655100	-0.96145600
H	-7.18427400	-3.38763600	0.68782300
H	-7.86252300	-1.76796100	0.40022400
C	-1.50809100	5.76671400	-1.09021700
H	-1.23696200	6.39908200	-0.23465700
H	-0.97816400	6.13876400	-1.97512800
H	-2.58577300	5.86732700	-1.26603200
C	3.82464500	-3.42889500	0.62719700
H	4.54543000	-3.61732000	1.43088200
H	2.95089600	-2.92997100	1.06127200
H	3.50379700	-4.39383600	0.21513500
C	-5.78078000	-0.80418300	-1.18315400
H	-4.76461900	-0.41456900	-1.31511900
H	-6.15484700	-1.10956900	-2.16882700
H	-6.41601200	0.00832000	-0.80720000
C	0.35936600	4.13573500	-0.57065200
H	0.60032800	3.08800700	-0.36441300
H	0.93838800	4.44604300	-1.45023000
H	0.68128800	4.73987300	0.28754200
C	5.66519100	-3.23897700	-1.10893400
H	6.08234900	-2.60480000	-1.90184000
H	6.45410100	-3.41172600	-0.36654000
H	5.38172500	-4.20389900	-1.54755000
C	4.68773500	1.47779600	-1.13030500
H	4.41590700	2.32456800	-1.77114100
H	5.67588100	1.67365400	-0.69899300
H	4.75303900	0.57518500	-1.74719700
H	2.40285300	-1.13103500	3.79515000
C	-0.16262900	-0.27650800	3.27876800
H	-1.14113400	-0.42886400	2.81652500
H	-0.07867500	-0.95705300	4.13336100
H	-0.09460300	0.75271400	3.64995900

Table S2.61 Transition state: activation of **3** derived from triisopropyl orthoformate (**2.2**) in int.**2** in acetonitrile (SMD) with **6** molecules of isopropanol





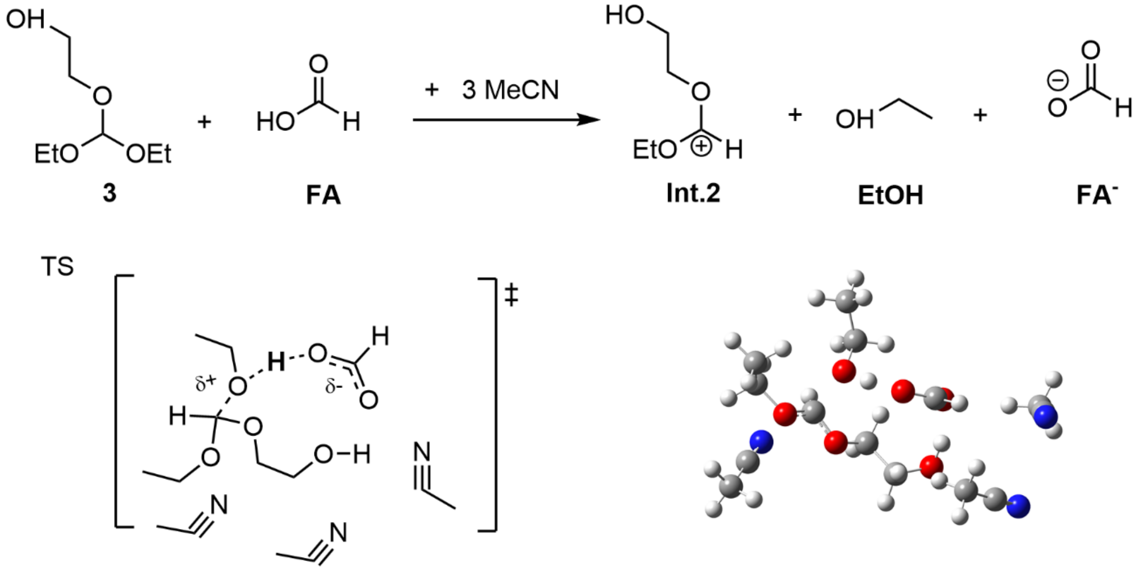


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1932.4835 Hartree
C 0.17405400 2.12996600 0.55718800	G = -1932.6532Hartree
H 0.82261000 2.42919300 1.37831300	
O -0.70438200 2.98626100 0.09401400	
O -0.82507000 1.00501700 1.60631900	
O 0.65862600 1.37373900 -0.39994800	
C -1.24872200 3.99130500 1.02288100	
H -1.05912200 4.94862700 0.53376600	
H -0.67903300 3.94359400 1.95413300	
C -2.72446500 3.73605700 1.23277700	
H -2.89346200 2.76284400 1.69969100	
H -3.12299300 4.51640900 1.89219200	
H -3.26858300 3.77868100 0.28370900	
C -0.27514900 0.60978500 2.89885300	
H 0.07569200 -0.42284600 2.82307900	
H 0.58808600 1.25706900 3.08199600	
C -1.32005200 0.78402100 3.98289400	
H -2.18081100 0.12992800 3.81263700	
H -0.87850200 0.52628800 4.95308400	
H -1.66747100 1.82226500 4.02659600	
C 1.68085800 0.41885100 -0.00075600	
H 2.50073500 0.95896400 0.47402500	
H 1.23577300 -0.27711300 0.71213900	
C 2.10576300 -0.33320300 -1.25711800	
H 1.25128300 -0.42421900 -1.93583300	
H 2.91290500 0.18302300 -1.78072100	
C -1.15447500 -1.87462200 -0.47857900	
H -1.71267300 -2.30704500 -1.32641200	
O -0.03573400 -2.39288500 -0.19548500	
O -1.71464000 -0.91958900 0.13041700	
H -1.11273100 0.19375200 1.05844800	
O 2.59639000 -1.62826900 -0.90036300	

H	1.81060000	-2.13192900	-0.60202500
C	-4.96813100	0.50196800	0.27208100
H	-4.38693800	1.36021700	-0.09827700
C	0.98203400	-4.24360500	-3.02166200
H	1.98725100	-3.91543000	-2.71311900
C	3.25163900	3.61731300	-0.90116500
H	3.22838400	2.58553000	-1.28052500
O	-4.47420200	-0.69535600	-0.34686300
H	-3.50787500	-0.75559000	-0.17739400
O	0.24973300	-4.65227600	-1.85401200
H	0.16506700	-3.87919800	-1.25291900
O	2.85173000	3.60007900	0.48957100
H	3.56023100	3.16743400	0.99858100
C	1.11983100	-5.46844400	-3.91480000
H	1.71384100	-5.23052100	-4.80509700
H	1.61549300	-6.28618000	-3.37826700
H	0.13169300	-5.81760900	-4.24168900
C	-6.41702600	0.67124800	-0.16228900
H	-7.02326100	-0.17515500	0.18597200
H	-6.83922600	1.59253500	0.25626600
H	-6.49093500	0.72341700	-1.25468900
C	2.21582800	4.44579300	-1.64474700
H	2.43859200	4.45224800	-2.71785300
H	1.21103300	4.03439100	-1.50699600
H	2.22094500	5.48181200	-1.28341100
C	0.28907200	-3.08361800	-3.73662700
H	0.20891700	-2.20712300	-3.08502600
H	0.85706100	-2.78725100	-4.62772000
H	-0.72178000	-3.37432800	-4.05030600
C	-4.82283900	0.43428600	1.79181000
H	-3.77467900	0.29812500	2.07922800
H	-5.18320700	1.35947000	2.25910600
H	-5.40301900	-0.40647400	2.19376900
C	4.66495000	4.16916800	-1.05257200
H	5.38598400	3.56666300	-0.48595900
H	4.96898700	4.15264900	-2.10631600
H	4.71545700	5.20424800	-0.69200200
C	-1.87615400	-4.16358200	2.40290600
H	-1.34665300	-5.08123100	2.68972900
H	-1.88161700	-4.09683800	1.30848100
H	-2.91738200	-4.24352500	2.74049600
C	-1.20399800	-2.94175500	3.02769500
H	-1.75877000	-2.04229500	2.72252900
C	-1.17713300	-3.01192800	4.54743000
H	-0.63034100	-3.90362700	4.88036600
H	-0.68548100	-2.12771900	4.96839700
H	-2.19651200	-3.06293200	4.94761700
C	5.61174600	-0.81873700	0.90938300
H	6.02357700	-1.39460000	0.06551800
C	6.55812100	-0.93957500	2.09586800
H	6.68466600	-1.98879600	2.38729300
H	7.54353000	-0.52894900	1.84633800
H	6.16225000	-0.38654500	2.95768300
C	5.43068500	0.63458200	0.46852200
H	6.39336900	1.06611000	0.16689000
H	4.74752200	0.70918400	-0.38435800
H	5.02541000	1.23657400	1.29217800
C	-2.57503700	1.49593800	-2.61320200
H	-2.79949100	1.18262700	-1.58682800
C	-1.62963600	0.47565700	-3.24211600

H -1.39339000 0.75716000 -4.27650700 H -0.69458100 0.41590200 -2.67658400 H -2.08683100 -0.52103700 -3.24964100 C -3.87749900 1.63481600 -3.38746100 H -4.38700500 0.66751900 -3.45968900 H -4.55058600 2.34502900 -2.89374300 H -3.67986100 1.99534300 -4.40550800 O -1.96095800 2.80268500 -2.56785600 H -1.39327800 2.83517800 -1.77904000 O 4.36157600 -1.40774500 1.30447700 H 3.78621900 -1.49445000 0.51409500 O 0.15923700 -2.81346400 2.58609100 H 0.15087500 -2.66513600 1.61607500	

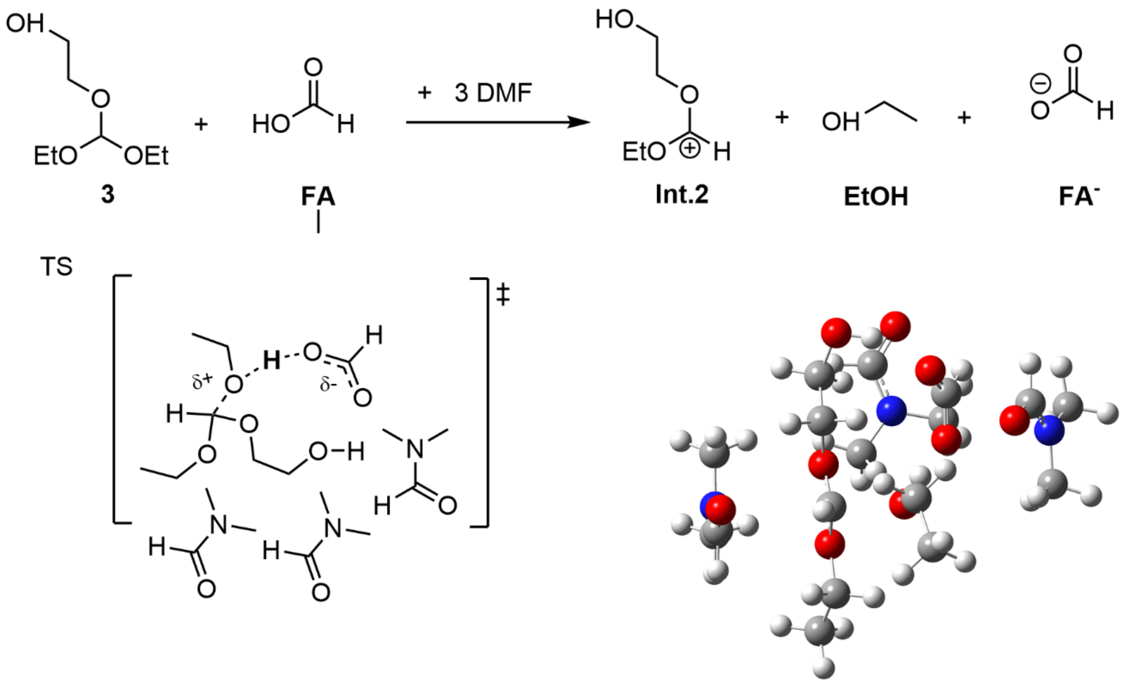
Table S2.62 Transition state: activation of **3** derived from **3** in int.**2** in acetonitrile (SMD) with **3** molecules of acetonitrile



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -2.40555700 -0.02227400 -0.04456800 H -2.80422800 0.18746100 -1.03631800 O -3.17265000 0.11508500 0.99961300 O -1.40905600 1.59448100 -0.06432500 O -1.51486200 -0.96988800 0.10045300 C -4.29468100 1.05987800 0.89302000 H -5.18766900 0.45798300 1.07369000 H -4.32473300 1.45105400 -0.12667300 C -4.12650500 2.15224800 1.92495700 H -3.21709100 2.73101600 1.74037300 H -4.99002100 2.82567600 1.86807100 H -4.08572500 1.73180400 2.93578000 C -1.35256300 2.33747500 -1.30441300 H -0.35810800 2.20148100 -1.74324300 H -2.08755500 1.89561600 -1.98660500 C -1.66257600 3.80303600 -1.05703900 H -0.93295500 4.24649700 -0.36972800 H -1.62164100 4.35409800 -2.00509600 H -2.66467300 3.92278300 -0.62995700	H= -1164.9909 Hartree G = -1165.1029 Hartree

C -0.68766300 -1.24266700 -1.07485400 H -1.30403700 -1.76416000 -1.81187500 H -0.33927900 -0.28983600 -1.47558900 C 0.50966800 -2.06629700 -0.61328300 H 0.84091000 -1.69790500 0.36653000 H 0.24857600 -3.12362300 -0.51318700 C 1.94340500 1.12894500 0.19335300 H 2.92096800 1.22576300 0.70491100 O 1.94287300 0.72036100 -0.99465000 O 0.93660600 1.46238500 0.89387700 H -0.44077100 1.47300400 0.31010000 O 1.55260100 -1.97326200 -1.57595300 H 1.88155500 -1.04890600 -1.51449000 C -4.99094600 -2.82191600 0.77199300 H -5.56766900 -3.75043700 0.71119600 H -4.03742500 -3.02337000 1.27055200 H -5.55418000 -2.08737800 1.35633800 C -4.74611500 -2.30334900 -0.56598000 N -4.53789100 -1.87690800 -1.62686000 C 3.65109000 -1.41983800 2.12512500 H 3.67803800 -2.09688800 2.98527000 H 4.04685700 -0.44399300 2.42233500 H 2.61488200 -1.30182600 1.79476100 C 4.45783700 -1.96708100 1.04374500 N 5.10676400 -2.40087600 0.18294100 C 5.32066300 0.80277500 -1.32427800 H 5.61155200 1.63252700 -1.97719000 H 4.22908000 0.69324500 -1.34376700 H 5.78424100 -0.11998400 -1.68670100 C 5.76191500 1.07187000 0.03656700 N 6.10386700 1.28466700 1.12710700	

Table S2.63 Transition state: activation of **3** derived from **3** in int.**2** in acetonitrile (SMD) with **3** molecules of acetonitrile

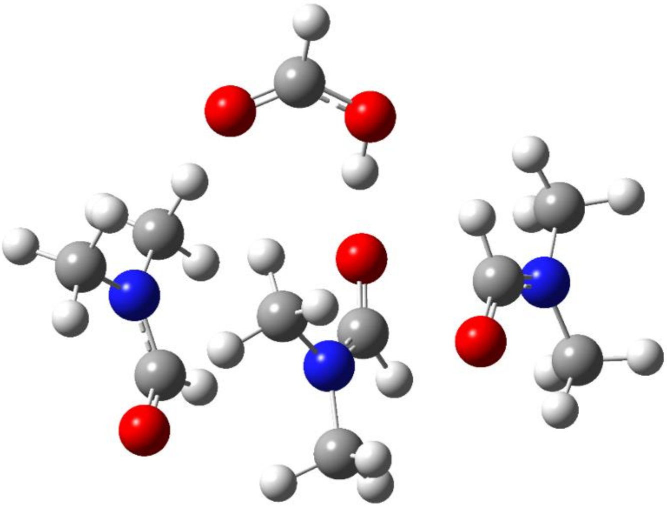


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.31953500 -1.41494200 0.17924100 H -1.21244500 -2.25958000 0.85708500 O -1.90174000 -1.55814100 -0.96790300 O 0.63573500 -1.68421000 -0.33783700 O -1.34010800 -0.20336700 0.63271500 C -1.98799900 -2.92597600 -1.50537700 H -2.28676600 -3.58743900 -0.68780800 H -0.98518200 -3.18900900 -1.84686100 C -2.99596700 -2.90727300 -2.62921600 H -2.68686700 -2.21878200 -3.42305200 H -3.06386100 -3.91500900 -3.05450300 H -3.98730300 -2.61584200 -2.26789600 C 1.41057100 -2.55870600 0.50669400 H 2.37364100 -2.08056900 0.70642500 H 0.89270400 -2.67529800 1.46902600 C 1.59223500 -3.90939300 -0.16152000 H 2.10345900 -3.80268100 -1.12501800 H 2.19564200 -4.56344400 0.48039000 H 0.62517600 -4.39671900 -0.33283500 C -0.74993500 0.01636700 1.95590100 H -1.34995600 -0.52635500 2.68975600 H 0.27137100 -0.36449800 1.93109000 C -0.72577500 1.52324200 2.19435000 H -0.50275100 2.02810600 1.24694100 H -1.69089400 1.88430200 2.55803000 C 2.17017700 1.35459300 0.28016300 H 2.49363900 2.37140400 -0.02666300 O 2.27705300 1.05986400 1.49819800 O 1.73224300 0.61909100 -0.65396200 H 1.08413700 -0.76303400 -0.39360100 O 0.24801900 1.83741500 3.18214500 H 1.11716600 1.66189300 2.75141800 O -3.89152700 -1.86325500 1.73711200 O 4.84446200 -1.97657600 1.52003900 O 0.36075300 5.17214600 -0.24831100 N -0.33422000 3.36014000 -1.49075300 C 0.78219600 3.37956500 -2.42460800 H 1.32140800 2.42809200 -2.36834300 H 0.41082200 3.52424800 -3.44690400 H 1.45300000 4.19897200 -2.16390100 C -1.32458000 2.30948700 -1.67693000 H -0.84684500 1.32863200 -1.59707600 H -2.09732300 2.38959500 -0.90908100 H -1.79169500 2.40225800 -2.66533200 C -0.43780700 4.25580100 -0.49072400 H -1.33830400 4.10328700 0.12583700 C 5.03848800 -0.89299100 0.95066100 H 5.29873500 0.01474400 1.51682900 N 4.97218800 -0.67805100 -0.37741500 C 4.62968500 -1.74217000 -1.30779500 H 3.71627100 -1.48136300 -1.85422300 H 5.44289400 -1.88449000 -2.03046600 H 4.47134900 -2.66678100 -0.75277000 C 5.24549200 0.63117400 -0.94954500 H 4.38994700 0.96585100 -1.54534300 H 5.42481500 1.35356900 -0.14953300 H 6.13106600 0.58683800 -1.59604500	H= -1512.1387 Hartree G = -1512.2663 Hartree

N -4.70877300 -0.17218100 0.40437800 C -4.31389900 0.91841900 1.28368100 H -3.60118600 1.57381400 0.77181900 H -5.19613100 1.50700500 1.56305800 H -3.85065400 0.50664000 2.17971600 C -5.32492200 0.19657400 -0.86153300 H -4.62468000 0.78742700 -1.46467000 H -5.59860300 -0.70467400 -1.41530400 H -6.22669900 0.79388600 -0.68299800 C -4.46656100 -1.45857300 0.71529100 H -4.83374900 -2.15927400 -0.05062300	

2.10.2.7.1 COMPUTATIONS FOR THE CALCULATION OF THE DISSOCIATION ENERGIES OF COMPLEX CATALYSTS-SOLVENTS

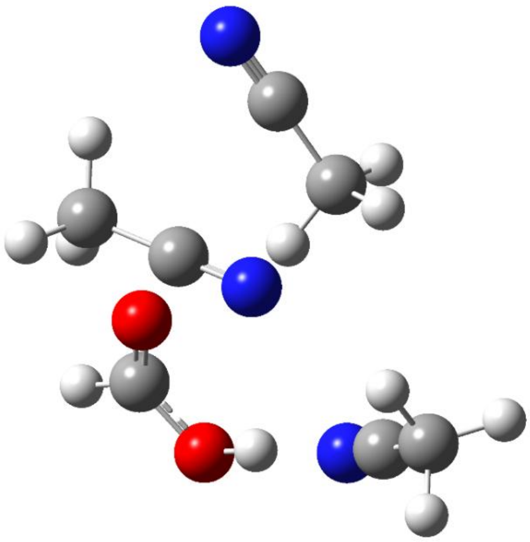
Table S2.64 Complex FA-3 molecules of DMF (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.33459800 3.21758500 0.73477600 O -1.45397700 2.75078100 0.82580500 O 0.68713600 2.67641800 0.08291500 H 0.42142400 1.81033500 -0.36358800 H -0.03842800 4.16819800 1.20298800 C 3.01910000 0.00850400 0.98049100 H 2.74123800 1.01716500 1.33084500 C 3.89353100 -1.21971900 -0.93984500 H 3.27782800 -1.40106400 -1.83080700 H 4.94370500 -1.16277900 -1.25252200 H 3.76860600 -2.04077300 -0.23269600 C 3.55265800 1.23697700 -1.07812000 H 2.89610800 1.16006700 -1.95292900 H 3.21337900 2.08063800 -0.47357500 H 4.58051400 1.42366000 -1.41409600 N 3.49066500 0.01560600 -0.29208100	H= -935.06127 Hartree G = -935.14854 Hartree

O 2.89060600 -0.98657000 1.69055200 C -2.93713800 -1.45466300 -0.67938100 H -2.52106100 -1.62148100 -1.68978800 C -3.93149600 0.25200700 0.76371300 H -3.35808700 1.07949900 1.19288200 H -4.96157000 0.58868500 0.58756100 H -3.94355600 -0.59639100 1.44879000 C -3.16960200 0.83713500 -1.52612500 H -2.56877500 1.66816200 -1.14588100 H -2.65946800 0.40186300 -2.38891200 H -4.15064800 1.21541900 -1.84315600 N -3.32539400 -0.17266000 -0.49037100 O -3.00765000 -2.36338700 0.14752400 C 0.35557400 -0.77963200 -0.91861700 H 0.70576400 -1.50444900 -1.66914000 C -0.45241000 -0.56679100 1.38177100 H -1.29176200 -1.11666800 1.81610000 H 0.33412600 -0.44118900 2.13343400 H -0.80635800 0.40276500 1.03593500 C 0.29668700 -2.75698400 0.50229200 H -0.64899300 -3.23384800 0.77698300 H 0.68447100 -3.22798400 -0.40469600 H 1.03454700 -2.86713800 1.30325000 N 0.06412100 -1.33780800 0.25616200 O 0.25731100 0.42461100 -1.22288200	

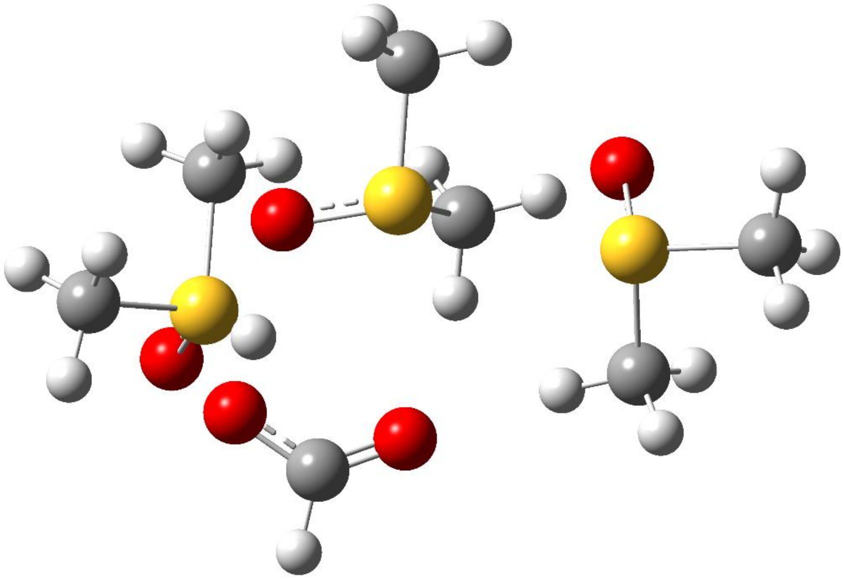
Table S2.65 Complex FA-3 molecules of MeCN (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.09710400 2.78125100 -0.31812300 O 0.11456500 2.06830600 -0.40534800 O 2.31609600 2.39253000 0.03210100	H= -587.91529 Hartree G = -587.98739 Hartree

H 2.33900000 1.41017700 0.19463800	
H 1.07964200 3.86105600 -0.52410900	
C -2.33203700 -0.02694700 1.54383700	
C -1.39249800 -0.99310400 -1.48763300	
C 2.29964700 -1.52834600 0.24128800	
N 2.44925300 -0.39116400 0.40501800	
N -3.44907700 0.08568400 1.24666200	
N -0.78609200 -1.91983200 -1.13868900	
C 2.09799800 -2.95638800 0.03232600	
H 2.17031400 -3.48953100 0.98559300	
H 1.10402700 -3.10534100 -0.40210000	
H 2.85984100 -3.34464300 -0.65096200	
C -0.91997700 -0.16625000 1.88709900	
H -0.31725000 0.43752800 1.20200500	
H -0.74498200 0.16651800 2.91516900	
H -0.61820500 -1.21284800 1.78883100	
C -2.15009500 0.17928300 -1.91179800	
H -3.12873100 0.17906900 -1.42298700	
H -1.60835000 1.08262300 -1.61438700	
H -2.28001900 0.16888800 -2.99862800	

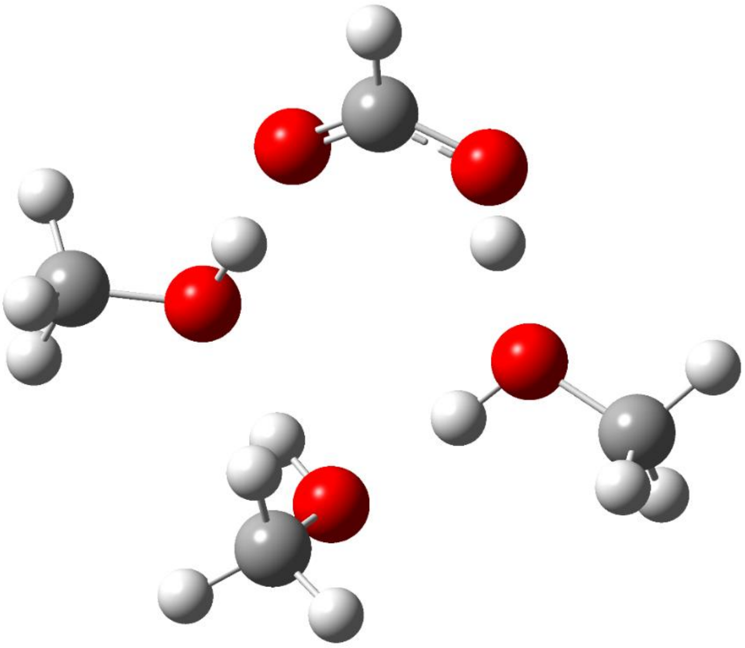
Table S2.66 Complex FA-3 molecules of DMSO (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1	H= -1849.1657 Hartree
C -0.73694100 -2.68065400 0.48833600	G = -1849.2501 Hartree
O 0.14567400 -2.19420000 -0.20283800	
O -1.47979100 -2.03539900 1.36556000	
H -1.25020500 -1.03914300 1.35832100	
H -1.00457500 -3.74658400 0.44371200	
C -3.42684400 1.81801800 -0.61931200	
H -2.70443500 2.10126700 0.14976300	

C -4.16253400 -0.21551400 1.02216500 H -4.29158600 -1.28583900 1.19361600 H -3.43587500 0.19190200 1.72886800 H -5.12629800 0.29804500 1.09125200 C 5.64578900 -0.05794500 -0.47593800 H 6.14326700 0.78680000 0.00599600 C 3.34029500 -1.47605100 -0.89808400 H 2.28498600 -1.64590900 -0.67294800 H 3.46947200 -1.20424700 -1.95025300 H 3.91630400 -2.37435500 -0.65365000 O -0.95753200 0.52806800 1.24596100 C 0.81448200 2.51241700 1.08313500 H 1.77054100 2.77515100 0.62562900 H -0.00364600 3.14041200 0.72004900 H 0.87936200 2.57564500 2.17178400 S 0.46864300 0.77672400 0.67097300 C 0.24178100 0.97279400 -1.12386300 H 1.20742500 1.25107900 -1.55030700 H -0.08748100 0.00182500 -1.49680700 H -0.52069600 1.73361000 -1.30648700 S -3.52800800 -0.01307700 -0.68490700 H -3.10037500 2.15948500 -1.60512700 O -4.68028400 -0.34964500 -1.62386600 S 3.92486900 -0.09325500 0.14104200 O 3.26564300 1.17671200 -0.40622100 H 6.15040100 -0.99152700 -0.20868700 H 5.63265000 0.08638700 -1.56015600 H -4.42314300 2.21703900 -0.40569800	

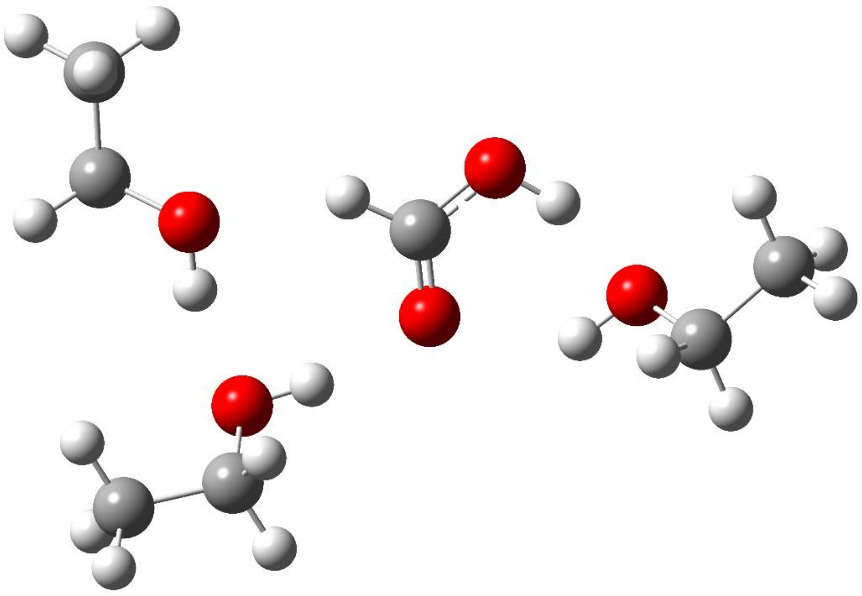
Table S2.67 Complex FA-3 molecules of MeOH (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.60306400 2.50150900 0.48977700 C 2.96275000 -1.23232600 -0.55485900	H= -536.80763 Hartree G = -536.87201 Hartree

H 2.95661600 -2.09327000 -1.23370900 H 3.77111600 -0.55655100 -0.84544800 H 3.13958500 -1.57975500 0.47210000 C -0.57750400 -2.14781500 1.37232700 H 0.24109900 -2.76665600 1.74951800 H -0.55605300 -1.17519600 1.88352200 H -1.52801900 -2.64969000 1.59491500 C -3.36841500 0.21179500 -0.40995300 H -3.77569100 1.11166400 -0.88768400 H -3.95547500 -0.65357500 -0.72811100 H -3.44525500 0.31763600 0.68072300 O -2.02300300 -0.01855400 -0.82137700 H -1.46257300 0.73235600 -0.52988000 O 1.73931300 -0.50620800 -0.65867100 H 0.97058900 -1.10261800 -0.44193200 O -0.39272000 -2.00422200 -0.03436900 H -1.09628300 -1.39540400 -0.37925900 O -0.50584100 2.04491400 0.24758500 O 1.75934700 1.90168600 0.32216400 H 1.66966900 0.95751800 -0.05944100 H 0.73453100 3.51362800 0.89826800	

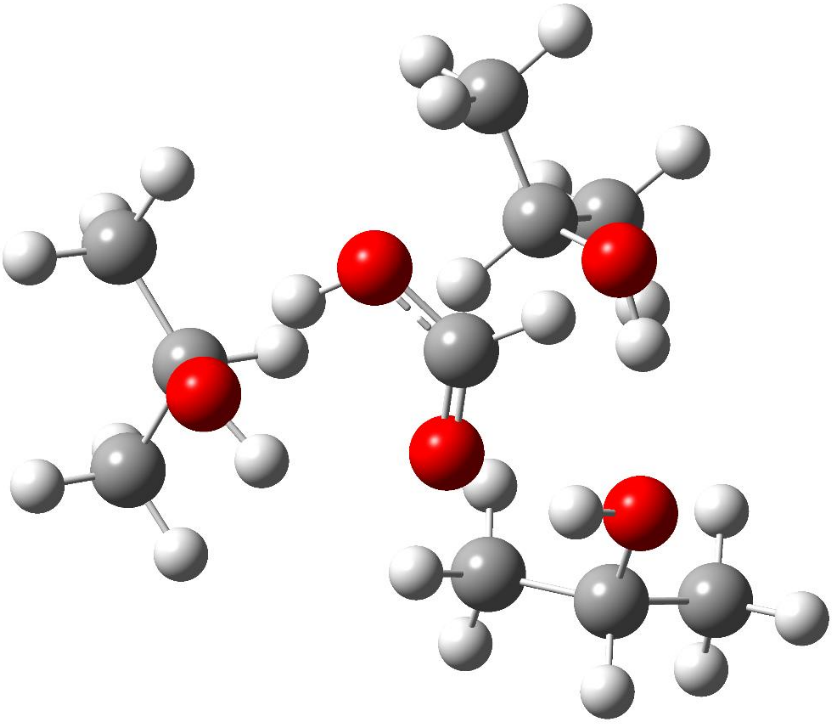
Table S2.68 Complex FA-3 molecules of EtOH (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.68020000 0.82862700 -0.15049000 C 4.46946100 -0.64574800 0.28890600 H 4.87247700 -1.58709500 -0.10653200 H 3.89454600 -0.87242100 1.19806500 C -3.64026300 1.53702800 -0.21919600 H -3.65813300 1.54464700 -1.32027500	H= -654.67908 Hartree G = -654.75507 Hartree

H -4.51271300 0.95788200 0.12274500 C -1.84628400 -2.58397400 0.28050700 H -1.42393300 -2.24919600 1.23954500 H -1.28392200 -3.47001100 -0.04770600 O -1.72011200 -1.54591300 -0.69761400 H -0.78260500 -1.25672900 -0.74022800 O 3.60388700 -0.05409200 -0.69721900 H 2.83419200 -0.63636400 -0.85462200 O -2.43689600 0.93661000 0.25148500 H -2.35581100 0.02606900 -0.11559400 O 0.80677900 -0.33471200 -0.53832200 O 1.68807200 1.66506600 0.02018700 H 2.54393600 1.19297100 -0.21541300 H -0.29682800 1.26895000 0.08694700 C -3.31979000 -2.91830500 0.43790300 H -3.74498900 -3.23685500 -0.52017200 H -3.45305800 -3.72806100 1.16479600 H -3.87879400 -2.04411900 0.79078700 C 5.58834200 0.33500600 0.58782500 H 5.18902700 1.26956100 0.99776500 H 6.28072400 -0.09337600 1.32139700 H 6.14800000 0.56873400 -0.32401200 C -3.71585100 2.95737300 0.31695600 H -2.86130500 3.54725700 -0.03398700 H -4.63718900 3.44833500 -0.01881200 H -3.70235900 2.95410800 1.41270400	

Table S2.69 Complex FA-3 molecules of ^{i}POH (computed in gas phase).



Coordinates of the TS (atom, X, Y, Z)	Energies
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C -2.49669100 -0.93046200 -0.75342100 H -1.52439200 -0.46539800 -0.96987900 C 0.62220400 1.89666600 -0.79657900 H 0.11551800 0.92326200 -0.91673600 C 2.70849300 -1.68782200 0.20079800 H 2.86376000 -2.56782200 0.84419000 O 2.40335300 -0.56444000 1.03982500 H 1.57290300 -0.73907100 1.53005400 O -2.64356700 -1.01365300 0.68540900 H -1.84897100 -1.44553500 1.05581100 O 1.26648700 1.92812000 0.47652100 H 1.85514300 1.14524200 0.54743800 O -0.20685200 -0.54749800 2.06796600 O -1.74543300 1.10292700 2.03345500 H -2.26952200 0.40762900 1.52871600 H 0.08824500 1.33285200 2.81595800 C 4.01264200 -1.36472800 -0.51509400 H 4.80202500 -1.14449100 0.21059900 H 4.33227000 -2.20956500 -1.13554100 H 3.88762600 -0.48845900 -1.16218900 C -3.61113200 -0.02451400 -1.25393400 H -3.53641600 0.97172400 -0.80506600 H -3.55097900 0.08542600 -2.34214300 H -4.58939800 -0.44840400 -1.00008700 C -0.43057300 2.99828100 -0.79695500 H 0.04948700 3.97581800 -0.67021700 H -0.98597400 3.00436300 -1.74234600 H -1.13730500 2.85407000 0.02598600 C -2.53803000 -2.32662100 -1.36502300 H -2.41044800 -2.27279800 -2.45261200 H -1.73454000 -2.95652600 -0.96499100 H -3.49700100 -2.81020100 -1.14770800 C 1.56176300 -1.98093600 -0.76849800 H 1.78703100 -2.86241400 -1.38101500 H 0.63142900 -2.17577600 -0.22286100 H 1.39525100 -1.12847900 -1.43724600 C 1.63402200 2.05949100 -1.93248300 H 2.38917400 1.26528000 -1.90206300 H 1.13743500 2.01849100 -2.91039500 H 2.14998100 3.02238600 -1.84169000	

2.11 MECHANISTIC STUDY OF DYNAMIC COVALENCE EXCHANGES TOWARD ORTHOESTERS (DCE)

2.11.1 MECHANISM OF DCE SEQUENCE TOWARD THE FORMATION OF 3, 4, 5, 6, 7, 10 AND 11

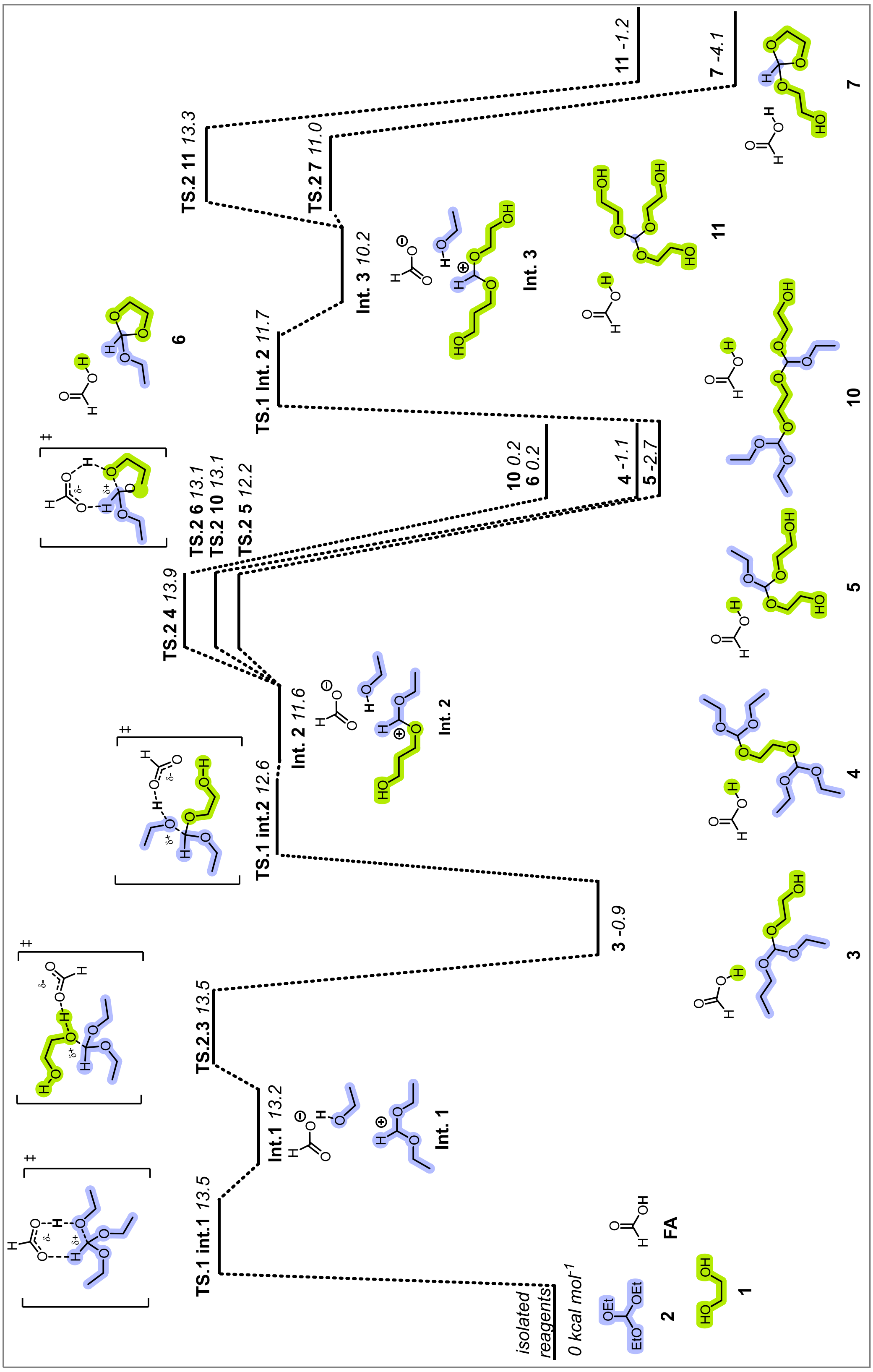


Figure S2.53 Energetic diagram of the DCE mechanism comprising the sequence of carbocation formation and subsequent substitution with a nucleophilic molecule into the production of **3**, **4**, **5**, **6**, **7**, **10** and **11**.

2.11.2 MECHANISM OF DCE TOWARD THE FORMATION OF 8, 9 AND 12

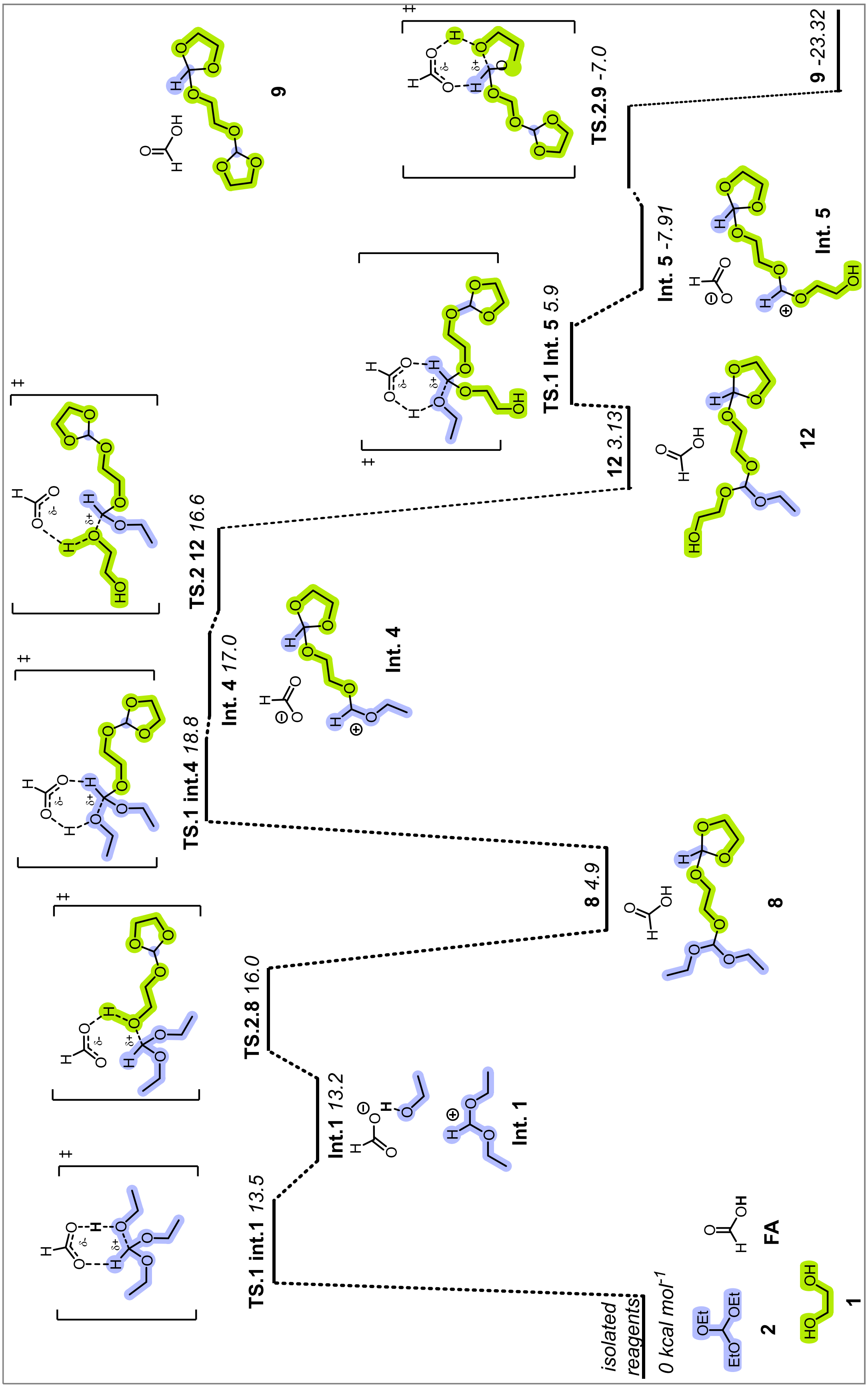


Figure S2.54 Energetic diagram of the DCE mechanism comprising the sequence of carbocation formation and subsequent substitution with a nucleophilic molecule into the formation of **8**, **9** and **12**.

2.11.3 Mechanism of carbene formation from 6 or carbocation from cyclic compounds 7, 8 or 9

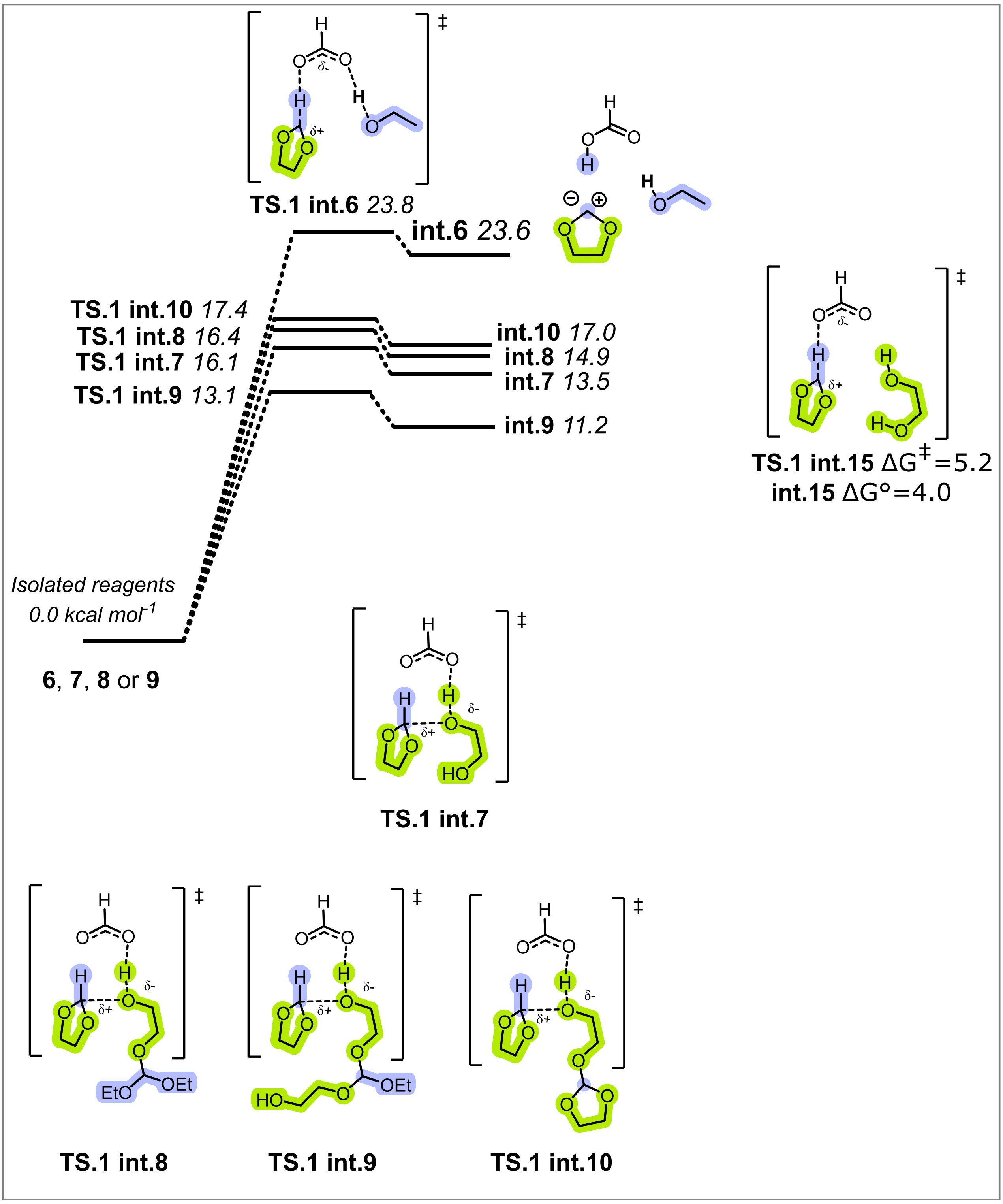


Figure S2.55 Elucidated mechanism for the formation of carbene from **6** or carbocation intermediates from **7**, **8** and **9**.

2.11.4 DFT COMPUTATIONS ON THE SCREENING OF CATALYSTS

Computational analysis identified the acid-mediated formation of carbocation intermediates as the rate demining step (RDS). Therefore, variations of the acid catalyst offered a straightforward way to modulate this step. The effect was evaluated first using DFT to compute the transition state for key compound **3** in presence of a selection organic acids (Figure 5a). The activation barriers ($\Delta G^{\ddagger}$) and Gibbs energies (ΔG°) for the formation of **int. 2** decreased linearly with decreasing pK_a of the acid (Figure 5b1) as a result of the greater proton exchange ability between the acid and substrate. Experimental data was collected using various organic acids including acetic acid (AA), pimelic acid (PA), benzoic acid (Bz), succinic acid (SA), oxalic acid (OA), trichloro- and trifluoro- acetic acid (TCl_3 and TF_3). Analysis of the data obtained focused on the conversion of **2** and formation of **3** and **6** after 45 min.

Use of AA ($pK_a = 4.76$) or PA ($pK_a = 4.71$) resulted in similar $\Delta G^{\ddagger}$ (17.7 vs 17.4 kcal mol^{-1}) and product distributions (Figure 5b), with ca. 41% conversion of **2** after 45 min, mostly due to the formation of **3** (ca. 30%) and modest amounts of **6** (>5%). Using more acidic catalyst Bz ($pK_a = 4.20$), a significantly increased the conversion of **2** (69%) and formation of **6** (21%) was observed.

Succinic acid (SA, $pK_a = 4.16$) led to a higher reagent conversion and production of **6** compared to Bz, despite having a similar pK_a. A catalyst loading of 5 mol% instead of 10 mol% was used for this dicarboxylic acid to maintain the active acid loading as the monocarboxylic acids (e.g. AA, PA, Bz, and FA). To explain the increase in reactivity, the TS was recalculated considering a possible intramolecular H bonding between the catalytically involved COOH and the second COOH (**TS.SA.H**, Figure 5a), which decreased the $\Delta G^{\ddagger}$ from 16.5 to 11.6 kcal mol^{-1}. A significant decrease of enthalpy variation (ΔH) was also observed for **TS.SA.H** (-4.6 kcal mol^{-1}), suggesting an important stabilizing effect of the hydrogen bond.

FA (pKa of 3.75) led to 83% conversion of **2** and formation of 67% of **6** over 45 min. All acids tested with lower pKa than FA resulted in varying degrees of hydrolysis of **2** and **3**, to afford ethyl formate (**13**) and 3-hydroxypropyl formate (**14**, Figure 5). Use of 5 mol% of dicarboxylate OA (pKa of 1.20) led to complete consumption of **2** in less than 30 seconds, yielding 85% of **6**. A stabilization effect comparable to that of SA was observed with dicarboxylate OA (**TS.OA.H**, Figure 5b), resulting in a similar $\Delta G^{\ddagger}$ value to the one obtained when using TF_3, despite the greater acidity of the latter. Experiments using TCl_3 ($pK_a = 0.77$) and TF_3 ($pK_a = 0.33$) led to a substantial product degradation, with more than 65% of combined **13** and **14**. The significant differences in the amount of degradation products obtained with OA compared to TCl_3 and TF_3 prompted us to calculate the TS involved in the hydrolysis of **3** in presence of OA, TCl_3 and TF_3, which revealed very little differences between the three acids. An alternative explanation was investigated, relying on the availability of water. Computation of **TS.OA.H** in presence of three molecules of water showed that the conjugated base was highly solvated, limiting water availability to attack **int.2**. On the other hand, TCl_3 and TF_3 resulted in more stable carboxylates that were less available to interact with water. The transition state for TF_3 catalysis shows a dispersed arrangement of the water molecules, more likely to promote hydrolysis. These findings strongly suggest that orthoester hydrolysis is influenced by both catalyst acidity and its water solvation ability. Hydrolysis products **13** and **14** were always produced in a 1:1 ratio, indicating that **2** and **3** underwent hydrolysis to the same extent, which agreed with $\Delta G^{\neq}$ values obtained by DFT for these reactions (Section 11 in Supporting information). Hydrolysis of **6** was highly unfavored compared to the acyclic compounds **2** and **3** due to the necessary formation of a carbene intermediate (**int.4**).

2.11.5 DFT COMPUTATIONS ON THE SCREENING OF SOLVENTS

Thus far, the DCE system has been studied using acetonitrile as solvent in both experiments and DFT calculations (implicit solvation). As the reaction progresses, ethanol is released, with the final solvent composition reaching a 1:13 ratio between acetonitrile and ethanol. We were interested in understanding better how differences in solvent properties impact the reaction system. A selection of metrics were selected to quantify the impact of the solvent: Hansen parameters measuring dispersion (δ_d), polarity (δ_p) and hydrogen bonding ability (δ_H) of a solvent; and donor (DN) and acceptor numbers (AN), developed by Guttman to quantify the Lewis basicity or acidity of a solvent. Aside from acetonitrile, three additional solvents were screened: dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and propylene carbonate (PC). Notably, the use of ethanol as solvent cannot be pursued because the involvement of ethanol in the DCE equilibria leads to convoluted results.

Reactions using each of these four solvents were monitored for 45 min and analyzed using **model VIII** to obtain the corresponding rate constants. In parallel, DFT computations of **TS.2** solvated by three molecules of solvent were performed for DMSO, DMF, MeCN, MeOH, EtOH and ^{i}PrOH.

In aprotic solvents (DN: DMF 26.6, DMSO 29.8, ACN 14.1), hydrogen-bond acceptor interaction with the acidic proton of the carbocation and the non-hydroxylated proton of formic acid were found to stabilize the transition state, reducing the activation barriers to 12.8, 9.3 and 11.6 kcal mol^{-1} versus to 13.5 kcal mol^{-1} calculated for the unsolved system.

In contrast, alcohols solvents exhibit dual hydrogen bond donor/acceptor behavior (high values of AN and moderate values of DN). While similar carbocation occurred, stabilization of formic acid proceeded via two simultaneous H-bonds involving catalyst oxygen atoms. This resulted in lower activation barriers of 6.8, 7.2, and 8.6 kcal mol^{-1} for systems involving MeOH, EtOH and ^{i}PrOH.

Dissociation energies (ΔE) were also calculated for the solvation of the catalysts with the various solvents. Methanol and dimethyl sulfoxide gave negative values of -6.8 and -2.3 kcal mol^{-1}, highlighting the favorable formation of FA-solvent complexes. In contrast, EtOH, ^{i}PrOH, DMF and MeCN exhibited positive dissociation energies of 0.6, 2.4, 4.2 and 6.0 kcal mol^{-1}, respectively, indicating that complex formation with formic acid is energetically unfavored to different extent.

Considering both the DFT and experimental results, although DMSO provided the highest stabilization of the **TS.2** compared to DMF and ACN, its complexation with FA was also favored, reducing catalyst availability for the DCE reactions. This likely resulted in a lowered formation of alcohol by-products and thus, negatively affecting the overall reaction kinetics as experimentally observed. DMF depicted a $\Delta\Delta G^{\ddagger}$ of 3.5 kcal mol^{-1} indicating a lower stabilization of the **TS2**, but exhibited a positive value ΔE, which was experimentally translated by similar reaction kinetic than this of DMSO.

Solvent with lower δ_H and DN values such as MeCN, exhibited lower affinity for the catalyst (ΔE = 6.0 kcal mol^{-1}), thereby promoting the reaction, which is further accelerated by the consequent release of EtOH. Other solvent parameters such as London dispersion forces (δ_d) or polarity (δ_p) appear to have little influence on reaction kinetics based on the data in Figure 6a1.

The reaction was also performed using different orthoester reagents, including trimethyl orthoformate (**2.1**) and triisopropyl orthoformate (**2.2**), following the same protocol described for triethyl orthoformate (**2**) (Figure 6a2). The rate constants varied depending on the reagent used and the by-product formed during the reaction, i.e. methanol (MeOH), ethanol and isopropanol (^{i}PrOH).

Triisopropyl orthoformate **2.2** exhibited the highest rate constants, attributed to its by-product ^{i}PrOH, which depicted lower affinity for FA ($\Delta E = 2.4$ kcal mol^{-1}), due to its low hydrogen bond donor ability ($\delta_H = 8$ cal mol$^{-1/2}$) and moderate DN of 21.1. Triethyl orthoformate **2** showed intermediate rate constants due to **EtOH** as its by-product ($\delta_H = 9.5$ cal mol$^{-1/2}$; DN = 19.2). Trimethyl orthoformate **2.1** resulted in the slowest rate due to the release of MeOH ($\delta_H = 10.9$ cal mol$^{-1/2}$; DN = 19.0), which exhibited a high affinity for FA ($\Delta E = -6.7$ kcal mol^{-1}). Overall, by-products and solvents that strongly stabilization **TS2.** (e.g DMSO and MeOH) were those that led to the most stable solvent-FA complexes, hence negatively affection the reaction kinetics.

2.11.6 MECHANISM OF HYDROLYSIS FOR SPECIES 2, 3 AND CYCLIC CARBOCATION (FROM CYCLIC SPECIES)

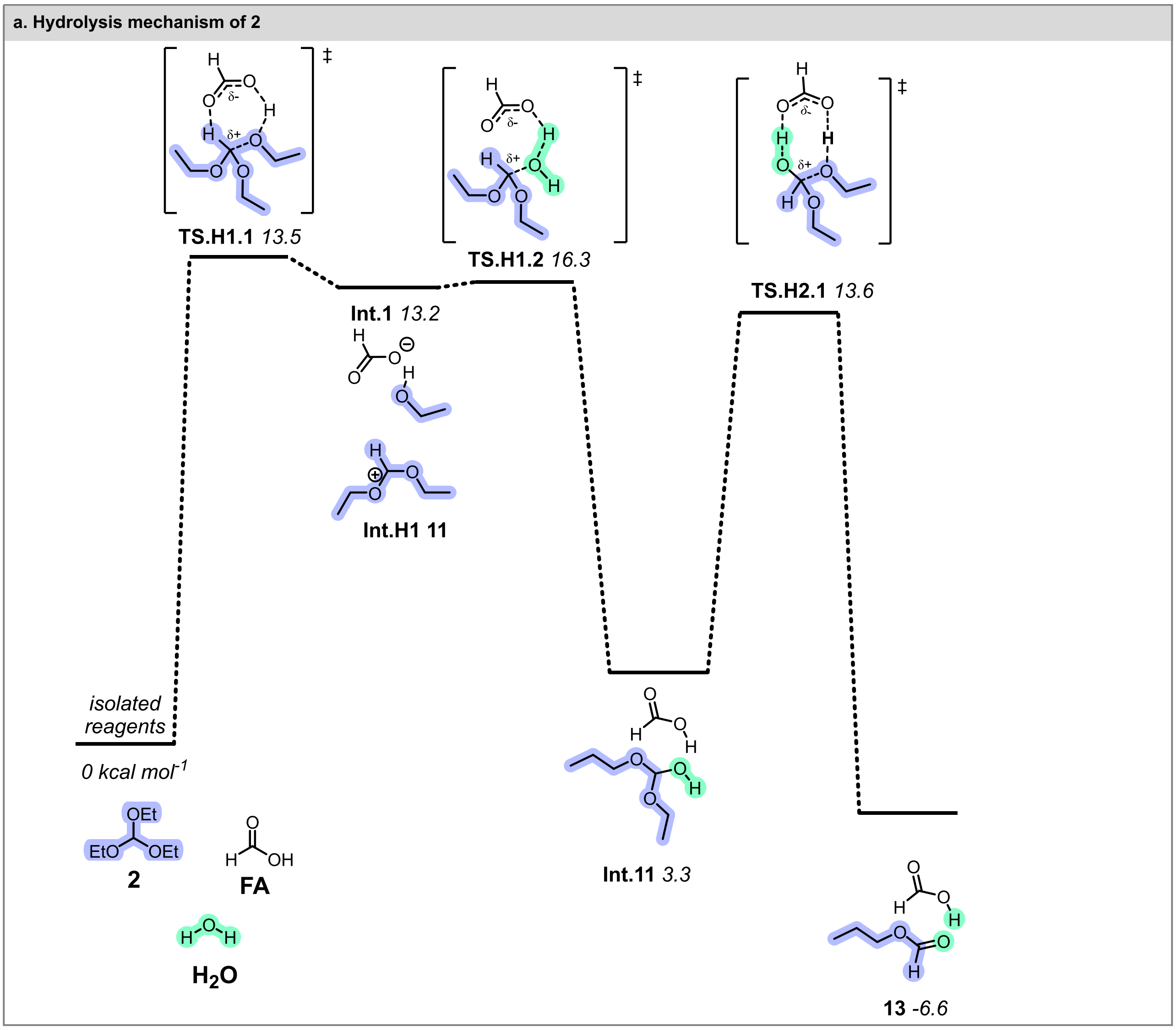


Figure S2.56 Elucidated mechanism for the hydrolysis of **2**.

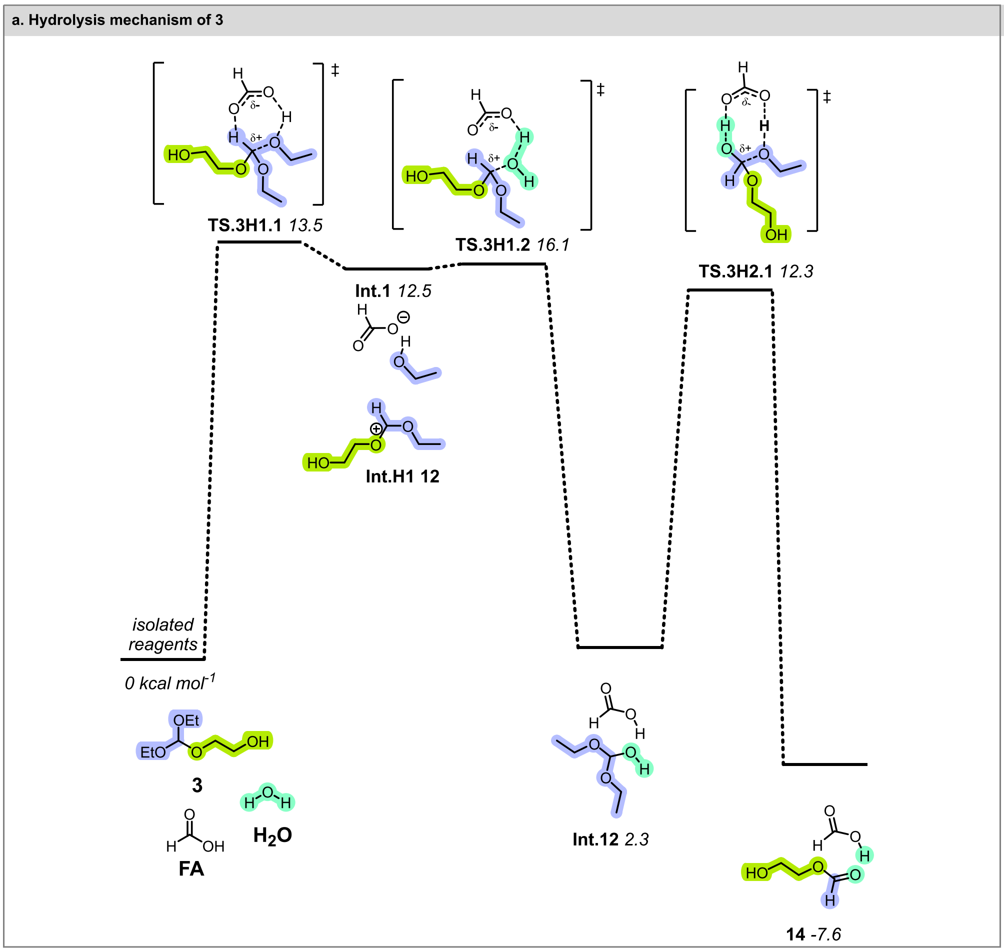


Figure S2.57 Elucidated mechanism for the hydrolysis of **3**.

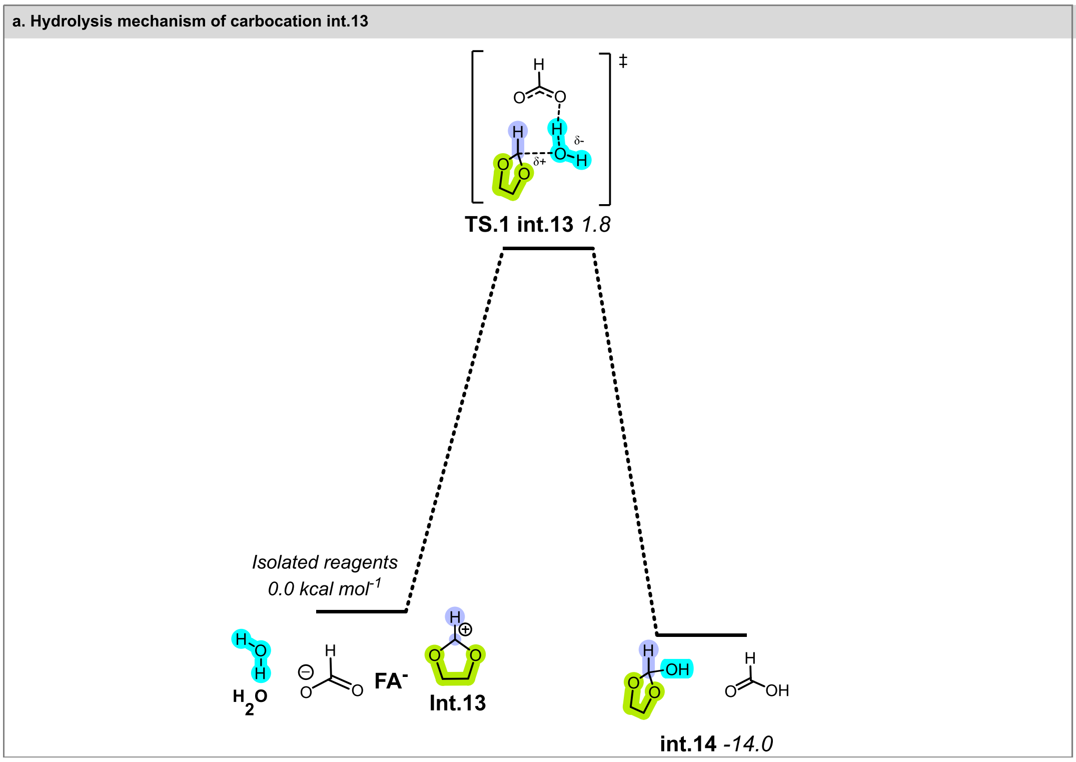


Figure S2.58 Mechanism of hydrolysis of carbocation intermediate **int.13**.

2.12 COPIES OF ^{1}H, ^{13} C NMR SPECTRA AND FRAGMENTATION OF THE PRODUCTS OBSERVED BY GC-MS

2.12.1 COMPOUND 1

2.12.1.1 ^{1}H-NMR SPECTRUM

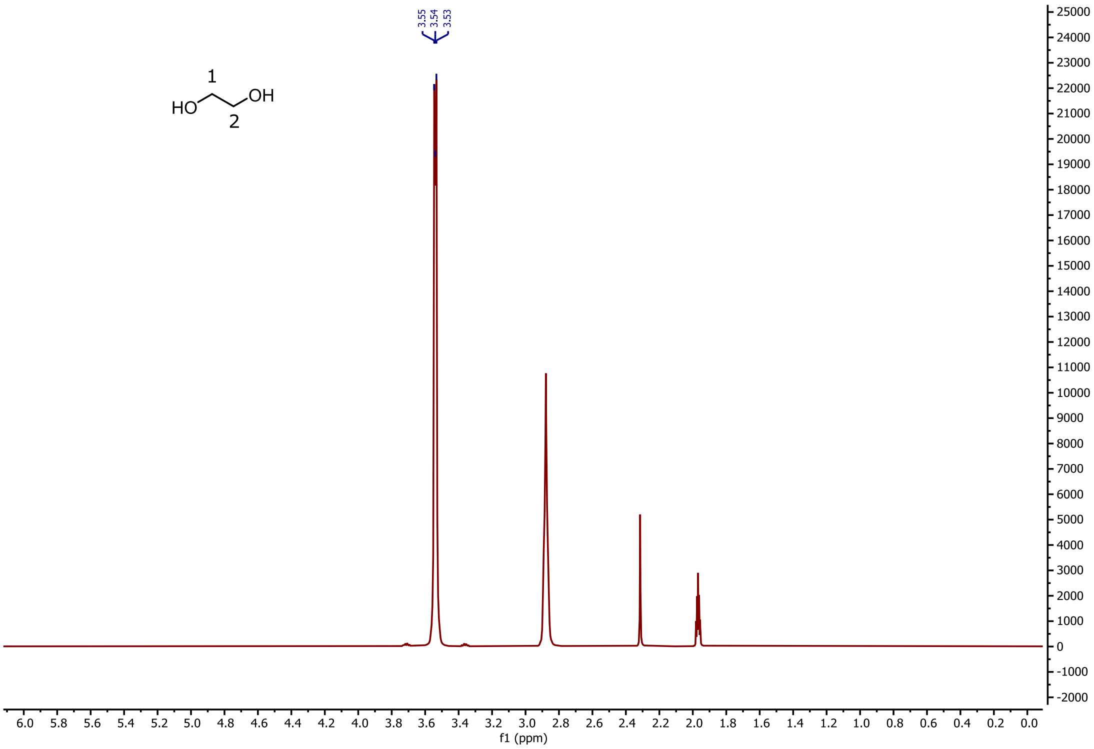


Figure S2.59 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **1** (éthane-1,2-diol – CAS 107-21-1).

2.12.1.2 ^{13}C-NMR SPECTRUM

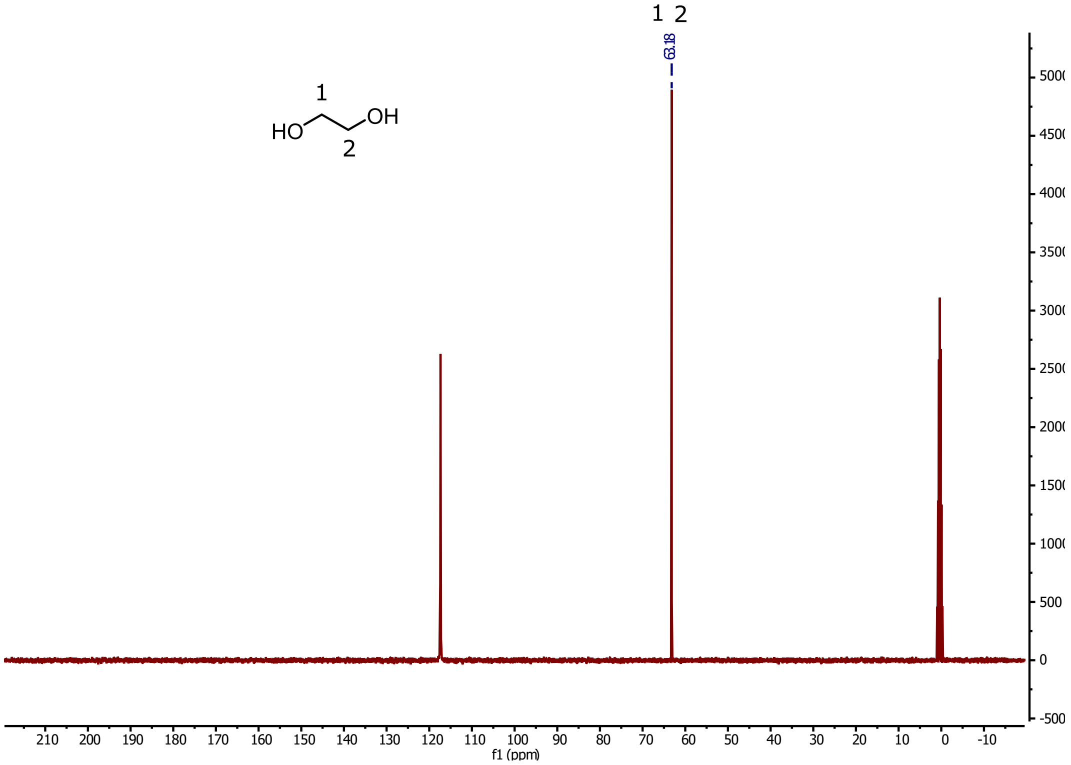


Figure S2.60 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **1**.

2.12.1.3 Mass spectrum and fragmentation

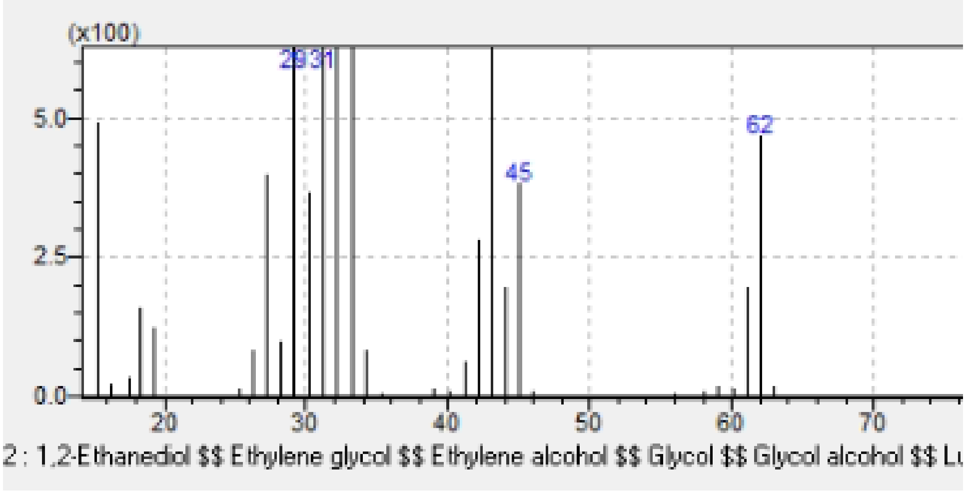


Figure S2.61 Mass spectrum obtained for 1.

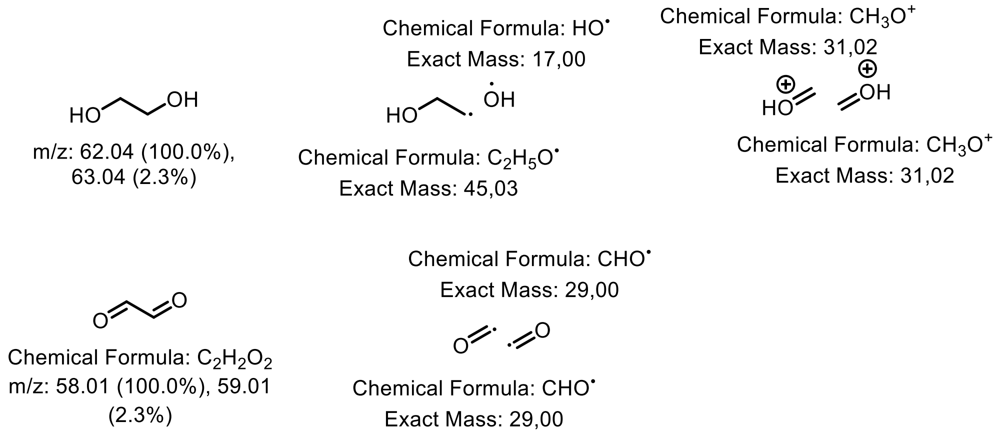


Figure S2.62 Fragmentation of **1**.

2.12.2 Compound 2

2.12.2.1 ^{1}H-NMR spectrum

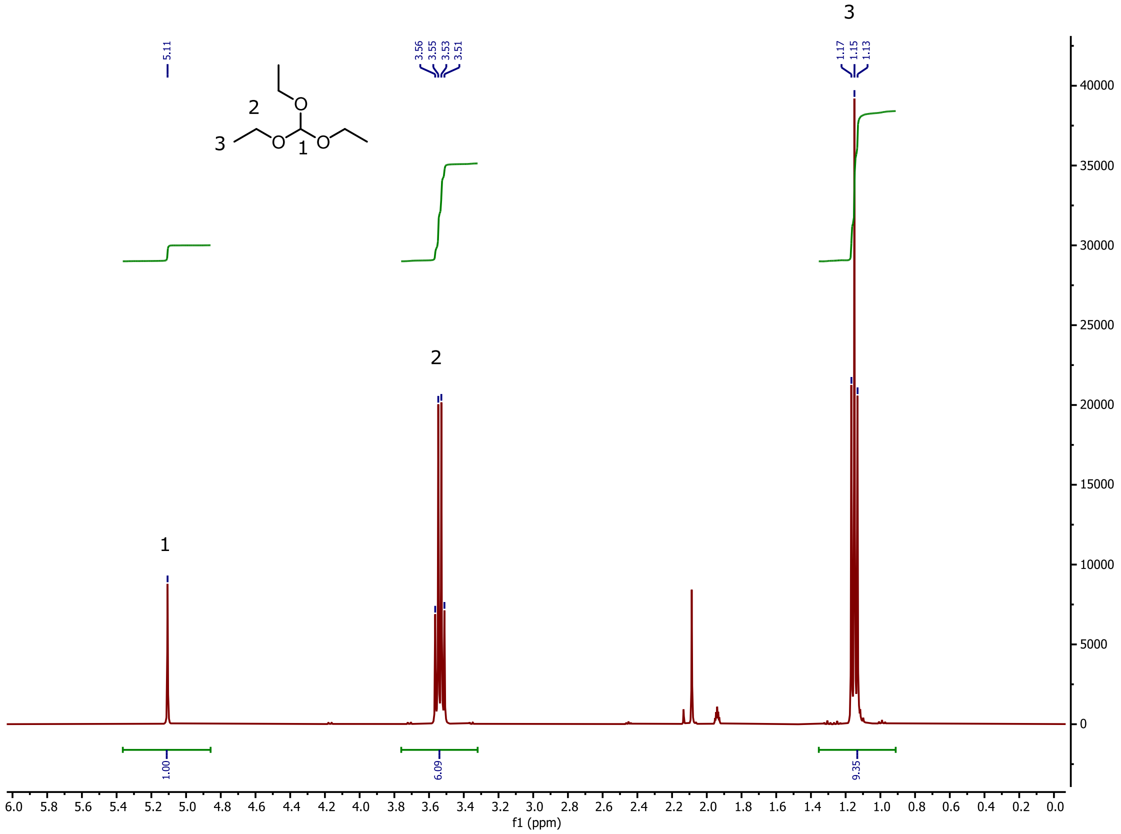


Figure S2.63 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **2**.

2.12.2.2 ^{13}C-NMR spectrum

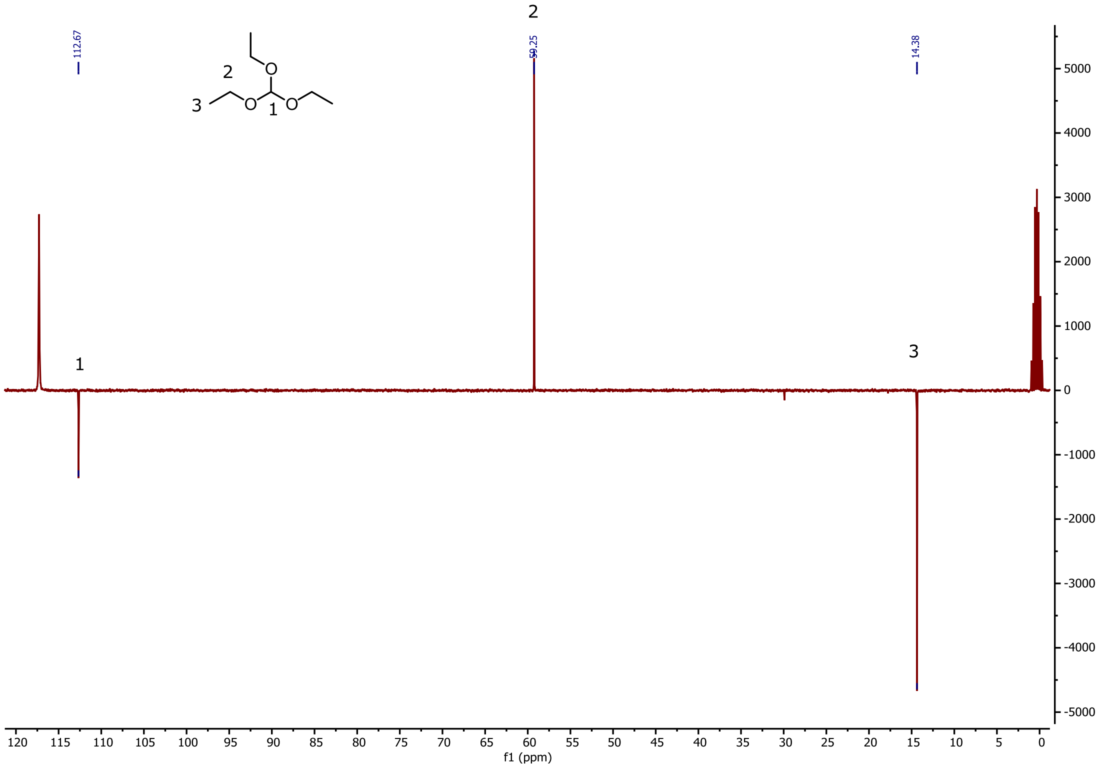


Figure S2.64 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **2**.

2.12.2.3 MASS SPECTRUM AND FRAGMENTATION

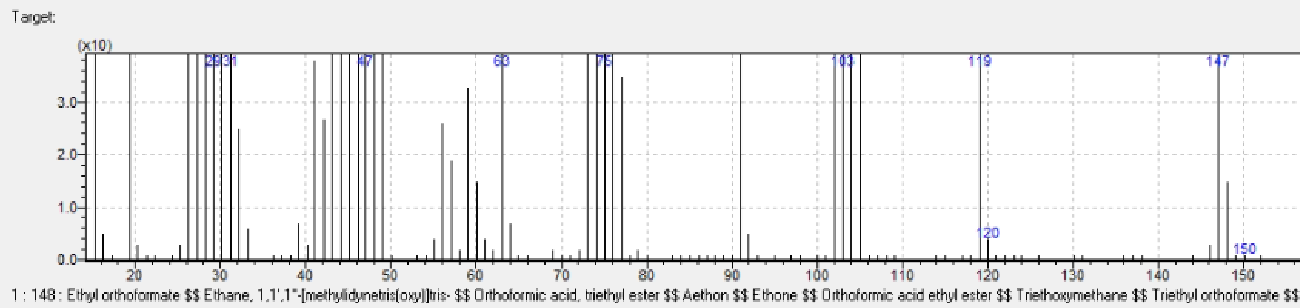


Figure S2.65 Mass spectrum obtained for **2**.

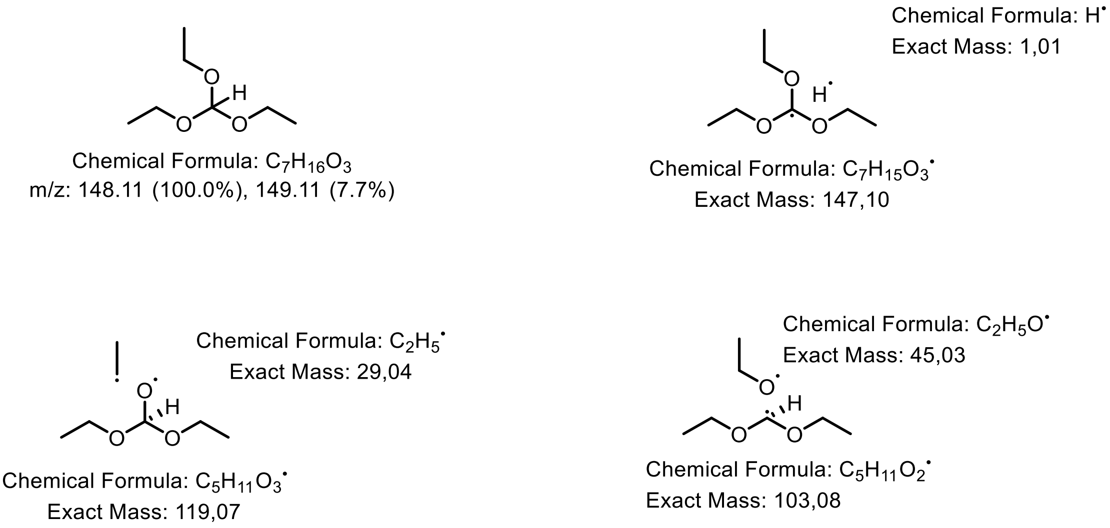


Figure S2.66 Fragmentation of **2**.

2.12.3 COMPOUND 3

Total purification of **3** was not succeeded, but the species remains in majority in the sample. Remaining content of **1** in the methyl group integration increased the value of 8 to 10 protons. Some minor amount of **4** was also observed, therefore contributing to the methyl group integration.

2.12.3.1 ^{1}H-NMR SPECTRUM

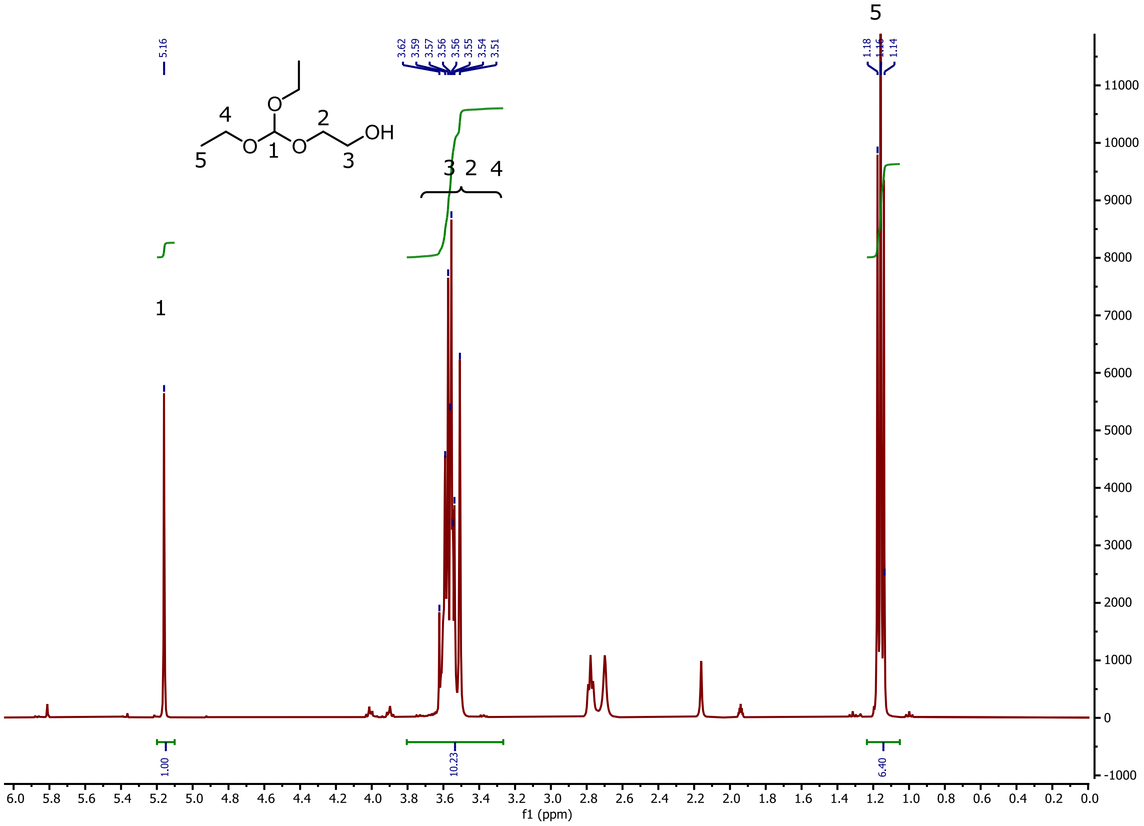


Figure S2.67 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **3**.

2.12.3.2 ^{13}C-NMR SPECTRUM

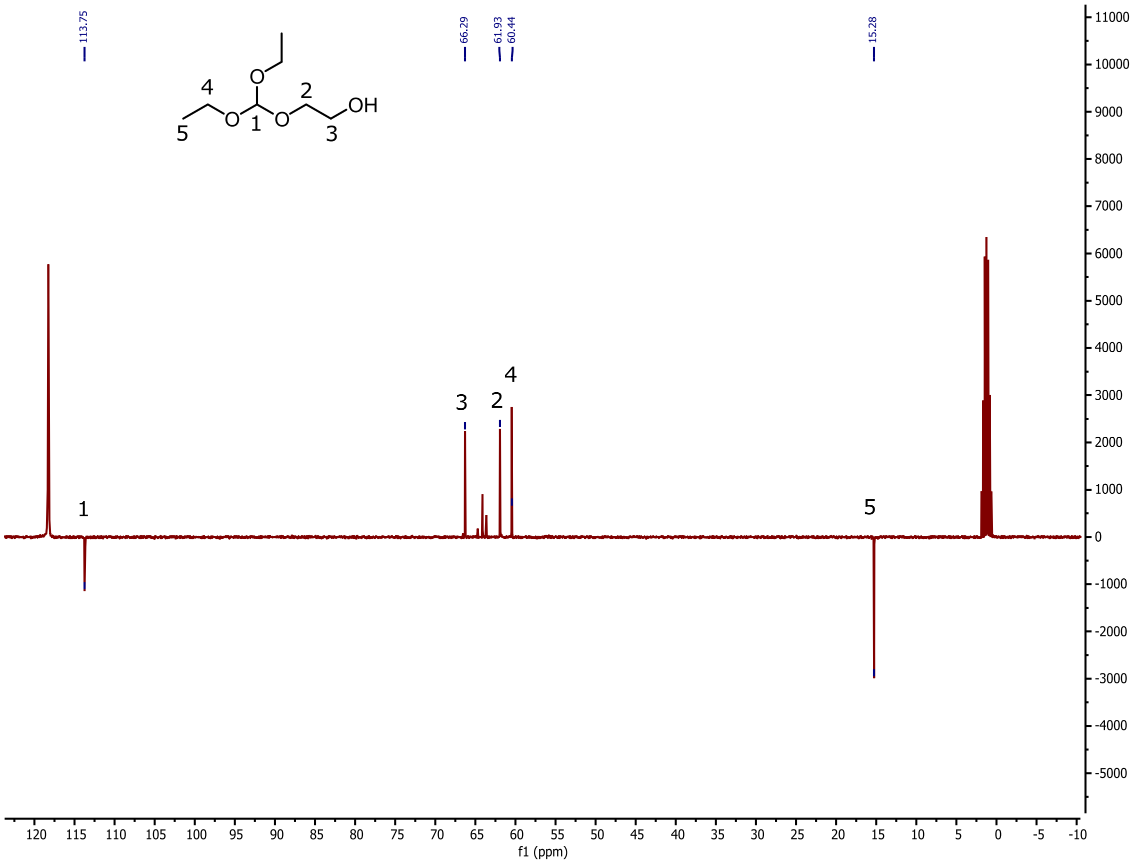
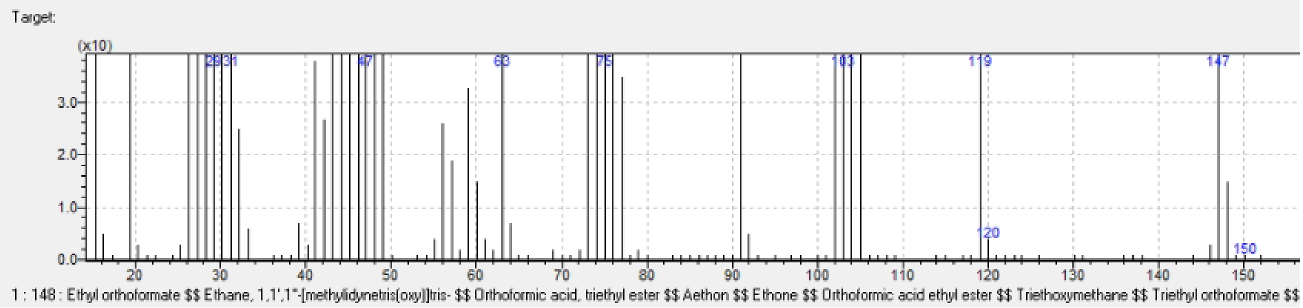


Figure S2.68 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **3**.

2.12.3.3 MASS SPECTRUM AND FRAGMENTATION



1 : 148 : Ethyl orthoformate $$ Ethane, 1,1',1''-[methylidynetris(oxy)]tris- $$ Orthoformic acid, triethyl ester $$ Aethon $$ Ethone $$ Orthoformic acid ethyl ester $$ Triethoxymethane $$ Triethyl orthoformate $$

Figure S2.69 Mass spectrum obtained for **3**.

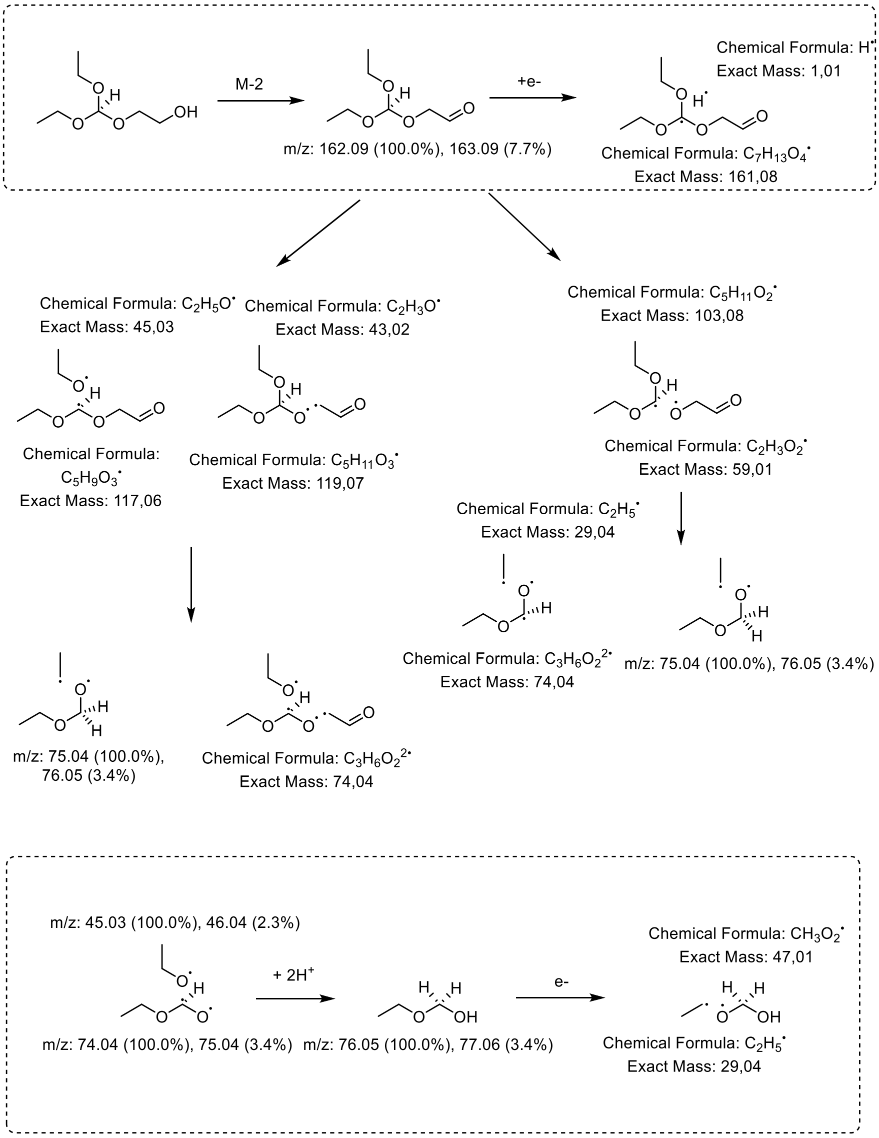


Figure S2.70 Fragmentation of **3**.

2.12.4 COMPOUND 4

2.12.4.1 ^{1}H-NMR SPECTRUM

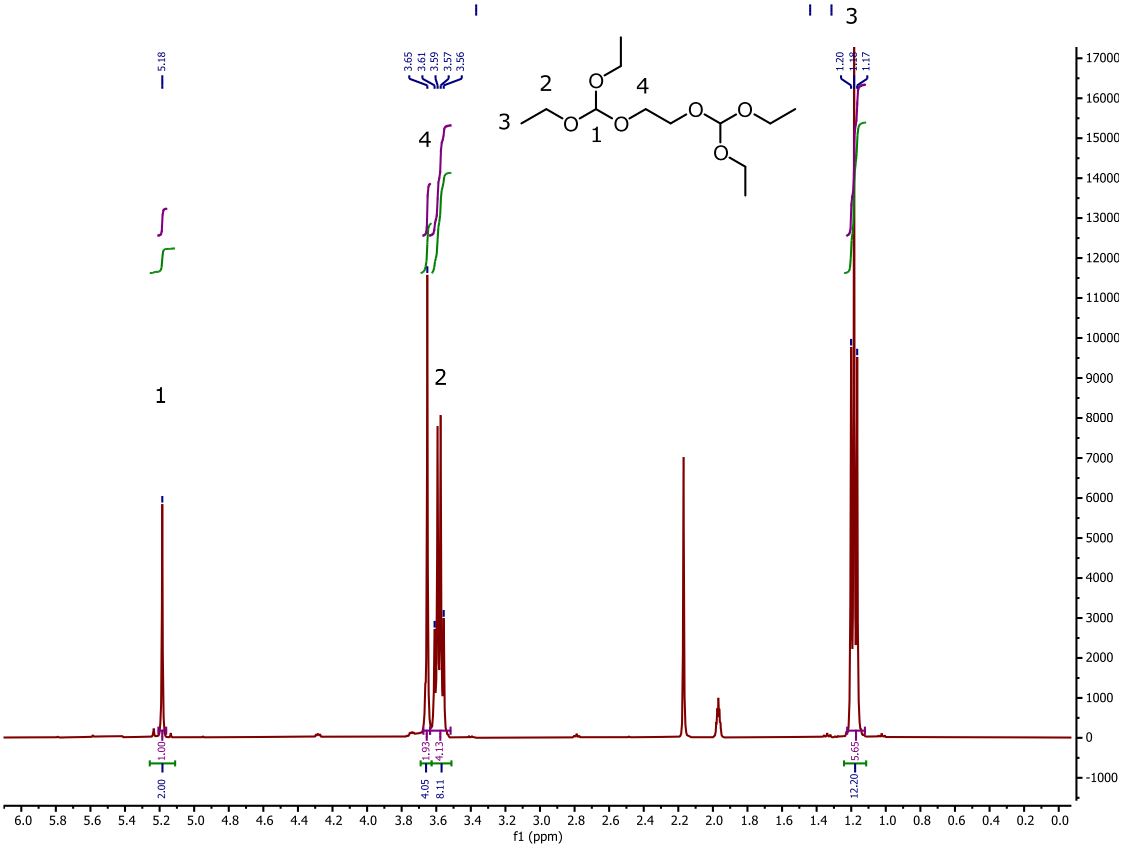


Figure S2.71 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **4**.

2.12.4.2 ^{13}C-NMR SPECTRUM

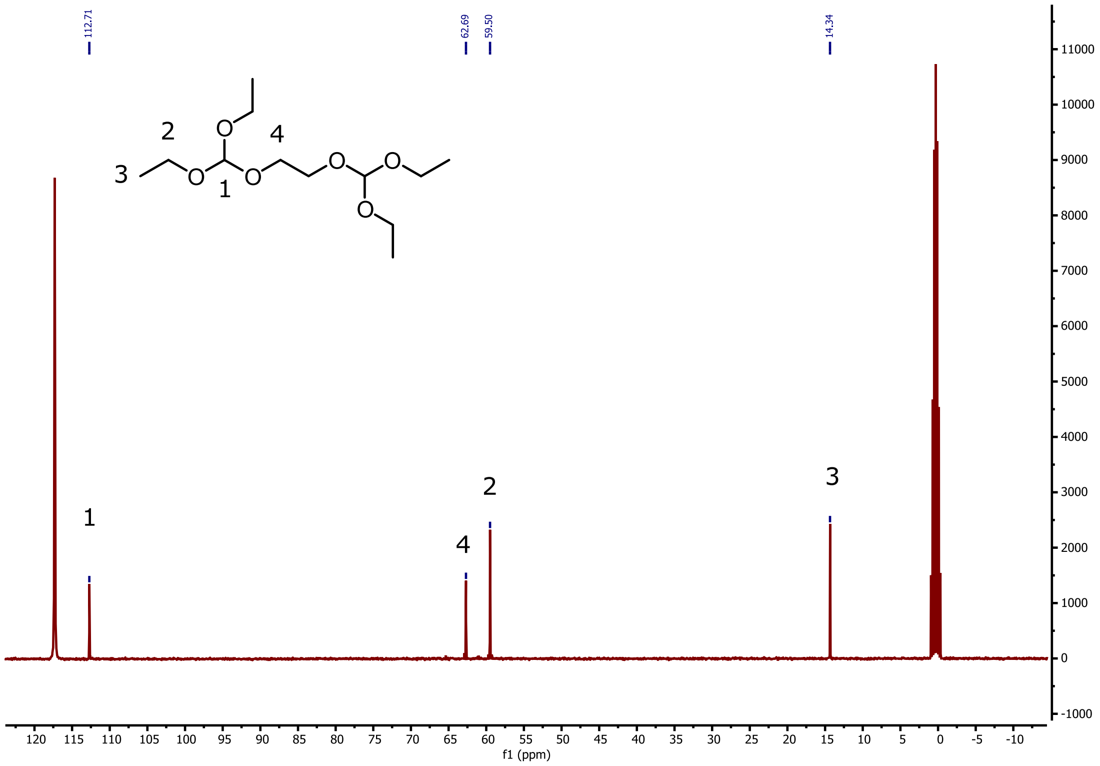


Figure S2.72 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **4**.

2.12.4.3 MASS SPECTRUM AND FRAGMENTATION

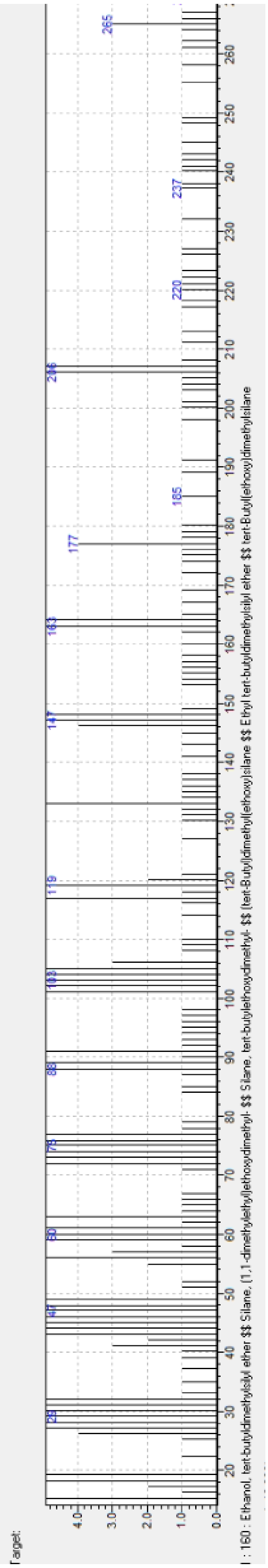


Figure S2.73 Mass spectrum obtained for **4**

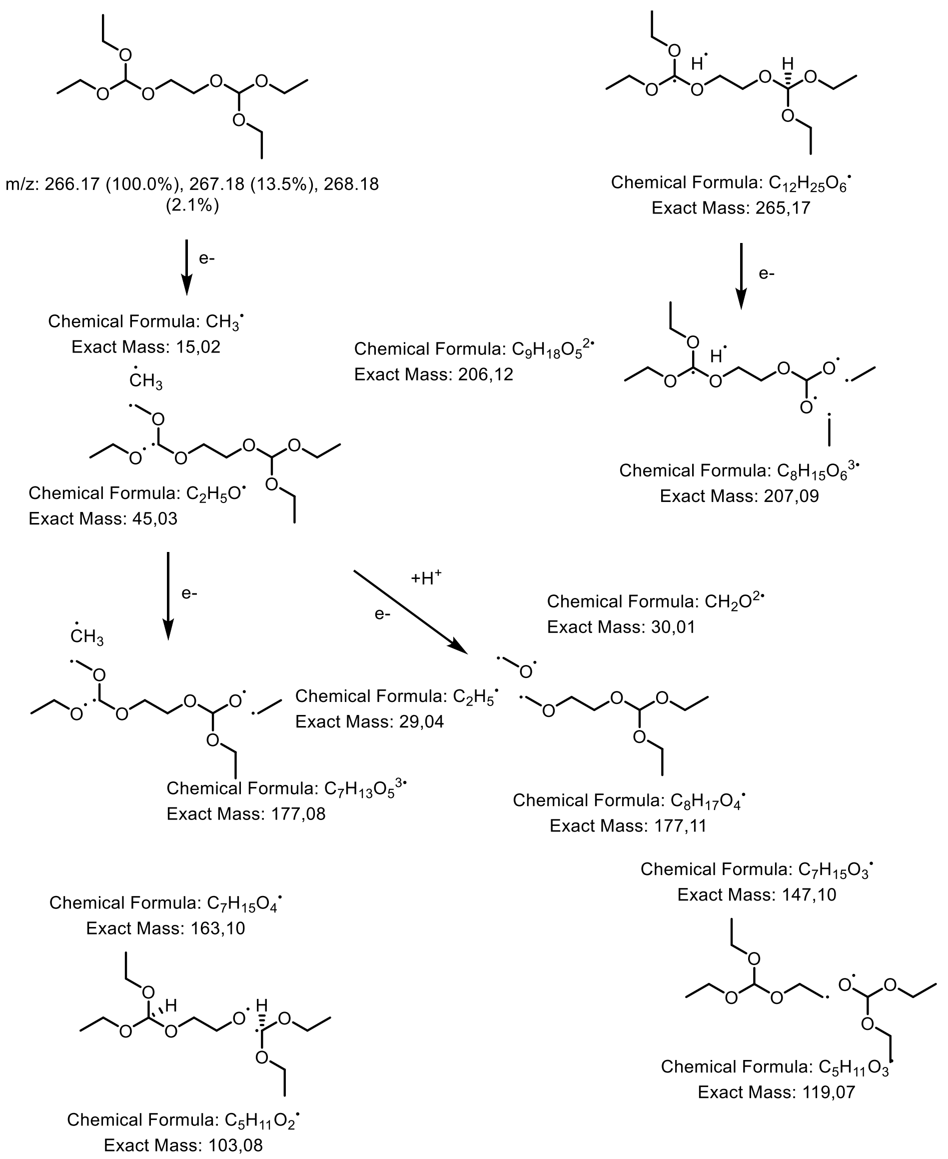


Figure S2.74 Fragmentation of **4**.

2.12.5 COMPOUND 5

2.12.5.1 ^{1}H-NMR SPECTRUM

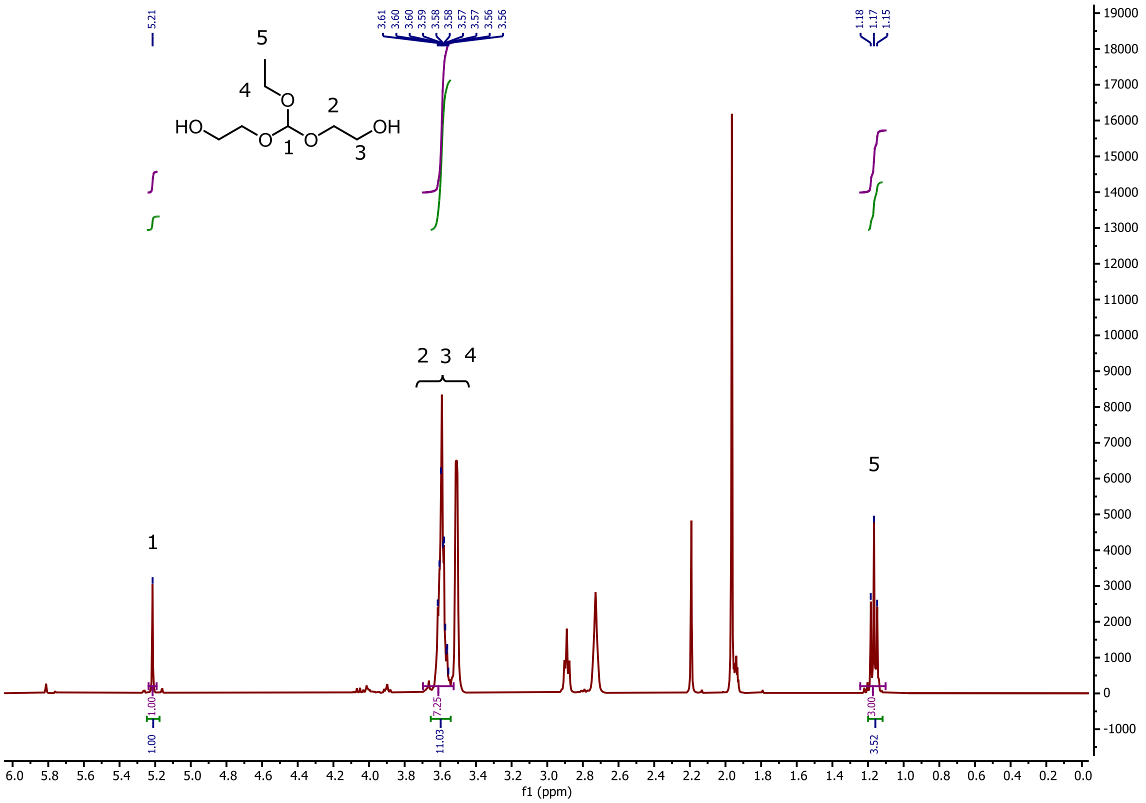


Figure S2.75 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **5**.

2.12.5.2 ^{13}C-NMR SPECTRUM

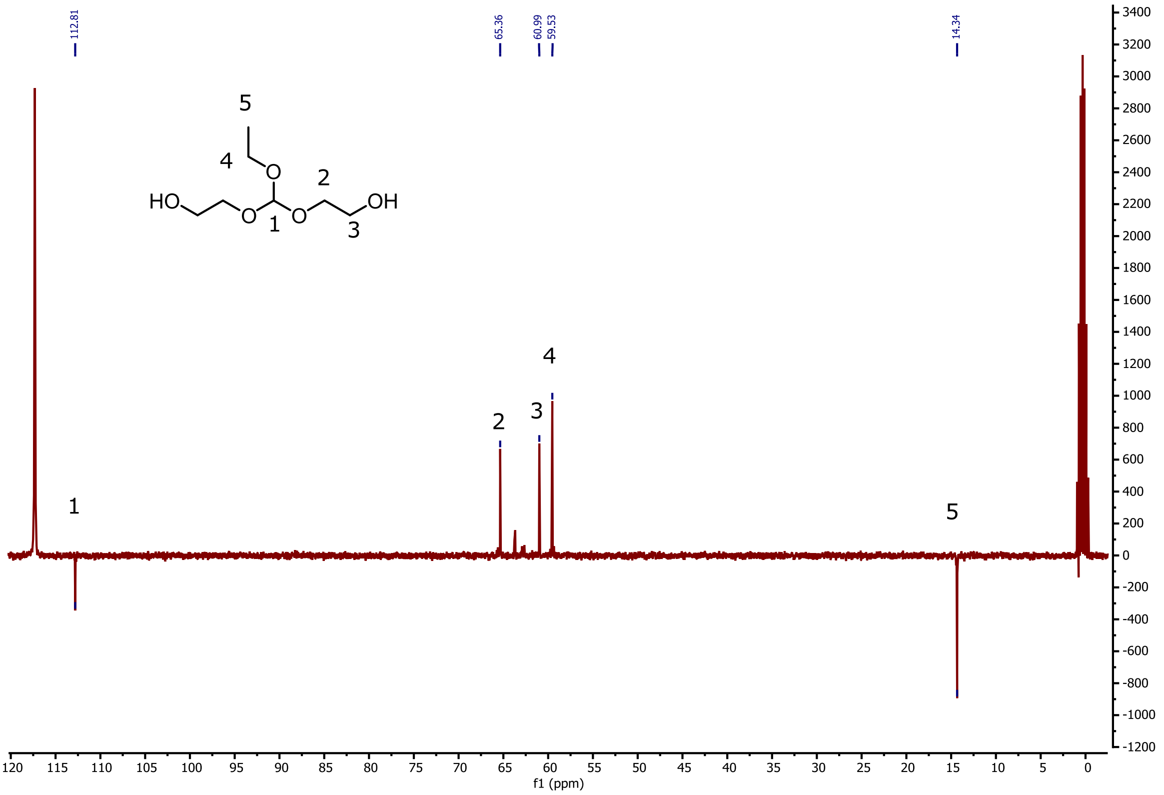


Figure S2.76 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **5**.

2.12.5.3 MASS SPECTRUM AND FRAGMENTATION

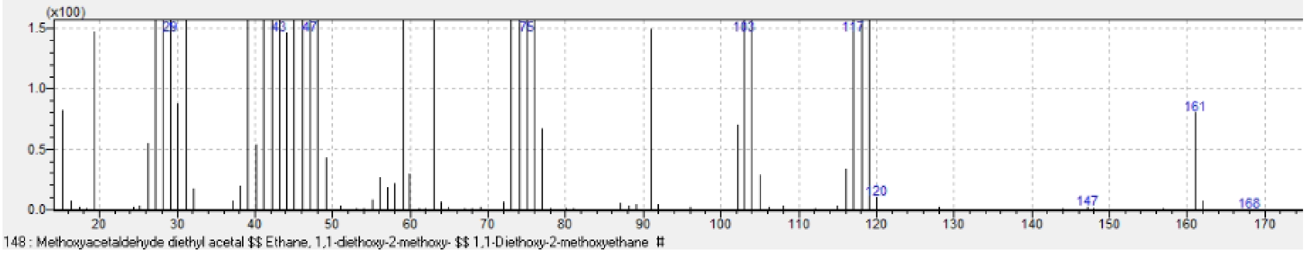


Figure S2.77 Mass spectrum obtained for **5**.

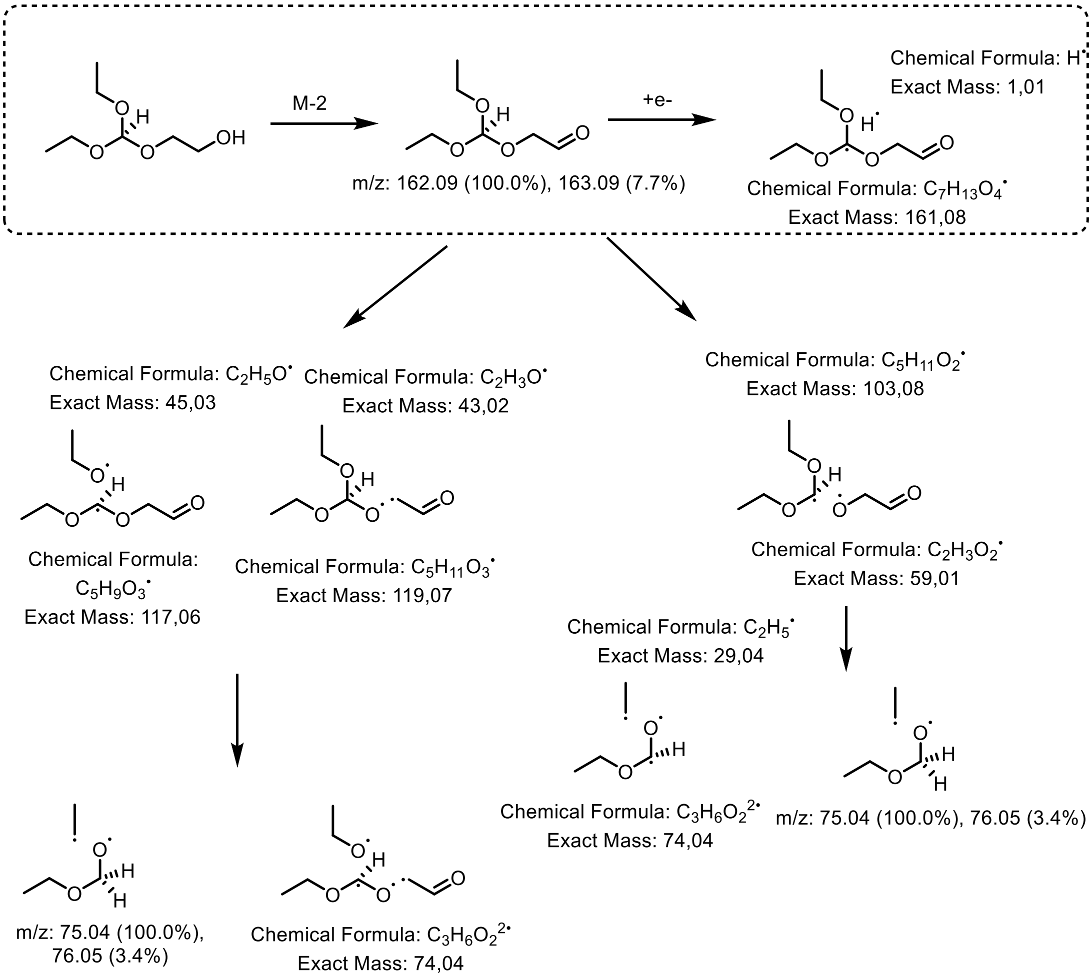


Figure S2.78 Fragmentation of **5**.

2.12.6 COMPOUND 6

2.12.6.1 ^{1}H-NMR SPECTRUM

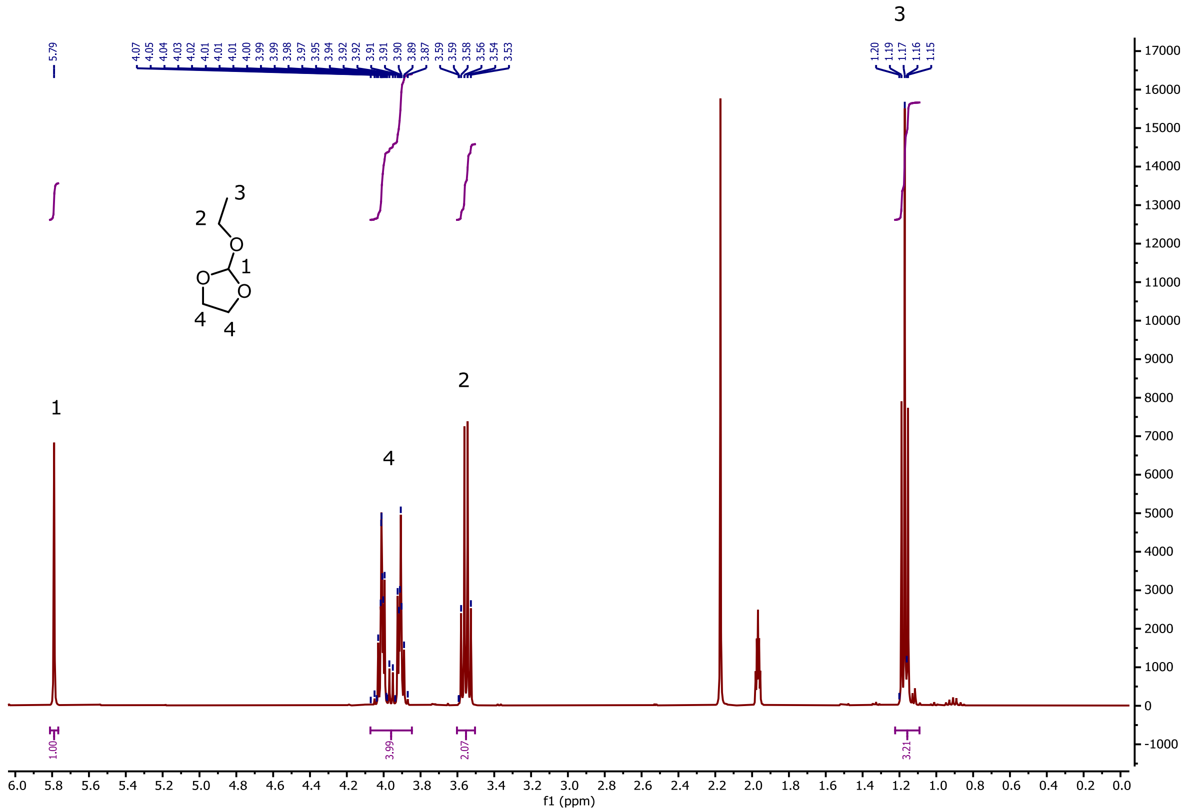


Figure S2.79 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **6**.

2.12.6.2 ^{13}C-NMR SPECTRUM

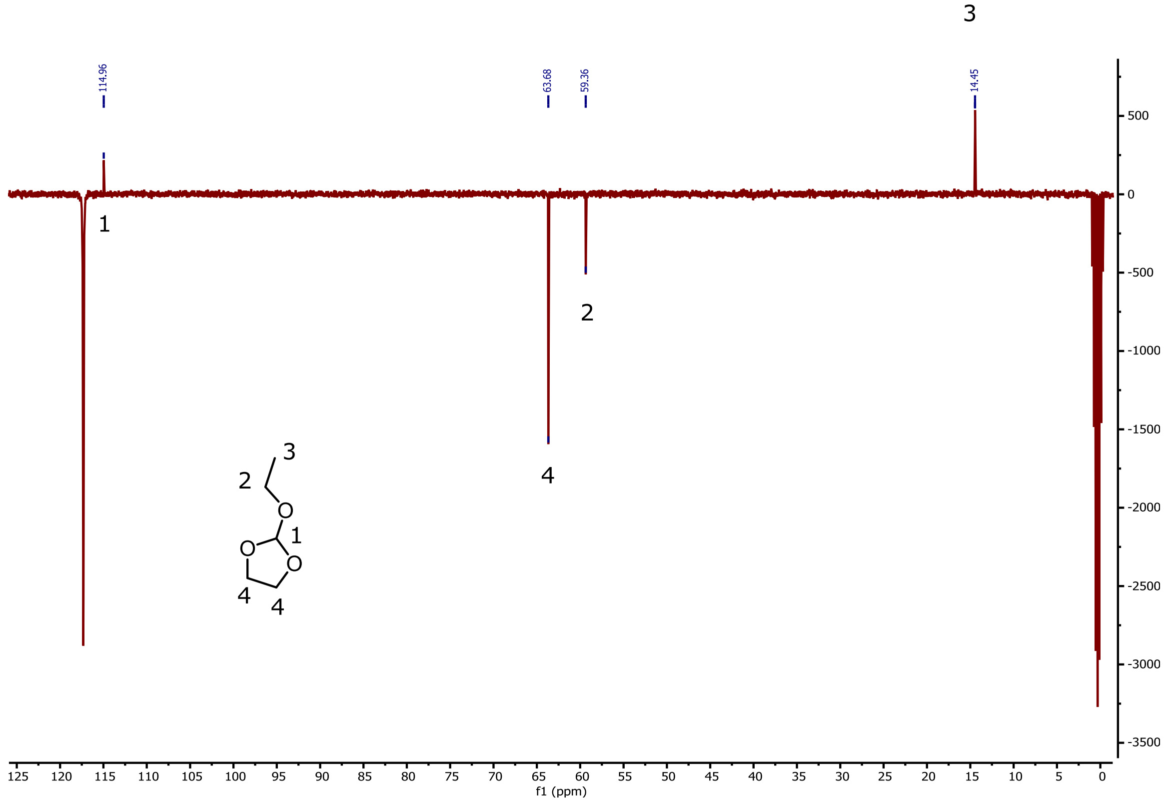


Figure S2.80 ^{13}C APT NMR spectrum **(101 MHz – CD_3CN)** of **6.**

2.12.6.3 MASS SPECTRUM AND FRAGMENTATION

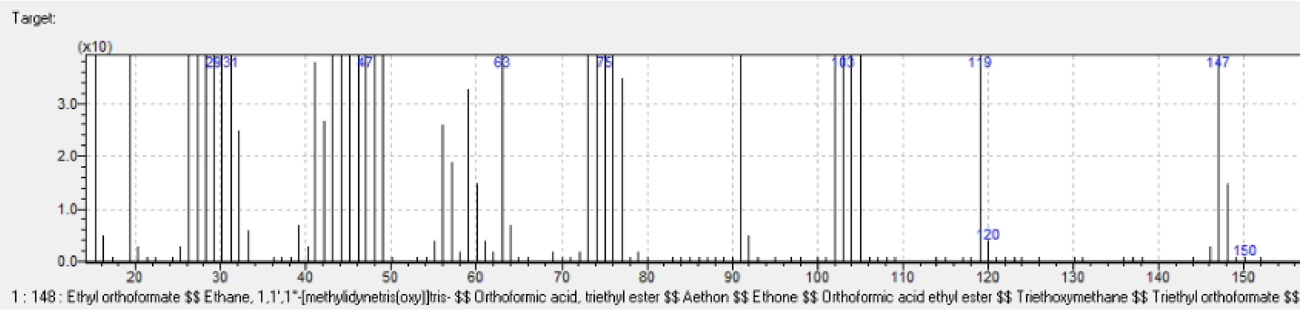


Figure S2.81 Mass spectrum obtained for **6**.

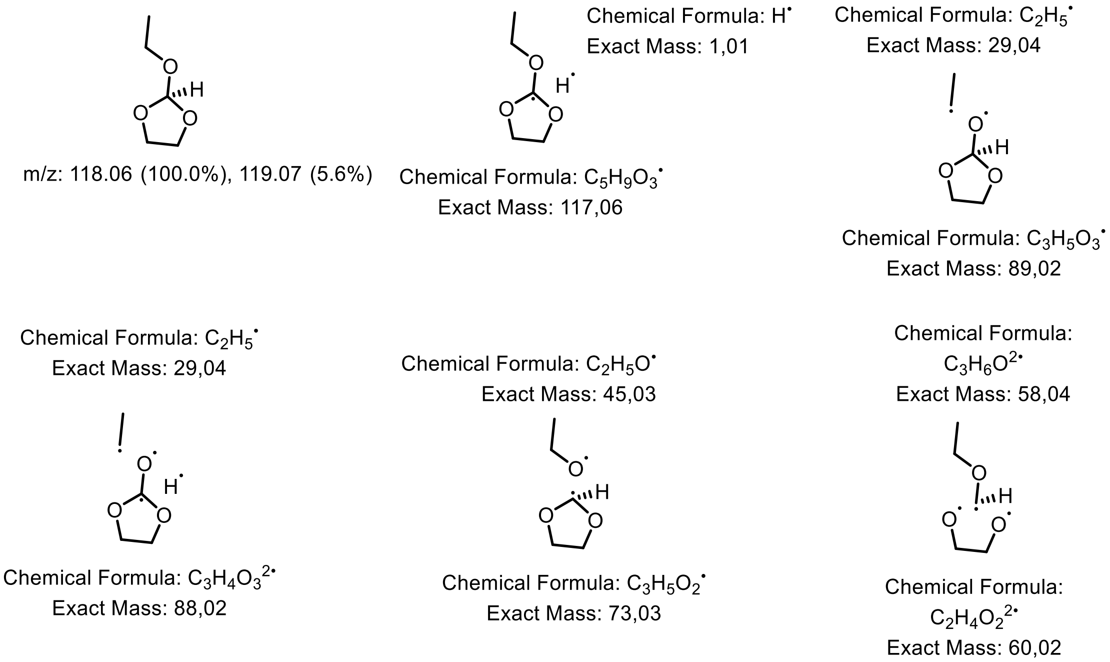


Figure S2.82 Fragmentation of **6**.

2.12.7 COMPOUND 7

2.12.7.1 ^{1}H-NMR SPECTRUM

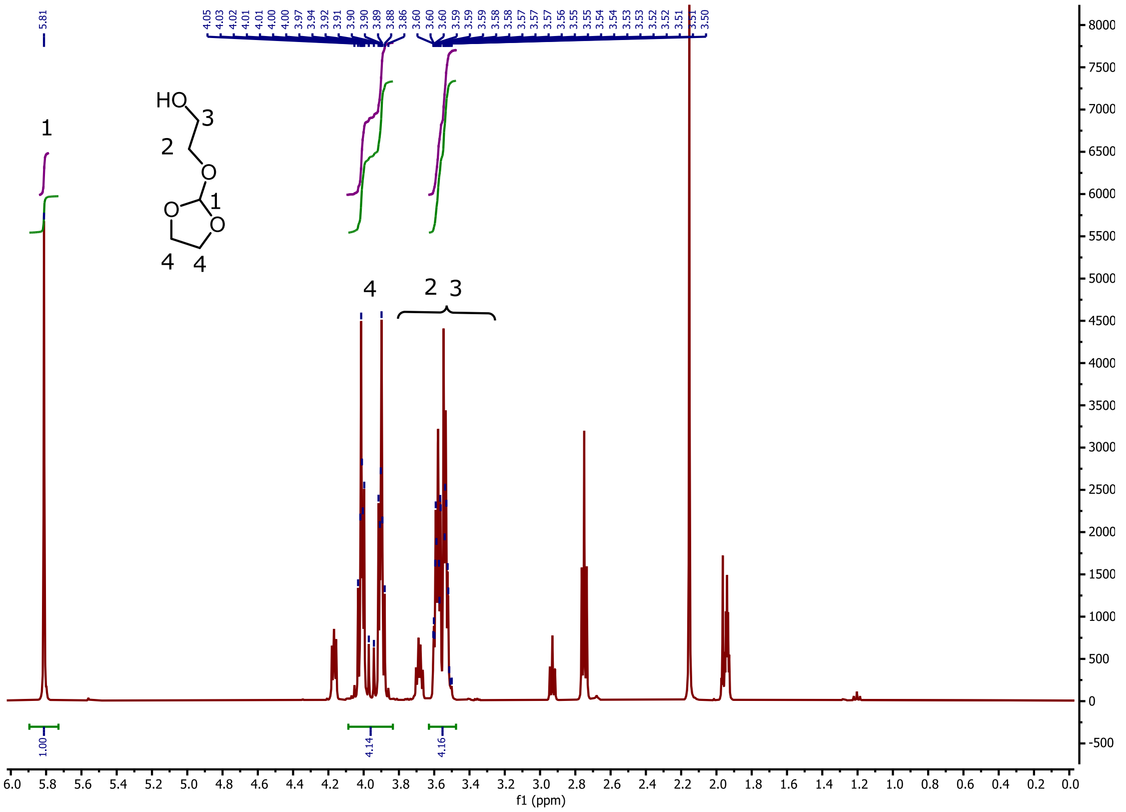


Figure S2.83 ^{1}H-NMR spectrum **(700 MHz – CD_3CN)** of **7**.

2.12.7.2 ^{13}C-NMR SPECTRUM

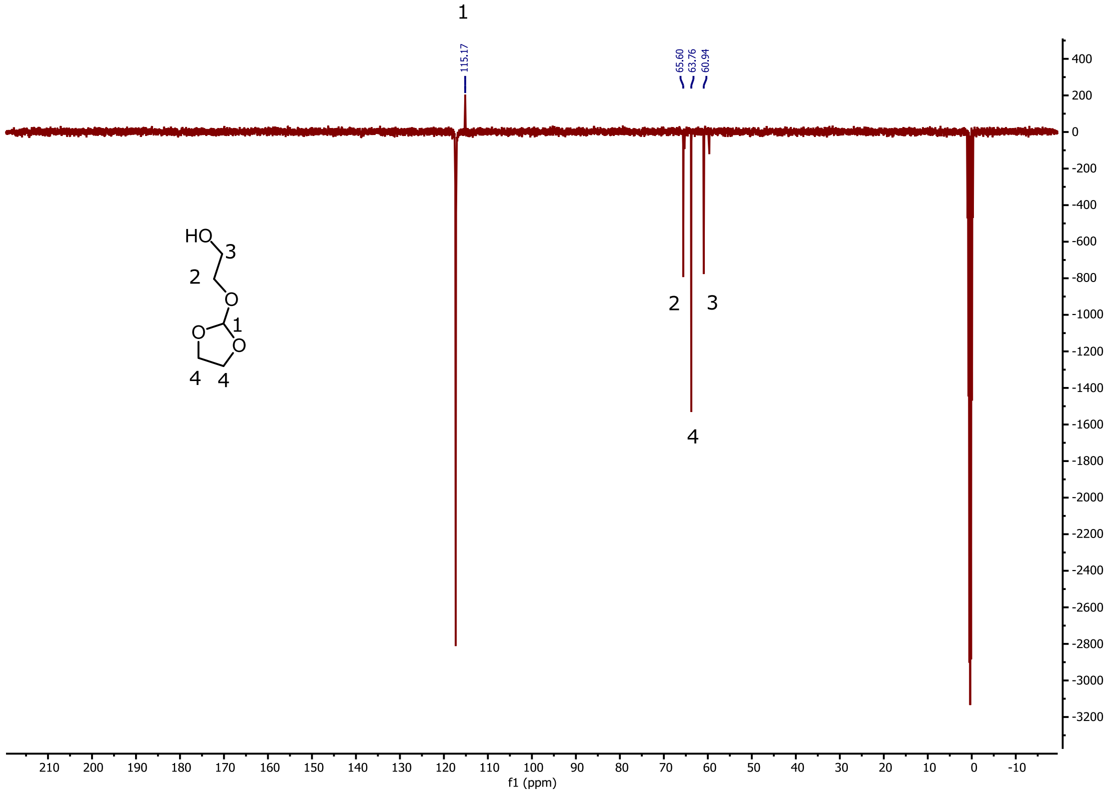


Figure S2.84 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **7**.

2.12.7.3 MASS SPECTRUM AND FRAGMENTATION

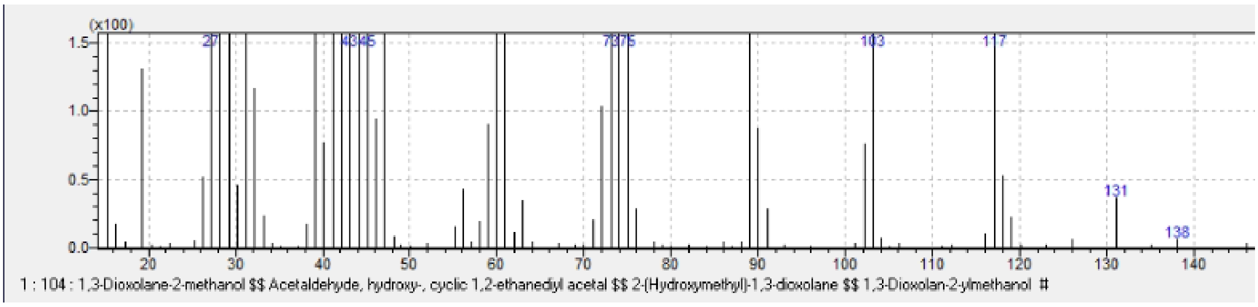


Figure S2.85 Mass spectrum obtained for **7**.

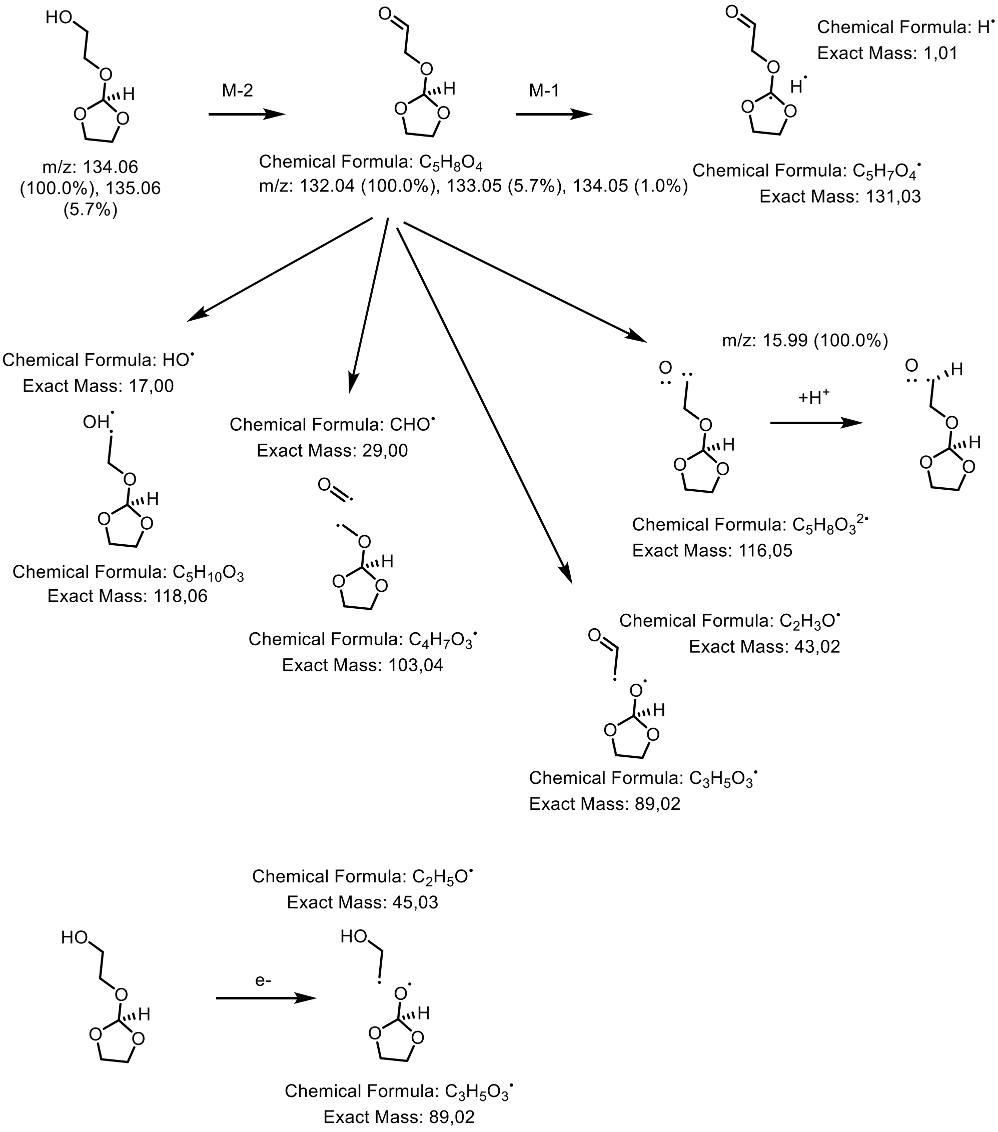


Figure S2.86 Fragmentation of **7**.

2.12.8 COMPOUND 8

2.12.8.12 D-HSQC AND HMBC NMR SPECTRA

The Figure S2.87 shows the correlations between the cyclic and acyclic acidic protons of **8**. Their proton chemical shifts are at 5.183 and 5.836 ppm respectively. Due to the very low content of **8**, it prevented to identify the carbon signals assigned to this species.

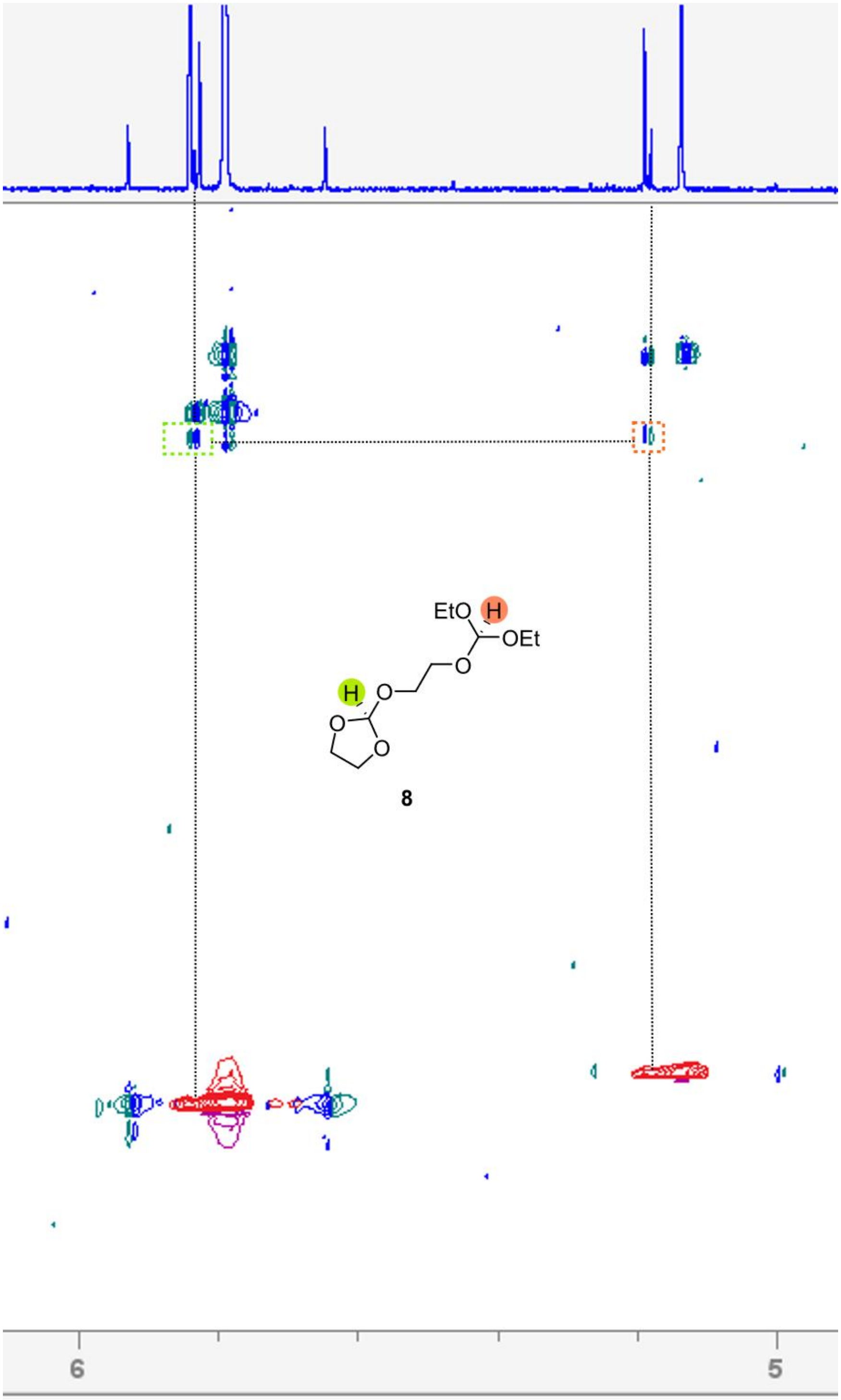


Figure S2.87 Superimposition of the 2D-HSQC (blue-green signals) and HMBC (red) spectra and corresponding assignments of the structural scaffold of products **8**.

2.12.8.2 MASS SPECTRUM AND FRAGMENTATION

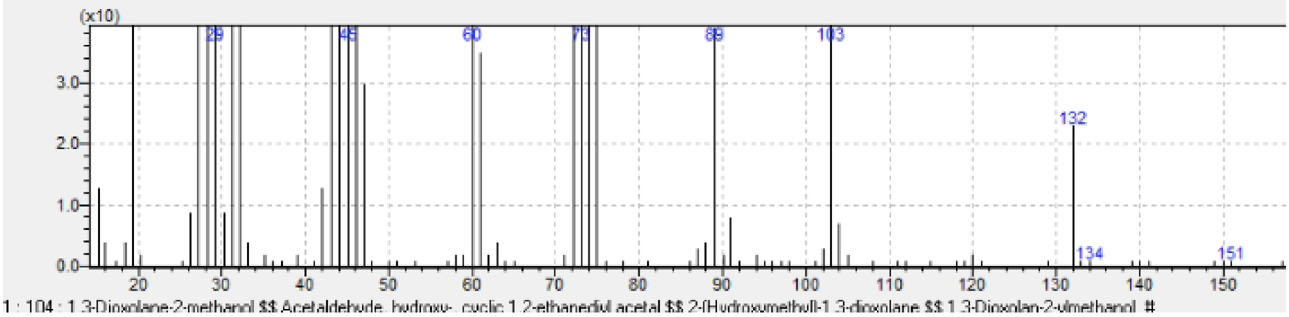


Figure S2.88 Mass spectrum obtained for **8**.

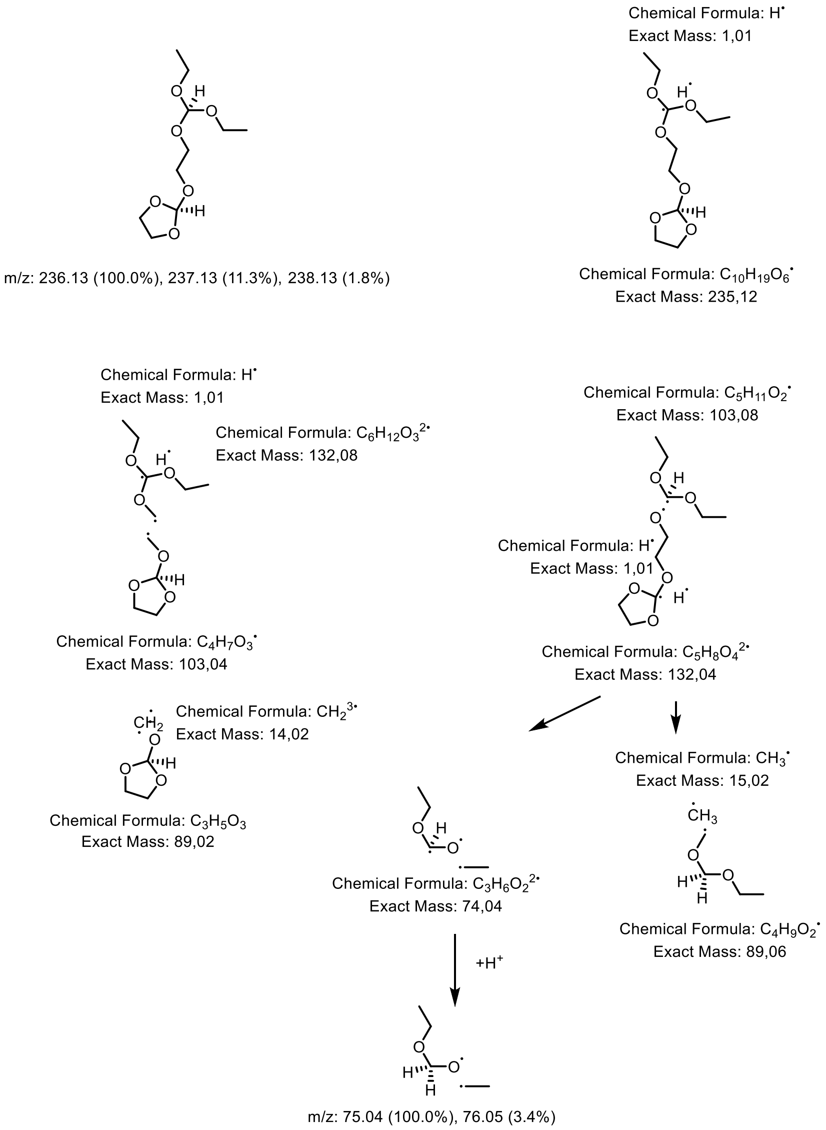


Figure S2.89 Fragmentation of **8**.

2.12.9 COMPOUND 9

2.12.9.1 ¹H-NMR SPECTRUM

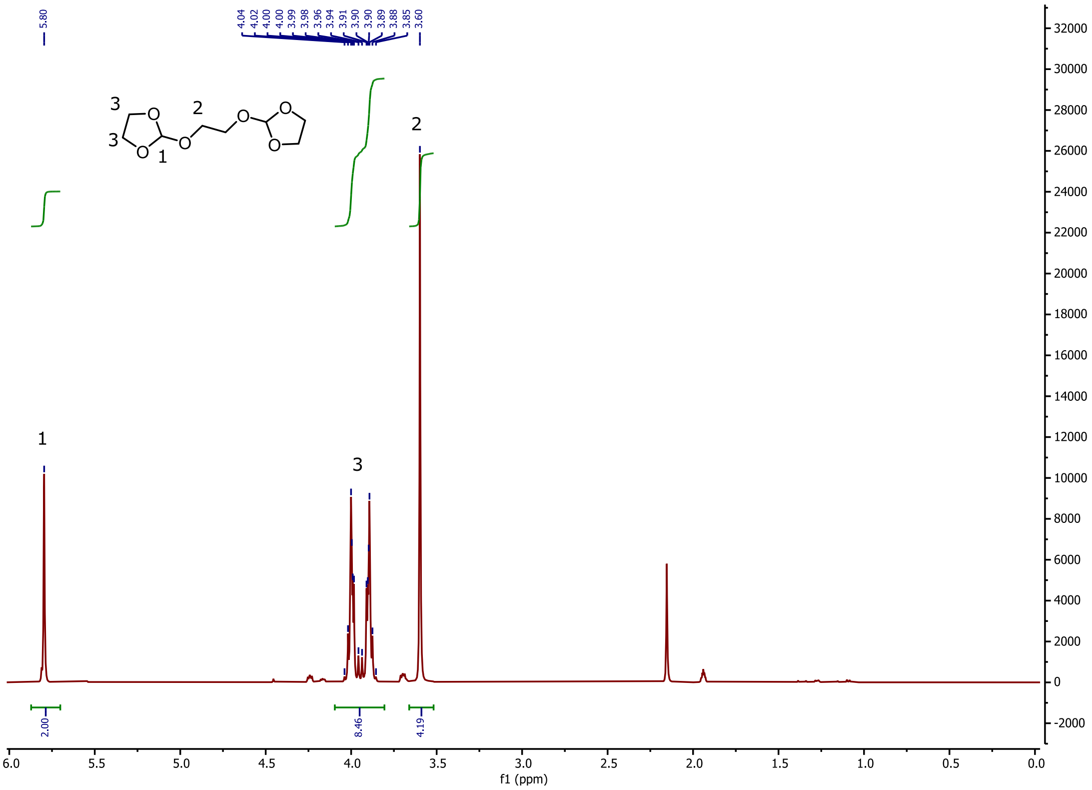


Figure S2.90 ¹H-NMR spectrum (700 MHz – CD_3CN) of **9**.

2.12.9.2 ¹³C-NMR SPECTRUM

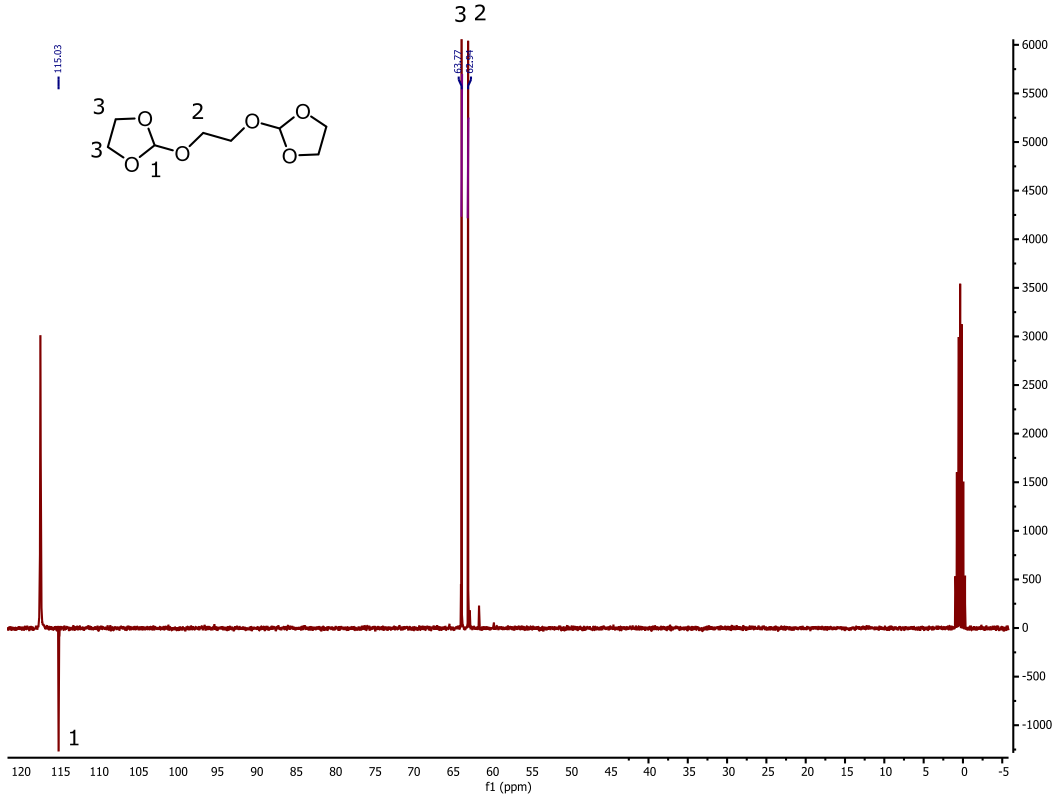


Figure S2.91 ¹³C APT NMR spectrum (101 MHz – CD_3CN) of **9**.

2.12.9.3 MASS SPECTRUM AND FRAGMENTATION

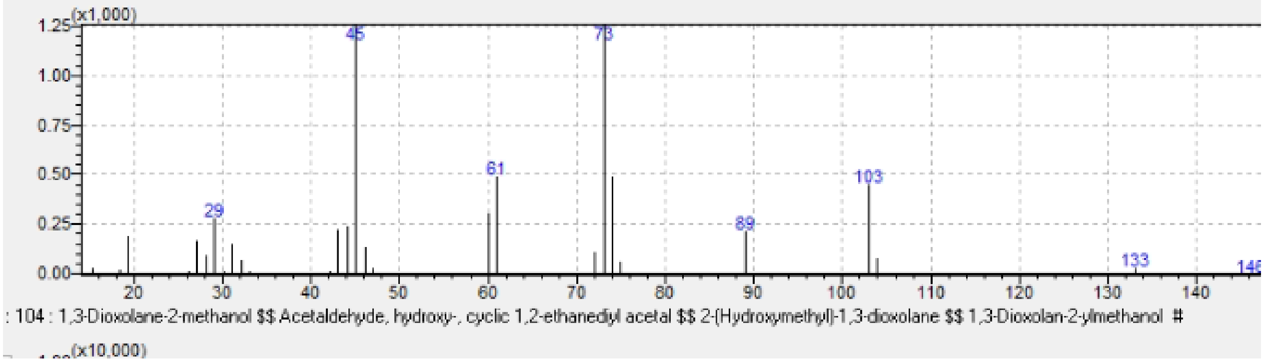


Figure S2.92 Mass spectrum obtained for **9**.

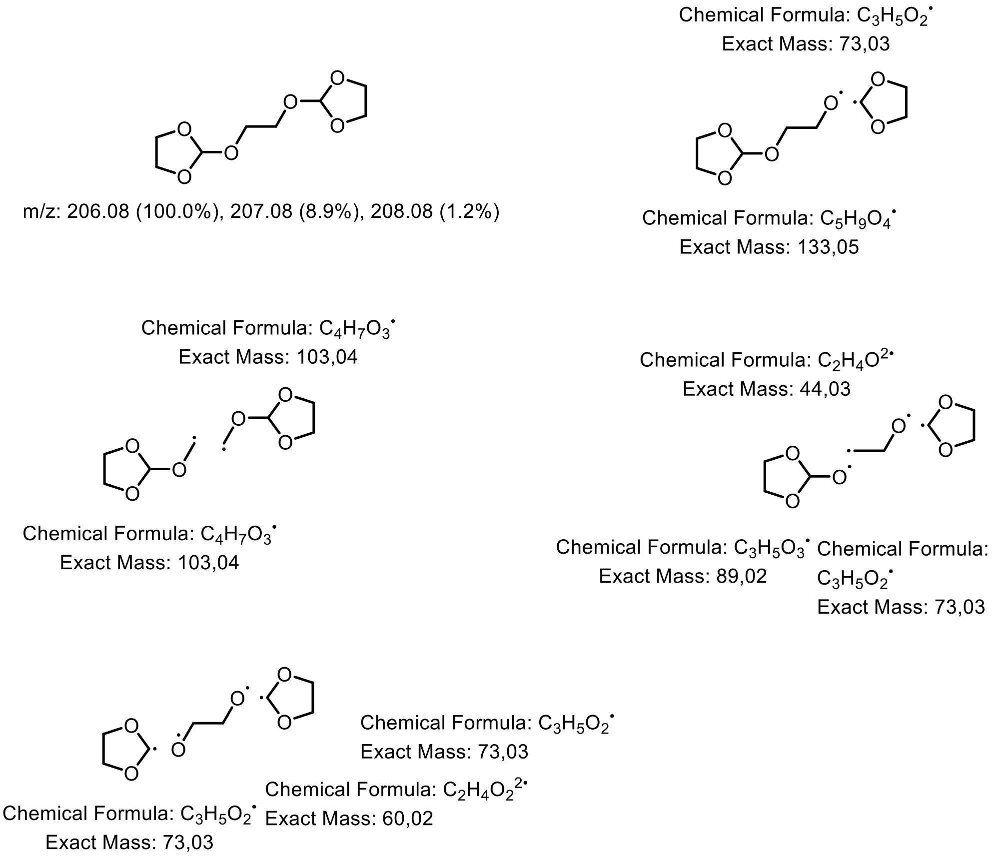


Figure S2.93 Fragmentation of **9**.

2.12.10 Compound 10

Compound **10** has never been observed or isolated but the hypothesis of its formation is strongly supported by the positive impact of its addition of the kinetic **model VIII**. This species was also included in the kinetic study starting from **4** (isolated and assigned), resulting in an improved model as well. Figure S2.94 shows the superimposition of a spectrum from a kinetic with an excess of **1**, promoting the formation of **3** and **5** (both isolated and assigned) versus the kinetic study using **3** as starting reagent. Due to the substitution of ethylene glycol moiety by **2**, it is expected that the acidic proton of **10** will be slightly more shielded compared to species **5**, explaining the difference of chemical shifts. Besides, **4** follows the same logic, with an acidic proton slightly more shielded than **3**. Due to its very low amount, no correlation with 2D HMBC or HSQC could be observed, similarly for the carbon spectrum.

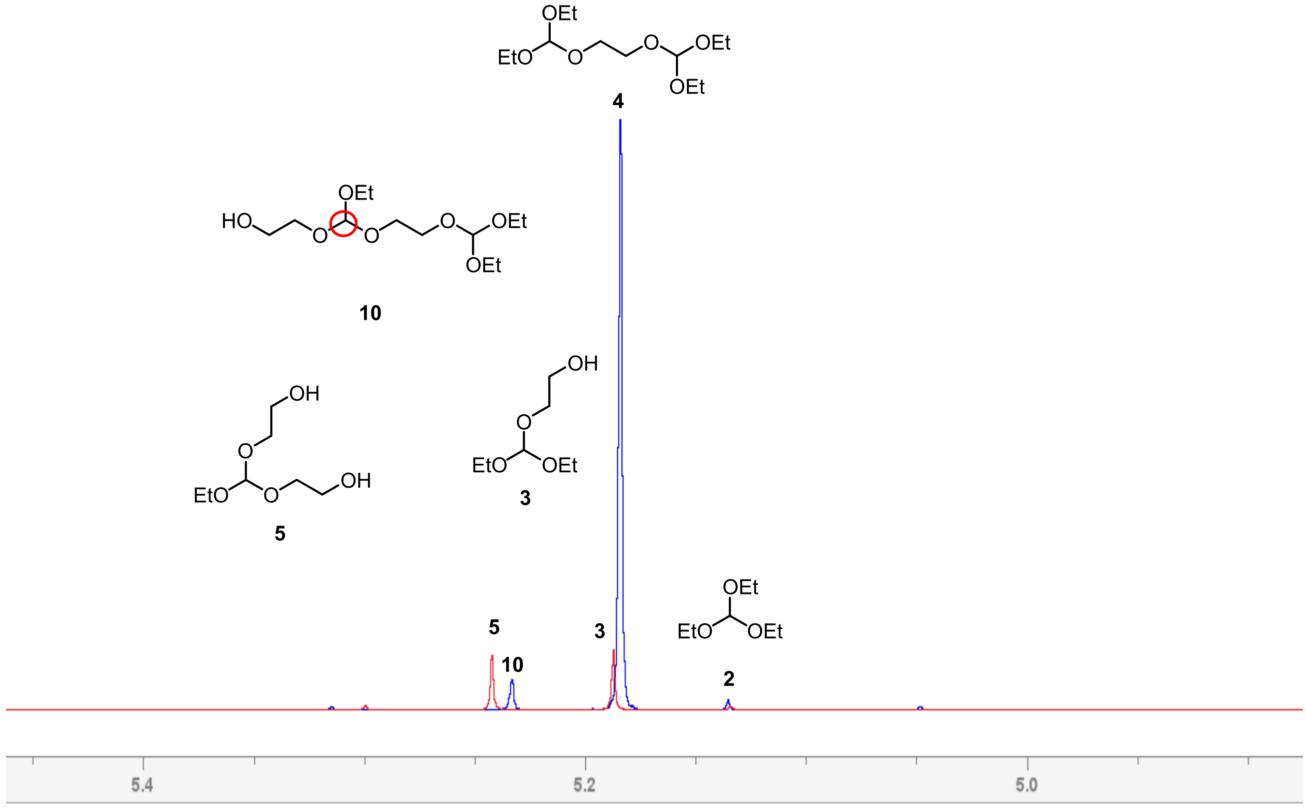


Figure S2.94 Superimposition of ^{1}H-NMR spectra of products **2**, **3**, **10** (blue spectrum) and **5** (red spectrum).

2.12.11 COMPOUND 11

2.12.11.1 ^{1}H-NMR SPECTRUM

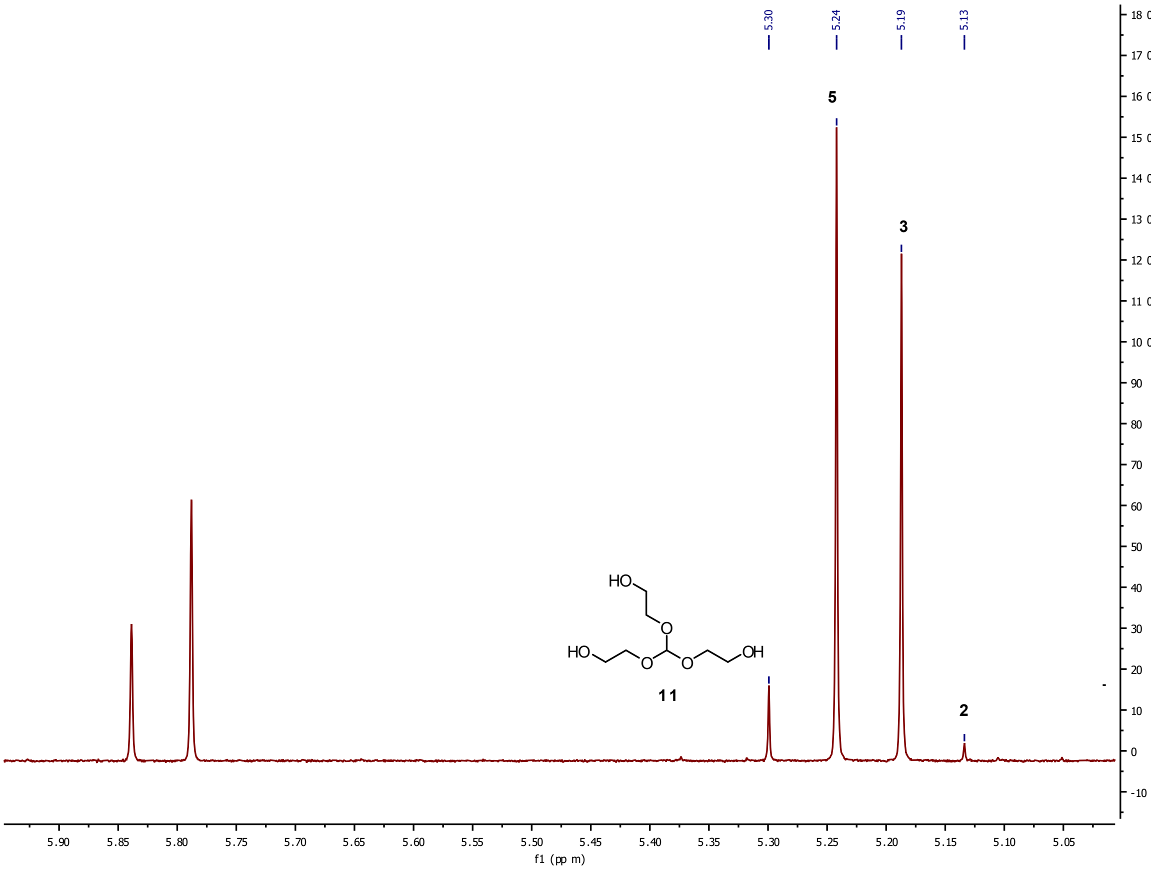


Figure S2.95 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **11** (spectral window between 5 and 5.9 ppm).

2.12.11.2 2D-HSQC AND HMBC NMR SPECTRA

The superimposition of the 2D-HSQC and HMBC spectra (Figure S2.96) reveals the proton-carbon correlation of the acidic proton of compound **11** at a chemical shift of 113.2 ppm (black box 1). The second box shows the two correlations of the "acidic carbon" with the two methylene groups (black box 2).

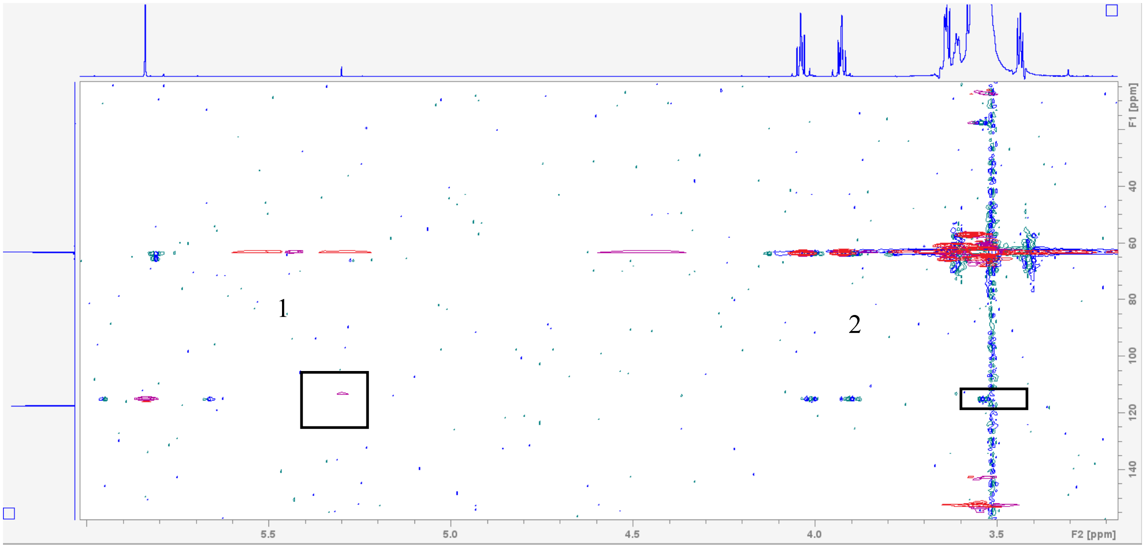


Figure S2.96 Superimposition of the 2D-HSQC (red signals) and HMBC (blue/green) spectra obtained from a typical crude of DCE and corresponding assignments of the structural scaffold of acyclic orthoester **11**.

2.12.12 COMPOUND 13 (COMMERCIAL REFERENCE)

2.12.12.1 ^{1}H-NMR SPECTRUM

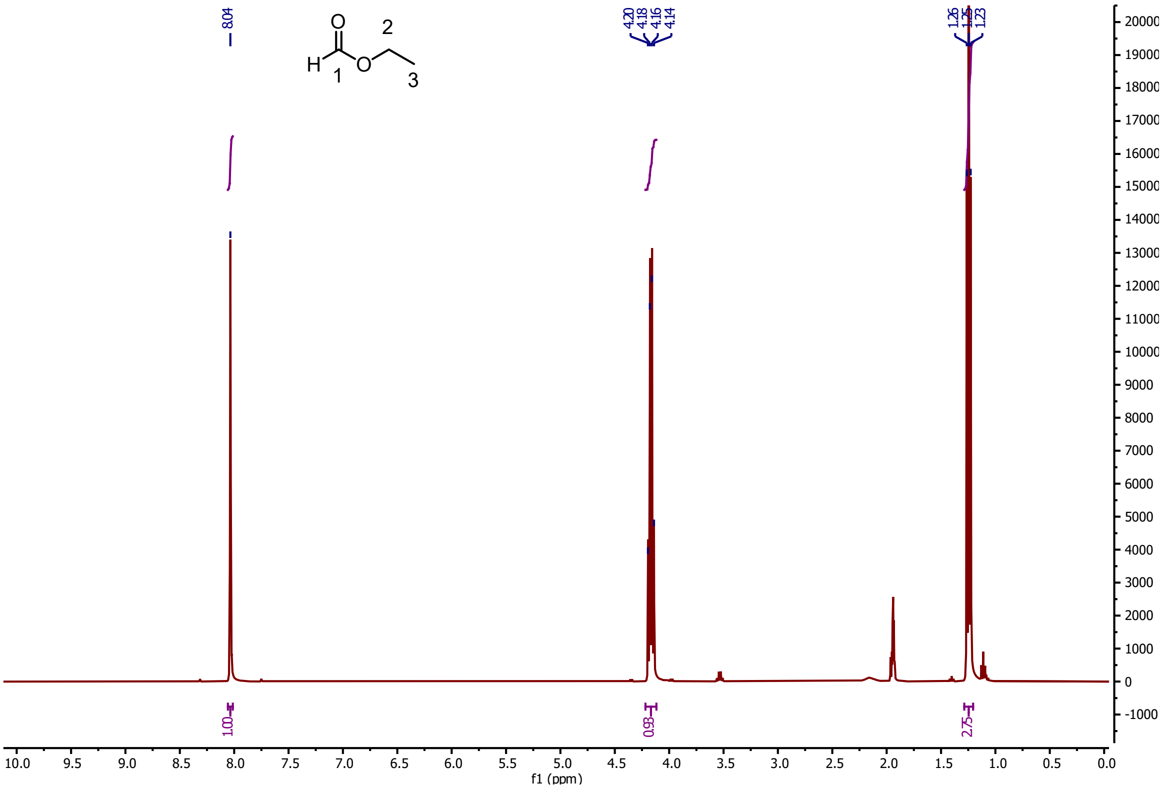


Figure S2.97 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **13**.

2.12.12.2 ^{13}C-NMR SPECTRUM

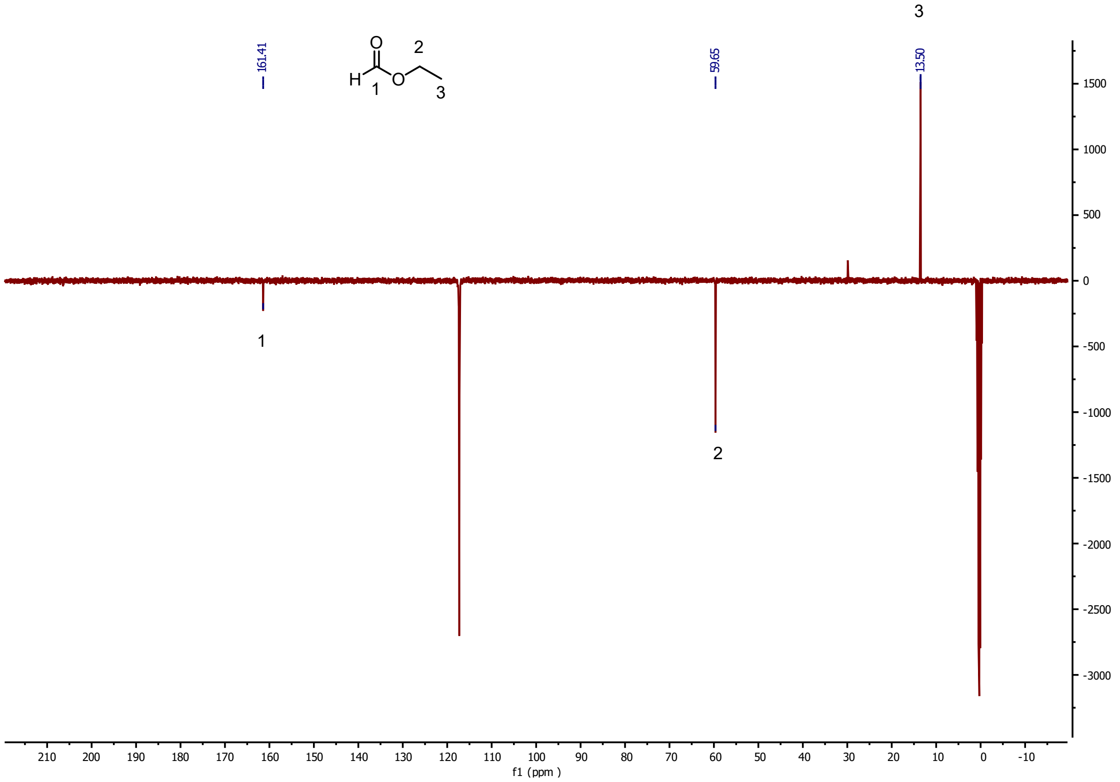


Figure S2.98 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **13**.

2.12.13 COMPOUND 14

2.12.13.1 ^{1}H-NMR SPECTRUM

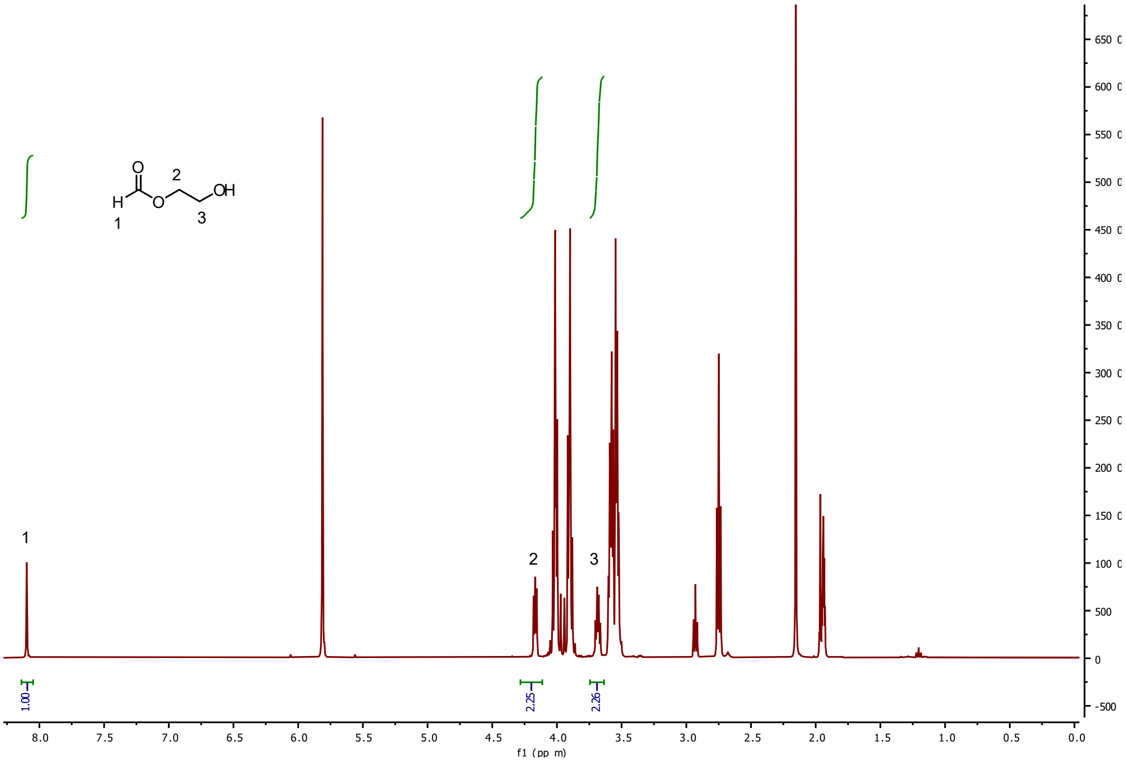


Figure S2.99 ^{1}H-NMR spectrum (700 MHz – CD_3CN) of **14**.

2.12.13.2 ^{13}C-NMR SPECTRUM

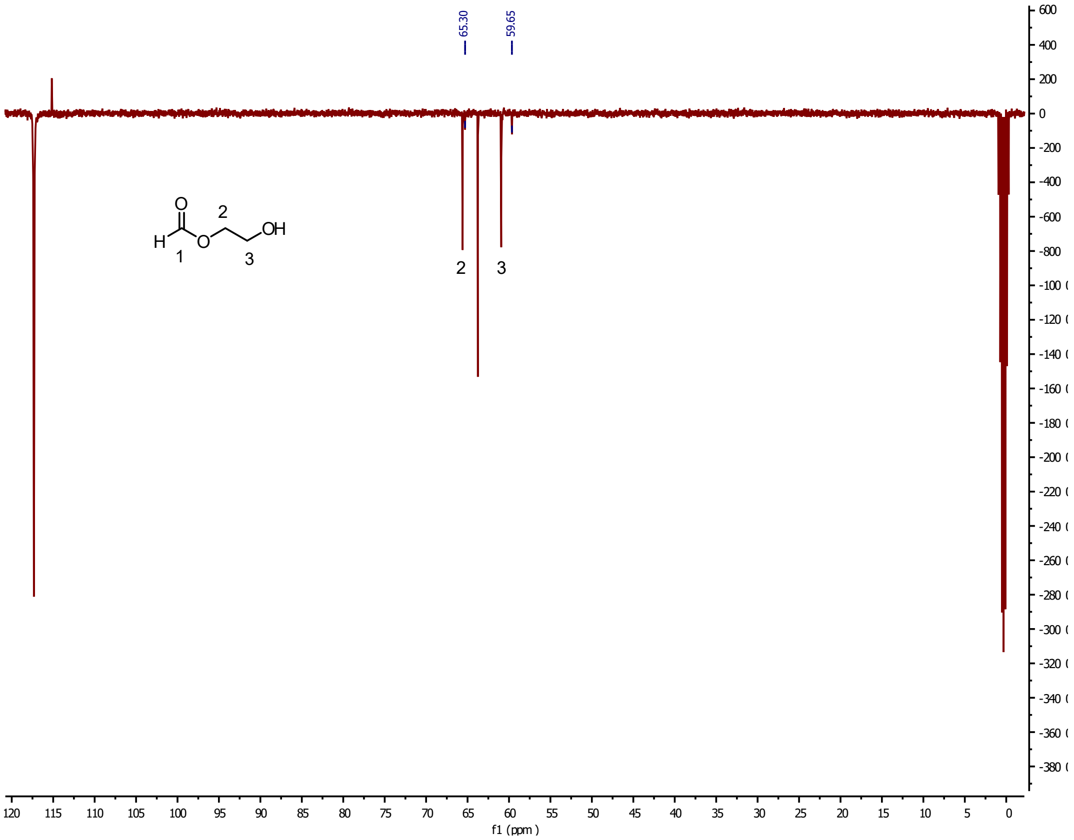


Figure S2.100 ^{13}C APT NMR spectrum (101 MHz – CD_3CN) of **14**.

The chemical shift of the quaternary carbon (1) was determined by 2D HMBC, at 161.33 ppm.

2.13 REFERENCES

[1] Newville, M., Stensitzki, T., Allen, D.B., Ingargiola, A., **2014**. https://doi.org/10.5281/zenodo.11813

[2] Liu,Y., Le Formal, F., Boudoire, F., Guijarro, N., ACS Appl. Energy Mater., **2019**, 2,6825-6833.

[3] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A., Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian Inc., Wallingford CT, **2016**.

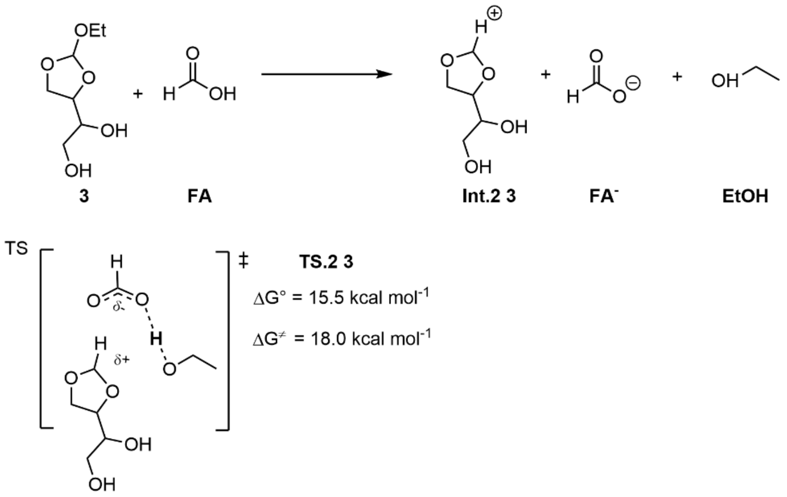
3 THE DEOXYDEHYDRATION REACTION OF BIO-BASED ORTHOESTERS

3.1 COMPUTATIONS

3.1.1 COMPUTATIONAL METHODS

DFT computations were performed using the Gaussian 16 (Revision C.01)[16] software package. Geometry optimizations were carried out at the B3LYP-D3/6-31+G* level of theory. The SMD method was used to model solvent effects using the built-in parameters for acetonitrile (MeCN, ε = 38.8). All possible stationary points were localized at the B3LYP-GD3BJ/6-31+G* level of theory. Stationary points were characterized by frequencies computations (local minima with only real frequencies and transition states with one imaginary frequency) and a systematic attempt to locate the lowest energy form was made. Transition states were verified by following the intrinsic reaction coordinates (IRC).

3.1.2 COMPUTATIONS OF THE FORMATION OF CARBOCATION FROM 3



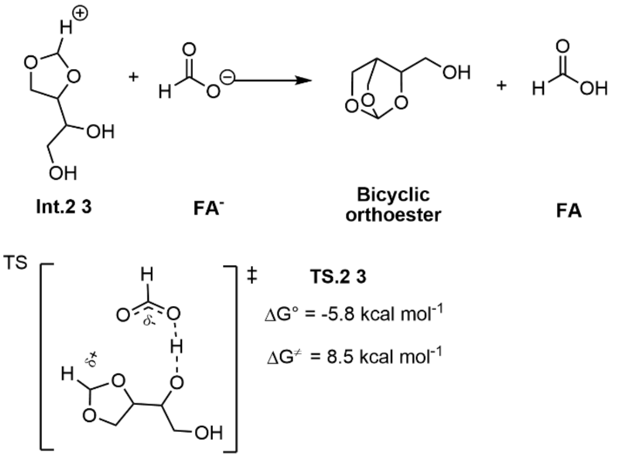
TS.2 3

ΔG° = 15.5 kcal mol^{-1}

ΔG$^{\neq}$ = 18.0 kcal mol^{-1}

Figure 3.1. Formation of carbocation from **3**.

3.1.3 COMPUTATIONS ON THE FORMATION OF BICYCLIC ORTHOESTER FROM INT.2 3



TS.2 3

ΔG° = -5.8 kcal mol^{-1}

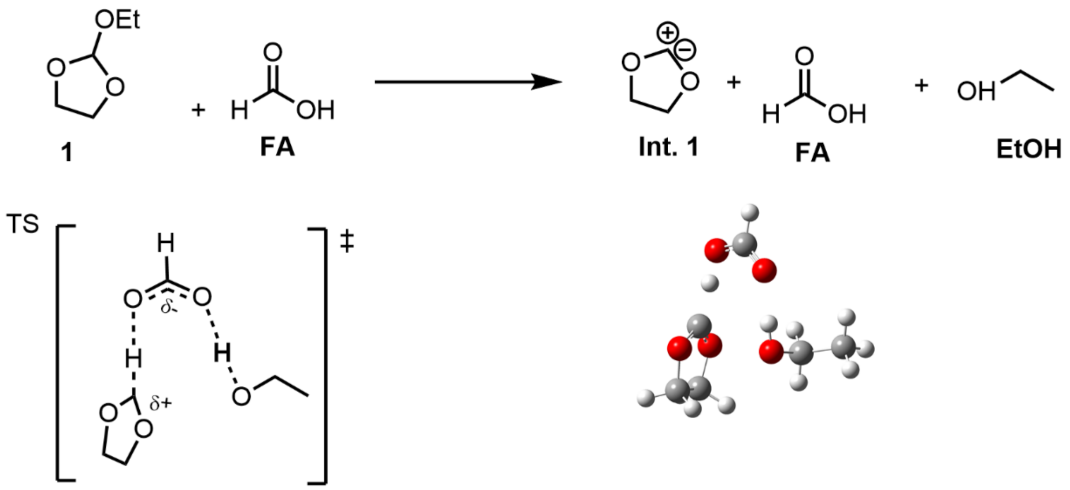
ΔG$^{\neq}$ = 8.5 kcal mol^{-1}

Figure 3.2 Formation of bicyclic orthoester from 3.

3.1.4 CARTESIAN COORDINATES AND ENERGIES FOR REPRESENTATIVE TRANSITION STATES

3.1.4.1 ASYNCHRONOUS FORMATION OF DIOXOCARBENES

Table S3.1 Transition state: activation of **1** in carbene **int.1.**



Coordinates of the TS (atom, X, Y, Z)	Energies
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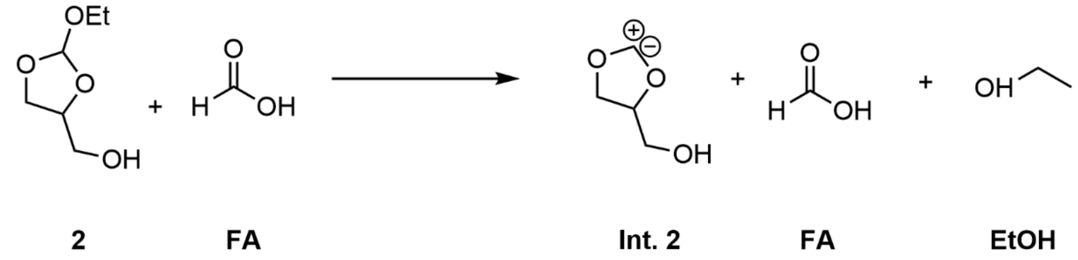
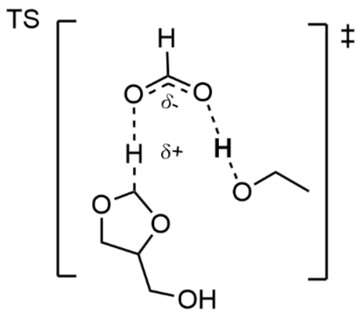
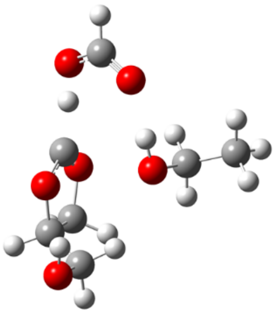
Table S3.2 activation of **2** in carbene **int.2**

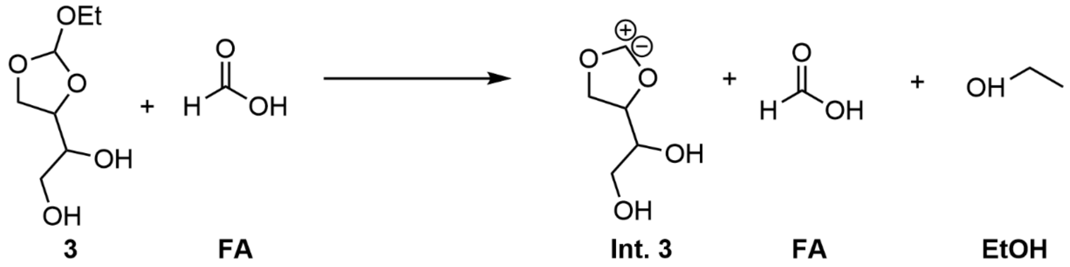


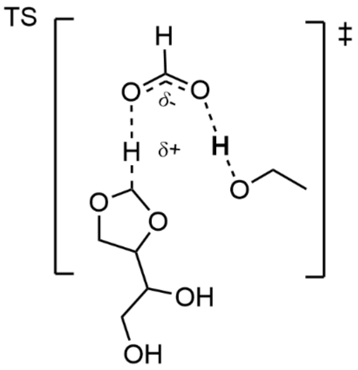


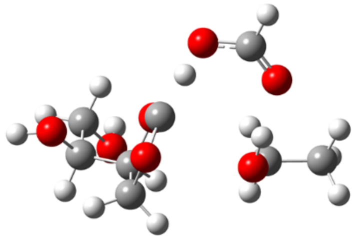


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.23875600 -1.20582500 0.63504500 H 1.12716800 -1.78969600 0.37659200 O -0.57792400 -0.60752400 1.74102600 O 0.67741100 1.20864400 -0.48282600 C -1.95329700 -0.06477800 1.65274900 H -1.87559000 1.01492000 1.78914900 C -2.39817300 -0.48165300 0.25503000 H -3.22156400 -1.19651900 0.25400800 O -1.20735300 -1.24013300 -0.23378600 H 1.40419900 0.60680900 -0.75952100 C 2.94212200 -1.65629900 -0.57885400 H 3.89083500 -2.19180400 -0.74201600 O 2.73773200 -0.56734800 -1.12580700 O 2.13027900 -2.29235200 0.21447200 C 1.14243100 1.99596500 0.61667600 H 1.58708000 1.34434700 1.38304400 H 0.25129100 2.45874200 1.05534100 C 2.13978700 3.06809400 0.19456400 H 2.44294300 3.66859700 1.06265700 H 3.04164300 2.61723200 -0.23838800 H 1.69641300 3.73900900 -0.55150600 C -2.65705800 0.67277400 -0.69670600 H -3.50229300 1.24826800 -0.30608800 H -1.77200300 1.31825300 -0.73405800 O -3.03087300 0.22749900 -1.99765100 H -2.23679300 -0.11936300 -2.44107200 H -2.52983600 -0.51874400 2.45740900	H = --726.31233 Hartree G = -726.37706 Hartree

Table S3.3 activation of **3** in carbene **int.3**







Coordinates of the TS (atom, X, Y, Z)	Energies
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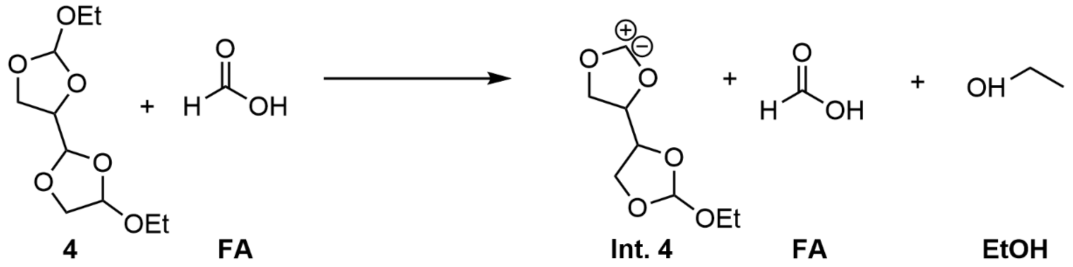
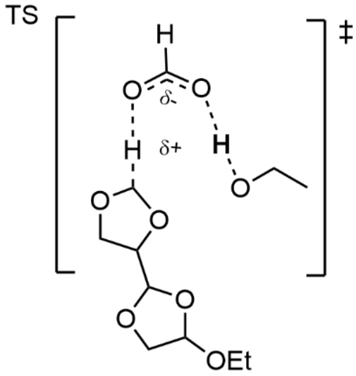
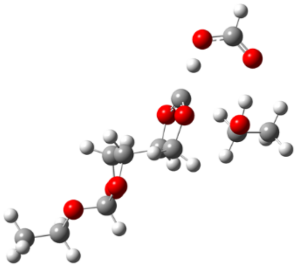
Table S3.4 activation of **4** in carbene **int.4**



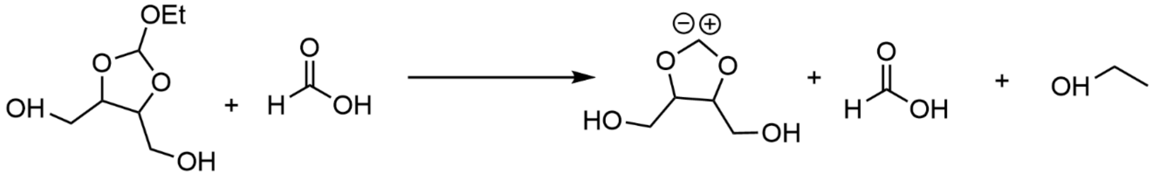




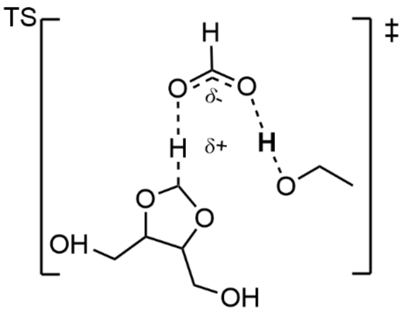
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.92143300 -1.26818900 0.08359900 H -3.17687900 -1.66682100 -0.59105700 O -0.98193700 -0.57648100 -0.49712200 O -3.07510700 1.15907400 0.90399200 C 0.08774900 -0.21555400 0.46596900 H 0.09452300 0.87342600 0.51982100 C -0.40239200 -0.87226100 1.75354900 H 0.25086800 -1.65820700 2.13272800 O -1.66252300 -1.52504900 1.32977800 H -3.85593000 0.68744100 0.53689500 C -5.17319100 -1.26401800 -0.92540700 H -6.07738400 -1.63094100 -1.43752900 O -5.22033800 -0.23538000 -0.24069900 O -4.13109700 -2.01301700 -1.13071400 C -2.69495100 2.18055900 -0.02201300 H -2.56835100 1.74885400 -1.02587300 H -1.71331100 2.53702000 0.30919700 C -3.68761700 3.33601700 -0.06891500 H -3.33762500 4.10987900 -0.76513400 H -4.67328500 2.99423200 -0.40910200 H -3.80258600 3.79014000 0.92297300 H -0.66153700 -0.16439700 2.53865300 C 1.40971100 -0.75111100 -0.07343000 H 1.34514900 -1.83298000 -0.22149700 C 3.33445000 0.45614900 0.38296900 O 2.41502500 -0.46771700 0.91822300 C 1.91449600 -0.01548500 -1.31752400 H 1.12685400 0.45299500 -1.90945400 H 2.51704900 -0.67281700 -1.95239100 O 2.72445800 1.02762200 -0.74789300 H 3.53848700 1.25755000 1.10107700 O 4.49538400 -0.25392700 0.07812400 C 5.60826700 0.58666800 -0.28573900 H 5.74831800 1.35016200 0.49288200	H = - 1032.7193Hartree G= - 1032.7998Hartree

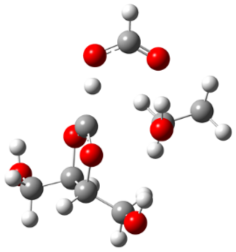
H 5.38419700 1.09678000 -1.23071900 C 6.83929300 -0.28701200 -0.41896800 H 6.69552700 -1.04922100 -1.19371200 H 7.70067300 0.33043900 -0.70004500 H 7.06803700 -0.78912200 0.52823900	

Table S3.5 activation of **5** in carbene **int.5**



5 **FA** **Int. 5** **FA** **EtOH**

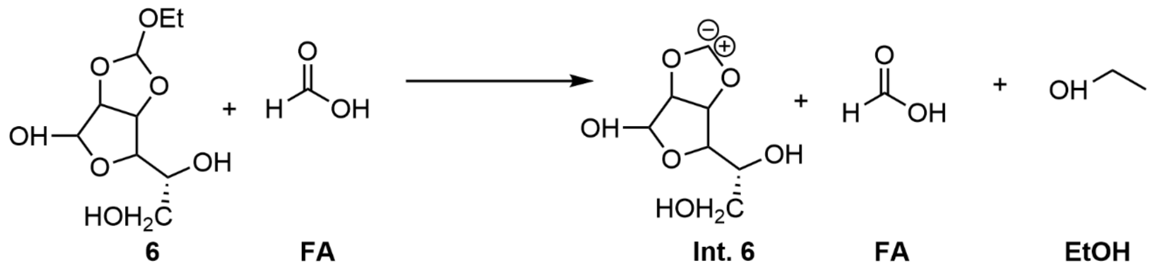


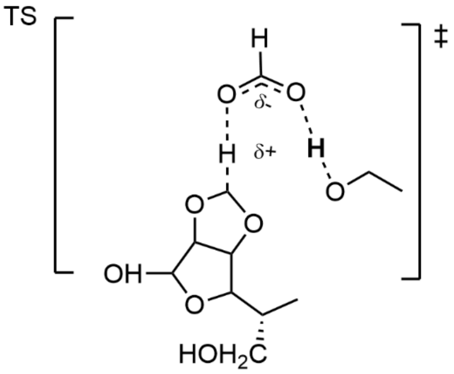


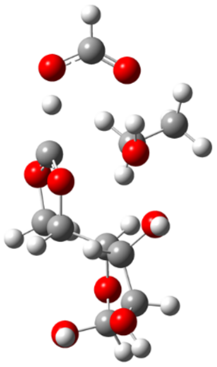
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.05683800 -0.96498300 -0.60959100 H 1.23906500 -1.68567300 -0.85730600 O -0.73401800 -1.06011800 0.49997100 O 1.42005500 1.18947100 0.34409900 C -1.95735700 -0.21242100 0.46003500 H -1.85788200 0.48554100 1.29369500 C -1.84282000 0.46389300 -0.90418800 H -2.66134600 0.21276200 -1.58151800 O -0.63189000 -0.18622300 -1.48003300 H 2.16107500 0.64748400 -0.00906200 C 3.29666900 -1.65438800 -0.95496400 H 4.17481600 -2.27687300 -1.18954200 O 3.44046800 -0.47146200 -0.62737200 O 2.17261100 -2.29944700 -1.06592500 C 1.43238600 1.09408600 1.77088900 H 1.49675300 0.03923400 2.07532600 H 0.46176800 1.47497300 2.10806900 C 2.56222300 1.89669000 2.40453700 H 2.51314900 1.82470500 3.49926800 H 3.54112300 1.51959100 2.08259800 H 2.49035100 2.95486700 2.12444500 C -3.17245500 -1.10704300 0.62857500 H -4.06689600 -0.48051900 0.55873900 C -1.60715400 1.96306400 -0.84336800 H -2.49576400 2.42507100 -0.40161400 H -0.74082700 2.17143000 -0.20620700 O -1.44502500 2.53496400 -2.13779100 O -3.20991700 -1.73358800 1.90576400	H = -840.82211 Hartree G = -840.89202 Hartree

H -3.20322100 -1.84738300 -0.18250700 H -2.51192700 -2.41123900 1.93744100 H -0.56643800 2.28387100 -2.47307600	

Table S3.6 activation of **6** in carbene **int.6**



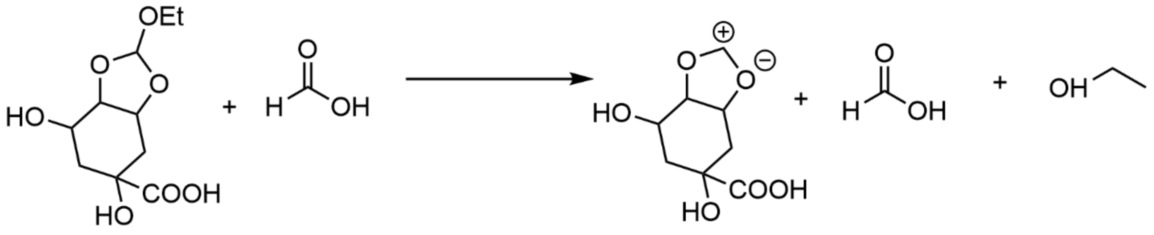




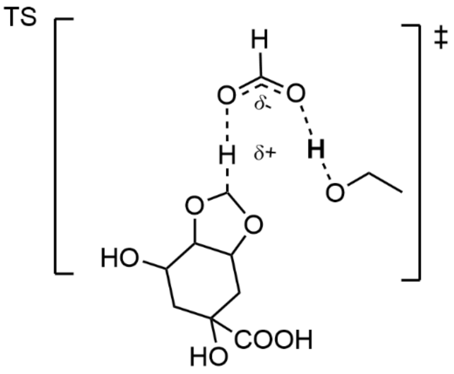
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.54762800 -1.14915000 1.05874100 H 2.83305200 -1.70934700 0.56596200 O 1.44242300 -0.33210100 2.06426500 O 1.90094500 1.12838200 -0.59307400 C 0.05762000 0.17980200 2.18606500 H 0.10476000 1.25553700 2.01905700 C -0.68518100 -0.58958600 1.09736400 H -1.40552000 -1.30289200 1.49761000 O 0.40465000 -1.39390800 0.48449700 H 2.60880900 0.53292300 -0.92692700 C 4.35492000 -1.60809100 -0.82189300 H 5.27609700 -2.10802600 -1.16220000 O 3.93769300 -0.60476600 -1.41166600 O 3.81357400 -2.18431900 0.21003000 C 2.51043500 2.15592300 0.19253200 H 3.18520100 1.70852600 0.93699300 H 1.69418300 2.64262900 0.73797000 C 3.26105300 3.17791900 -0.65277700 H 3.68104300 3.96573000 -0.01321000 H 4.08810400 2.70618500 -1.19818100 H 2.58880100 3.64666100 -1.38194700 H -0.28071400 -0.04342800 3.19662000 C -1.30757200 0.27783200 0.00724700 C -2.12456300 -0.50755400 -1.03170100 H -0.52280300 0.86416100 -0.47752600 C -3.49319600 0.19206000 -1.02275500 C -3.55457500 0.80220600 0.38657400 H -3.50475700 0.99082200 -1.77146000 H -4.16479100 1.70607800 0.46776800 O -4.52312100 -0.76290000 -1.26552600	H= -1068.6518 Hartree G = -1068.7298 Hartree

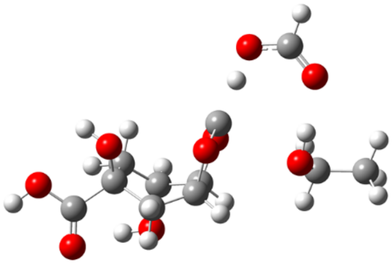
H -5.32235100 -0.29642100 -1.57023200 O -3.99015100 -0.15941900 1.33283800 H -4.48242000 -0.84639700 0.84047400 H -2.26043100 -1.54921400 -0.71503000 O -1.46368200 -0.46577900 -2.29149100 H -1.90095800 -1.10251700 -2.88400800 O -2.22417000 1.19366200 0.65036200	

Table S3.7 activation of **7** in carbene **int.7**



7 **FA** **Int. 6** **FA** **EtOH**

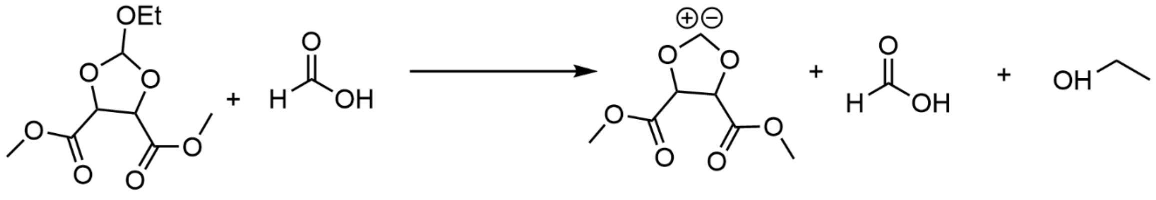




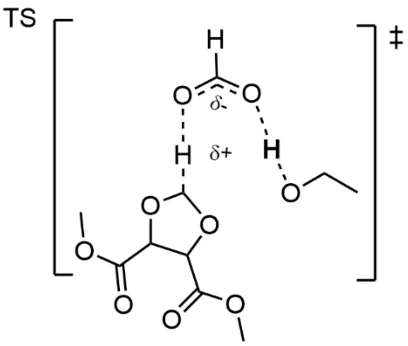
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.10251400 0.80881600 0.24907300 H -2.12011800 1.87043600 0.53180700 O -0.83692600 -0.16623700 1.07732500 O -3.04581500 -0.86968700 -0.97243200 O -0.44353700 0.71748100 -0.86207700 H -3.55962000 -0.05970700 -0.75831500 C -4.07154700 2.46859300 0.32197400 H -4.77584900 3.28533400 0.54767400 O -4.45474700 1.46638000 -0.29119200 O -2.86904700 2.69719300 0.76228700 C -3.44250300 -1.90512700 -0.06977500 H -3.35310900 -1.55264600 0.96859000 H -2.71852200 -2.71601000 -0.20621500 C -4.85593700 -2.41111500 -0.33287000 H -5.10289500 -3.22755300 0.35886100 H -5.59327200 -1.61100900 -0.19048300 H -4.94866700 -2.78797900 -1.35891400 C 1.78753400 -0.26843400 -1.28682800 C 2.58845900 0.50112400 -0.22693000 C 2.19226400 0.11325700 1.23618400 C 1.36467400 -1.16526800 1.36423800 C 0.11954800 -1.12337600 0.48236300 C 0.34457600 -0.54711900 -0.91958100 H 1.82824300 0.28334700 -2.23073000 H 3.07511500 0.03438800 1.88052000 H -0.37870000 -2.09150800 0.46872600	H= -1106.7946 Hartree G = -1106.8735 Hartree

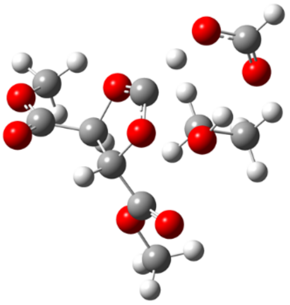
H -0.14061400 -1.14291300 -1.69122800 H 1.04326200 -1.26671600 2.40893300 H 1.59660100 0.94136100 1.63621400 H 2.25938300 -1.23958100 -1.45226700 O 2.06317300 -2.34066000 0.94647900 H 2.94688300 -2.34028600 1.35504000 O 2.34103700 1.88963600 -0.45634500 H 2.84926100 2.40986900 0.19182700 C 4.08625500 0.19753400 -0.40382500 O 4.84886600 1.24561100 -0.03895200 H 5.79259800 0.98583300 -0.10001800 O 4.55139200 -0.86321400 -0.77061200	

Table S3.8 activation of **8** in carbene **int.8**



8 **FA** **Int. 8** **FA** **EtOH**

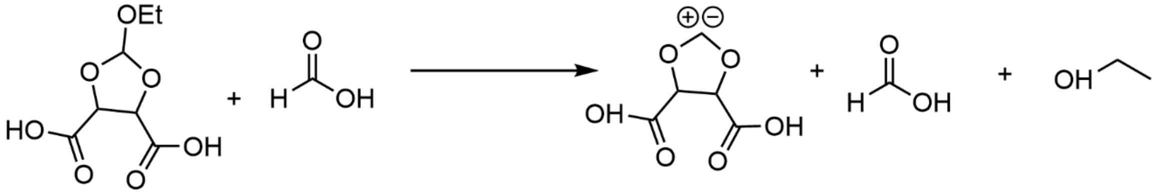




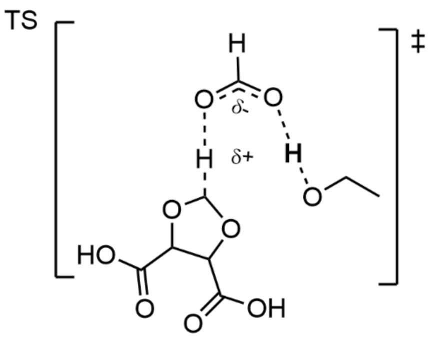
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.49971400 -1.43838400 -0.81668200 H 1.70821800 -2.11334400 -0.83583600 O -0.30404700 -1.45237200 0.20464300 O 1.44538000 0.92355800 0.44100400 C -1.37432500 -0.44405900 0.02820200 H -1.28795800 0.25410500 0.85600600 C -1.02344000 0.17925900 -1.31894900 H -1.80642900 0.02021600 -2.06297700 O 0.14344200 -0.61278300 -1.74734500 H 2.25036100 0.38199700 0.27393400 C 3.75555200 -1.89557300 -0.42617000 H 4.74679700 -2.37945800 -0.44565900 O 3.65409200 -0.72350700 -0.03184300 O 2.79515400 -2.65836500 -0.83805400 C 1.28729700 1.07791300 1.85508000 H 1.24095300 0.08977500 2.33682800 H 0.31587200 1.56338900 1.99698100 C 2.39043600 1.92023500 2.48207900 H 2.20943200 2.04016400 3.55833300 H 3.37068900 1.44471900 2.35346100 H 2.42516500 2.91612300 2.02400700 C -2.70817700 -1.20663500 0.03507800	H= -1067.4849 Hartree G = -1067.5628 Hartree

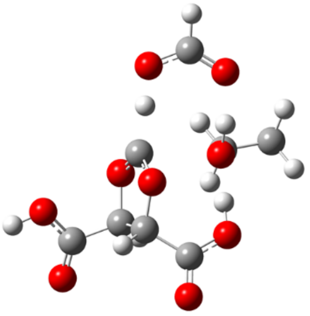
C -0.61310500 1.65018400 -1.32773900 O -1.17782800 2.30910500 -0.32018500 O -3.33533100 -1.40089300 -0.98692800 O 0.06796900 2.13246100 -2.20583700 C -0.87823300 3.72410200 -0.22038500 H -1.23877100 4.24555000 -1.11005600 H -1.40867400 4.06483700 0.66799600 H 0.19877300 3.86234400 -0.10619800 C -2.47548700 -1.40253100 2.45670300 H -3.03958700 -1.96536300 3.19942100 H -1.44282100 -1.75379800 2.43269900 H -2.52741500 -0.33449000 2.68065400 O -3.14832900 -1.68268300 1.19668200	

Table S3.9 activation of **9** in carbene **int.9**



9 **FA** **Int. 9** **FA** **EtOH**

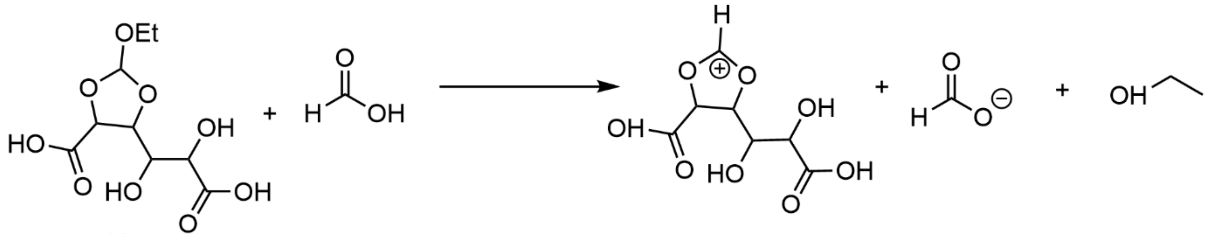




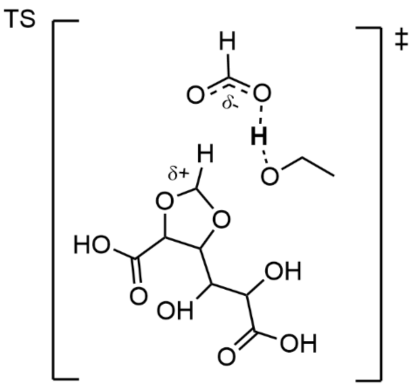
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.17693200 -1.12525600 -0.26463300 H 1.37343100 -1.87472800 -0.36339700 O -0.54178900 -0.99542500 0.81060100 O 1.68688400 0.91303400 0.19840800 C -1.70413700 -0.12444300 0.57513900 C -1.51899900 0.28042500 -0.90718400 H -2.32536800 -0.06485200 -1.55213400 O -0.31857600 -0.48330900 -1.28472500 H 2.43340900 0.38901600 -0.20451400 C 3.44580600 -1.91130900 -0.74633500 H 4.30676600 -2.57017700 -0.94002600 O 3.59707200 -0.67875200 -0.79292800 O 2.34995400 -2.54643000 -0.48682100 C 1.92749200 1.14905900 1.60048000 H 2.16547300 0.19091700 2.07842500 H 0.97703200 1.50552800 2.00896700 C 3.03328900 2.16638800 1.82538100 H 3.17048400 2.33457900 2.90106000 H 3.98466000 1.81102800 1.41164800 H 2.78242000 3.12398200 1.35415000 C -1.32898400 1.78575000 -1.14848000	H= -988.94228 Hartree G = -989.01207 Hartree

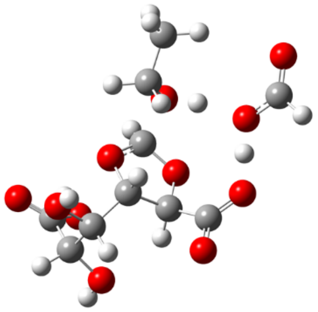
O -2.29577400 2.44684400 -1.47708900 O -0.13098500 2.31722200 -0.98618900 H 0.58601600 1.71331300 -0.59576100 C -2.99509600 -0.89592500 0.81809800 O -2.88248300 -2.18154200 0.47189100 O -4.00006200 -0.36451300 1.23559300 H -1.63910300 0.70648300 1.27671100 H -3.74696200 -2.63026000 0.60015300	

Table S3.10 activation of **10** in carbene **TS.2 10**



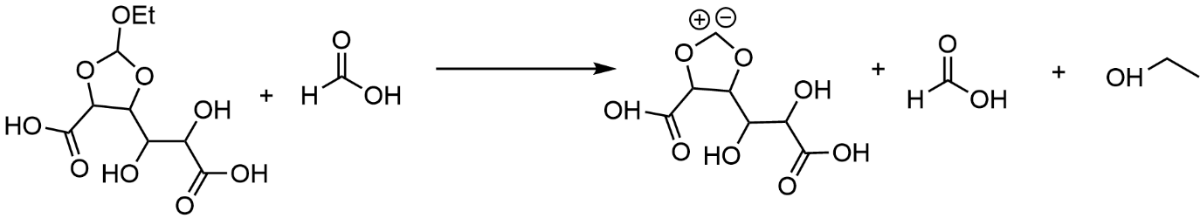
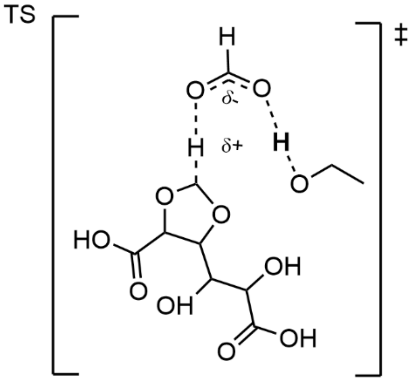
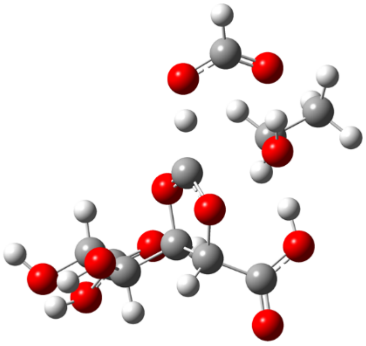
10 **FA** **Int. 10** **FA⁻** **EtOH**





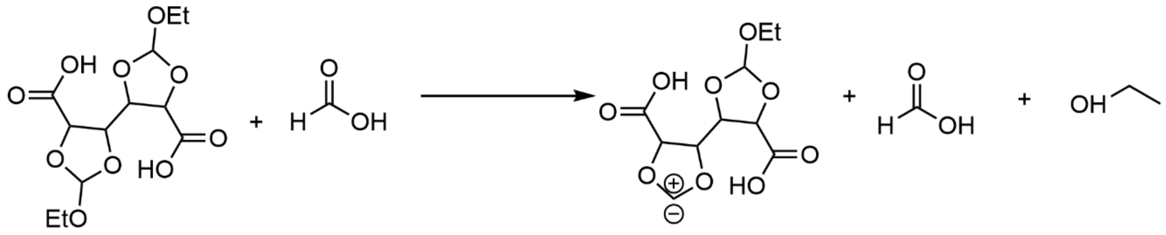
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.22679900 -0.90657000 -0.93431100 H -0.10323600 -1.57833700 -1.77832100 O -0.41132100 0.38871400 -1.25098700 O -1.68220500 -1.46082100 -0.40679700 C 0.30300200 1.22683800 -0.29035000 C 0.82068000 0.20611900 0.74489600 H 0.16557100 0.17534900 1.62089200 O 0.67615300 -1.06625200 0.04117900 H -2.37294000 -0.72482400 -0.58096400 C -4.49435100 0.73251000 -0.38858800 H -4.73437400 1.72237000 0.03165300 O -3.21512900 0.58054700 -0.71219500 O -5.33357000 -0.13433100 -0.55009300 C -1.82039400 -1.96161500 0.98299700 H -0.93660500 -2.57336800 1.15550100 C 2.26009200 0.36401000 1.23734700 H -1.81302600 -1.09694100 1.65079900 C -0.55131500 2.32899100 0.35351200 C -3.10060000 -2.76022900 1.07798000 H -3.18803200 -3.14499100 2.10098100 H -3.97933600 -2.14128800 0.86985000 H -3.08572500 -3.60962900 0.38719900 O -1.80842100 2.39123000 0.11336700 H -2.54357000 1.41307900 -0.39196200 O 0.08859500 3.10353500 1.07973100	H= -1217.9713 Hartree G = -1218.0475 Hartree

H 1.11666900 1.69732900 -0.84079300 C 3.38337700 0.32072000 0.17559300 H 4.31898800 0.22842000 0.73843900 C 3.33698000 -0.90272700 -0.74574100 O 2.55992300 -0.64428900 2.19542400 H 2.03316800 -0.47274400 2.99682600 O 3.33035200 1.55303700 -0.52561200 H 4.07787700 1.59714100 -1.14781500 O 3.73712200 -2.00208900 -0.42104200 O 2.85538700 -0.62149700 -1.97223600 H 2.88200500 -1.44511600 -2.50409100 H 2.32344900 1.36298400 1.68588800	

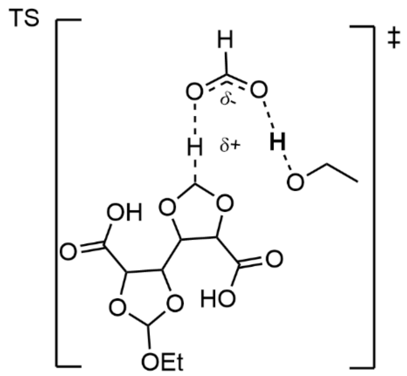
Table S3.11 activation of **10** in carbene **int.10**	
 **10** **FA** **Int. 10** **FA** **EtOH**  	
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.99911900 -0.95684400 -0.78828200 H 2.05313600 -1.93191700 -0.61838700 O -0.02742900 -0.83406300 -0.00763300 O 2.50846000 0.73165100 0.62417800 C -0.90378700 0.28431200 -0.43683400 H -0.95699900 0.97329400 0.40397200 C -0.13888700 0.83796100 -1.65244400 H -0.69988600 0.73879600 -2.57927900 O 1.01088600 -0.07629800 -1.75302000 H 3.23220700 0.07693200 0.43459800 C 4.05009400 -2.33140100 -0.16200900 H 4.81809200 -3.12041600 -0.14355300 O 4.35584900 -1.16901700 0.14661900 O 2.88050200 -2.75449400 -0.52231500 C 2.12785500 0.67922700 2.01290800 H 1.97466800 -0.36928200 2.29635700 H 1.16276400 1.19089400 2.07831000 C 3.15674000 1.34530500 2.91123200 H 2.82138300 1.30446200 3.95541700 H 4.12594900 0.83660400 2.84360900	H= -1217.9702Hartree G = -1218.0509Hartree

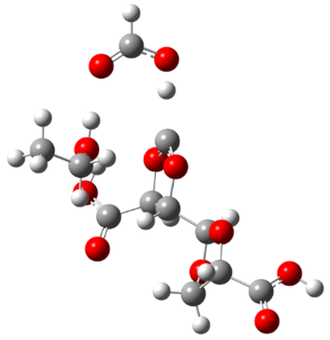
H 3.29331700 2.39678200 2.63220800 C -2.27382200 -0.27322700 -0.78499700 H -2.89532800 0.57709200 -1.10200000 C 0.31347700 2.29293100 -1.51249500 O 1.43162700 2.56100400 -0.85894800 H 1.86694300 1.78437800 -0.37563100 O -0.37848600 3.17045400 -1.99609700 O -2.09047200 -1.19028700 -1.84926800 H -2.96760000 -1.52028700 -2.11470800 C -2.97398300 -0.98823700 0.39414600 C -3.30536300 -0.03111900 1.54444100 O -4.60914900 0.13392400 1.78860100 O -2.45311200 0.54171100 2.19413000 H -5.10618200 -0.42700000 1.14827600 O -4.18621700 -1.54007100 -0.13005000 H -4.24457600 -2.48236800 0.11182300 H -2.32620500 -1.77752000 0.78540600	

Table S3.12 activation of **11** in carbene **int.11**



11 **FA** **Int. 11** **FA** **EtOH**

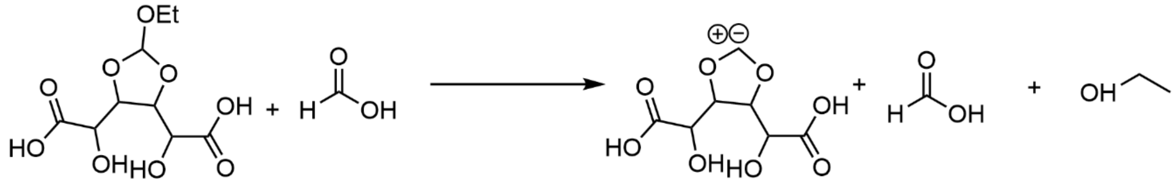




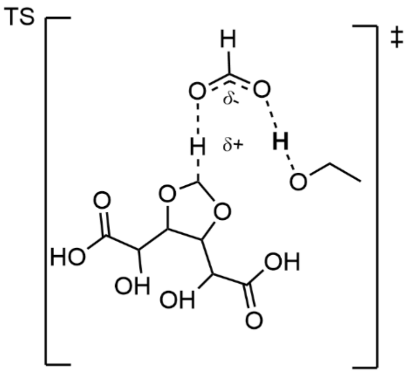
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.44590900 -1.03435100 -1.01251500 H 2.72118600 -2.17288100 -0.96212200 O 0.44949200 -1.01281700 -0.17336600 O 2.74418600 0.70582600 0.77137000 C -0.38355100 0.19675300 -0.32755200 H -0.37328400 0.71724500 0.62899100 C 0.34595200 0.94500300 -1.43756500 H -0.27075900 1.10076300 -2.32713000 O 1.41542400 0.00891200 -1.81773200 H 3.38023000 -0.03707500 0.69198100 C 4.48467400 -2.50186600 -0.15992200 H 5.29436900 -3.24443600 -0.13628400 O 4.54675200 -1.45718900 0.48245500 O 3.49229500 -2.87662400 -0.93635700 C 2.21695500 0.70864700 2.10346300	H= -1256.0472 Hartree G = -1256.1293 Hartree

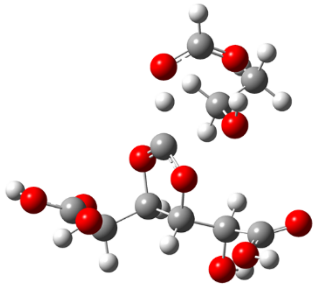
H 1.75238900 -0.26398000 2.32277100 H 1.42458600 1.46442600 2.10806700 C 3.27002200 1.04085400 3.15218400 H 2.81440900 1.06664200 4.15078400 H 4.06734800 0.28714000 3.16278900 H 3.72104300 2.02042600 2.95230000 C 0.92897000 2.29851300 -1.04104800 O 2.15131000 2.59230200 -1.48962100 H 2.60953900 1.78674100 -1.80589600 O 0.26067100 3.10640700 -0.43386100 C -1.80374600 -0.24462400 -0.69754300 H -1.80104000 -0.82174200 -1.62795900 C -3.42438200 -0.31296500 0.95606500 C -3.24292500 1.11699600 0.41965500 H -3.33183500 -0.35577700 2.04320800 H -4.17180400 1.66403600 0.25731400 H -2.57559300 1.69018300 1.07161500 O -2.34179100 -1.02744900 0.36195900 O -2.63527800 0.87781000 -0.86091400 C -4.78691600 -0.88388800 0.58478800 O -4.77524400 -1.65588200 -0.51095200 H -5.69333600 -1.95555300 -0.68424500 O -5.79196800 -0.62636900 1.22124000	

Table S3.13 activation of **12** in carbene **int.12**



12 **FA** **Int. 12** **FA** **EtOH**



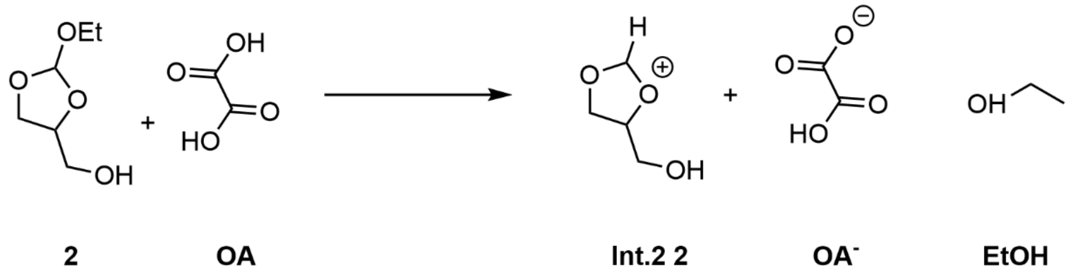


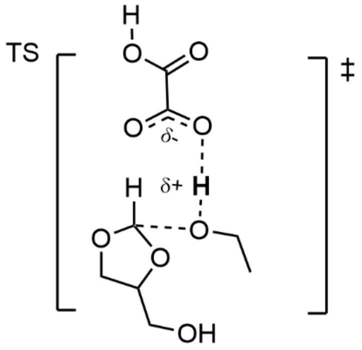
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.23337200 -0.75997500 -0.96641300 H 1.14568300 -1.74445100 -1.55528600 O -0.70176300 -1.04380000 -0.10819700 O 2.06293100 -0.46010400 0.98145400 C -1.44477600 0.17502800 0.29234700 H -1.39670500 0.23117100 1.37819600 C -0.65399500 1.27685200 -0.41042400 H -1.26430900 1.88224200 -1.07805400 O 0.28025200 0.51149900 -1.25613400 H 2.68284400 -0.83066000 0.31194500	H= -1217.9579 Hartree G = -1218.0422 Hartree

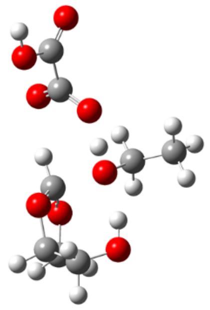
C 3.08019900 -2.47210100 -1.76747900 H 3.69427900 -3.20296600 -2.31805200 O 3.61138800 -1.69805200 -0.96093900 O 1.81828800 -2.53639100 -2.06672100 C 1.78598000 -1.48093000 1.94598600 H 1.52669900 -2.41861000 1.43319400 H 0.89733600 -1.14784800 2.49335600 C 2.94600000 -1.70620300 2.90730000 H 2.68162400 -2.47158400 3.64901600 H 3.84058400 -2.04667100 2.37094500 H 3.19368000 -0.77972900 3.43977000 C -2.88464600 0.02576600 -0.17836100 H -3.42348200 0.92688500 0.15218900 C 0.16811600 2.14129500 0.54049700 O -2.86717400 -0.08524600 -1.58474600 H -3.77903700 -0.05597000 -1.92385300 C -3.54765200 -1.15355100 0.54177900 O -4.24131900 -1.94306800 -0.28831200 H -4.67173900 -2.65094500 0.23840000 C 1.13197500 3.08772600 -0.18114900 O -0.77907200 2.91834400 1.27239300 H -0.39281600 3.13944300 2.13898500 H 0.76805900 1.50380600 1.19470100 O 0.61391600 3.59716400 -1.31106400 H 1.25258100 4.23581200 -1.69446200 O 2.22405200 3.38935000 0.25699000 O -3.47683900 -1.32136700 1.74334100	

3.1.4.2 FORMATION OF CARBOCATION DERIVED FROM 2 CATALYZED BY OXALIC ACID

Table S3.14 activation of **2** in carbene **int.2 2** catalyzed by OA without intramolecular stabilization



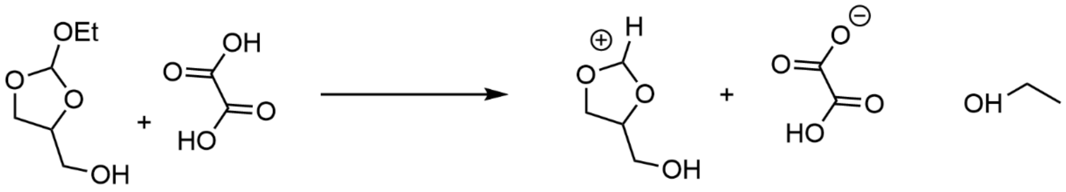




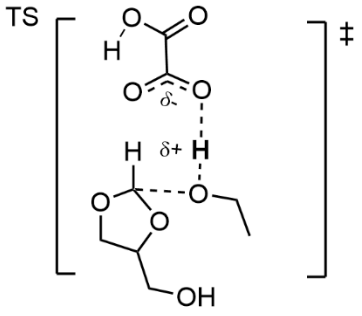
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.05280900 -0.55178600 -1.04568600 H 0.09400500 -0.52759100 -1.55807500 O 0.65116300 0.91124500 0.06546100 C 3.30790900 -0.70978100 -0.97389800 H 3.88125500 0.13992100 -0.60453500	H= -914.90225Hartree G = -914.97002Hartree

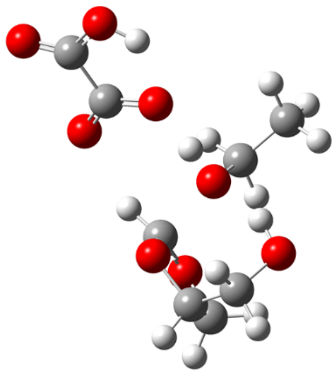
H 3.88134600 -1.28844700 -1.69662800 C 2.70011000 -1.56101900 0.15161900 H 2.96305400 -2.61669100 0.07483100 O 1.24849600 -1.49553500 -0.15232700 H -0.33674800 0.71276500 0.36292200 C -2.40573000 -0.15553500 -0.17688300 O -1.73584900 0.40965000 0.74501500 O -2.03149300 -0.49079100 -1.31576400 O 2.13620700 -0.18250200 -1.69104000 C 2.95930900 -1.06420100 1.56666100 H 2.29565500 -1.60776500 2.25320900 H 3.99299300 -1.32159100 1.81983800 O 2.83813500 0.34198800 1.72656900 C 0.69685200 2.20476600 -0.60203200 H -0.04696700 2.20449900 -1.40648500 H 1.69412600 2.28121500 -1.03969300 C 0.44412700 3.31721700 0.39818400 H 0.50549800 4.28288100 -0.11795600 H -0.55203700 3.23179200 0.84602800 H 1.19457500 3.30457300 1.19676400 H 1.96450700 0.62695600 1.38857500 C -3.87462100 -0.41573100 0.17369000 O -4.05285500 -1.61763300 0.75124600 O -4.77961000 0.36470700 -0.05557600 H -5.00939500 -1.73511400 0.94259600	

Table S3.15 activation of **2** in carbene **int.2 2** catalyzed by OA with intramolecular stabilization



2 **OA** **Int.2 2** **OA⁻** **EtOH**



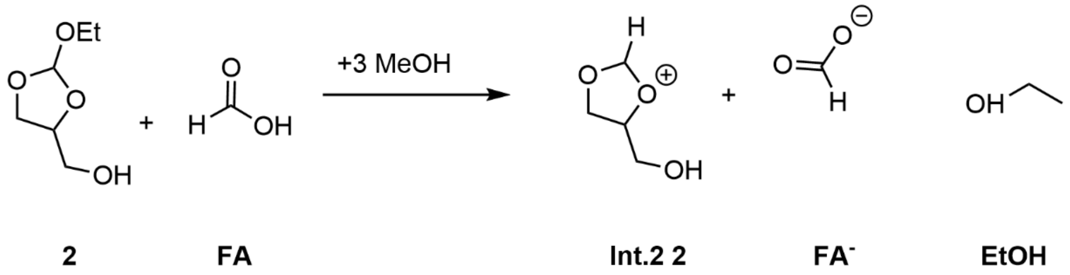


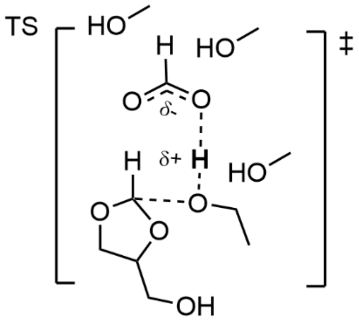
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.07467900 -0.71298200 -0.97037200 H 0.13661400 -0.79293900 -1.51334400 O 0.63162600 0.87856100 -0.11871900 C 3.32794200 -0.81808800 -0.80945500 H 3.86900000 0.09187700 -0.55143400 H 3.94133300 -1.48276100 -1.41591900	H= -914.90627 Hartree G = -914.97267Hartree

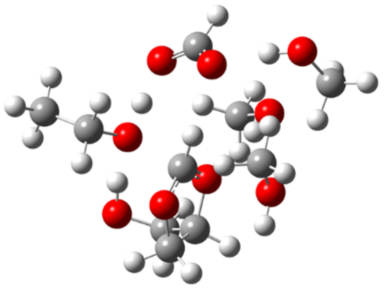
C 2.69682400 -1.50837500 0.40964200 H 2.97289600 -2.56019400 0.49186900 O 1.25440000 -1.50914200 0.06181300 H -0.34881200 0.71421100 0.20590400 C -2.41424700 -0.26232000 -0.22198000 O -1.75615800 0.45001300 0.61815900 O -2.02097200 -0.75276900 -1.28550900 O 2.17426700 -0.43571200 -1.63706300 C 2.91153600 -0.81133100 1.74541200 H 2.23503500 -1.26092500 2.48529100 H 3.94053900 -1.01389800 2.05947600 O 2.77129600 0.60186600 1.69990400 C 0.65598500 2.05934700 -0.97514200 H -0.10909200 1.93754900 -1.74941300 H 1.64129500 2.06749000 -1.44459000 C 0.42708000 3.30675500 -0.14329900 H 0.46649600 4.18483500 -0.79907100 H -0.55438200 3.28817900 0.34313400 H 1.20193200 3.41444100 0.62405400 H 1.90683000 0.82385800 1.29939200 C -3.89094700 -0.49607700 0.22559600 O -4.17848700 0.08761900 1.39947000 O -4.71174200 -1.13139900 -0.39876300 H -3.34662000 0.53438200 1.68789200	

3.1.4.3 FORMATION OF CARBOCATION DERIVED FROM 2 SOLVATED BY THREE MOLECULES OF SOLVENT

Table S3.16 activation of **2** in carbene **int.2 2** solvated by three molecules of methanol



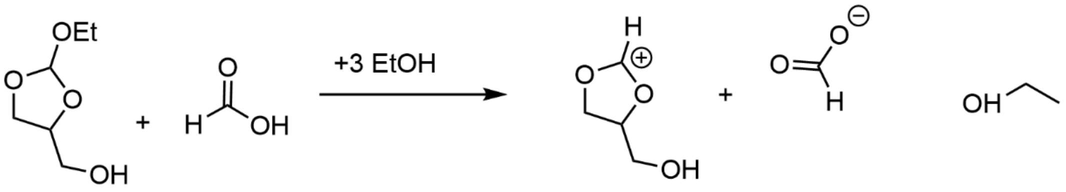




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.40358900 -0.81434600 0.42808900 H 0.39323500 -0.40834000 1.04245200 O -1.60066200 0.62804900 0.89006900 C -1.71047400 -2.47556800 -0.37764700 H -2.78172900 -2.49622900 -0.18303400	H= -1073.444 Hartree G = -1073.5422 Hartree

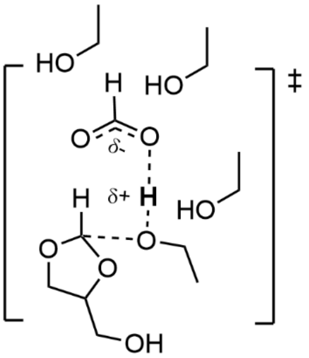
H -1.30960200 -3.48172200 -0.49144600 C -1.32833500 -1.53134700 -1.52588600 H -0.78505500 -2.03308800 -2.32696400 O -0.33575300 -0.63992600 -0.87248900 H -0.98078500 1.50882200 0.77677300 C 1.07211100 2.37545600 0.75074300 H 1.76122600 3.19069000 0.46406700 O -0.16791700 2.61353300 0.57546200 O 1.55766800 1.31744200 1.22008500 C 4.19270300 0.12549100 -0.50659400 H 5.18799200 -0.29529300 -0.68280200 H 4.02305500 0.93012900 -1.23512300 H 3.44922200 -0.66383500 -0.68188300 C 0.23312300 2.08620400 -2.87858500 H 0.62824800 2.95545600 -3.41180200 H -0.43185400 2.43615000 -2.08035600 H -0.34245200 1.47632900 -3.58782200 C 2.41246700 -2.54386000 1.46935400 H 2.94306300 -1.59106400 1.51874900 H 1.61089100 -2.54700800 2.21956800 H 3.11749500 -3.35255900 1.70012400 O 1.89015300 -2.66573700 0.13989100 H 1.44100500 -3.52103500 0.07057400 O 1.35408300 1.37144000 -2.35281500 H 1.01358700 0.66578400 -1.78386000 O 4.15509400 0.60556600 0.83469400 H 3.23916200 0.92269100 1.01153300 O -1.05260500 -1.88840000 0.79936700 C -2.46707700 -0.70329900 -2.10036600 H -2.03831200 0.07929600 -2.73948900 H -3.06246500 -1.36831200 -2.73434000 O -3.34390700 -0.16396300 -1.12349800 C -2.10434000 0.55595500 2.24445200 H -1.26796200 0.69839600 2.93887000 H -2.49939500 -0.45420200 2.37820900 C -3.18804200 1.59708300 2.46391700 H -3.56936500 1.51450400 3.48779300 H -2.79787300 2.61050800 2.32522100 H -4.02276600 1.44358800 1.77193000 H -2.81908900 0.32569600 -0.45794500	

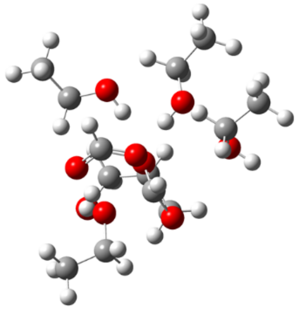
Table S3.17 activation of **2** in carbene **int.2 2** solvated by three molecules of ethanol



2 **FA** **Int.2 2** **FA⁻** **EtOH**

TS



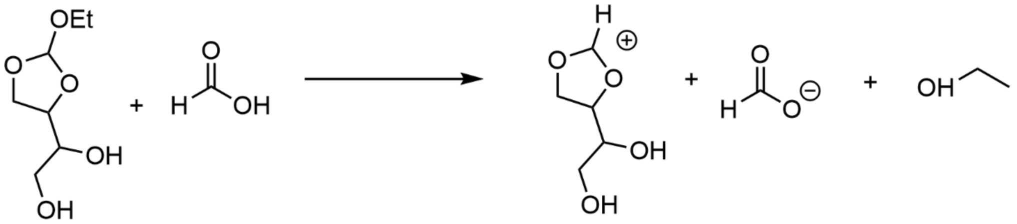


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.93230400 0.95919200 -0.63740200 H -0.20967700 0.55635300 -1.34246100 O -2.20287500 -0.46213200 -1.00854000 C -2.16222000 2.58483600 0.33851000 H -3.24673700 2.55399500 0.24136100 H -1.79742600 3.60411500 0.43998500 C -1.62998600 1.63753200 1.42283300 H -0.98227500 2.13938100 2.14050400 O -0.73426500 0.74534100 0.64279100 H -1.57789900 -1.33925700 -1.04440200 C 0.47698200 -2.21339000 -1.30283500 H 1.17775200 -3.05596900 -1.15758900 O -0.74411800 -2.45992000 -1.03584100 O 0.93489600 -1.12008400 -1.71735900 C 4.06846500 -0.86927900 -0.38596700 H 3.86381500 -1.88762400 -0.02083900 H 3.51660400 -0.17399900 0.26260100 C -0.17115900 -2.25770500 2.34201700 H -0.91509200 -2.37841600 1.54564200 H -0.66410500 -1.78364900 3.20335800 C 2.02653500 2.42948300 0.02328200 H 1.95734800 1.50795800 0.60589900 H 1.80244100 2.18286700 -1.02368000 O 1.00120800 3.28908000 0.55202900 H 1.02237900 4.12052800 0.05405100 O 0.90844500 -1.43176500 1.87857000 H 0.52480200 -0.66538900 1.42820500 O 3.63904900 -0.73237800 -1.74085700 H 2.66594600 -0.88647000 -1.76780800 O -1.59027500 2.05410300 -0.91002700 C -2.67627800 0.79914500 2.13824000 H -2.16015200 0.03141600 2.72968800 H -3.20440300 1.46050700 2.83281800	H= -1191.3427 Hartree G = -1191.4475 Hartree

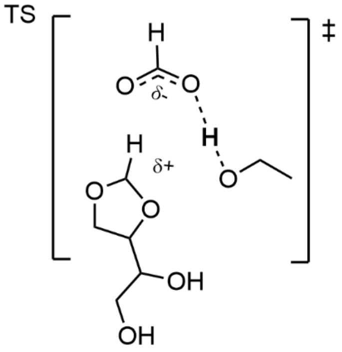
O -3.65296600 0.23124300 1.27862800 C -2.90292300 -0.31034700 -2.26533300 H -2.18253500 -0.41851400 -3.08478900 H -3.29798900 0.70843700 -2.28260800 C -4.02348400 -1.32955100 -2.37631200 H -4.55102400 -1.18758100 -3.32615300 H -3.63337600 -2.35212000 -2.35168500 H -4.74402900 -1.20811300 -1.56072400 H -3.20584100 -0.22856100 0.53962900 C 3.41761400 3.03174500 0.13926400 H 4.16459800 2.33316700 -0.25399600 H 3.49070000 3.96288800 -0.43592400 H 3.66252600 3.24858300 1.18485300 C 5.55677300 -0.58153600 -0.30214100 H 5.90587300 -0.67757200 0.73232600 H 6.12514300 -1.28371600 -0.92289000 H 5.77545300 0.43602700 -0.64545700 C 0.39290500 -3.60848400 2.73947200 H -0.40631500 -4.25432200 3.12004400 H 0.85589700 -4.10241600 1.87795600 H 1.14930100 -3.50028600 3.52515700	

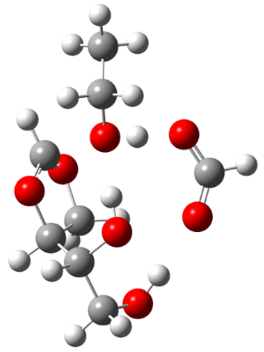
3.1.4.4 FORMATION OF CARBOCATION INTERMEDIATE FROM 3

Table S 3.18 activation of **3** in carbene **int.2 3.**



3 **FA** **Int.2 3** **FA⁻** **EtOH**



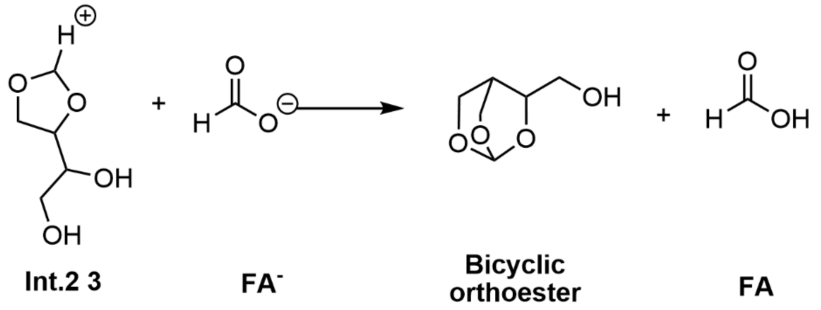


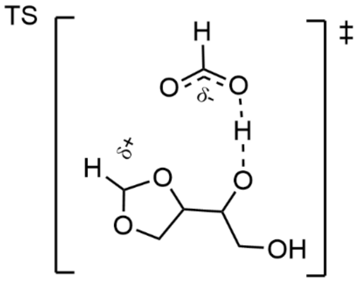
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.90296000 -1.57854700 0.86652700 H 1.86735700 -2.06400600 0.95428100 O 0.48353600 -0.80876400 1.82809300 O 1.48889700 -0.23533400 -0.45807800 C 2.70193200 -0.54157300 -1.18615400 H 2.60628800 -1.58371700 -1.50700000 H 2.71045600 0.09008600 -2.08162300 C -0.89526500 -0.39997700 1.47654900 H -0.82068300 0.61219300 1.08331700	H= -840.83512 Hartree G = -840.89795 Hartree

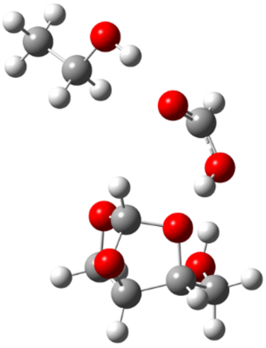
H -1.48090900 -0.43207600 2.39240000 C 3.95099200 -0.32721200 -0.34817200 H 4.83580200 -0.59024100 -0.94076800 H 4.04326700 0.72022900 -0.04072700 H 3.94273300 -0.95535200 0.55041500 C -1.32063200 -1.45826800 0.44278700 H -1.97879000 -2.21290600 0.87560700 O -0.03530800 -2.16243100 0.16906300 H 1.49052800 0.76374400 -0.10427800 C 0.51205500 2.92067500 0.29868800 H 0.72867800 3.99825400 0.45756300 O 1.54707200 2.17319600 0.27219500 O -0.68473600 2.58269400 0.17622800 C -1.89830000 -0.98879900 -0.89289100 O -1.02984100 -0.13696200 -1.62753400 C -3.21160900 -0.23115100 -0.70509700 H -3.59689300 0.01518100 -1.70478800 H -3.94676800 -0.86738500 -0.20212000 O -3.06572900 0.94208700 0.08780700 H -2.11371100 -1.89802300 -1.47414700 H -2.27555400 1.44190600 -0.20723300 H -0.09573000 -0.24465700 -1.34651500	

3.1.4.5 FORMATION OF BICYCLIC ORTHOESTERS FROM INT.2 3

Table S3.19 Formation of bicyclic orthoester from **int.2 3**.





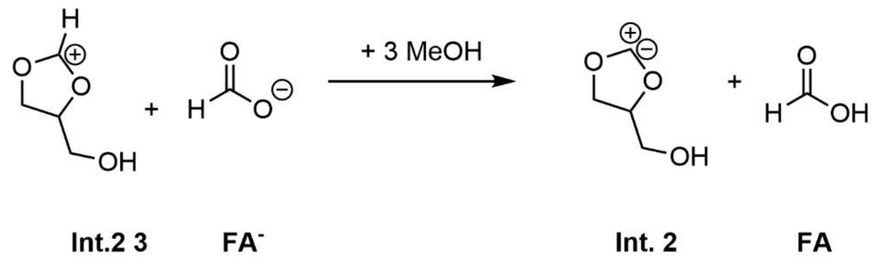


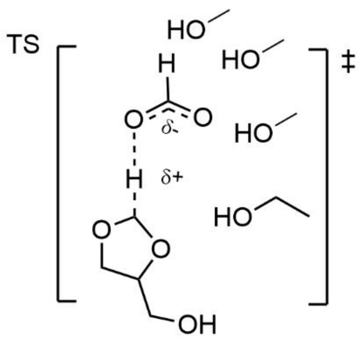
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.77783000 -1.38558200 -0.99188500 H -0.15433200 -1.40746900 -1.87729700 O -0.22011700 -1.23673100 0.18584100 O 4.08064200 0.44832800 -0.63576800 C -1.32083900 -1.45476500 1.16630800	H= -840.82291 Hartree G = -840.88931 Hartree

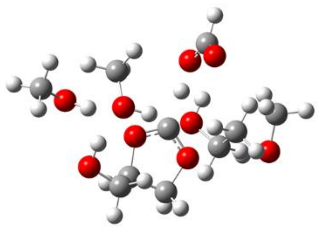
H -1.27723000 -0.65204100 1.89619100 H -1.17106100 -2.43811100 1.61477000 C -2.52518600 -1.39655700 0.23527500 H -3.39558000 -1.96368100 0.55551500 O -1.92816700 -2.03318800 -0.96534600 H 3.18499900 0.77058400 -0.89901900 C 0.99000200 1.93632700 -0.29509100 H 1.65694300 2.46321800 0.41453200 O -0.26336800 2.12956200 -0.11683000 O 1.49730100 1.22819300 -1.18818800 C -2.83927500 0.00491800 -0.33200100 O -1.69382200 0.31132400 -1.17192300 C -3.17955900 1.10685900 0.67713600 H -3.43463800 2.01236300 0.11052300 H -4.07842300 0.78492400 1.21269900 O -2.18794100 1.38259500 1.65634300 H -3.70093100 -0.09600000 -0.99879600 H -1.42439000 1.81451700 1.21242200 H -1.08673100 1.06624400 -0.78800400 C 3.90490500 -0.46826200 0.44639900 H 3.37296800 0.02194400 1.27708500 H 3.29167100 -1.32465600 0.12404800 C 5.26563500 -0.95283100 0.91485800 H 5.15324200 -1.66192500 1.74450900 H 5.79970700 -1.45851600 0.10071000 H 5.88042800 -0.11269700 1.26110300	

3.1.4.6 FORMATION OF DIOXOCARBENES FROM CARBOCATIONS SOLVATED BY THREE MOLECULES OF SOLVENT

Table S3.20 Formation of dioxocarbene **int.2** from **int.2 2** solvated by three molecules of methanol.



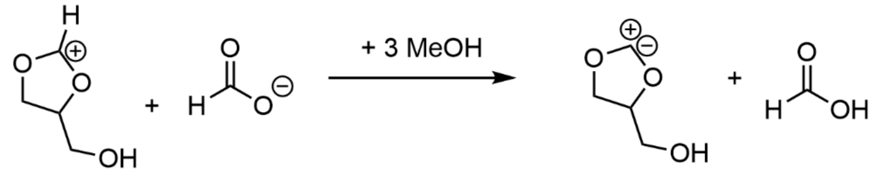




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.15352000 -0.49973000 -1.17103900 H 0.65705900 0.79515500 -1.59423700 O 0.84296800 -1.60586000 -1.15853900	H= -1073.3784 Hartree G = -1073.474 Hartree

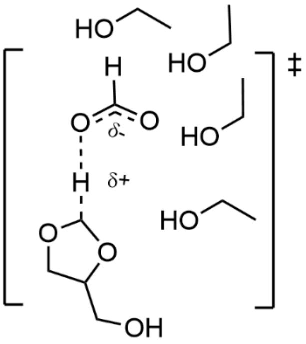
O 0.89507500 0.26067300 1.31249500 C 0.01424300 -2.75251400 -0.69997400 H 0.51601500 -3.17336700 0.17214200 C -1.32687300 -2.09751400 -0.38616800 H -2.14314000 -2.44707200 -1.01767400 O -1.08106000 -0.68377500 -0.81307500 H 1.31782100 1.03840600 0.86717800 C 1.59216000 2.63255900 -1.21826600 H 1.90815300 3.57528400 -1.69265600 O 1.81921800 2.44410300 -0.01485400 O 0.99901500 1.82074100 -2.03533900 C 1.87054700 -0.47432800 2.06805100 H 2.67002400 -0.80960500 1.39495900 H 1.34999700 -1.36287000 2.43900500 C 2.44243800 0.33445000 3.22266500 H 3.15685700 -0.27570900 3.79016300 H 2.97060800 1.22371900 2.85719000 H 1.64598700 0.65761600 3.90372600 C -1.71115100 -2.10174900 1.08660900 H -1.94307600 -3.13955300 1.35415800 H -0.85002300 -1.78485100 1.68801600 O -2.84775900 -1.30133200 1.34578600 H -2.51976800 -0.38899200 1.54544800 H -0.01483100 -3.46682000 -1.52116500 O -1.60421600 1.04552600 1.99788600 H -0.66734500 0.75316800 1.86888600 C -1.79906500 2.21920000 1.20186000 H -2.84978100 2.50539000 1.28904500 H -1.17507100 3.04582100 1.56589000 H -1.56286200 2.03422100 0.14632800 O -3.58039500 0.44985800 -1.92960600 H -2.76228600 0.25812600 -1.44184700 C -4.48869500 1.11466900 -1.04752100 H -4.15517000 2.13492100 -0.81577100 H -5.45122800 1.17057300 -1.56462900 H -4.62239900 0.55854400 -0.11063000 C 4.09627000 -0.05310900 -1.26948800 H 5.18515800 0.05066200 -1.27227900 H 3.69160900 0.46317100 -2.15033700 H 3.69968700 0.42104400 -0.36323900 O 3.81226500 -1.45541500 -1.30274600 H 2.84676300 -1.56474900 -1.27410300	

Table S3.21 Formation of dioxocarbene **int.2** from **int.2 2** solvated by three molecules of ethanol.



Int.2 3 **FA⁻** **Int. 2** **FA**

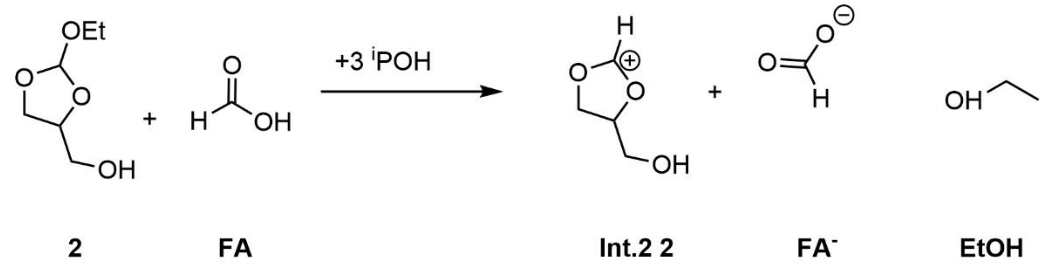
TS

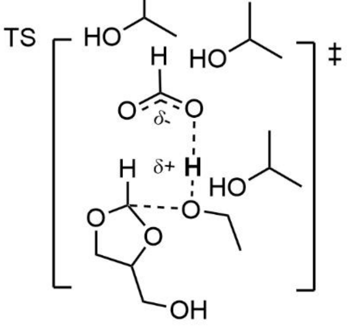


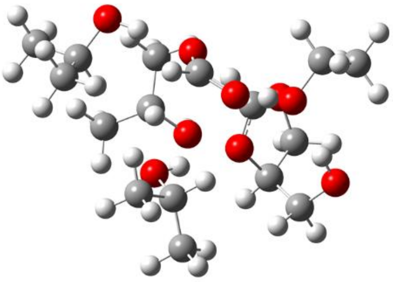
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.19063300 -0.92808000 -0.81555800 H 0.47716700 0.29645200 -1.53906300 O 1.01035500 -1.92576600 -0.64171400 O 1.01363400 0.44953800 1.35316200 C 0.35881000 -3.03403700 0.10716100 H 0.97269500 -3.22052500 0.98911400 C -1.02113800 -2.46480600 0.42175000 H -1.83843300 -3.02341600 -0.03347300 O -0.98428100 -1.16113100 -0.31200500 H 1.33434100 1.12501500 0.70300500 C 1.22953400 2.25029100 -1.66589300 H 1.35353600 3.10562300 -2.34896100 O 1.66438500 2.32048100 -0.50793400 O 0.61560000 1.24590200 -2.20706700 C 2.11018400 -0.02362000 2.15001600 H 2.85150900 -0.50129100 1.49608500 H 1.69276600 -0.79624800 2.80309200 C 2.75261800 1.08412500 2.97138600 H 3.56252800 0.67280700 3.58739400 H 3.17970300 1.85833400 2.32222800 H 2.01646000 1.55320000 3.63514400 C -1.27699900 -2.18973700 1.89727300 H -1.35453100 -3.16427900 2.39413800 H -0.41508900 -1.66318800 2.32515900 O -2.47745300 -1.47474700 2.11220100 H -2.25091200 -0.51134200 2.07340600 H 0.34954700 -3.89705800 -0.55682900 O -1.53706800 1.09641200 2.07214100 H -0.57742600 0.91257200 1.91715300 C -2.00296700 1.93140700 0.99728500 H -3.09427000 1.93341600 1.07142900 H -1.73162200 1.47798300 0.03525800 O -3.47771600 -0.59570000 -1.81942500 H -2.68396500 -0.59983300 -1.25841400 C -4.41105800 0.35575300 -1.28361900 H -3.99299600 1.37005700 -1.35032300	H= -1191.2673 Hartree G = -1191.3738 Hartree

H -4.60030400 0.13829300 -0.22296100 C 4.00450600 -0.13470300 -1.44321000 H 3.41266000 0.17098800 -2.31772900 H 3.60030900 0.38635200 -0.56616800 O 3.90551800 -1.55703000 -1.25853300 H 2.97485600 -1.76691400 -1.07147700 C -5.69970300 0.26570600 -2.07884400 H -6.42913000 0.99022600 -1.69667900 H -5.51985900 0.48571500 -3.13834100 H -6.13705400 -0.73720000 -2.00175100 C 5.46362900 0.22633100 -1.64493800 H 5.56501800 1.30802300 -1.79597200 H 6.06041600 -0.05618800 -0.76905100 H 5.87474600 -0.28336600 -2.52495200 C -1.45655400 3.34853400 1.08738300 H -0.36338000 3.35548300 1.01126600 H -1.85641300 3.95604200 0.26490100 H -1.74563700 3.81762300 2.03562000	

Table S3.22 activation of **2** in carbene **int.2 2** solvated by three molecules of isopropanol





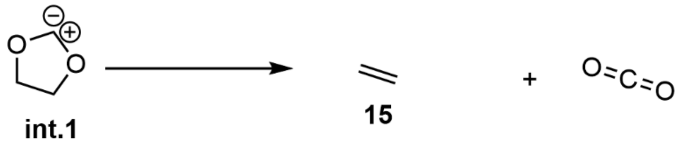


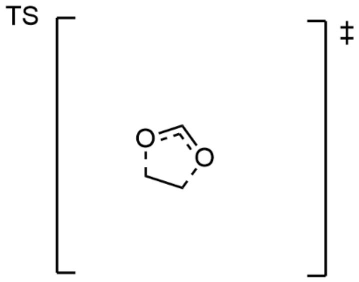
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.30144800 0.89849000 -0.58683100 H -0.48112900 0.59816700 -1.23588600 O -2.42435500 -0.54868600 -1.22848200 C -2.70251600 2.39176500 0.37298000 H -3.76917700 2.36525100 0.15480400 H -2.36379700 3.39920800 0.60309900 C -2.27787600 1.35391100 1.42037800 H -1.75691600 1.79777100 2.26758600 O -1.24288000 0.58154200 0.68640200 H -1.72832300 -1.37540200 -1.25483000 C 0.38108900 -2.05409300 -1.57122800 H 1.14700600 -2.84920900 -1.52153500	H= -1309.2425 Hartree G = -1309.3549 Hartree

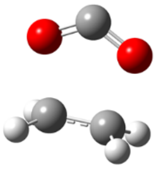
O -0.80204200 -2.41121300 -1.25777700 O 0.73424700 -0.90533500 -1.93232300 C 3.94131600 -0.34357700 -0.81831200 H 3.23454800 0.11071100 -0.10912300 C 0.20966800 -2.31192400 2.14799100 H -0.58395700 -2.48236300 1.40858700 C 1.58274600 2.52256300 0.51668500 H 1.40151100 1.44390900 0.52329900 O 0.36887600 3.08826500 1.05867600 H 0.46790400 4.05343300 1.05467000 O 0.94078000 -1.12865500 1.76630600 H 0.29509600 -0.46223100 1.48995300 O 3.39309000 -0.25500500 -2.14037400 H 2.44874700 -0.53106000 -2.09694900 O -1.98986600 1.97805100 -0.84672800 C -3.37232200 0.41077500 1.89331600 H -2.90545600 -0.40762900 2.45678700 H -4.01126500 0.97250100 2.58230600 O -4.20773300 -0.07743600 0.85446000 C -2.96219800 -0.32659200 -2.55266800 H -2.13384100 -0.31213500 -3.27069400 H -3.42871800 0.66165100 -2.54009500 C -3.97619400 -1.40226700 -2.90132200 H -4.38300500 -1.20870500 -3.90015800 H -3.51435000 -2.39486200 -2.90696000 H -4.80554100 -1.40419300 -2.18622600 H -3.64878800 -0.46537500 0.15079100 C 2.77289900 2.82937100 1.41948000 H 3.67742800 2.33954300 1.04425300 H 2.96098600 3.91015700 1.45376700 H 2.58544400 2.47601000 2.43872100 C 5.23544000 0.45845500 -0.80152800 H 5.69037000 0.43929400 0.19467900 H 5.95382700 0.03658000 -1.51513700 H 5.04941000 1.50178200 -1.07662100 C 1.18694400 -3.47658600 2.09685300 H 0.68640000 -4.40876300 2.37955300 H 1.59572200 -3.59457300 1.08844200 H 2.01925100 -3.30870900 2.79091600 C 1.80341200 2.98488500 -0.91964400 H 2.67134800 2.48052600 -1.35601500 H 0.92985100 2.76040200 -1.53970800 H 1.98255900 4.06735700 -0.95118400 C 4.16423900 -1.80114000 -0.41342900 H 4.55170600 -1.86619400 0.61033000 H 3.22669800 -2.36482500 -0.45478900 H 4.88490000 -2.27838200 -1.08858800 C -0.41593800 -2.13449400 3.52945700 H -1.08130000 -1.26419700 3.54660400 H -1.00516200 -3.01723600 3.80434500 H 0.36352500 -1.98768900 4.28666000	

3.1.4.8 FORMATION OF OLEFIN FROM THE DEOXYDEHYDRATION OF DIOXOCARBENES

Table S3.23 Formation of olefin **15** from dioxocarbene **int.1.**

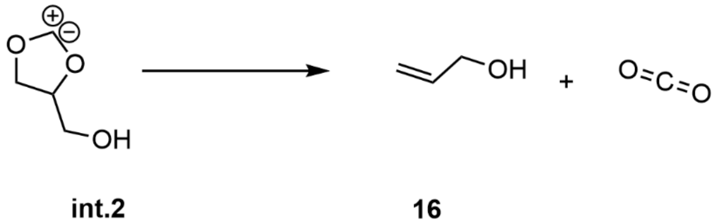


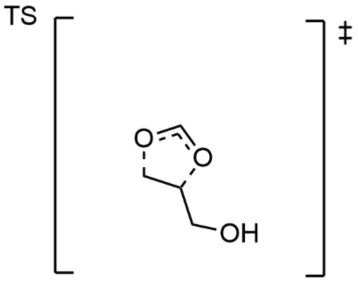


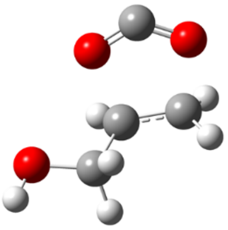


Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -1.28372000 -0.00000500 0.00000100 O -0.70542500 1.09828200 0.00022400 C 1.12483900 0.71278100 -0.00029500 C 1.12484000 -0.71277300 0.00029600 O -0.70541200 -1.09828700 -0.00022600 H 1.37248500 1.23364400 -0.91981500 H 1.37249700 -1.23363000 0.91981600 H 1.37299300 -1.23450000 -0.91858500 H 1.37297000 1.23451500 0.91858800	H= -267.03862 Hartree G = -267.07165 Hartree

Table S3.24 Formation of olefin **16** from dioxocarbene **int.2.**







Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.57547200 -1.04336400 -0.16620300 O 2.09186000 0.07324400 -0.35260800 C 0.83012400 1.32503800 0.17356100 C -0.30222300 0.52899200 0.52033500 O 0.43133000 -1.22371600 0.27097800	H= -381.54493 Hartree G = -381.58442 Hartree

H -0.52057900 0.39584800 1.57650100 H 0.79985200 1.88821600 -0.75519400 C -1.49174900 0.50093000 -0.39421400 H -1.16828800 0.33538700 -1.43105000 H -1.98028600 1.48661700 -0.34726800 O -2.39598200 -0.51665400 0.03717800 H -3.22340700 -0.41437000 -0.46366700 H 1.40530300 1.77573700 0.97541900	

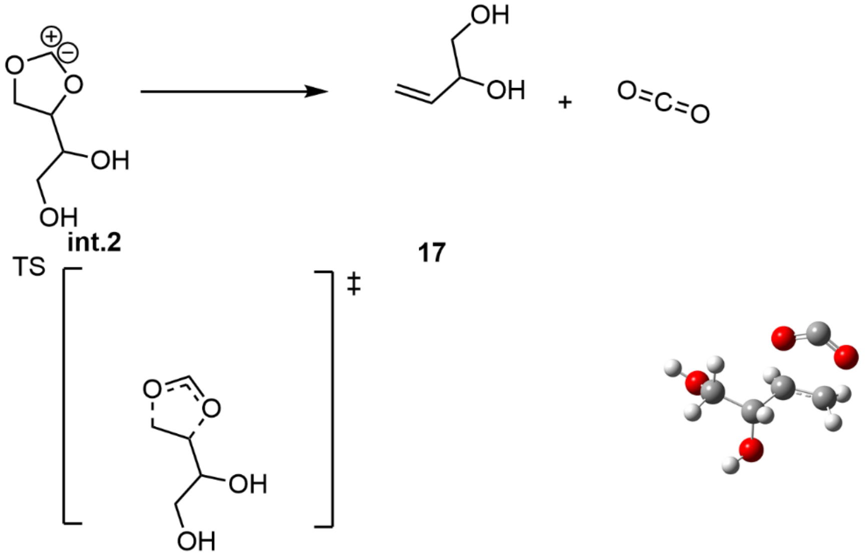
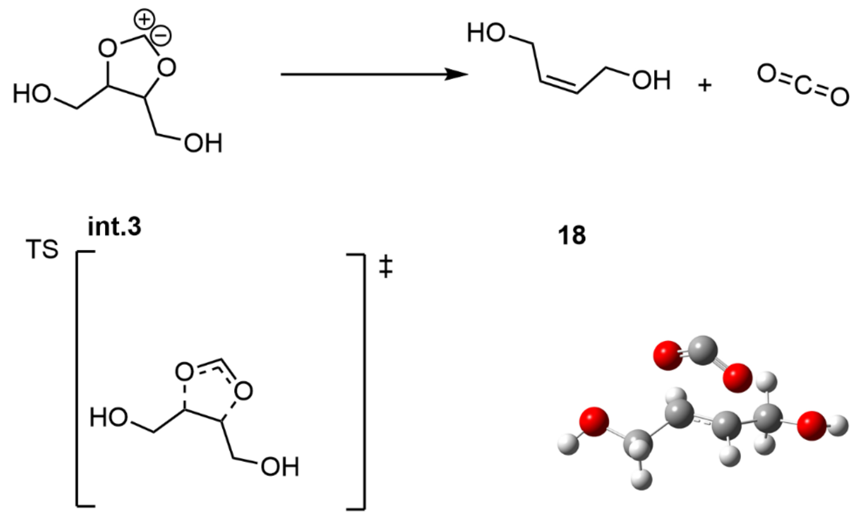
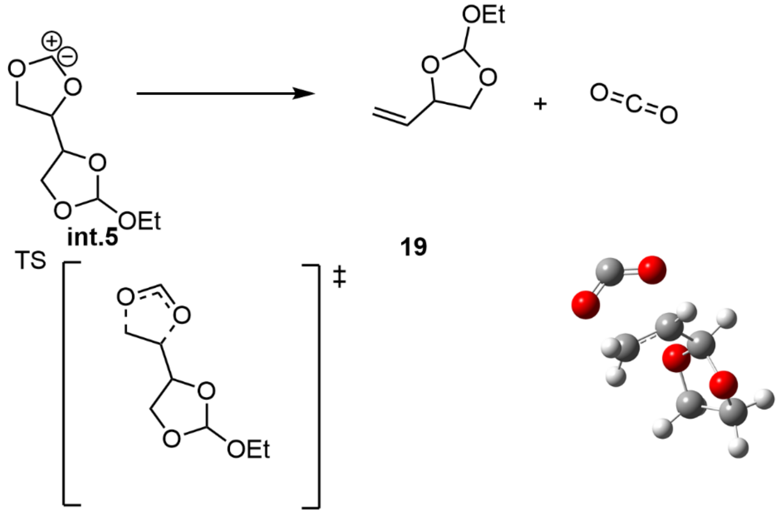
Table S3.25 Formation of olefin **17** from dioxocarbene **int.3.**	
	
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.22927300 -1.02150700 -0.30014600 O 1.05184700 -1.30617000 -0.04070800 C 0.24649800 0.32126000 0.53221800 C 1.37225000 1.19715000 0.48436900 O 2.72478200 0.11048300 -0.16950100 H 1.40899900 1.94792200 -0.29957500 H -0.06676400 -0.04230300 1.50548600 C -0.85369800 0.47841400 -0.49626900 H -0.40033600 0.58379400 -1.49272900 H 1.85400700 1.46929100 1.41783200 C -1.81852700 -0.69942100 -0.55847200 H -2.62689600 -0.45255600 -1.26320200 H -1.28495600 -1.57496700 -0.94664400 O -1.52162800 1.70421900 -0.14081200 H -2.29706900 1.80440100 -0.72286100 O -2.34964200 -0.96103900 0.74331500 H -2.88463300 -1.77090700 0.69314600	H= -496.05073 Hartree G = -496.09677 Hartree

Table S3.26 Formation of olefin **18** from dioxocarbene **int.4.**



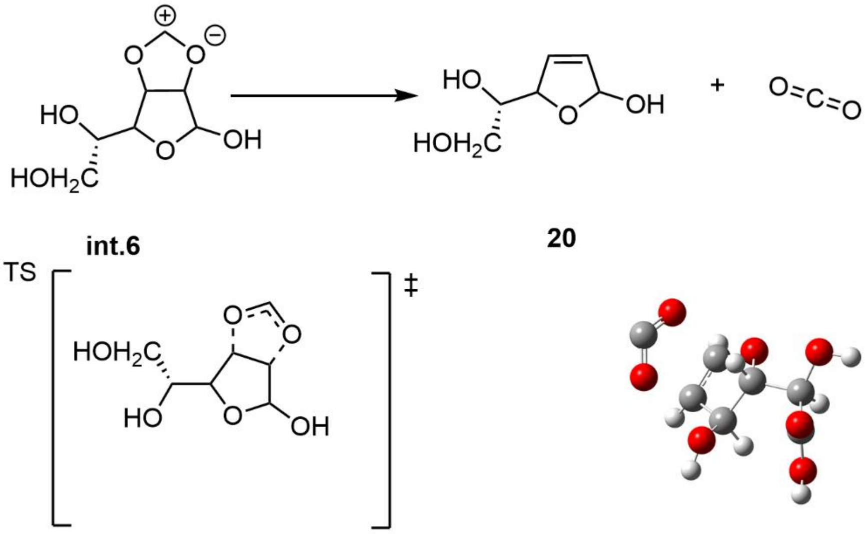
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.00000300 1.96498700 0.00000200 O 0.95531200 1.38827600 0.54326000 C 0.64890100 -0.46681300 0.29867300 C -0.64890000 -0.46681200 -0.29868100 O -0.95531600 1.38827800 -0.54325800 H -0.71017900 -0.72346900 -1.35436300 H 0.71017800 -0.72347600 1.35435400 C -1.82975100 -0.87629300 0.53163000 H -1.81848800 -0.34454300 1.49286000 H -1.74141700 -1.95384400 0.74109800 C 1.82975600 -0.87628400 -0.53163600 H 1.81850100 -0.34452200 -1.49285900 H 1.74142400 -1.95383300 -0.74111900 O -3.03142500 -0.61412800 -0.19368200 H -3.77118000 -1.00770200 0.30013700 O 3.03142300 -0.61412900 0.19369100 H 3.77118300 -1.00770000 -0.30012400	H= -496.05138 Hartree G = -496.09742 Hartree

Table S3.27 Formation of olefin **19** from dioxocarbene **int.5.**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.61747200 0.43297700 -0.58455300 O 1.88035400 -0.38439900 -1.15259000 C 0.65559500 -0.95990700 0.17497500 C 1.14377100 -0.25676000 1.31437400 O 2.53577900 0.73711600 0.61788600 H 0.56004200 0.57603000 1.69239600 H 0.87721300 -2.01975700 0.08965200 H 1.71357000 -0.81162600 2.05209400 C -0.63448800 -0.53053200 -0.48274900 C -2.79761900 -0.12541200 0.05909500 C -2.07137000 1.21366100 0.06213300 H -3.28287800 -0.32440400 -0.90605800 H -3.51537900 -0.24648700 0.87215800 H -2.54587700 1.96761600 -0.57136500 H -1.94347600 1.60681500 1.07740000 H -0.68495800 -0.89596600 -1.51820200 O -1.71974000 -1.05288800 0.26943900 O -0.77869700 0.88812300 -0.49070200	H= -534.14694 Hartree G = -534.19222 Hartree

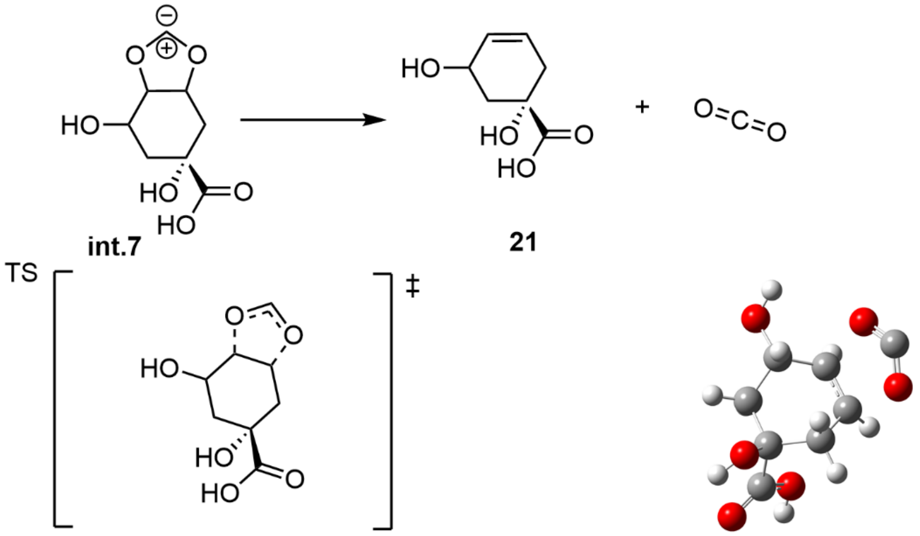
Table S3.28 Formation of olefin **20** from dioxocarbene **int.6.**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 3.16896300 -0.10940000 -1.07872900 O 3.10076000 0.99998500 -0.53878000 O 2.60332500 -1.13887600 -0.64674600 C 1.70381200 -0.69914700 0.87671800 C 0.22781300 -0.92568900 0.56882400 C -0.18285700 0.44647200 0.00664400 C 1.84740800 0.71662200 0.99752100 H 2.23565200 -1.36091300 1.54917900 H -0.28456100 -1.11997300 1.52095400 H 0.01011100 0.47363200 -1.07321800 H 2.49290700 1.24166000 1.68846400 O 0.71653200 1.38119200 0.65947500 C -1.61385900 0.90099300 0.27469600 H -1.73834500 1.06406500 1.35204300 C -2.60639800 -0.18587500 -0.16367300 O -1.80763600 2.09510100 -0.45738500	H= -797.94476 Hartree G = -797.99918 Hartree

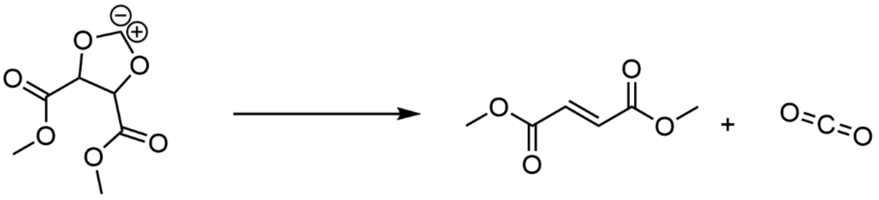
H -2.68588700 2.45777000 -0.24364500 O -3.11726300 -0.25787000 -1.26075200 O -2.86230100 -1.04356800 0.84095200 H -3.45397900 -1.75192400 0.50778000 O -0.10051800 -1.92115100 -0.37915400 H -0.10837800 -2.78667800 0.06555100	

Table S3.29 Formation of olefin **21** from dioxocarbene **int.7.**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 3.20191500 -1.11868300 0.35340300 O 2.27157700 -1.93913300 0.31745100 O 3.12424000 0.04904600 -0.07049800 C 1.37945700 0.26085100 -0.71349400 C 0.82954300 1.41268900 0.09847400 C -0.69913100 1.38458300 -0.03360800 C -1.30258500 0.05746200 0.52103600 C -0.24082000 -1.07669600 0.63591500 C 0.79675100 -1.02266000 -0.45685600 H 1.66019000 0.49745200 -1.73592000 H 1.10239400 1.29102700 1.15451800 H -1.13682800 2.21559800 0.52649900 H 0.24191800 -0.91079500 1.60425000 H 0.69078300 -1.70127700 -1.29552000 H -0.95050900 1.52284800 -1.09083800 H -0.73085000 -2.05205700 0.67618700 O 1.28519700 2.67700300 -0.37675000 H 2.23419300 2.75569700 -0.17282000 C -2.46263100 -0.35426600 -0.38437800 O -1.81027900 0.23685100 1.83878900 H -2.73929600 0.52741800 1.76164600 O -2.05581100 -0.83648500 -1.56715500 H -2.84258900 -1.04932100 -2.11353500 O -3.63297300 -0.23181600 -0.07151400	H= -762.03116 Hartree G = -762.08459 Hartree

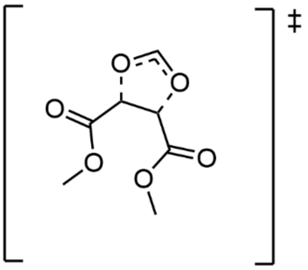
Table S3.30 Formation of olefin **22** from dioxocarbene **int.8.**

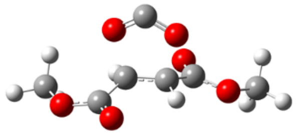


int.8

22

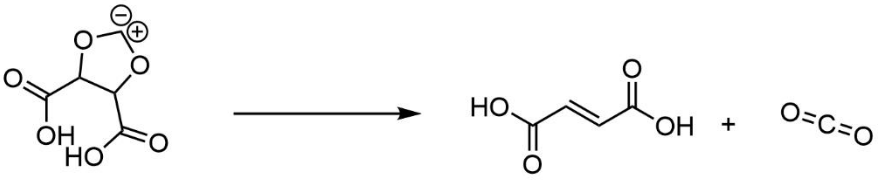
TS





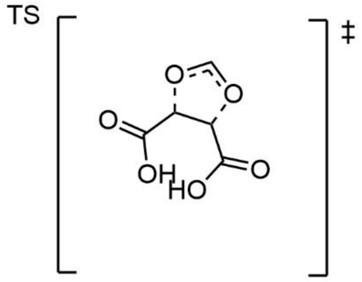
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C -0.27330400 2.22099800 -0.57190300 O -1.17767900 1.41690600 -0.87085600 C -0.71985100 -0.16066500 -0.11939600 C 0.54628400 0.16835000 0.48810000 O 0.71873200 1.88459400 0.11103700 H 0.57706100 0.22291000 1.57072300 H -0.67992900 -0.76718800 -1.01635200 C 1.78012800 -0.37079800 -0.17774000 O 2.80612700 -0.39191400 0.67356000 C -1.89375600 -0.34207400 0.80409400 O 1.83133000 -0.71417400 -1.34543600 O -3.03094700 -0.82973000 0.29794000 O -1.84605800 -0.03225000 1.98192800 C -3.15433800 -1.22054400 -1.09456700 H -2.49494900 -2.06357800 -1.31471400 H -4.19432800 -1.52712000 -1.20435300 H -2.94673100 -0.37558600 -1.75431400 C 4.07705800 -0.84602500 0.14368800 H 4.39519900 -0.19128400 -0.67115200 H 4.77148400 -0.78528000 0.98099900 H 3.98683000 -1.87577200 -0.20987600	H= -722.73119 Hartree G = -722.7865 Hartree

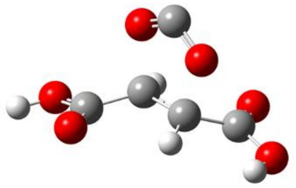
Table S3.31 Formation of olefin **23** from dioxocarbene **int.9.**



int.9

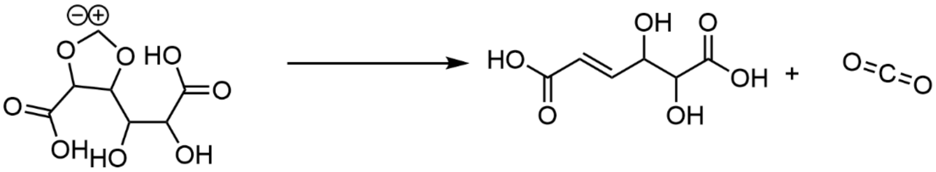
23





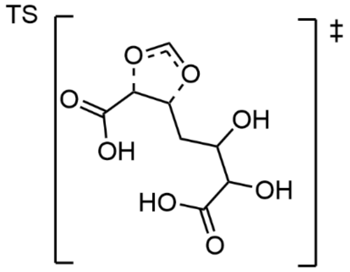
Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.02905900 2.12708500 -0.04847800 O 0.88199000 1.52966600 0.63974100 C 0.57939700 -0.21662800 0.42664300 C -0.57664800 -0.21424300 -0.43617100 O -0.83554800 1.51562800 -0.71146600 H -0.43331600 -0.53784300 -1.46140800 H 0.40999000 -0.49038600 1.46396300 C -1.88995300 -0.57580400 0.19182300 O -2.79057900 -0.93140300 -0.73572500 H -3.64225000 -1.12964800 -0.28929400 C 1.89201300 -0.62669300 -0.18491800 O 2.08344900 -0.68349400 -1.38163000 O 2.88695800 -0.89951800 0.67684900 H 2.59503000 -0.82904200 1.60904500 O -2.11785300 -0.52780300 1.38526900	H= -644.17596 Hartree G = -644.22373 Hartree

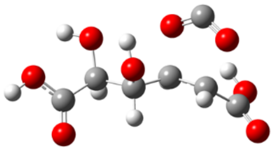
Table S3.32 Formation of olefin **24** from dioxocarbene **int.10.**



int.10

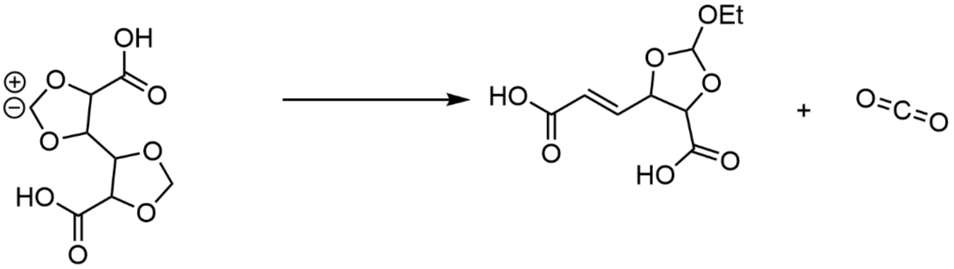
24





Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 1.70539900 2.11651500 0.30979300 O 2.48197900 1.32058300 0.85676900 C 1.78248700 -0.37497600 0.45251800 C 0.62824600 -0.01306400 -0.33538300 O 0.71663500 1.76105600 -0.36475900 H 0.67408400 -0.20298000 -1.40561000 H 1.59777000 -0.71071400 1.46725700 C -0.73380700 -0.31026400 0.28932000 C 2.98468600 -1.02747700 -0.14690000 O 3.59990400 -1.89625700 0.44084800 O 3.40112400 -0.63685200 -1.37026800 H 2.86779000 0.09466600 -1.74036700 C -1.91478700 -0.06152500 -0.66363200 H -1.69994900 -0.55371900 -1.62384700 C -3.15521800 -0.75986600 -0.10329300 O -3.18548700 -1.93950000 0.18606700 O -4.21429200 0.06007300 -0.00543600 H -4.98590900 -0.45667100 0.31240900 O -0.91667200 0.36561700 1.52173300 H -1.07944100 1.30580200 1.31667500 O -2.06888200 1.33585300 -0.82011200 H -2.93469600 1.52207000 -1.22259600 H -0.73616800 -1.37909500 0.52281400	H= -873.19034 Hartree G = -873.25044 Hartree

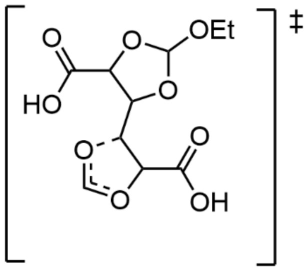
Table S3.33 Formation of olefin **25** from dioxocarbene **int.11.**

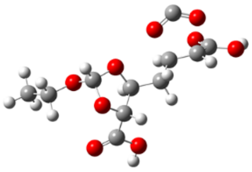


int.11

25

TS

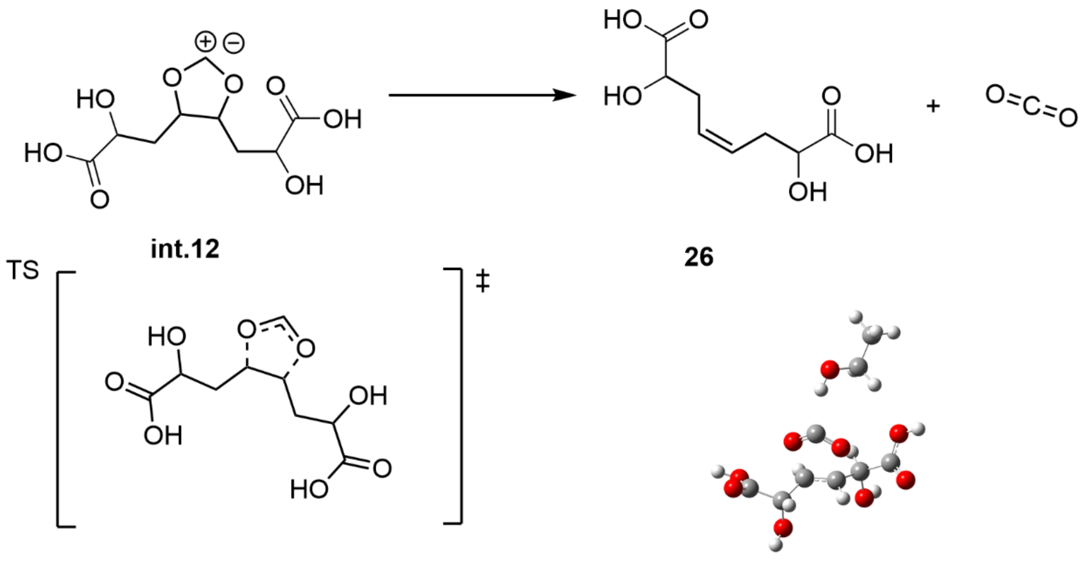




Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 2.92868200 -2.17680600 -0.63624800 O 3.89428200 -1.43958700 -0.87592100 C 3.31288200 0.26908200 -0.27925600 C 1.95328600 -0.03514600 0.09393400 O 1.86011400 -1.77063000 -0.13044100 H 1.75927600 -0.02131700 1.16385900 H 3.48755200 0.81174800 -1.20223000 C 0.84913200 0.53599800 -0.76687700	H= -1104.3917 Hartree G = -1104.4654 Hartree

H 0.96898400 0.22934900 -1.81199000 H 0.96598800 1.62698300 -0.73618200 C 4.31269900 0.46679500 0.80000600 O 5.40688900 1.11402400 0.35166400 H 6.03902800 1.20457000 1.09576200 C -0.55966700 0.22718600 -0.28783500 C -1.65750400 1.05775400 -1.02618000 H -0.63059100 0.37355800 0.79589700 H -1.25004000 1.53931300 -1.92175900 C -2.31707000 -1.11768300 -0.77504100 H -2.62433200 -1.93844200 -1.43077400 O -0.93784500 -1.12281500 -0.60683300 O -2.62765900 0.10546500 -1.43046500 O -2.91513300 -1.20928800 0.48023700 O 4.18697300 0.08467500 1.95139400 C -4.35393900 -1.27271600 0.43992700 H -4.65559600 -2.08931100 -0.23240600 H -4.74108000 -0.32979000 0.03955100 C -4.85614300 -1.51422300 1.84912900 H -5.95161500 -1.56211100 1.84670100 H -4.46981600 -2.45900800 2.24901700 H -4.54960600 -0.69990000 2.51610700 C -2.25486200 2.13528300 -0.13508500 O -3.38962200 2.17366400 0.28751000 O -1.32473800 3.07746700 0.12953700 H -1.71923200 3.75740900 0.71615700	

Table S3.34 Formation of olefin **26** from dioxocarbene **int.12.**



Coordinates of the TS (atom, X, Y, Z)	Energies
0 1 C 0.48252600 -1.15579400 -0.33041400 O -0.55506300 -1.40431900 0.29817100 C -1.54530500 0.20209900 0.29581500 C -0.62457300 1.10259700 -0.32135200 O 0.77029400 -0.04986500 -0.81027200 H -0.85095300 1.45047600 -1.32591500 H -1.66947100 0.26813700 1.37300100 H 2.21415900 -2.48109700 -0.43615600 O 3.14111800 -2.77173500 -0.32745600 C 3.90013000 -1.63518000 0.11450900	H= -1028.1684 Hartree G = -1028.2476 Hartree

C 5.32844700 -2.07758800 0.37089700 H 3.45734600 -1.22189500 1.03246100 H 3.87794700 -0.84722100 -0.65234600 H 5.36465500 -2.84991900 1.14881900 H 5.78092100 -2.48308200 -0.54234000 H 5.93229800 -1.22445500 0.70366400 C 0.12451500 2.08643400 0.55167600 H 0.37256400 1.61946300 1.51006700 C -2.76360700 -0.23790000 -0.48478700 H -2.50566300 -0.35714300 -1.54139700 C -3.32467900 -1.58038000 -0.00402700 O -3.75173900 0.78241400 -0.31126600 H -4.38955100 0.71752600 -1.04585200 O -3.57721300 -2.51088400 -0.74386700 O -3.54789200 -1.59845200 1.31969800 H -3.93857400 -2.46466800 1.56213000 O -0.74866400 3.19999300 0.73437700 H -0.42280000 3.72749300 1.48742900 C 1.41601000 2.54478300 -0.14046400 O 1.45351500 3.12547200 -1.20552100 O 2.50487400 2.24116700 0.58576900 H 3.30248600 2.54163000 0.09826400	

4 THE CATALYTIC COUPLING OF CO_2 AND GLYCIDOL TOWARD GLYCEROL CARBONATE

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[c] Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liège, Allée du Six Août 13, B-4000 Liège (Sart Tilman), Belgium
[d] Federation of Researchers in Innovative Technologies for CO_2 Transformation (FRITCO$_2$T technology platform), University of Liege, Allée de la Chimie, B6a, 4000 Liège, Belgium.
[e] WEL Research Institute, Avenue Pasteur, 6, 1300 Wavre, Belgium.

4.1 DETAILED ANALYSIS FOR THE SYNTHESIS FOR THE PREPARATION OF SELECTED CATALYSTS AND E-FACTORS

4.1.1 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 3[1]

Table S4.1 Detailed analysis for the synthesis of catalyst **3**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
3,5-Dimethylpyrazole CAS Number: 67-51-6 (Sigma-Aldrich)	40.1€/5 g	8020		8.5	1	96.13	0.8	6.55
Benzyltriethylammonium chloride CAS Number: 56-37-1 (Sigma-Aldrich)	25.9€/25 g	1036		0.42	0.05	227.78	0.1	0.10
Potassium carbonate CAS Number: 584-08-7 (Sigma-Aldrich)	23.80€/100 g	238		8.4	0.99	138.20	1.2	0.28
Potassium hydroxide CAS Number: 1310-58-3 (Sigma-Aldrich)	56.7€/1 kg	56.7		9	1.06	56.10	0.5	0.03
Methylene chloride (25 mL) CAS Number: 75-09-2 (VWR)	54.5€/500 mL	109.0	1.33	391.50	46.06	84.93	33.3	3.62

Intermediate	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
(3,5-dimethyl)pyrazolylmethane	89	204.28	1.55	6.85

Step number 2 Reagents and references	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
4,4′-Bis(diethylamino)benzophenone CAS Number: 90-93-7 (VWR)	48€/50 g	960		4.89	1	204.28	1.6	1.52
nBuLi (1.6 M in hexane) 3 mL for 4.89 mmol CAS Number: 109-72-8 (Sigma-Aldrich)	44.2€/50 mL	884		4.89	1	324.47	0.3	0.28
NH$_4$Cl (aq sat) 6g/15 mL H$_2$O 53.49 g/mol CAS Number: 12125-02-9 (Sigma-Aldrich)	89.4€/1 kg	89.4		4.89	1	64.06	0.5	0.0005
Tetrahydrofuran (THF) 70 mL CAS Number: 109-99-9 (Sigma-Aldrich)	124€/500 mL	248	0.89	0.11	0.02	53.49	62.3	15.45

Intermediate 2	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
1,1-bis(4-(diethyl(methyl)-l4-azaneyl)phenyl)-2,2-bis(3,5-dimethyl-1H-pyrazol-1-yl)ethan-1-ol	85	558.82	2.32	7.43

Step number 3 Reagents and references	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Iodomethane (2.28 g/mL) CAS Number: 74-88-4 (Sigma-Aldrich)	502€/L	220		8.4	3.5	141.94	1.19	0.26
Acetonitrile (70 mL) CAS Number: 75-05-08 (Sigma-Aldrich)	24.32€/L	30.94	0.786	1340.3		41.05	55.02	1..7

Intermediate 3	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g	
4-(1-(4-(diethyl(methyl)-l4-azaneyl)phenyl) -2,2-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1-hydroxyethyl)- N,N-diethyl-N-methylbenzenaminium	82	812.63	1.60	1.23	

Step number 4 Reagents and references	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
AlMe$_3$ (2 M) in toluene (0.66 mL for this scale) CAS Number: 75-24-1 (Sigma-Aldrich)	420€/ 1 L			1.32	1	141.94	0.2772	0.28
Acetonitrile (70 mL) CAS Number: 75-05-8 (Sigma-Aldrich)	24.32€/ 1 L	30.94	0.786	957.37	725.28	41.05	39.3	1..22

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
3	71	886.71	0.81	
Total mass of reagents (g)	For X g of **3**	Mass of used catalyst (g)	Total mass of reagents for X g of **3**	Cumulated price (€)/g **3**
195.82	0.81	0.072	17.34	17.34

		Molar mass (g/mol)	Mass (g)
Catalyst **3** n (mmol)	0.083	866.710	17.34
GD n (mmol)	1.700	74.8	0.13
CO$_2$ (35°C, 1 bar, 0.01 L)	0.39	44.01	0.02
Yield of **GLC** %	91	118.09	0.18
E factor	94.71		

4.1.2 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 20[2]

Table S4.2 Detailed analysis for the synthesis of catalyst **20**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
2,4-di tert-butyl phenol CAS Number: 96-76-4 (Sigma-Aldrich)	46.3€/500 g	92.6		40	1	96.13	0.8	6.55
Hexamethylenetetraamine CAS Number: 100-97-0 (Sigma-Aldrich)	54.3€/1 kg	54.3		3.3	0.08	227.78	0.1	0.10
Formaldehyde solution (aq) CAS Number: 50-00-0 (Sigma-Aldrich)	93.8€/1 L	93.8		14.2	0.36	138.20	1.2	0.28
Water from formaldehyde solution							0.8	0

Step number 2 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Trimethylaluminum solution hexane (2 M) CAS Number: 75-24-1 (Sigma-Aldrich)	727€/0.8 L	872.4		2.98	4	72.09	0.2	0.19
THF 20 mL CAS Number: 109-99-9 (VWR)	124€/500 mL	248	0.89	863.96	579.84	72.11	62.3	15.45

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
20	-	768.12	0.96	
Total mass of reagents (g)	For X g of **20**	Mass of used catalyst (g)	Total mass of reagents for X g of **20**	Cumulated price (€)/g **20** (g)
72.44	0.96	0.001	0.06	16.2

		Molar mass (g/mol)	Mass (g)
Catalyst **20** n (mmol)	0.001	866.710	0.06
GD n (mmol)	1	74.8	0.07
Methyl Ethyl Ketone (MEK) 1 mL 0.804 g/mL CAS Number: 78-93-3 (VWR)		72.11	0.80
CO_2 (35°C, 1 bar, 0.01 L)	17.274	44.01	0.76
Yield of **GLC** %	93	118.09	0.11
E factor	14.44		

4.1.3 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 32[3]

Table S4.3 Detailed analysis for the synthesis of catalyst **32**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Picolinaldehyde CAS Number: 1121-60-4 (VWR)	228€/500 mL	92.		4	1	96.1	0.8	6.55
Iron iodide CAS Number: 7783-86-0 (Sigma-Aldrich)	340€/10 g	54.3		3.3	0.08	227.78	0.1	0.10
3-Amino-1-propanol CAS Number: 156-87-6 (Sigma-Aldrich)	79€/500 g	93.8		14.2	0.36	138.20	1.2	0.28
1-(3-Aminopropyl)imidazole CAS Number: 5036-48-6 (Sigma-Aldrich)	165€/250 g						0.8	0
Methanol 6 mL CAS Number: 67-56-1 (VWR)	37.44€/1L	37.4	0.7913	148.18	98.79	32.04	4.7	0.18

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
32	75	855.22	0.32	
Total mass of reagents (g)	For X g of **32**	Mass of used catalyst (g)	Total mass of reagents for X g of **32**	Cumulated price (€)/g **32**
5.23	0.32	0.004	0.07	17.57

		Molar mass (g/mol)	Mass (g)
Catalyst **32** n (mmol)	0.00475	85522	0.0043
GD n (mmol)	4.75	74.8	0.35
TBD-HI	0.0475		0.01
CO_2 (50°C, 3 bar, 0.05 L)	5.58312	44.01	0.25
Yield of **GLC** %	79	118.09	0.44
E factor	0.39		

4.1.4 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 40[4]

Table S4.4 Detailed analysis for the synthesis of catalyst **40**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Merrifield resin CAS Number: 9003-70-7 (Sigma-Aldrich)	382€/100 g	3820			1		0.5	1.91
Anthranilic acid CAS Number: 118-92-3 (Sigma-Aldrich)	125€/500g	250		0.002	-	137.14	0.3	0.06
N,N-Dimethylformamide (DMF) 5mL CAS Number: 68-12-2 (VWR)	92€/500 mL	194.9	0.944	64.58	-	73.09	5.7	1.10

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
6,6',6''-(nitrilotris(methylene))tris(2,4-di-tert-butylphenol)	75	-	0.75	4.10

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Zinc chloride CAS Number: 7646-85-7 (Sigma-Aldrich)	145€/1 kg	145					0.1	0.0145
Ethanol (EtOH) 10 mL CAS Number: 64-17-5 (VWR)	32.64 €/2.5 L	13.0	0.7849	85.19		46.07	5.7	0.07

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
40	-	-	1.10	
Total mass of reagents (g)	For X g of **40**	Mass of used catalyst (g)	Total mass of reagents for X g of **40**	Cumulated price (€)/g **40**
12.18	1.10	0.05	0.55	4.18

		Molar mass (g/mol)	Mass (g)
Catalyst **40** n (mmol)	-	-	0.55
GD n (mmol)	5	74.8	0.37
TBAB	0.083	-	0.03
CO_2 (25 °C, 1 bar, 0.1 L)	4.03	44.01	0.18
Yield of **GLC** %	89	118.09	0.11
E factor	1.15		

4.1.5 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 52[5]

Table S4.5 Detailed analysis for the synthesis of catalyst **52**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Polyethylene glycol dimethyl ether 500 CAS Number: 24991-55-7 (Sigma-Aldrich)	102€/500 mL	204					1.1	0.22
Calcium iodide CAS Number: 10102-68-8 (Sigma-Aldrich)	49€/10 g	4900		3.3	0.08	227.78	0.6	2.88

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
52	-	824.54	1.65	
Total mass of reagents (g)	For X g of **52**	Mass of used catalyst (g)	Total mass of reagents for X g of **52**	Cumulated price (€)/g **52**
5.23	0.32	0.004	0.07	1.88

		Molar mass (g/mol)	Mass (g)
Catalyst **52** n (mmol)	0.00475	855.22	0.0043
GD n (mmol)	40	74.08	0.35
CaI_2	2	-	0.01
Polyethylene glycol dimethyl ether 500	2	530.65	1.06
CO_2 (25 °C, 10 bar, 0.045 L)	18.15	44.01	0.80
Yield of **GLC** %	75	118.09	3.58
E factor	0.51		

4.1.6 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 61[6]

Table S4.6 Detailed analysis for the synthesis of catalyst **70**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
3-bromopropylamine CAS Number: 5003-71-4 (Sigma-Aldrich)	178€/100 g	1780		10	1	218.92	2.2	3.90
Triphenylphosphine CAS Number: 603-35-0 (Sigma-Aldrich)	167/1 kg	167		10	1	262.29	2.6	0.44

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
Phosphorous based catalyst	82	400.3	3.28	1.51

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Polyacrylonitrile CAS Number: 25014-41-9 (Sigma-Aldrich)	240€/100 g	2400					1	2.4
Dichloroethane 6 mL	120.28€/2.5 L	48.11	1.25	75.8	-	98.96	7.5	0.4

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
61	-	-	1.32	
Total mass of reagents (g)	For X g of **61**	Mass of used catalyst (g)	Total mass of reagents for X g of **61**	Cumulated price/g **61** (g)
41.46	1.32	0.007	0.21	1.80

		Molar mass (g/mol)	Mass (g)
Catalyst **61** n (mmol)	0.025	400.3	0.21
GD n (mmol)	5	74.8	0.37
CO_2 (80 °C, 1 bar, 0.01 L)	0.34	44.01	0.01
Yield of **GLC** %	75	118.09	0.45
E factor	0.32		

4.1.7 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST BB[7]

Table S4.7 Detailed analysis for the synthesis of catalyst **BB.**

Step number 1 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Tetramethylurea CAS Number: 632-22-4 (Sigma-Aldrich)	91.7€/100 g	917		500	1	116.16	58.1	53.26
Oxalyl chloride CAS Number: 79-37-8 (Sigma-Aldrich)	154€/100 g	1540		500	1.1	126.93	69.8	107.51
Toluene 80 mL CAS Number: 108-88-3 (Sigma-Aldrich)	253€/1L	293	0.8623	748.7		92.14	69.0	20.24

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
-	-	-	-	181.01

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
tert-Butylamine CAS Number: 75-64-9 (Sigma-Aldrich)	66.10€/1L	95	0.696	550	1	73.14	40.2	3.82
Triethylamine CAS Number: 121-44-8 (Sigma-Aldrich)	160€/2L	110	0.7276	1	101.19	101.19	0.1	0.01
Acetonitrile 300 mL	24.32€/L	30.94	0.786	5744.2	41.05	41.05	424.44	13.13

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
BB	82	171.29	70.23	
Total mass of reagents (g)	For X g of **BB**	Mass of used catalyst (g)	Total mass of reagents for X g of **BB**	Cumulated price (€)/g **BB**
661.64	70.24	0.0031	0.029	1.80

		Molar mass (g/mol)	Mass (g)
Catalyst **BB** n (mmol)	0.018	171.29	0.003
GD n (mmol)	1.8	74.8	0.13
CO_2 (1 equiv)	1.8	44.01	0.08
MEK CAS Number: 78-93-3 (VWR)			0.71
Yield of **GLC** %	78	118.09	0.17
E factor	4.56		

4.1.8 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 69[8]

Table S4.8 Detailed analysis for the synthesis of catalyst **69**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/G)
4-tert-butylphenol CAS Number: 98-54-4 (Sigma-Aldrich)	980€/kg	98		50	1	15035	7.5	0.74
N,N-dimethylethylenediamine CAS Number: 110-70-3 (Sigma-Aldrich)	3500€/kg	3500		25	0.5	88.15	2.2	7.70
36% aqueous formaldehyde CAS Number: 50-00-0 (Sigma-Aldrich)	93.8€/L	86.61	1.083	50	1	30.03	4.1	0.36
Methanol 25 mL CAS Number: 67-56-1 (Sigma-Aldrich)	37.44€/L	37.04	0.7913	617.43	12.35	32.04	19.8	0.74

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product/g
2,2'-(((2-(dimethylamino)ethyl)azanediyl)bis(methylene))bis(4-tert-butyl)-phenol)	89	412.31	9.20	181.01

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/G)
Methyl iodide CAS Number: 74-88-4 (Sigma-Aldrich)	502€/1 L	220.18	2.28	12	4.0	141.94	1.7	0.37
Acetonitrile 25 mL	24.32€/ 1 L	30.94	0.786	478.68	9.57	41.05	19.65	0.01

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
69	89	426.33	1.50	
Total mass of reagents (g)	For X g of **69**	Mass of used catalyst (g)	Total mass of reagents for X g of **69**	Cumulated price (€)/g **69**
56.16	1.50	0.085	3.19	1.69

		Molar mass (g/mol)	Mass (g)
Catalyst **69** n (mmol)	0.2	426.33	3.16
GD n (mmol)	10	74.8	0.74
CO_2 (1 equiv)	4.03	44.01	0.18
Yield of **GLC** %	99	118.09	1.17
E factor	2.52		

4.1.9 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 74[9]

Table S4.9 Detailed analysis for the synthesis of catalyst **74**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
N,N-dimethyl-butylamine CAS Number: 85409-22-9 (Sigma-Aldrich)	274€/1 L	380.0	0.721	100	1	101.19	10.1	3.85
1-Iodobutane CAS Number: 92-62-8 (TCI)	222€/250 mL	548.2	1.62	100	1	184.02	18.4	10.09
EtOH 100 mL CAS Number: 64-17-5 (Sigma-Aldrich)	32.64€/2.5 L	13.0	0.7849	1703.71	17.04	46.07	4.7	0.06

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
N-allyl-N,N-dimethyl-N-butylammonium iodide	100	-	26.92	0.52

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
9-borabicyclo[3.3.1]nonane (9-BBN) (21 mL) CAS Number: 74-88-4 (Sigma-Aldrich)	371€/800 mL	331.67	0.894	11	1.1	122.01	18.8	6.23
9-BBN (THF 0.5 M)								

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
74	100	533.46	3.92	
Total mass of reagents (g)	For X g of **74**	Mass of used catalyst (g)	Total mass of reagents for X g of **74**	Cumulated price (€)/g **74**
52.23	3.92	0.0028	0.04	2.11

		Molar mass (g/mol)	Mass (g)
Catalyst **74** n (mmol)	0.005	533.46	2.88
GD n (mmol)	27	74.8	2
CO_2 (80 °C, 20 bar, 0.05 L)	34.05	44.01	1.50
Yield of **GLC** %	99	118.09	3.03
E factor	1.11		

4.1.10 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 98-99[10]

Table S4.10 Detailed analysis for the synthesis of catalyst **98-99**.

Step number 1 Reagents and references	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
1-Vinylimidazole CAS Number: 1072-63-5 (Sigma-Aldrich)	37.6€/100 g	376.0		10	1	94.11	0.9	0.35
Chloroacetic acid CAS Number: 79-11-8 (Sigma-Aldrich)	183€/2 kg	91.5		10	1	167.98	1.0	0.09
EtOH 5 mL	32.64€/2.5L	13.0	0.7849	85.19	8.52	46.07	3.9	0.09

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
CEImCl **98**	95	182.22	10.39	1.58

Step number 2 Reagents and references	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€)
CEImCl **98**				10	1	189	1.89	0.49
1,8-diazabicyclo[5.4.0]undec-7-ene CAS Number: 229-713-7 (Sigma-Aldrich)	1.580€/2.5kg	632		15	1.1	152.24	2.3	1.44
Ethanol								

Intermediate 2	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€) /g
CCIm **99**	-	152	1.52	1.30

Step number 3 Reagents and references	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
CEImCl **98**				10	1	189.20	1.52	
CCIm **99**				10	1	152.24	1.3	
Divinyl benzene CAS Number: 1321-74-0 (Sigma-Aldrich)	225€/1L	245.0	0.918	10	1.00	130.19	1.3	0.32
2,2′-Azobis(2-methylpropionitrile) AIBN CAS Number: 78-67-1 (Sigma-Aldrich)	194€/100g	1940.0		1	0.10	164.21	0.1	0.16
EtOH 15 mL	32.64€/2.5L	13.0	0.7849	85.19	8.52	46.07	11.8	0.15
Ethyl acetate 15 mL CAS Number: 141-78-6 (Sigma-Aldrich)	65.76€/2.5L	29.2	0.902	153.56	15.36	88.11	13.5	0.39

		Molar mass (g/mol)	Mass (g)
Catalyst **99-98** n (mmol)	0.003	-	0.43
GD n (mmol)	15	74.8	1.11
CO_2 (80 °C, 20 bar, 0.05 L)	17.03	44.01	0.75
Yield of **GLC** %	86	118.09	1.52
E factor	0.50		

4.1.11 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 101[11]

Table S4.11 Detailed analysis for the synthesis of catalyst **101**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Imidazole CAS Number: 288-32-4 (Sigma-Aldrich)	827€/1 kg	827.0		60	1.00	68.08	4.1	3.37
Potassium Hydroxide	87.4/1 kg	87.4		90	1.5	56.11	5.0	0.44
Potassium Carbonate	74.3€/1 kg	74.3		60	1.00	138.21	8.3	0.62
Tetra-n-butylammonium bromide (TBAB) CAS Number: 1643-19-2 (Sigma-Aldrich)	160€/250 g	640.0		1.30	0.02	322.37	0.4	0.42
Dichloromethane 45 mL	152€/2.5 L	45.8	1.325	702.0	11.70	84.93	59.625	2.7
Ethyl 4-bromobutyrate CAS Number: 2969-81-5 (Sigma-Aldrich)	189€/520 g	756		60.0	1.00	195.05	11.7	8.8

Intermediate 1	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product/g
1-ethoxycarbonyl propyl imidazole	95	182.22	10.39	1.58

Step number 2 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Hydrobromic acid 47% CAS Number: 10035-10-6 (Sigma-Aldrich)	314€/1 L	210.7	1.49	20	1.33	80.91	2.7	34.48
Toluene 30 mL	253€/1 L	293	0.8623	280.8	18.72	92.14	25.09	7.59
Highly cross-linked PS-Cl (Merrifield resin) CAS Number: 9003-70-7 (Sigma-Aldrich)	382€/100 g	3820					4.0	15.2

Intermediate 2	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	Price product (€)/g
1-ethoxycar- bonyl propyl imidazole bromide	-	262.1	7.93	7.23

Step number 3 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€)
1,1,3,3-tetramethylguanidine CAS Number: 80-70-6 (Sigma-Aldrich)	168€/500 mL	366.01	0.918	15	1	115.18	1.7	0.63
MeOH 30 mL	37.44€/1 L	37.4	0.7913	740.92	12.35	32.04	23.7	0.89

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product	
101	-	-	9.66	
Total mass of reagents (g)	For X g of 101	Mass of used catalyst (g)	Total mass of reagents for X g of **101**	Cumulated price (€)/g **101**
144.49	9.66	0.31	4.77	1.78

		Molar mass (g/mol)	Mass (g)
Catalyst **101** n (mmol)	0.15	-	4.77
GD n (mmol)	5	74.8	0.37
CO$_2$ (80 °C, 1 bar, 0.05 L)	17.03	44.01	0.07
Yield of **GLC** %	82	118.09	0.48
E factor	9.78		

4.1.12 DETAILED ANALYSIS FOR THE SYNTHESIS OF CATALYST 11112

Table S4.12 Detailed analysis for the synthesis of catalyst **111**.

Step number 1 **Reagents and references**	Price	€/kg	Density (g/ mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
4,4'-bipyridine CAS Number: 553-26-4 (Sigma-Aldrich)	58.20€/10 g	5820		2	1	156.18	0.3	1.82
Acetonitrile 10 mL	24.32€/1 L	30.94	0.786	191.5			7.86	0.24
Propargyl bromide CAS Number: 106-96-7 (TCI)	305€/500 g	610		5	2.5	118.96	0.7	0.45

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product (g)	
111	-	-	9.66	
Total mass of reagents (g)	For X g of **111**	Mass of used catalyst (g)	Total mass of reagents for X g of **111**	Cumulated price (€)/g **111**
8.92	0.85	0.04	0.42	2.94

		Molar mass (g/mol)	Mass (g)
Catalyst **111** n (mmol) Degree of functionalization 0.47 mmol per g	0.15	-	0.42
GD n (mmol)	2	74.8	0.15
CO$_2$ (30 °C, 1 bar, 0.025 L)	0.99	44.01	0.04
Yield of **GLC** %	85	118.09	0.20
E factor	2.04		

4.1.13 DETAILED ANALYSIS FOR THE SYNTHESIS OF GLC THROUGH THE REACTION OF GLYCEROL WITH DIMETHYL CARBONATE [13-15]

Table S4.13 Detailed analysis for the synthesis of **GLC**.

Catalyst Ce-S	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
$Ce(NO_3)_3\,6H_2O$ CAS Number: 10294-41-4 (Sigma-Aldrich)	243€/500 g	486		0.0024		434.22	1.042	0.51
Urea CAS Number: 57-13-6 (Sigma-Aldrich)	48.6€/1 kg	48.6	0.786	0.008			0.384	0.02
Mass of product (g)	1.43							
Price (€)/ g of product	0.37							

Dimethyl carbonate (DMC)	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
CO_2 (150 °C, 50 bar, 0.1 L)	58.20€/10 g	486		142	1.42	44.01	6.25	3.04
2-cyanopyridine CAS Number: 100-70-9 (Sigma-Aldrich)	24.32/1 L	270		50	0.5		5.2	1.40
Methanol (MeOH) 6 mL	305€/500 g	37.4	0.7913	100	1	32.04	3.2	0.12
Catalyst Ce-S		370					0.1	0.037

Final product	Isolated yield (%)	Molar mass (g/mol)	Mass of product	
Dimethyl carbonate (**DMC**)	-	90.08	5.49	
Total mass of reagents (g)	For X g of DMC	Mass of used catalyst (g)	Total mass of reagents for X g of **DMC**	Cumulated price (€)/g **DMC**
14.75	5.49	0.203	0.544	1.27

		Molar mass (g/mol)	Mass (g) – price (€) per mass used (g)
Catalyst TBAB n (mmol)	0.035	322.37	0.0112 – 0.009
GLY n (mmol)	1	7492.08	0.09 – 0.017
DMC (2.25 equiv.)	2.3	90.08	0.20 – 0.182
Yield of **GLC** %	95	118.09	0.11
E factor	4.77	Total price	1.86

4.1.14 DETAILED ANALYSIS FOR THE END-TO-END SYNTHESIS OF GLC STARTING FROM GLY[7]

Table S4.14 Detailed analysis for the end-to-end synthesis of **GLC** starting from **GLY**.

Glycidol	Price	€/kg	Density (g/mL) 25 °C	n (mmol)	Equiv.	Molar mass (g/mol)	Mass (g)	Price per mass (€/g)
Glycerol CAS Number: 56-81-5 (Sigma-Aldrich)	234€/1 L	185.71	1.26	0.11	1	92.08	0.0105	0.00197
HCl 35% CAS Number: 7647-01-0 (VWR)	14.48€/1 L	12.27	1.18	0.68	6	36.45	0.025	0.00031
Sodium hydroxide 4M CAS Number: 1310-73-2 (Sigma-Aldrich)	20.6€/1 kg	20.6		1.03	9	40.00	0.041	0.00085
Acetic acid CAS Number: 64-19-7 (Sigma-Aldrich)	64.5€/1 L	61.43	1.05	0.03	0.3	60.05	0.002	0.00013

		Molar mass (g/mol)	Mass (g) – price (€) per mass used (g)
Catalyst **BB** n (mmol)	0.018	171.28	0.003 – 0.02
GD n (mmol	1.8	74.08	0.13 – 0.07
MEK (0.805 g/l) CAS Number: 78-93-3 (VWR)			0.71 – 0.04
CO_2 (1 equiv.)	1.8	44.01	0.71 – 0.04
Yield of **GLC** %	78	118.09	0.17
E factor	13.73	Total price	0.76

4.2 Guidelines on penalty points and color code implemented for the calculation of Ecoscores16

For the efficiency assessment of the catalyzed coupling of GD and CO_2, we are introducing a scoring system inspired by the EcoScale.[16] All reactions start with a score of 100 and penalty points are withdrawn based on categories of impactful factors (yield, catalytic loading, use of additive, use of solvents, pressure of CO_2, technical specificities of the setup, process temperature, reaction time). These scores are indicative only, and do not take the scale (or potential for scalability into account).

Table S4.15 Guidelines of penalty points and color caode for Ecoscores **16**

additive (mol%)	none	≤ 1 mol%	1 ≤ 5 mol%	> 5 mol%
color code	🟩	🟨	🟥	⬛
penalty	0	1	4	8
solvent	none	low bp (<100°C)	high bp (>100°C)	
color code	🟩	🟨	🟥	
penalty	0	1	4	
T (°C)	25°C	25°C≤ 50°C	50°C≤ 85°C	> 85°C
color code	🟩	🟨	🟥	⬛
penalty	0	1	2	3
P CO_2 (bar)	1 bar	1 ≤ 5 bar	5 ≤ 10 bar	> 10 bar
color code	🟩	🟨	🟥	⬛
penalty	0	1	2	3
t (h)	0 ≤ 4h	4 ≤ 10h	10h ≤ 24h	> 24h
color code	🟩	🟨	🟥	⬛
penalty	0	2	4	8
yield (%)	≥ 90%	90 ≥ 70%	70 ≥ 50%	< 50%
color code	🟩	🟨	🟥	⬛
penalty	(100-yield)/2			

4.2.1 Details for the Ecoscores presented in Figure 3

Table S4.16 Catalyst **3.**

Catalyst **3**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	5	1
Additive	/	0
Solvent	Neat	0
Technical setup	batch	0
Temperature	35	1
Time	24	4
Pressure	1	0
Sum		10.5
Score		89.5

Table S4.17 Catalyst **5.**

Catalyst **5**		
Parameter	Value	Penalty
Yield	92	4
Catalytic loading	0.5	0
Additive	/	0
Solvent	Neat	0
Technical setup	Autoclave	3
Temperature	85	2
Time	18	4
Pressure	10	2
Sum		15
Score		85

Table S4.18 Catalyst **7.**

Catalyst **7**		
Parameter	Value	Penalty
Yield	89	5.5
Catalytic loading	0.5	0
Additive	0.5	1
Solvent	Neat	0
Technical setup	Autoclave	3
Temperature	50	1
Time	8	2
Pressure	10	2
Sum		14.5
Score		85.5

Table S4.19 Catalyst **9.**

Catalyst **9**		
Parameter	Value	Penalty
Yield	74	13
Catalytic loading	5	1
Additive	5	4
Solvent	Neat	0
Technical setup	batch	0
Temperature	25	0
Time	24	4
Pressure	1	0
Sum		22
Score		78

Table S4.20 Catalyst **11.**

Catalyst **11**		
Parameter	Value	Penalty
Yield	63	18.5
Catalytic loading	5	1
Additive	5	4
Solvent	Neat	0
Technical setup	batch	0
Temperature	50	1
Time	24	4
Pressure	1	0
Sum		28.5
Score		71.5

4.2.2 Details for the Ecoscores presented in Figure 4

Table S4.21 Catalyst **12.**

Catalyst **12**		
Parameter	Value	Penalty
Yield	80	10
Catalytic loading	0.1	0
Additive	0.2	1
Solvent	/	0
Technical setup	Autoclave	3
Temperature	50	1
Time	24	4
Pressure	10	2
Sum		21
Score		79

Table S4.22 Catalyst **14.**

Catalyst **14**		
Parameter	Value	Penalty
Yield	53	23.5
Catalytic loading	0.25	0
Additive	/	0
Solvent	Neat	0
Technical setup	batch	0
Temperature	50	1
Time	24	4
Pressure	1	0
Sum		28.5
Score		71.5

Table S4.23 Catalyst **17.**

Catalyst **17**		
Parameter	Value	Penalty
Yield	87	6.5
Catalytic loading	1.7	1
Additive	1.7	2
Solvent	Neat	0
Safety	1 bar	0
Technical setup	batch	0
Temperature	80	2
Time	24	4
Pressure	1	0
Sum		15.5
Score		84.5

4.2.3 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 6

Table S4.24 Catalyst **20.**

Catalyst **20**		
Parameter	Value	Penalty
Yield	93	3.5
Catalytic loading	1	0
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	75	2
Time	2	0
Pressure	10	2
Sum		11.5
Score		88.5

4.2.4 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 8

Table S4.25 Catalyst **30.**

Catalyst **30**		
Parameter	Value	Penalty
Conversion	78	11
Catalytic loading	0.025	0
Additive	0.4	1
Solvent	/	1
Technical setup	Autoclave	3
Temperature	100	3
Time	22	4
Pressure	20	3
Sum		26
Score		74

Table S4.26 Catalyst **31.**

Catalyst **31**		
Parameter	Value	Penalty
Conversion	72	14
Catalytic loading	0.5	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	80	2
Time	20	4
Pressure	5	1
Sum		24
Score		76

Table S4.27 Catalyst **32.**

Catalyst **32**		
Parameter	Value	Penalty
Conversion	79	10.5
Catalytic loading	0.1	0
Additive	1	1
Solvent	/	0
Technical setup	Autoclave	3
Temperature	50	1
Time	20	4
Pressure	3	1
Sum		20.5
Score		79.5

Table S4.28 Catalyst **33.**

Catalyst **33**		
Parameter	Value	Penalty
Conversion	78	11
Catalytic loading	0.25	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	80	2
Time	15	4
Pressure	3	1
Sum		21
Score		79

4.2.5 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 10

Table S4.29 Catalyst **40.**

Catalyst **40**		
Parameter	Value	Penalty
Yield	89	5.5
Catalytic loading	8.3	4
Additive	5	4
Solvent	/	0
Technical setup	Batch	0
Temperature	25	0
Time	5	2
Pressure	1	0
Sum		15.5
Score		84.5

Table S4.30 Catalyst **41.**

Catalyst **41**		
Parameter	Value	Penalty
Conversion	95	2.5
Catalytic loading	0.3	0
Additive	/	0
Solvent	/	0
Technical setup	batch	0
Temperature	100	3
Time	16	4
Pressure	1	0
Sum		9.5
Score		90.5

Table S4.31 Catalyst **42.**

Catalyst **42**		
Parameter	Value	Penalty
Conversion	90	5
Catalytic loading	$7.5*10^{-5}$	0
Additive	0.08	1
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	7	2
Pressure	10	2
Sum		16
Score		84

Table S4.32 Catalyst **45**

Catalyst **45**		
Parameter	Value	Penalty
Conversion	94	3
Catalytic loading	0.2	0
Additive	0.2	1
Solvent	/	0
Technical setup	Autoclave	3
Temperature	50	1
Time	12	4
Pressure	10	2
Sum		14
Score		86

Table S4.33 Catalyst **46.**

Catalyst **46**		
Parameter	Value	Penalty
Conversion	99	0.5
Catalytic loading	1.25	4
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	60	2
Time	12	4
Pressure	15	3
Sum		16.5
Score		83.5

4.2.6 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 11

Table S4.34. Catalyst **47.**

Catalyst **47**		
Parameter	Value	Penalty
Yield	98	1
Catalytic loading	5	1
Additive	5	4
Solvent	/	0
Technical setup	Batch	0
Temperature	60	2
Time	18	4
Pressure	1	0
Sum		12
Score		88

Table S4.35. Catalyst **48.**

Catalyst **48**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	0.0284	0
Additive	2.12	4
Solvent	/	0
Technical setup	Batch	0
Temperature	25	0
Time	10	4
Pressure	1	0
Sum		8.5
Score		91.5

4.2.7 Details for the Ecoscores presented in Figure 12

Table S4.36 Catalyst **49.**

Catalyst **49**		
Parameter	Value	Penalty
Yield	37	31.5
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	23	0
Time	24	4
Pressure	1	0
Sum		36.5
Score		63.5

Table S4.37 Catalyst **50.**

Catalyst **50**		
Parameter	Value	Penalty
Yield	83	8.5
Catalytic loading	10	4
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	50	1
Time	6	2
Pressure	1	0
Sum		15.5
Score		84.5

Table S4.38 Catalyst **51.**

Catalyst **51**		
Parameter	Value	Penalty
Yield	42	29
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	23	0
Time	24	4
Pressure	1	0
Sum		34
Score		66

Table S4.39 Catalyst **52**.

Catalyst **52**		
Parameter	Value	Penalty
Yield	**75**	**12.5**
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	25	0
Time	24	4
Pressure	10	2
Sum		22.5
Score		77.5

Table S4.40 Catalyst **53.**

Catalyst **53**		
Parameter	Value	Penalty
Yield	87	6.5
Catalytic loading	1	0
Additive	5	4
Solvent	/	0
Technical setup	Batch	0
Temperature	25	0
Time	6	2
Pressure	1	0
Sum		12.5
Score		87.5

4.2.8 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 13

Table S4.41 Catalyst **54.**

Catalyst **54**		
Parameter	Value	Penalty
Yield	56	22
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		33
Score		67

Table S4.42 Catalyst **57.**

Catalyst **57**		
Parameter	Value	Penalty
Yield	82	9
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	23	0
Time	48	8
Pressure	10	2
Sum		23
Score		77

Table S4.43 Catalyst **60.**

Catalyst **60**		
Parameter	Value	Penalty
Yield	58	21
Catalytic loading	1	0
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	45	1
Time	6	2
Pressure	10	2
Sum		26
Score		74

Table S4.44 Catalyst **61.**

Catalyst **61**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	0.5	0
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	80	2
Time	24	4
Pressure	1	0
Sum		6.5
Score		93.5

4.2.9 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 15

Table S4.45 Catalyst **DMAP.**

Catalyst **DMAP**		
Parameter	Value	Penalty
Yield	90	5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		17
Score		83

Table S4.46 Catalyst **TEA.**

Catalyst **TEA**		
Parameter	Value	Penalty
Yield	78	11
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		23
Score		77

Table S4.47 Catalyst **TMG.**

Catalyst **TMG**		
Parameter	Value	Penalty
Yield	95	2.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		14.5
Score		85.5

Table S4.48 Catalyst **DBU.**

Catalyst **DBU**		
Parameter	Value	Penalty
Yield	95	2.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		14.5
Score		85.5

Table S4.49 Catalyst **TBD.**

Catalyst **TBD**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		16.5
Score		83.5

Table S4.50. Catalyst **MTBD.**

Catalyst **MTBD**		
Parameter	Value	Penalty
Yield	90	5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	Autoclave	3
Temperature	45	1
Time	18	4
Pressure	10	2
Sum		17
Score		83

Table S4.51 Catalyst **PS-TBD.**

Catalyst **PS-TBD**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	2900	8
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	70	2
Time	0.5	0
Pressure	13	3
Sum		14.5
Score		85.5

4.2.10 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 16

Table S4.52 Catalyst **TMG.**

Catalyst **TMG**		
Parameter	Value	Penalty
Yield	52	24
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		31
Score		69

Table S4.53 Catalyst **DBU.**

Catalyst **DBU**		
Parameter	Value	Penalty
Yield	86	7
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		14
Score		86

Table S4.54 Catalyst **TBD.**

Catalyst **TBD**		
Parameter	Value	Penalty
Yield	86	7
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		14
Score		86

Table S4.55 Catalyst **BB.**

Catalyst **BB**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		11.5
Score		88.5

Table S4.56 Catalyst **P1-t-Oct.**

Catalyst **P1-t-Oct**		
Parameter	Value	Penalty
Yield	79	10.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		17.5
Score		82.5

Table S4.57 Catalyst **VB.**

Catalyst **VB**		
Parameter	Value	Penalty
Yield	81	9.5
Catalytic loading	5	1
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		16.5
Score		83.5

Table S4.58 Catalyst **BB** (pilot scale).

Catalyst **BB** (pilot scale)		
Parameter	Value	Penalty
Yield	78	11
Catalytic loading	1	0
Additive	/	0
Solvent	MEK	1
Technical setup	CF	0
Temperature	140	3
Time	0.03	0
Pressure	10	2
Sum		17
Score		83

4.2.11 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 17

Table S4.59 Catalyst **63.**

Catalyst **63**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	1	0
Additive	2	4
Solvent	/	0
Technical setup	Batch	0
Temperature	70	2
Time	24	4
Pressure	1	0
Sum		10.5
Score		89.5

Table S4.60 Catalyst **DBU HI.**

Catalyst **DBU HI**		
Parameter	Value	Penalty
Yield	65	17.5
Catalytic loading	10	4
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	70	2
Time	4	0
Pressure	1	0
Sum		23.5
Score		76.5

4.2.12 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 18

Table S4.61 Catalyst **65**

Catalyst **65**		
Parameter	Value	Penalty
Yield	96	2
Catalytic loading	2	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	25	0
Time	6	2
Pressure	10	2
Sum		10
Score		90

Table S4.62 Catalyst **70**

Catalyst **70**		
Parameter	Value	Penalty
Yield	80	10
Catalytic loading	1	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	80	2
Time	18	4
Pressure	5	1
Sum		20
Score		80

Table S4.63 Catalyst **CVI/BINOL**

Catalyst **CVI/BINOL**		
Parameter	Value	Penalty
Yield	61	19.5
Catalytic loading	2	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	50	1
Time	24	4
Pressure	50	3
Sum		31.5
Score		68.5

4.2.13 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 19

Table S4.64 Catalyst **71**

Catalyst **71**		
Parameter	Value	Penalty
Yield	70	15
Catalytic loading	1	0
Additive	1	1
Solvent	/	0
Technical setup	Batch	0
Temperature	80	2
Time	24	4
Pressure	1	0
Sum		22
Score		78

4.2.14 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 20

Table S4.65 Catalyst **74**

Catalyst **74**		
Parameter	Value	Penalty
Yield	95	2.5
Catalytic loading	0.02	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	120	3
Time	8	2
Pressure	20	3
Sum		13.5
Score		86.5

4.2.15 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 22

Table S4.66 TBAX +HBD GD

TBAX +HBD GD		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	5	1
Additive	GD	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	60	2
Time	3	0
Pressure	10	2
Sum		8.5
Score		91.5

Table S4.67 TBAX +HBD 77

TBAX +HBD 77		
Parameter	Value	Penalty
Yield	85	7.5
Catalytic loading	4	1
Additive	2	4
Solvent	/	0
Technical setup	Batch	0
Temperature	25	0
Time	24	4
Pressure	1	0
Sum		16.5
Score		83.5

Table S4.68 TBAX +RB

TBAX +RB		
Parameter	Value	Penalty
Yield	64	18
Catalytic loading	5	1
Additive	5	4
Solvent	/	0
Technical setup	Batch	0
Temperature	100	3
Time	12	4
Pressure	1	0
Sum		34
Score		70

4.2.16 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 23

Table S4.69 Catalyst **78**

Catalyst **78**		
Parameter	Value	Penalty
Yield	90	5
Catalytic loading	2	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	60	2
Time	24	4
Pressure	1	0
Sum		15
Score		85

Table S4.70 Catalyst **79**

Catalyst **79**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	80	2
Time	24	4
Pressure	5	1
Sum		15.5
Score		84.5

4.2.17 Details for the Ecoscores presented in Figure 24

Table S4.71 Catalyst **81**

Catalyst **81**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	3	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	120	3
Time	9	2
Pressure	26	3
Sum		16.5
Score		83.5

Table S4.72 Catalyst **82**

Catalyst **82**		
Parameter	Value	Penalty
Yield	45	27.5
Catalytic loading	0.4	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	16	4
Pressure	5	1
Sum		38.5
Score		61.5

Table S4.73 Catalyst **83**

Catalyst **83**		
Parameter	Value	Penalty
Yield	94	3
Catalytic loading	6.75	4
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	70	2
Time	2	0
Pressure	1	0
Sum		9
Score		91

Table S4.74 Catalyst **84**

Catalyst **84**		
Parameter	Value	Penalty
Yield	27	36.5
Catalytic loading	1.87	2
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	50	1
Time	3	0
Pressure	25	3
Sum		45.5
Score		54.5

4.2.18 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 26

Table S4.75 Catalyst **86**

Catalyst **86**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	0.75	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	80	2
Time	1	0
Pressure	10	2
Sum		7.5
Score		92.5

Table S4.76 Catalyst **87**

Catalyst **87**		
Parameter	Value	Penalty
Yield	92	4
Catalytic loading	5	1
Additive	/	0
Solvent	DMSO	4
Technical setup	Batch	0
Temperature	90	3
Time	8	2
Pressure	1	0
Sum		14
Score		86

Table S4.77 Catalyst **88**

Catalyst **88**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	27	8
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	90	3
Time	0.5	0
Pressure	6	2
Sum		16.5
Score		83.5

4.2.19 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 28

Table S4.78 Catalyst **90**

Catalyst **90**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	27	8
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	40	1
Time	72	8
Pressure	1	0
Sum		17.5
Score		82.5

Table S4.79 Catalyst **91**

Catalyst **91**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	0.2	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	130	3
Time	10	2
Pressure	10	2
Sum		10.5
Score		89.5

Table S4.80 Catalyst **94**

Catalyst **94**		
Parameter	Value	Penalty
Yield	88	6
Catalytic loading	4.54	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	1	0
Pressure	10	2
Sum		15
Score		85

Table S4.81 Catalyst **96**

Catalyst **96**		
Parameter	Value	Penalty
Yield	96	2
Catalytic loading	5.4	4
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	90	3
Time	2	0
Pressure	5	1
Sum		13
Score		87

4.2.20 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 30

Table S4.82 Catalyst **98**/**99**.

Catalyst 98/99		
Parameter	Value	Penalty
Yield	95	2.5
Catalytic loading	4.5	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	90	3
Time	1	0
Pressure	10	2
Sum		11.5
Score		88.5

Table S4.83 Catalyst **100**

Catalyst **100**		
Parameter	Value	Penalty
Yield	92	4
Catalytic loading	1.6	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	110	3
Time	8	2
Pressure	10	2
Sum		15
Score		85

4.2.21 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 31

Table S4.84 Catalyst **101**

Catalyst **101**		
Parameter	Value	Penalty
Yield	82	9
Catalytic loading	3	1
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	80	2
Time	4	0
Pressure	1	0
Sum		12
Score		88

Table S4.85 Catalyst **102**

Catalyst **102**		
Parameter	Value	Penalty
Yield	48	26
Catalytic loading	5	1
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	60	2
Time	7	2
Pressure	1	0
Sum		31
Score		69

Table S4.86 Catalyst **103**

Catalyst **103**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	25	8
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	30	1
Time	24	4
Pressure	1	0
Sum		17.5
Score		82.5

Table S4.87 Catalyst **104**

Catalyst **104**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	4.54	1
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	4	0
Pressure	10	2
Sum		9.5
Score		90.5

4.2.22 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 33

Table S4.88 Catalyst **108**

Catalyst **108**		
Parameter	Value	Penalty
Yield	92	4
Catalytic loading	0.3	0
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	5	2
Pressure	10	2
Sum		14
Score		86

Table S4.89 Catalyst **110**

Catalyst **110**		
Parameter	Value	Penalty
Yield	98	1
Catalytic loading	6.75	4
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	100	3
Time	4	0
Pressure	20	3
Sum		14
Score		86

Table S4.90 Catalyst **111**

Catalyst **111**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	27.02	8
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	30	1
Time	72	8
Pressure	1	0
Sum		21.5
Score		87.5

Table S4.91 Catalyst **113**

Catalyst **113**		
Parameter	Value	Penalty
Yield	99	0.5
Catalytic loading	52.63	8
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	60	2
Time	48	8
Pressure	1	0
Sum		18.5
Score		81.5

4.2.23 DETAILS FOR THE ECOSCORES PRESENTED IN FIGURE 35

Table S4.92 Catalyst **117**

Catalyst **117**		
Parameter	Value	Penalty
Yield	58	21
Catalytic loading	15	8
Additive	/	0
Solvent	/	0
Technical setup	Batch	0
Temperature	50	1
Time	6	2
Pressure	1	0
Sum		32
Score		68

Table S4.93 Catalyst **118**

Catalyst **118**		
Parameter	Value	Penalty
Yield	97	1.5
Catalytic loading	7.19	4
Additive	/	0
Solvent	/	0
Technical setup	Autoclave	3
Temperature	120	3
Time	3	0
Pressure	30	3
Sum		14.5
Score		85.5

Table S4.94 Catalyst **119**

Catalyst **119**		
Parameter	Value	Penalty
Yield	91	4.5
Catalytic loading	4.2	4
Additive	1	1
Solvent	/	0
Technical setup	Batch	0
Temperature	130	3
Time	5	2
Pressure	1	0
Sum		14.5
Score		85.5

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5 INTENSIFIED CONTINUOUS FLOW PROCESS FOR THE SCALABLE PRODUCTION OF BIO-BASED GLYCEROL CARBONATE

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5.1 GENERAL INFORMATION

Conversions and yields for the hydrochlorination and the dechlorination reactions were determined by Gas Chromatography (GC) coupled to Flame Ionization Detection (GC-FID). The GC-FID is equipped with a 14% cyanopropylphenyl / 86% dimethyl polysiloxane (0.25 mm ID x 0.25 µm x 30 m) column while the program of temperature consisted in a plateau at 30 °C hold 4 min, a 5 °C min^{-1} ramp to 35 °C hold 1 min and a 12.5 °C min^{-1} ramp to 220 °C hold 2 min. Selectivity was calculated as the ratio between the yield and the conversion. GC quantification was performed using 1-butanol as internal standard, as well as calibrations curves with commercial references of 3-chloropropane-1,2-diol (**3-MCH**), propane-1,2,3-triol (**1**), 2-chloropropane-1,3-diol (**2-MCH**), 1,3-dichloropropan-2-ol (**1,3-DCH**) and 2,3-dichloropropan-1-ol (**1,2-DCH**).

Conversions and yields for the carbonation reaction were determined by ^{1}H NMR spectroscopy conducted on a high field Bruker Avance spectrometer 400 MHz in CD_3CN. The chemical shifts were reported in ppm relative to the solvent residual peak. 1,3,5-trimethylbenzene or octamethylcyclotetrasiloxane was used as internal standard. Preparation of the samples consisted in the prior weighing of the internal standard (6-8 mg), its further solvation in 600 CD_3CN and the final addition of 100 µl of reactional crude. Commercial references of 2,3-epoxy-1-propanol (**2**), 4-(hydroxymethyl)-1,3-dioxolan-2-one (**3**), propane-1,2,3-triol (**1**) and methyl ethyl ketone (MEK) were used to perform peaks assignment on a ^{1}H NMR spectrum obtained from a typical reactional crude. Given that all signals arising from the ^{1}H spectrum were identified and assigned, a mass balance could be calculated for the determination of both the conversion as well and yields of all products. For each set of process parameters, three aliquots of the reactor effluent were subsequently collected over a 1 min. Yields and conversions reflect the average values of the triplicate and standard deviation (SD) is provided.

5.2 REAGENTS AND SOLVENTS

The reagents and solvents are purchased from commercial sources; these compounds are used without purification (Table S5.1).

Table S5.1 Chemicals and suppliers.

Solvents	Purity (%)	CAS number	Supplier
Ethanol (absolute)	>99%	64-17-5	VWR
Ethyl acetate	>99.5%	141-78-6	VWR
Methyl ethyl ketone	>99%	78-93-3	VWR
D3-acetonitrile	>99.8%	2206-26-0	Eurisotop
Petroleum spirit 40-60 °C	/	8032-32-4	VWR
Chemicals	Purity (%)	CAS number	Supplier
1,2,3-Propanetriol (**1**)	99%	56-81-5	ABCR
Hydrochloric acid 36 wt.-%	/	7647-01-0	Merck
2-Chloropropane-1,3-diol	≥97%	497-04-1	Carbosynth Ltd.
3-Chloropropane-1,2-diol	99%	96-24-2	Acros Organics
1,3-Dichloropropan-2-ol	99%	96-23-1	Acros Organics
2,3-Dichlorpropan-1-ol	≥98%	616-23-9	TCI
2,3-Epoxy-1-propanol (**2**)	96%	556-52-5	Acros Organics
2-(Chloromethyl)oxirane	99%	106-89-8	Acros Organics
Acetic Acid	99%	64-19-7	VWR
Sodium Hydroxide	98.5%	1310-73-2	Acros Organics
4-(Hydroxymethyl)-1,3-dioxolan-2-one (**3**)	>90%	931-40-8	Sigma-Aldrich
1,8-Diazabicyclo[5.4.0]undec-7-ene (**DBU**)	>99%	6674-22-2	Merck/Sigma Aldrich
2,8,9-Trimethyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (**VB**)	/	120666-13-9	Merck/Sigma Aldrich
1,1,3,3-Tetramethylguanidine (**TMG**)	99%	80-70-6	Merck/Sigma Aldrich
2-tert-Butyl-1,1,3,3-tetramethylguanidine (**BB**)	≥97%	29166-72-1	Merck/Sigma Aldrich
tert-Octyliminotris(dimethylamino) phosphorane (**P_1-*t*-Oct**)	≥97%	161118-69-0	Merck/Sigma Aldrich
1,5,7-Triazabicyclo[4.4.0]dec-5-ene (**TBD**)	98%	5807-14-7	Merck/Sigma Aldrich
Octamethylcyclotetrasiloxane	98%	556-67-2	Merck/Sigma Aldrich

5.3 EXPERIMENTAL SETUPS ASSEMBLY

5.3.1 MICROFLUIDIC SETUPS AND PARTS

All microfluidic setups were assembled with commercially available components (see details in Table S5.2).

5.3.1.1 PUMPS AND MASS FLOW CONTROLLERS

Chemyx Fusion 6000® High Force syringe pumps equipped with stainless steel syringes (6 or 20 mL) with Dupont™ Kalrez® Spectrum™ AS-568 O-rings (0.549 x 0.103") or Asia syringe pumps (Syrris) using Asia Blue Syringes (1 mL / 2.5 mL) equipped with an internal sensor of pressure were used to carry out the liquid feeds. Gaseous CO_2 was handled with a Bronkhorst EL FLOW Prestige mass flow controller (flow rate: 0-250 mL_N min, maximum pressure: 35 bar, $\Delta p = 10$ bar).

5.3.1.2 MICROFLUIDIC PROTOTYPE (PFA COIL REACTORS)

Coil reactors, collections and feed lines were constructed with high purity PFA tubing (1.58 mm outer diameter and 762 µm of internal diameter).

5.3.1.3 CONNECTORS, FERRULES AND MIXERS

Unions, arrowhead and static mixers, PEEK connectors and ferrules were purchased from IDEX/Upchurch; details can be found in Table S5.2.

5.3.1.4 CHECK VALVES

Check valves (with PEEK check valve holders) were inserted on feed lines downstream the pumps/MFC and were purchased from IDEX/Upchurch Scientific.

5.3.1.5 BACK PRESSURE REGULATORS

A dome-type BPR (BPR-10 from Zaiput Flow Technologies) was inserted downstream the microfluidic prototype. Cracking pressure setpoints were regulated with compressed nitrogen gas (AirLiquide).

5.3.1.6 THERMOREGULATORY DEVICES

Thermoregulation of PFA coil reactors was performed with a Heidolph™ MR Hei-Tec® equipped with a Pt-1000 temperature sensor.

5.3.2 SETUP PARTS AND VENDORS

Continuous flow parts and vendors are gathered in Table S5.2.

Table S5.2 Connectors, ferrules, and unions (outer diameter = o.d.)

Part	Details	Vendor	Reference
Connectors	One-Piece Fingertight, PEEK, 10-32 Coned, for 1/16” o.d.	IDEX/Upchurch Scientific	F-120X
	Super Flangeless Nuts, natural PEEK 1/4-28 thread for 1/16” o.d. tubing	IDEX/Upchurch Scientific	P-255X
	Super Flangeless Ferrule Tefzel (ETFE) and SS ring 1/4-28 thread for 1/16” o.d. tubing	IDEX/Upchurch Scientific	P-259X
Mixers	T-mixer, natural PEEK 1/4-28 thread for 1/16" o.d. tubing, 0.02" through hole	IDEX/Upchurch Scientific	P-712
	High Pressure Static Mixing Tee (arrowhead), PEEK, 10-32 Coned thread for 1/16" o.d. tubing, 0.02" through hole, embedded with a UHMWPE Frit	IDEX/Upchurch Scientific	U-466
Tubing	High-purity PFA tubing, 1.58 mm outer diameter, 762 µm internal diameter	VICI (Valco Ins. Co. Inc.)	JR-T-4002-M25
	High-purity 1/8” and 1/4” PFA tubing, including appropriate PFA connections	Swagelok	PFA-T2-030-100 PFA-T4-047-100
Check-valve	Check-valve inline cartridge 1.5 psi	IDEX/ Upchurch Scientific	CV-3001
Dome-type BPR	Dome-type BPR, metal-free, with adjustable set point	Zaiput Flow Techn.	BPR-10

5.3.3 MESOFLUIDIC SETUPS AND PARTS

5.3.3.1 PUMPS

A Teledyne ISCO 500D dual syringe pump system was used to continuously handle the liquid feeds.

5.3.3.2 MASS FLOW CONTROLLER

Gaseous CO_2 was handled with a Bronkhorst EL FLOW Prestige mass flow controller (flow rate: 0-250 mL_N min^{-1}, maximum pressure: 35 bar, $\Delta p = 10$ bar).

5.3.3.3 MESOFLUIDIC REACTORS

Scalability trials relied on commercial mesofluidic glass reactors (Corning® Advanced-Flow Reactors™). Intermediate scalability trials were carried out with a Corning® AFR™ G1/LF skid equipped with 5 glass fluidic modules connected in series (2.7 mL internal volume each, 13.5 mL of total internal volume). Pilot scale trials were carried out with a Corning® AFR™ G1 Reactor equipped with 7 glass fluidic modules connected in series (8 mL internal volume each, 56 mL of internal volume). All fluidic modules were equipped with standard Swagelok connectors and PFA tubing (1/4”).

5.3.3.4 BACK-PRESSURE REGULATOR

A dome-type BPR (Zaiput Flow Technologies – BPR-1000) was inserted downstream the mesofluidic setups to set the system pressure (connected to a compressed nitrogen tank).

5.3.3.5 THERMOREGULATORY DEVICE

The fluidic modules were thermoregulated at working temperature with a LAUDA Integral XT 280 thermostat (LAUDA Therm 180 silicone oil).

5.4 DETAILED CONTINUOUS FLOW SETUPS AT MICROSCALE AND MESOSCALE

5.4.1 MICROSCALE SETUP FOR THE HYDROCHLORINATION AND DECHLORINATION OF 1

Microfluidic reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 508 or 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a PEEK high-pressure static mixing assembly. The liquid feeds were handled with high force Chemyx Fusion 6000 syringe pumps equipped with Stainless Steel syringes and check valves on each inlet (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type backpressure regulator (BPR-10, Zaiput Flow Technologies) set at the working pressure with a cylinder of compressed air. Thermoregulation of the reactor was performed with a Heidolph MR Hei-TEC® equipped with a Pt-1000 temperature sensor. A dome-type BPR (Zaiput Flow Technologies – BPR-1000) was utilized to set the system pressure (connected to a compressed nitrogen tank).

5.4.1.1 HYDROCHLORINATION SETUP

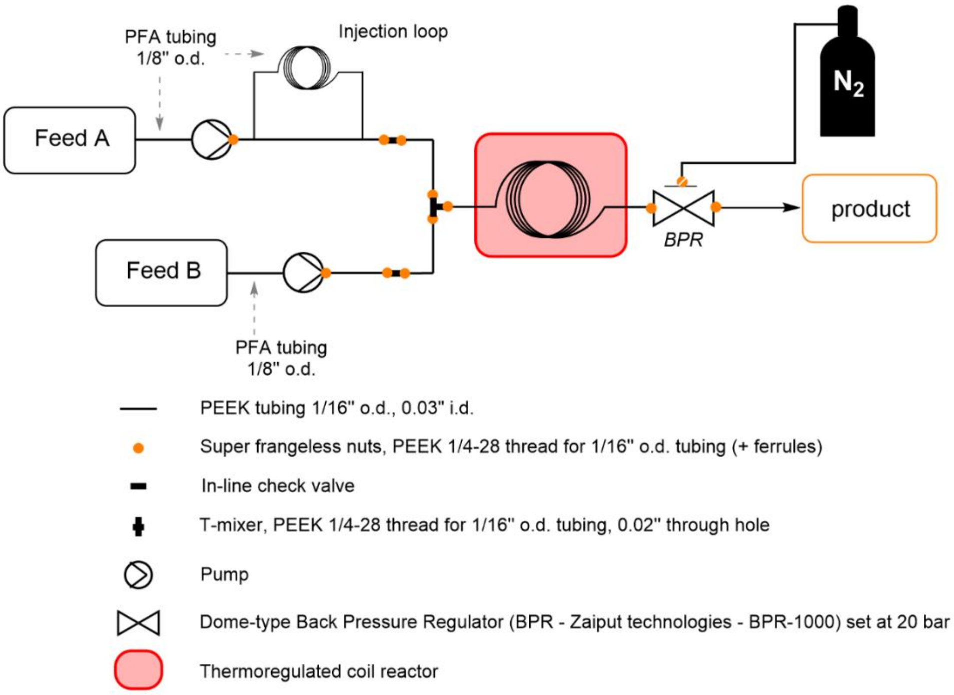


Figure S.5.1 The setup for the hydrochlorination of **1.**

5.4.1.2 Dechlorination setup

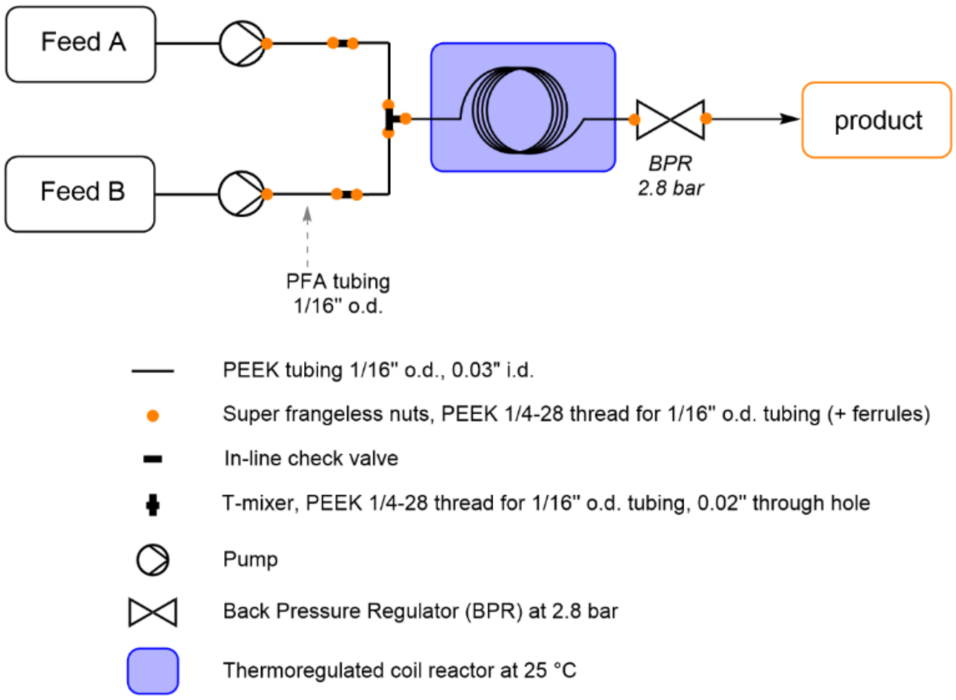


Figure S5.2 The setup for the dechlorination toward glycidol (**2**) and epichlorohydrin**.**

5.4.1.3 Concatenation of the hydrochlorination and dechlorination reactions

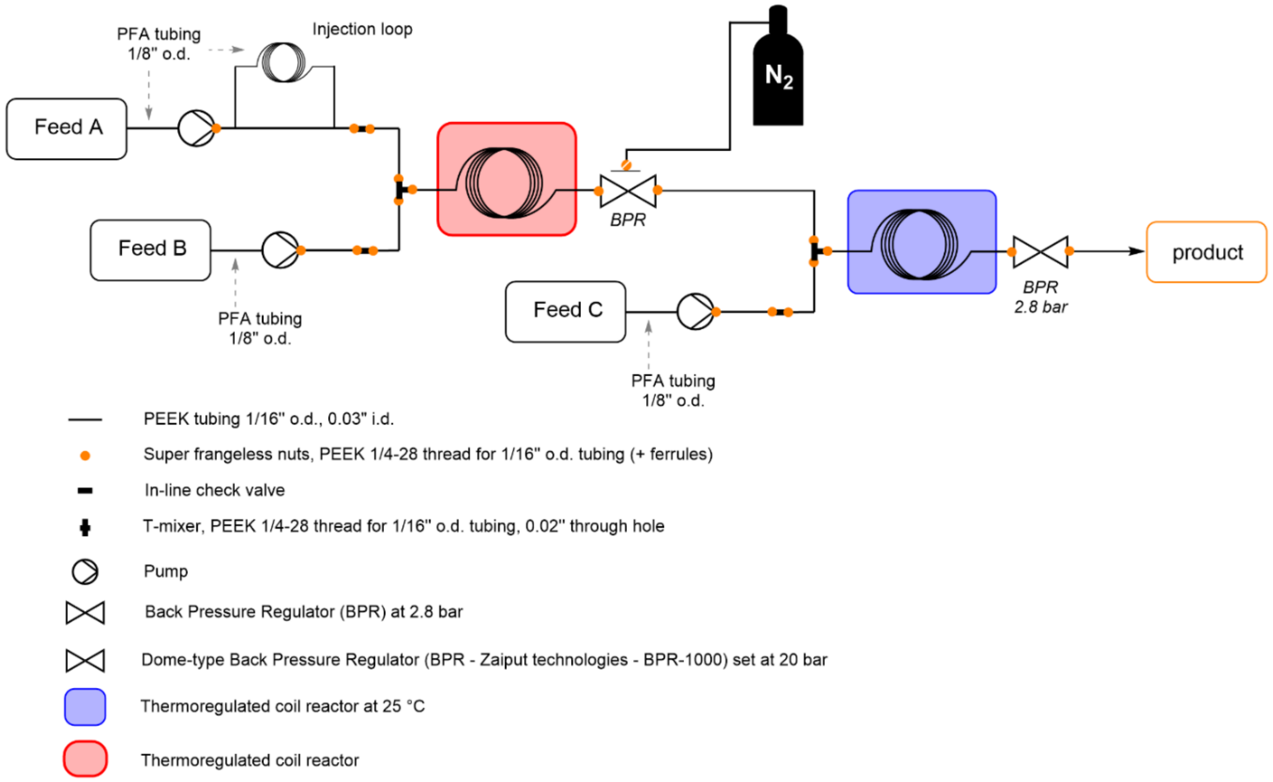


Figure S5.3 Concatenated setup for the hydrochlorination and subsequent dechlorination toward glycidol (**2**) and epichlorohydrin.

5.4.2 HOMOGENEOUS CARBONATION OF GLYCIDOL (2) AT MICROSCALE

Microfluidic reactors consisted in modular coil assemblies constructed with high purity PFA capillaries (1.58 mm of outer diameter and 762 µm of internal diameter) equipped with Super Flangeless nuts and ferrules (IDEX/Upchurch Scientific), as well as a High-Pressure Static Mixing Tee (arrowhead). The liquid feed was handled with a Syrris Asia Syringe Pump and the gaseous feed was regulated with a Bronkhorst EL FLOW Prestige mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). The downstream pressure was regulated with a dome-type backpressure regulator (BPR-10 Zaiput Flow Technologies). A digital pressure gauge (0-34.47 bar) was added upstream of the backpressure regulator to monitor the stability of the system. Thermoregulation of the reactor was performed with a Heidolph MR Hei-TEC® equipped with a Pt-1000 temperature sensor.

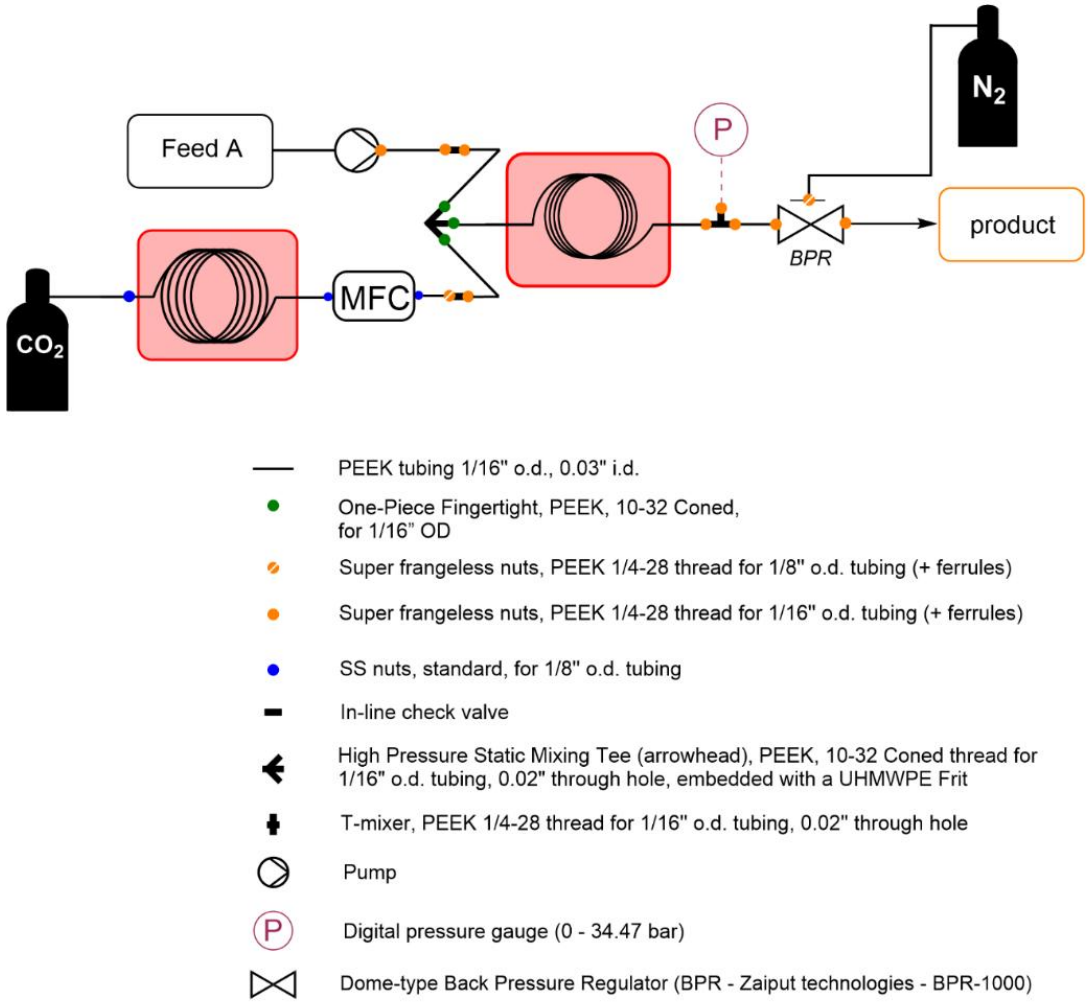


Figure S5.4 The setup for the carbonation of glycidol (**2**) at microscale.

5.4.3 HOMOGENEOUS CARBONATION OF GLYCIDOL (2) AT MESOSCALE (LAB SCALE)

Mesofluidic experiments were performed in a commercial lab scale (Corning® Advanced-Flow™ (AFR) Lab Reactor of 13.5 mL of internal volume – 2.7 mL per fluidic module). The AFR reactor was thermoregulated with a LAUDA® XT Integral 280. The liquid feed was handled with a Syrris Asia Syringe Pump while the gaseous feed was regulated with a Bronkhorst EL FLOW Prestige mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). Downstream pressure was regulated with a dome-type backpressure (BPR-1000 Zaiput Flow Technologies). A digital pressure gauge (0-34.47 bar) was added upstream of the backpressure regulator to monitor the stability of the system.

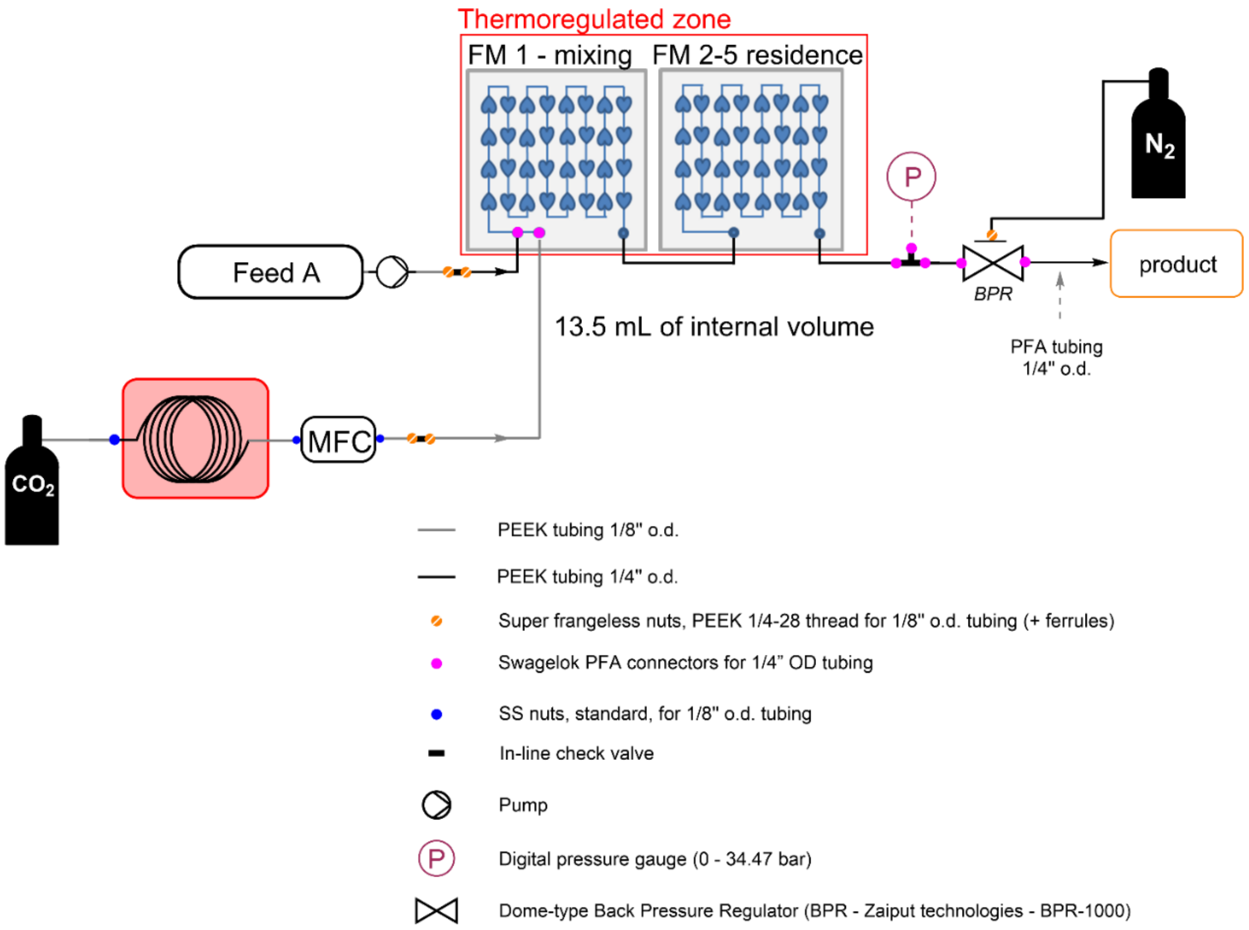


Figure S5.5 The setup for the carbonation of glycidol (**2**) at mesoscale (Corning® AFR™ LF Reactor).

5.4.4 HOMOGENEOUS CARBONATION OF GLYCIDOL (2) AT MESOSCALE (PILOT SCALE)

Mesofluidic experiments were performed in a commercial pilot-scale (Corning® Advanced-Flow™ (AFR) G1 Reactor of 56 mL of internal volume – 8 mL per fluidic module). The AFR reactor was thermoregulated with a LAUDA® XT Integral 280. The liquid feed was handled with a Teledyne ISCO 500D dual pump system while the gaseous feed was regulated with a Bronkhorst EL FLOW Prestige mass flow controller, both equipped with check valves (IDEX/Upchurch Scientific). Downstream pressure was regulated with a dome-type backpressure (BPR-1000 Zaiput Flow Technologies). A digital pressure gauge (0-34.47 bar) was added upstream of the backpressure regulator to monitor the stability of the system.

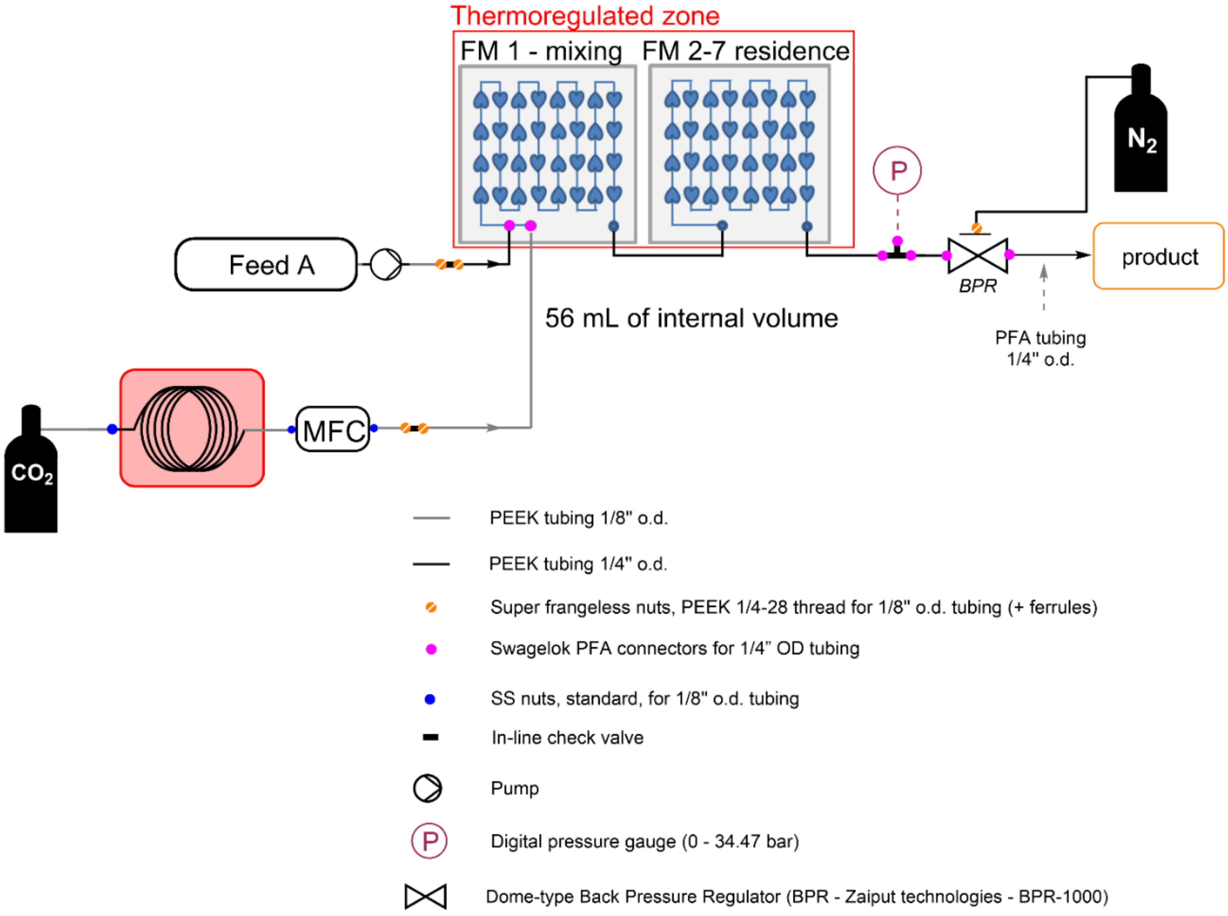


Figure S5.6 The setup for the carbonation of glycidol (**2**) at pilot (Corning AFR G1 Reactor).

5.5 MICROFLUIDIC PRODUCTION OF GLYCIDOL (2) FROM GLYCEROL (1)

The preliminary phase of this study aimed at designing an integrated production scheme feeding upon biobased **1**. An intensified process for the continuous production of epichlorohydrin (**ECH**) starting from **1** based on a chlorination/dechlorination sequence was already reported by us a few years ago.[1]The process was very appealing since it only fed on neat **1**, concentrated aqueous HCl and aqueous NaOH. The downstream section of the process included a selective in-line extraction, eventually leading to the selective recovery of **ECH** and **2**.[1]This process was here revisited and optimized (Figure S5.7) to favor the formation of **2** for feeding the needs of the carbonation step.

The hydrochlorination step of **1** (Figure S5.7a) led to a mixture of monochlorohydrins (**MCH**) and dichlorohydrins (**DCH**). The selectivity of the process was tuned toward **MCH** with 0.3 equiv. of acetic acid (AcOH) and 6 equiv. of concentrated aqueous HCl (36%). These conditions achieved the highest conversion of **1** (89%) as well as the best selectivity toward MCH (79%) within 80 s of residence time at 160 °C (20 bar of counter-pressure). This clearly demonstrated the successful intensification in comparison to our former process (140 °C, 20 min and 8 bar).[1]

The dechlorination of **MCH** and **DCH** toward **2** and **ECH** was triggered at room temperature with a 4 M aqueous solution of NaOH (Figure S5.7b). Complete conversion of **MCH** and **DCH** was achieved within 30 s of residence time, and led to a mixture of oxiranes (**2** and **ECH**, respectively). After the formal validation of both individual steps under intensified flow conditions, concatenation of both steps successfully led **2** in 75% yield, with **ECH** as a side product (17%).

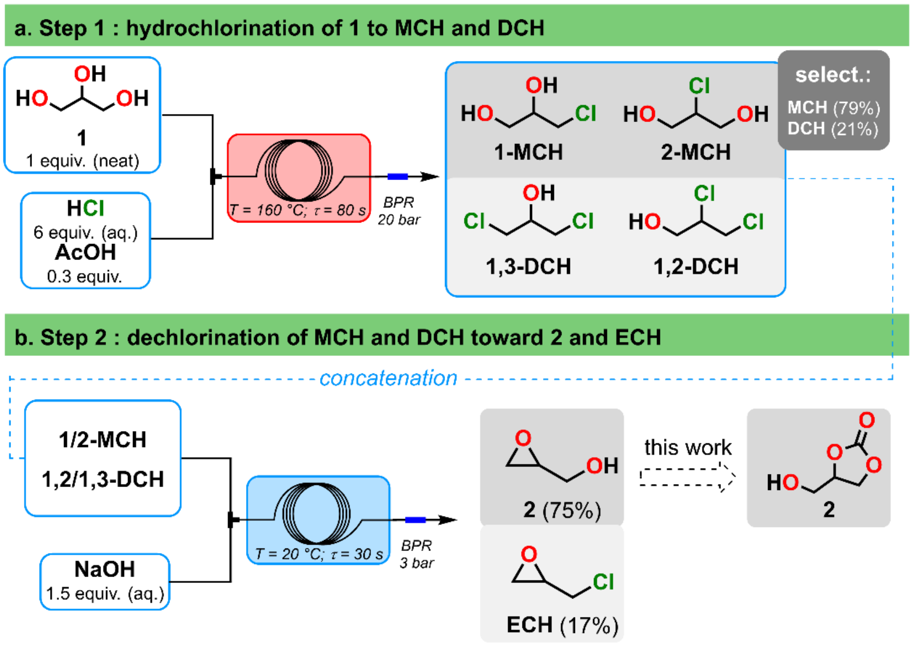


Figure S5.7 Continuous flow setup for the telescoped process composed of two main modules. a. Hydrochlorination and b. Dehydrochlorination from **1** toward **2** and **ECH**.

5.5.1 OPTIMIZATION OF THE HYDROCHLORINATION OF GLYCEROL (1) AT MICROSCALE

Despite the promising results, additional optimization was carried out for further intensification of the process. Reaction temperature (up to 160 °C) was leveraged to shorten the residence time. A counter-pressure of 20 bar was adopted downstream of the hydrochlorination reactor to maintain the reaction mixture in the liquid phase. Residence times from 30 to 120 s were next assessed, and the corresponding results are presented in Table S5.3. It became clear that increasing the residence time to 120 s had a positive impact on the conversion of **1** (76 to 95%), but also promoted the formation of undesired dichlorohydrins (**DCH**), from 15 to 29% (see Table S5.3, Entries 1 and 8). Entry 4 shows the compromise for a high conversion of **1** toward **MCH** (79% combined selectivity) within 80 s of reaction time at 160 °C (Figure S5.8).

Table S5.3 Optimization of the hydrochlorination of 1 under continuous flow conditions (substrate conversion and selectivity toward MCH (%) and DCH (%)).[a]

Entry	t (s)	**1** conv (%) [b]	**MCH** yield (%)[b]	**DCH** yield (%)[b]
1	30	76	58	15
2	60	86	68	15
3	70	91	71	18
4	80	89	79	19
5	90	90	74	20
6	100	92	74	20
7	110	93	76	24
8	120	95	72	29

[a] 6 equiv. HCl, 0.3 equiv. AcOH, 160 °C, 20 bar. [b] Determined by GC-FID with 1-butanol as internal standard and selectivity calculated as the ratio between the yield and the conversion.

Typical run

A feed solution containing aqueous HCl 36% wt (11.18 M) and 0.3 equiv. of AcOH (0.58 M, *vs* **1**) was loaded in an injection loop (PFA tubing, 1/8'', 20 mL internal volume). The volume of acetic acid was considered as neglectable for the preparation of the liquid solution. This solution was delivered with a syringe pump (flow rate = 0.467 mL min^{-1}) and mixed with a feed of neat **1** (flow rate = 0.0621 mL min^{-1}) through a PEEK T-mixer. The reaction medium was next reacted in a PFA coil reactor (1/16'', internal volume = 0.73 mL; residence time = 80 s; length = 1.60 m) heated at 160 °C with a 20 bar counter-pressure (See Figure S5.1 for detailed setup in section S5.4). After sufficient equilibration (3 residence times), the reaction effluent was collected, neutralized with Na_2CO_3, and then diluted in absolute ethanol (25 mL) prior GC-FID analysis.

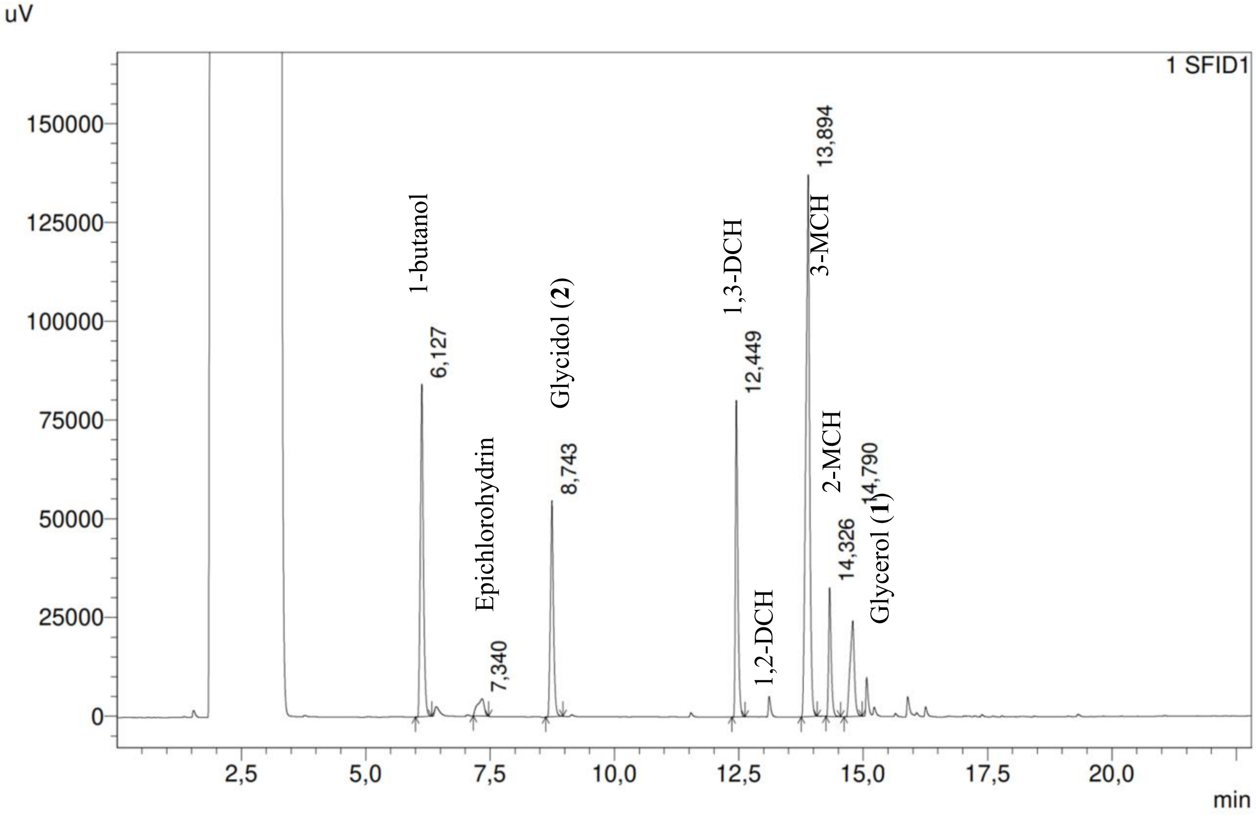


Figure S5.8 Gas chromatogram of the reaction crude obtained from the hydrochlorination step of **1** (6 equiv. HCl, 0.3 equiv. AcOH, 160 °C, 20 bar counter-pressure and 1.2 min of residence time).

5.5.2 DECHLORINATION AT MICROSCALE

The dechlorination step was also revisited to both intensify the process and optimize the selectivity toward **2**. The dechlorination step was assessed with 3 different residence times (30, 60 and 120 s) in the presence of 1.5 equiv. of NaOH (per HCl equivalent) to trigger the dechlorination step at room temperature. Results indicated that the complete conversion of all **MCH** and **DCH** species into their corresponding epoxides, namely, **2** and **ECH** was reached for all residence times (Figure S5.9).

Typical run

A representative feed solution was prepared with the successive addition of 0.8 M of 3-chloropropane-1,2-diol, 0.2 M of **1**, 0.12 M of 1,3-dichloropropan-2-ol and finally, 8.35 M of HCl. Next, this solution was loaded in a PFA injection loop (20 mL internal volume). This feed solution was delivered with a syringe pump (flow rate = 0.236 mL min^{-1}) and mixed with a 4 M solution of NaOH (flow rate = 0.764 mL min^{-1}) through a PEEK T-mixer. The reaction medium was then reacted in a PFA coil reactor (1/16'', internal volume = 1 mL; residence time = 30 s) at room temperature with a counter-pressure of 2.8 bar (See Figure S5.2 for detailed setup in section S5.4). the reaction effluent was collected, neutralized with Na_2CO_3, and then diluted in absolute ethanol (25 mL) prior GC-FID analysis.

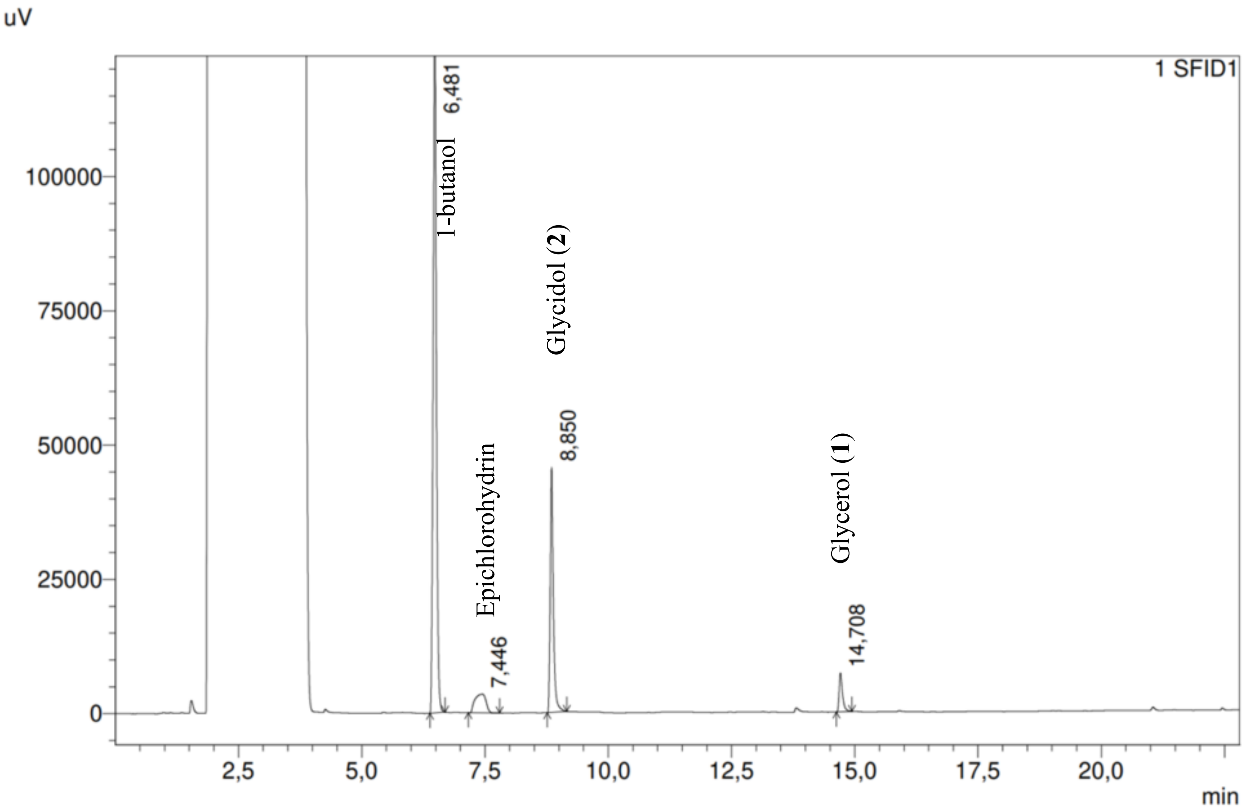


Figure S5.9 Gas chromatogram of the reaction crude obtained from the dehydrochlorination step of the model solution with a 4 M solution of NaOH (0.5 min of residence time).

5.6 OPTIMIZATION OF THE CARBONATION OF GLYCIDOL (2)

All the results presented below displayed a standard deviation between 0 and 5%.

5.6.1 PRELIMINARY OPTIMIZATION AT THE MICROFLUIDIC SCALE

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (**TBD**) was selected as a model catalyst for the direct coupling of gaseous CO_2 with **2** was investigated.

The results are summarized in Table S5.4. Increasing the temperature has a positive impact to boost substrate conversion, ranging from 10-25% at 60 °C to 53-97% at 100 °C. Similar conversion and selectivities toward **3** were observed under 10 or 20 bar of counter-pressure; therefore, the lowest operational counter-pressure was selected for further work to limit mechanical stress on the equipment. Excellent conversion and selectivity were maintained with 1 equiv. of CO_2 (10 mL_N min^{-1}). Next, the impact of the residence time on products distribution was studied in Figure S5.10 (dark blue – **3**, blue **- 2** and light blue – **1**). These experiments clearly demonstrated that a high conversion of **2** and a high yield in **3** are both achievable within unexpectedly short residence times at higher process temperatures. For every residence time assessed, rising the temperature enhanced the formation of **3**, yet it was also counterbalanced with an increase of **1** as a side product. At 10.5, 4, and 2 min, the yield in **3** increased from 81 to 89%, from 38 to 80% and from 56 to 86%, respectively. The only exception lies with the experiments carried out within 1 min of residence time, where the yield plateaued at 77-78 % with a significant increase in **1**, from 15 to 22%. Therefore, the trial at 140 °C and 2 min residence time (10 bar and 10 mL_N min^{-1}) was identified as the optimum, balancing both yield and selectivity under intensified conditions.

Table S5.4 Preliminary optimization for the coupling of $\mathbf{CO_2}$ and **2** under microfluidic conditions.

Entry	T (°C)	P (bar)	CO_2 (mL$_N$ min^{-1})	**2** conv. (%)[a]	**3** yield (%)[b]	**1** yield (%)[c]
1	60	10	15	16	16	/[a]
2	60	10	35	10	10	/[a]
3	60	20	15	25	25	/[a]
4	60	20	35	12	12	/[a]
5	100	10	10	94	83	11
6	100	10	15	93	79	14
7	100	10	35	53	45	8
8	100	20	15	97	86	11
9	100	20	35	73	63	10

[a] Conversion of glycidol (**2**). [b] Yield of glycerol carbonate (**3**). [c] Yield of glycerol (**1**) (hydrolysis product). [d] **1** was not detected in the crude ^{1}H NMR.

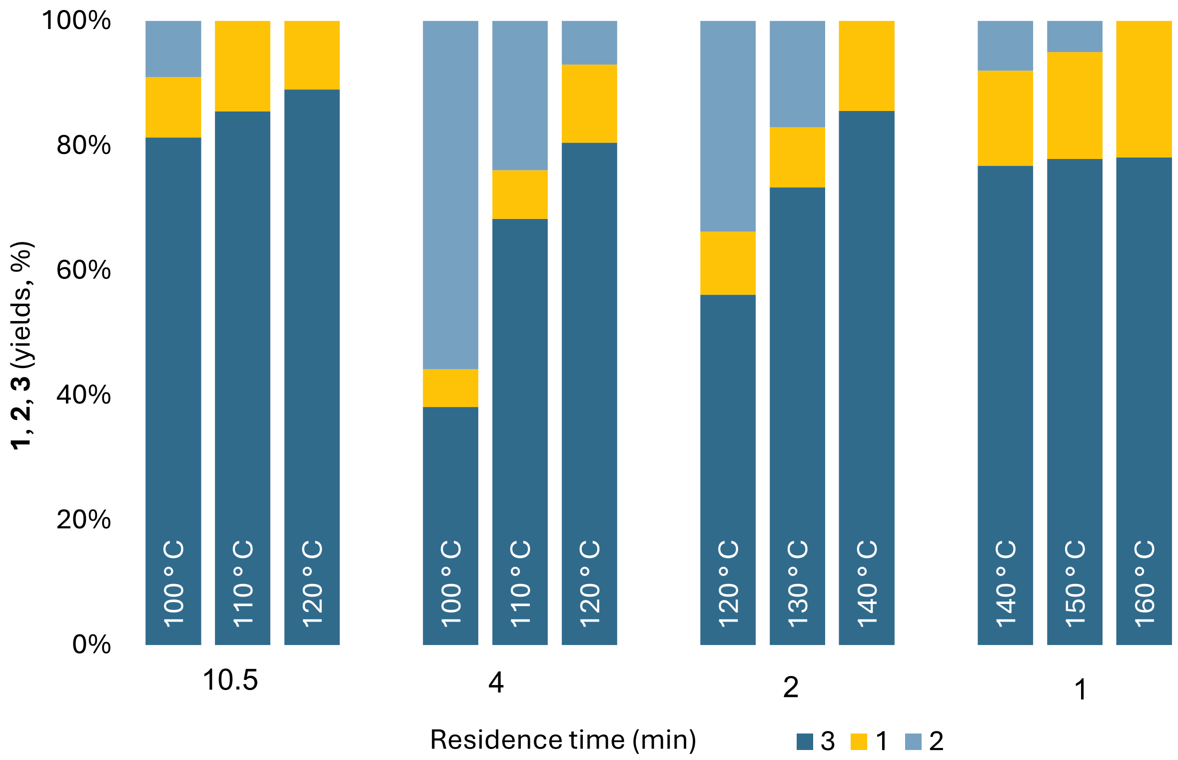


Figure S5.10 Evolution of the yields (%) for **3** and **1**, as well as the conversion of **2** at different residence times (10.5, 4, 2 and 1 min) and various temperatures with TBD (5 mol%) as a model organocatalyst (dark blue – **3**, blue - **2** and light blue – **1**).

5.6.2 CATALYST LOADING OF BARTON'S BASE (MICROSCALE)

Generally, all conditions led at least to some conversion of **2** into **3** (Figure S5.11), although the best yields are achieved for the highest catalytic loading of Barton's base (**BB**), *i.e.* 1 mol% (82%). It also became clear that for a given catalytic loading, the temperature only had a moderate impact on the formation of **3**. For instance, at 1 mol%, the yield toward **3** only increased from 69 to 82% with a raise of temperature from 140 to 170 °C. When using a lower catalytic loading, the extent of the competitive formation of **1** became marginal, with yields in the range of 6 to 9%, 5 to 8%, and 1 to 2%, at 1, 0.5 and 0.1 mol%, respectively.

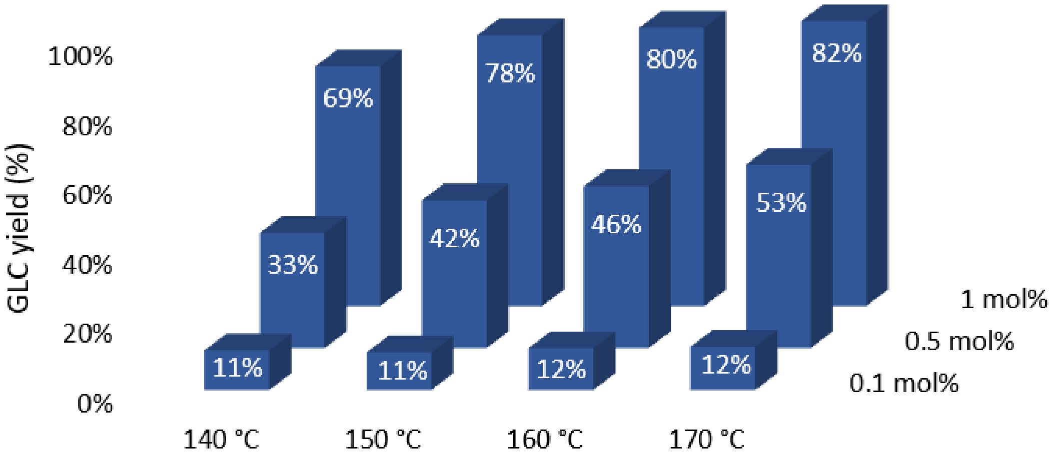


Figure S5.11 Comparison of the impact of different loadings of Barton's base (1, 0.5 and 0.1 mol%) on the yield toward **3** at various temperatures (140, 150, 160 and 170 °C) and 10 bar of counter-pressure.

5.6.3 Catalyst loading of DBU (microscale)

A similar screening of the impact of the catalytic loading of **DBU** was also considered given its high catalytic efficiency, as well as its lower cost compared to Barton's base. Likewise, conversion of **2** to **3** was detected even at the lowest catalytic loading (Figure S5.12). However, a more pronounced effect of the temperature on the reaction outcome was noticed with **DBU**. More specifically, increasing the temperature from 150 to 160 °C led to a significant increase in the yield toward **3**, rising from 45 to 73% at 1 mol% of **DBU**. However, higher process temperatures with **DBU** were also accompanied with a higher formation of **1** (up to 10%).

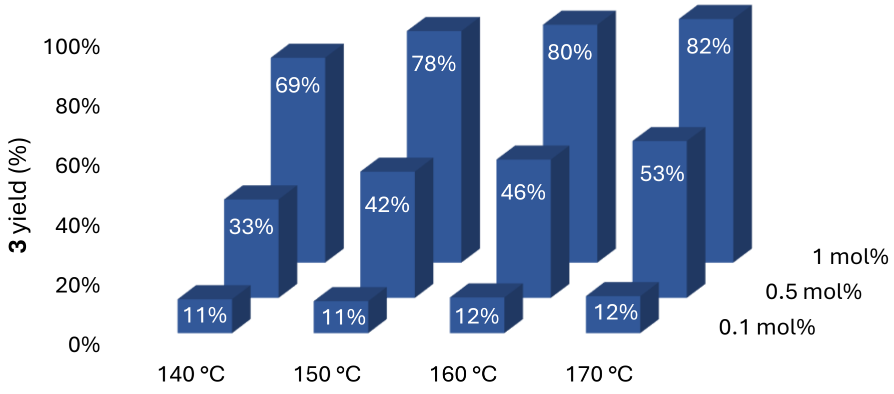


Figure S5.12 Investigation of the impact of various DBU loadings (1, 0.5 and 0.1 mol%) on the yield toward **3** for various temperatures (140, 150, 160 and 170 °C).

5.6.4 Optimized carbonation of glycidol (2) (microscale)

5.6.4.1 Typical run

A solution of **2** in methyl ethyl ketone (MEK, 1.8 M) containing 5 mol% of organocatalyst was delivered at 0.25 mL min^{-1} with an Asia Syrris pump. The gaseous CO_2 feed was injected at a flow rate of 10 mL$_N$ min^{-1} with a mass flow controller. Both streams were mixed through a High-Pressure

Static Mixing Tee (arrowhead-head type, equipped with at UHMWPE frit) and were subsequently reacted into to a capillary PFA coil reactor (1/16'', internal volume = 1.05 mL; residence time determined experimentally = 120 s) heated at 140 °C with a counter-pressure of 10 bar (See Figure S5.4 for detailed setup in section S5.4.2). After sufficient equilibration, the reaction effluent was collected, diluted with d_3-MeCN containing mesitylene as internal standard prior to ^{1}H NMR analysis.

The stoichiometry of CO_2 (SCO_2) was determined according the ideal gas law, and calculated as the ratio between n1 (number of moles per min of CO_2) and n2 (number of moles per min of **2** with a solution at 1.8 M):

$$n1 = \frac{P * V'}{R * T} = \frac{101325 * 10 * 10^{-6}}{8.31 * 273.15} = 0.00044592\, mol\ min^{-1}$$

Where P is the atmospheric pressure (Pa), V' is the flow rate of the gas (m^3) in the standard conditions (25 °C and 1 atm), R is the ideal gas constant ($m^3PaK^{-1}mol^{-1}$) and T, the temperature in Kelvin.

$$n2 = FR * C = 0.25 * 10^{-3} * 1.8 = 0.00045\, mol\ min^{-1}$$

Where FR is the flow rate of the liquid feed of **2** (L/min) and C is the concentration of the solution **2** (mol/L).

$$SCO2 = \frac{n2}{n1} = 0.9915$$

The experimental residence time was determined through the implementation of a typical run as describe above. Three residence times were waited for the equilibration time and followed by the change of the colorless MEK solvent with a colored solution of MEK using Rose Bengal. The experimental time was determined starting from the visual observation of the injection of the feed in the continuous flow set-up up to the crossing of the feed through the downstream BPR section. This experiment was performed as indicative information as the CO_2 injected in the set-up was gradually consumed over the reaction and thus, modified the flow rate accordingly.

5.6.4.2 COMPETITION EXPERIMENT – CO_2 COUPLING WITH A 2/ECH MIXTURE

The same experiment as described in S6.4.1 was performed with a **2**/**ECH** ratio of 2.3 (1.8 M of **2** and 0.792 M of **ECH** in MEK) and 1 mol% of Barton's base. ^{1}H analysis of the crude only showed the conversion of **2** (Figure S5.13) whereas the quantification (with internal standard) confirmed the absence of conversion of **ECH**. It was worth mentioning that glycerol signals were overlapped with the CH_2 of **ECH**, therefore preventing the quantification of **1**.

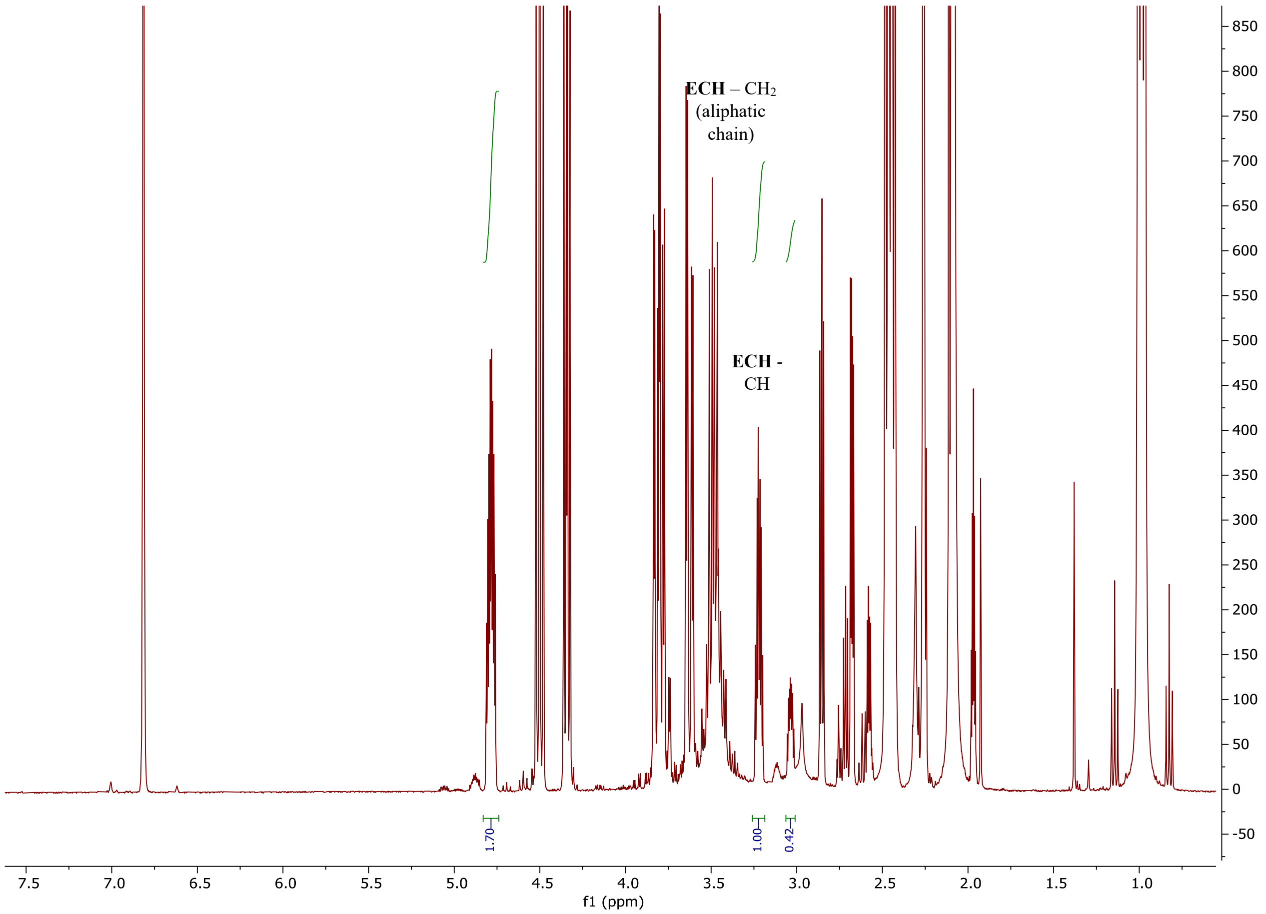


Figure S5.13 ^{1}H NMR spectrum (400 MHz - CD_3CN) of a typical crude obtained with 2.3 ratio of **2**/**ECH** after reaction (1mol% of Barton's base, 140 °C, 10 bar of counter-pressure, 10 mL_N min^{-1} of CO_2 and 2 min residence time).

5.6.5 SCALABILITY TRIALS

First, an intermediate scalability trial was successfully carried out in a lab scale mesofluidic system (Corning® AFR™ G1/Lab skid equipped with 5 glass fluidic modules connected in series, 2.7 mL internal volume each, 13.5 mL of total internal volume, see Figure S5.5, section S5.4.3 for details). The conditions were next transposed in a pilot scale mesofluidic reactor (Corning® AFR™ G1 Reactor equipped with 7 glass fluidic modules connected in series, 8 mL internal volume each, 56 mL of internal volume, see Figure S5.6, section S5.4.4 for details).

5.6.5.1 OPTIMIZED CARBONATION OF GLYCIDOL (**2**) AT MESOSCALE WITH A CORNING® AFR™ LF REACTOR

Typical run: a solution of **2** in methyl ethyl ketone (MEK, 1.8 M) containing 1 mol% of Barton's Base was delivered at 1.82 mL min^{-1} with an Asia Syrris pump. The gaseous CO_2 feed was injected at a flow rate of 72.9 mL_N min^{-1} with a mass flow controller. Both streams were injected into Corning® Advanced-Flow™ Lab Reactor composed of 5 fluidic modules connected in series (total internal volume = 13.5 mL; residence time = 1 min) operated at 140 °C with a counter-pressure of 10 bar (Figure S5.5 for detailed setup in section S5.4.3). After sufficient equilibration, the reaction effluent was collected, diluted with CD_3CN containing mesitylene as internal standard prior to ^{1}H NMR analysis.

5.6.5.2 STABILITY EVALUATION OF CARBONATION OF GLYCIDOL (2) UNDER MESOFLUIDIC CONDITIONS (CORNING® AFR™ LAB REACTOR)

The stability of the carbonation of **2** was investigated over a 250 min run using the Corning® AFR™ Lab Reactor. Three aliquots of 0.5 min (0.92 mL) were collected every 30 minutes and analyzed by quantitative NMR spectroscopy. Results showed that the production of **3** was constant over the entire time of the experiment, with product yield ranging between 82 and 84% (standard deviation of 2%) (Figure S5.14). The average yield of **3** calculated from the samples collected (every 30 min) was (83 ± 2)%.

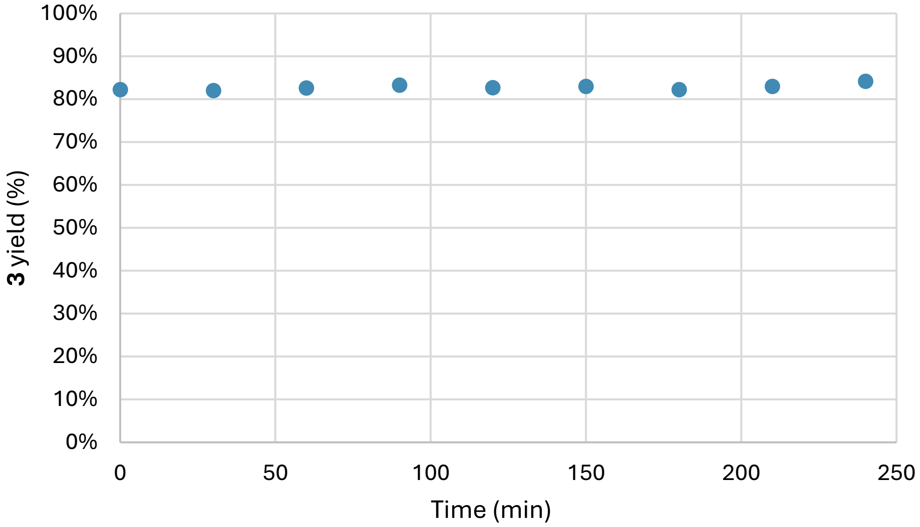


Figure S5.14 Evaluation of the stability of the system (Corning® AFR™ Lab Reactor) over 250 min of continuous operation.

5.6.5.3 OPTIMIZED CARBONATION OF GLYCIDOL (2) AT PILOT SCALE WITH A CORNING® AFR™ G1 REACTOR

Typical run: a solution of **2** in MEK (1.8 M) containing 1 mol% of **BB** was delivered at 16 mL min^{-1} with Teledyne ISCO 500D dual pump system. The gaseous CO_2 feed was injected at a flow rate of 650 mL$_N$ min^{-1} with a mass flow controller. Both streams were injected into a Corning® Advanced-Flow™ G1 Reactor composed of 7 fluidic modules connected in series (total internal volume = 56 mL; residence time = 28 s) operated at 140 °C with a counter-pressure of 10 bar (See Figure S5.6. for detailed setup in section S5.4.4). After sufficient equilibration, the reaction effluent was collected, diluted with CD_3CN containing mesitylene as internal standard, and cooled at 2 °C prior to ^{1}H NMR analysis.

5.6.5.4 Stability evaluation of carbonation of glycidol (2) at mesofluidic conditions (CORNING® AFR™ G1 REACTOR)

The stability of the carbonation of **2** was investigated over a 60 min run using a Corning® AFR™ G1 Reactor. Three aliquots of 1 min (16 mL) were collected every 10 minutes and analyzed by quantitative NMR spectroscopy. Results showed that the production of **3** was constant over the entire time of the experiment with product yield ranging between 71 and 74% (standard deviation of 2%) (Figure S5.15). The average yield of **3** calculated from the 7 samples collected (every 10 min) was (73 ± 1)%.

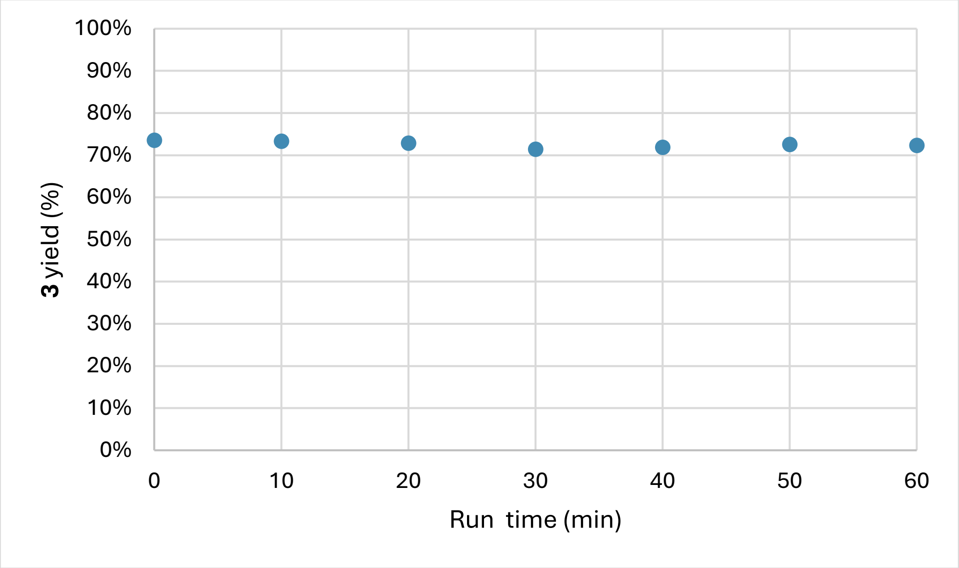


Figure S5.15 Evaluation of the stability of the system (Corning® AFR™ G1 Reactor) over 60 min of continuous operation.

5.6.5.5 BARTON BASE'S THERMAL STABILITY ASSESSMENT

The thermal stability of Barton's base (**BB**) was performed under microwave conditions using a Discover sp synthesizer apparatus. A solution of 0.1 M of **BB** dissolved in MEK was heated at 140 °C (300 W) under 4.6 bar of pressure during 10 min at high stirring rate. Then, an aliquot of the resulting heated solution was recovered and diluted into d_3-MeCN prior NMR analysis. The thermally shocked sample was compared with a sample of the initial solution of **BB** (Figure S5.16).

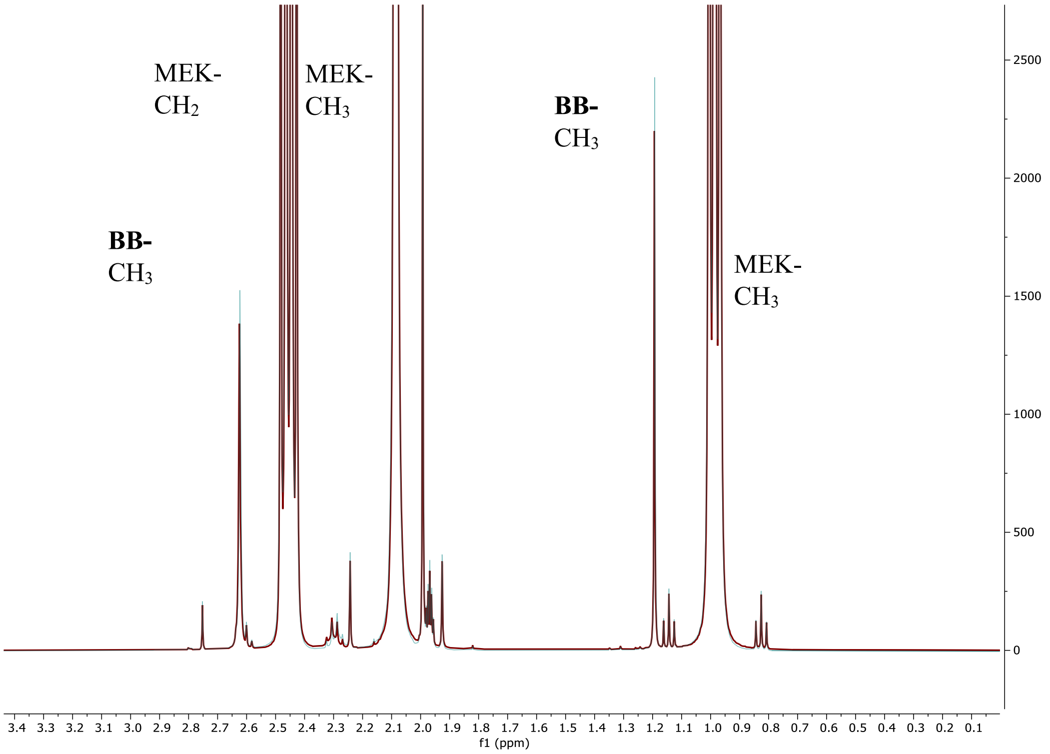


Figure S5.16 Overlapping ^{1}H spectra of the solution of BB prior the thermic treatment and after 10 min under microwave conditions (140 °C, 300 W, 10 min and high stirring).

These spectra (Figure S5.16) clearly demonstrate the absence of thermal degradation of **BB** during this experiment. Therefore, it can be concluded that **BB** maintained its structural integrity during the various runs performed under continuous flow conditions.

5.6.5.6 FOOTPRINT AND PROCESS METRICS

The global efficiency of the CO_2 coupling process was assessed through the calculation of representative metrics. The Environmental factor[2] (E-factor) was calculated with the inclusion of the catalyst, the solvent and the hydrolysis side product **1** in order to obtain the most accurate estimation of waste generation. While the production of fine chemicals is usually associated with E-factor values ranging between 5 and 50,[3] the upstream carbonation process is associated with an E-factor of 4.7, therefore highlighting its reduced environmental footprint. When the downstream extraction is included in the calculation, the E-factor increases to 53.07, considering MIBK, MEK, **BB**, unreacted glycerol, sodium chloride and water as waste compounds. However, since MIBK and MEK can be recycled by vacuum distillation, this leads to end-to-end E-factor (carbonation process + extraction) of 6.55 with the recycling of MIBK (MEK, **BB**, unreacted glycerol, sodium chloride and water as waste compounds) or of 1.99 with the recycling of MIBK and MEK (**BB**, unreacted glycerol, sodium chloride and water as waste compounds. An example of a detailed E-factor calculation is provided below.

$$E-factor = \frac{\sum_j m_{input,j} - m_{product}}{m_{product}}$$
$$= \frac{(133.34 + 79.22 + 3.08 + 240 + 2.4 + 6.63) - (155.17)}{155.17} = 1.99$$

Considering 1 L of feed containing 1.8 M of 2 and 0.018 M of BB dissolved in MEK :

m_2 = 133.34 g
m_{CO2} = 79.22 g
m_{BB} = 3.08 g
m_{H2O} = 240.00 g

$m_{NaCl} = 2.4$ g
$m_{MIBK} = 7220$ g
$m_{MEK} = 706.68$ g
$m_1 = 6.63$ g
$m_3 = 155.17$ g

Moreover, according to CHEM21 solvent selection guide, MEK is recommended as a green solvent[4] and its favorable physico-chemical properties (boiling point: 80 °C) to ease its potential downstream recyclability. Lastly, this process meets several core principles of Green Chemistry: (a) use of renewable feedstocks in stochiometric amount, (b) catalysis, (c) safer implementation and (d) energy efficiency, the latter both inherently related to continuous flow technology. The attractiveness of this process is emphasized by its high throughput and low footprint, which translates with a Space Time Yield (STY) of 2.7 kg h^{-1} L^{-1}.

5.7 PURIFICATION OF GLYCEROL CARBONATE (3)

5.7.1 GENERAL PROCEDURE

The reactional effluent of carbonation produced from the mesofluidic synthesis of **3** in a Corning® AFR™ Lab Reactor (S6.5.2) was evaporated to recover MEK. Then, the remaining crude was dissolved in 1 mL of aqueous solution of various percentage of NaCl (0, 1, 5 wt% and a saturated solution of NaCl) and extracted with 3 times 5 mL of methyl isobutyl ketone (MIBK). The organic phases were combined, dried over $MgSO_4$ and filtered before an additional step of purification using activated charcoal (and subsequent filtration). Finally, 10 µl of the resulting crude were analyzed by quantitative ^{1}H NMR using octamethylcyclotetrasiloxane as internal standard.

5.7.2 RESULTS

In absence of NaCl, the organic phase was miscible in the aqueous crude solution, therefore preventing any purification step. Subsequent trials focused on aqueous solutions with 1 and 5 wt%, achieving both the same results with an isolated yield of **3** of 71% and with a purity >95% (established with octamethylcyclotetrasiloxane as internal standard). The ^{1}H NMR spectrum of glycerol carbonate (**3**) is presented in Figure S5.17 (with the internal standard). An additional test was also performed with a saturated aqueous solution of NaCl, but further liquid-liquid separation led to the partial precipitation of salt, preventing any reliable recovery as well as an accurate analysis of the purified crude by NMR. As the purification procedure was implemented on a large quantity of crude, a large amount of MIBK was required. MIBK contains impurities that can be clearly observed in Figure S5.18 and are also detected in the purified **3**, due to their concentration in the crude during the evaporation of MIBK. Filtration on activated charcoal is optional, yet it removed yellowish impurities (not detectable by NMR).

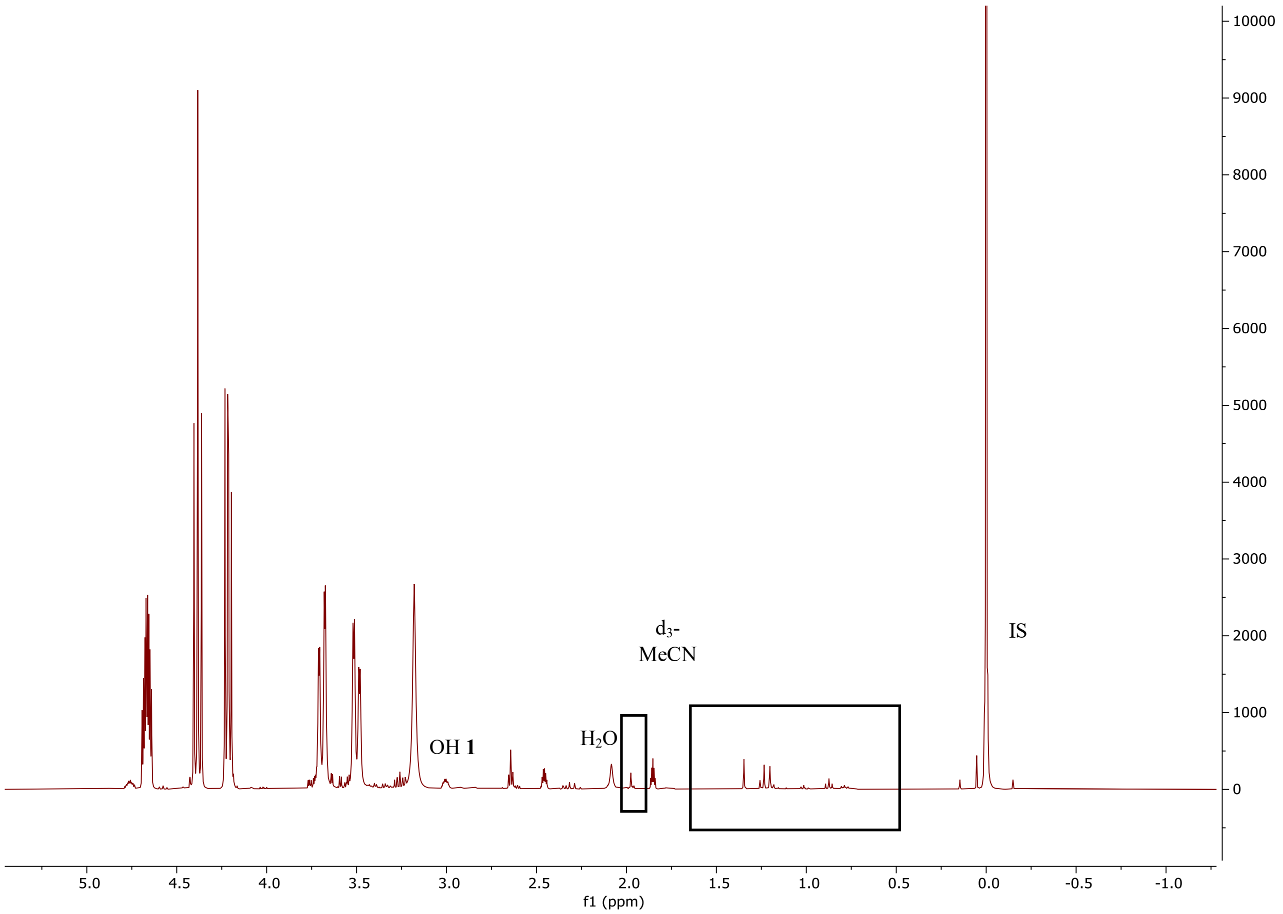


Figure S5.17 ^{1}H NMR spectrum (400 MHz - CD_3CN) of a typical purified sample of glycerol carbonate (**3**) obtained after liquid-liquid extraction using an aqueous solution of 1 wt% NaCl and MIBK.

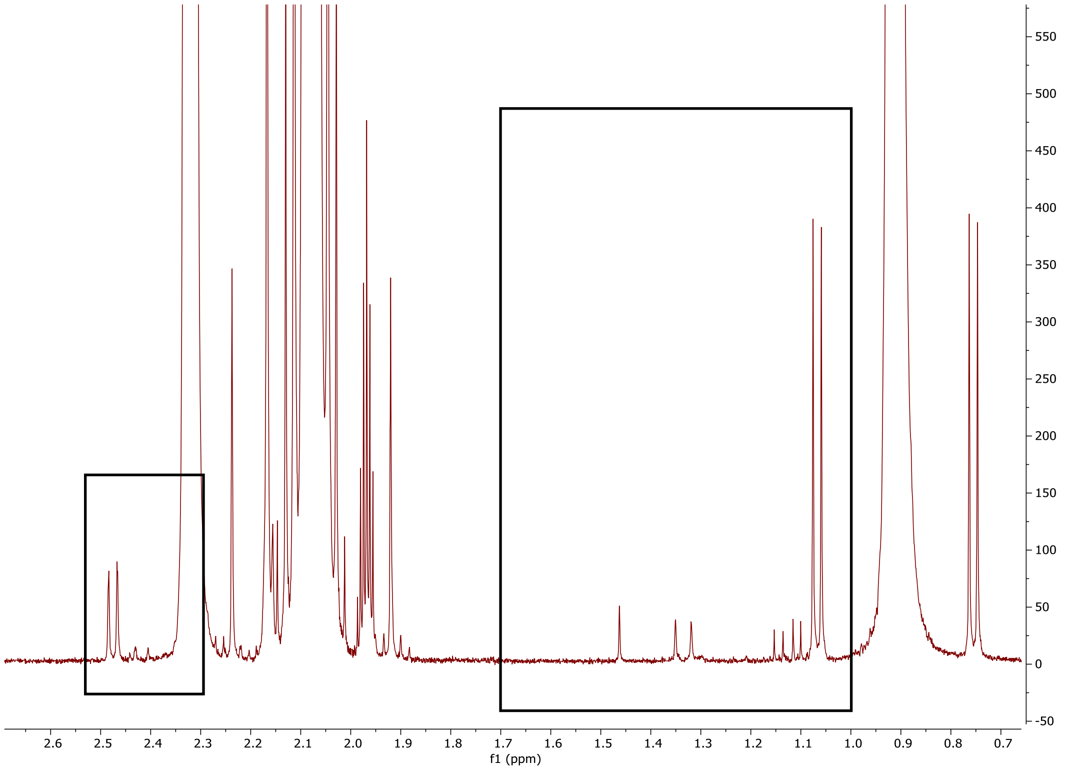


Figure S5.18 ^{1}H NMR spectrum (400 MHz - CD_3CN) of neat MIBK used for the liquid-liquid extraction of crude 3, emphasizing impurities.

5.8 ASSIGNMENTS OF 1H NMR SPECTRUM OF TYPICAL CRUDE

5.8.1 COMPLETE ^{1}H NMR SPECTRUM OF A TYPICAL CRUDE FROM CARBONATION OF GLYCIDOL (2)

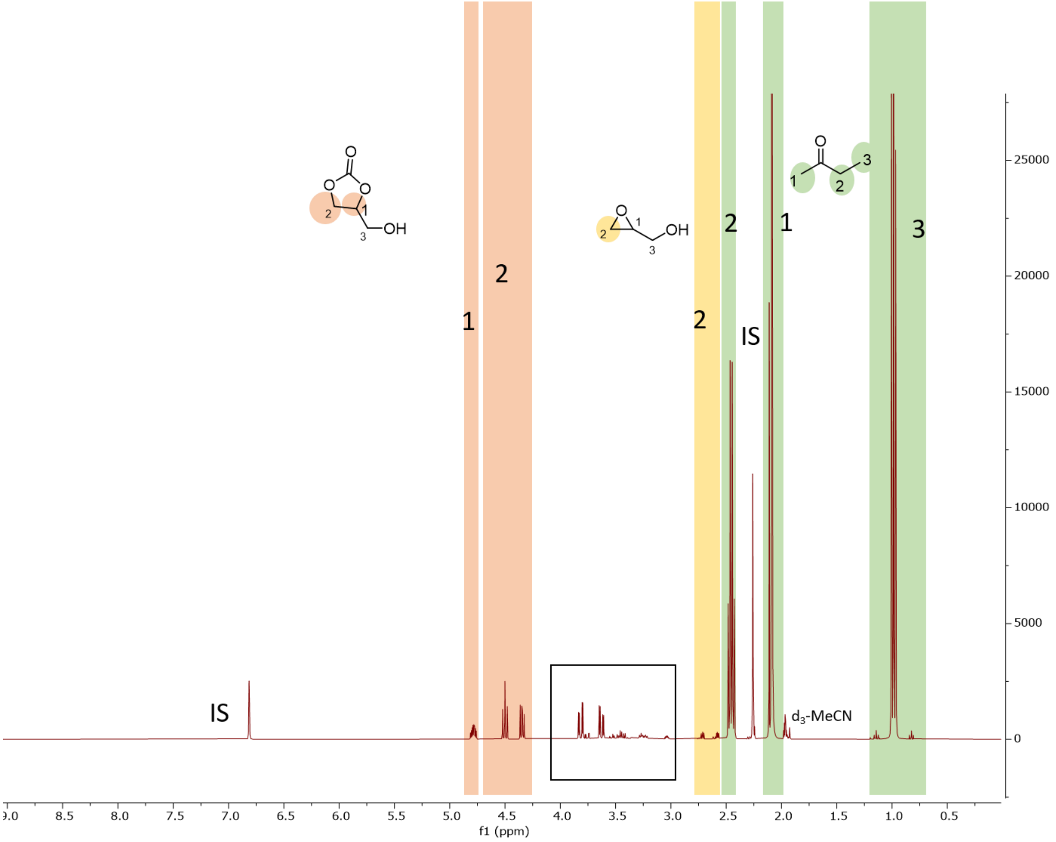


Figure S5.19 ^{1}H NMR spectrum (400 MHz - CD_3CN) of a typical crude obtained after reaction (100 °C, 10 bar of counter-pressure, 15 mL_N min^{-1} of CO_2 and 14 min residence time) while the black square corresponds to spectral area of the section S5.8.2).

5.8.2 Expansion of the 3-4 ppm region of the ^{1}H NMR spectrum of a typical crude from carbonation of glycidol (2)

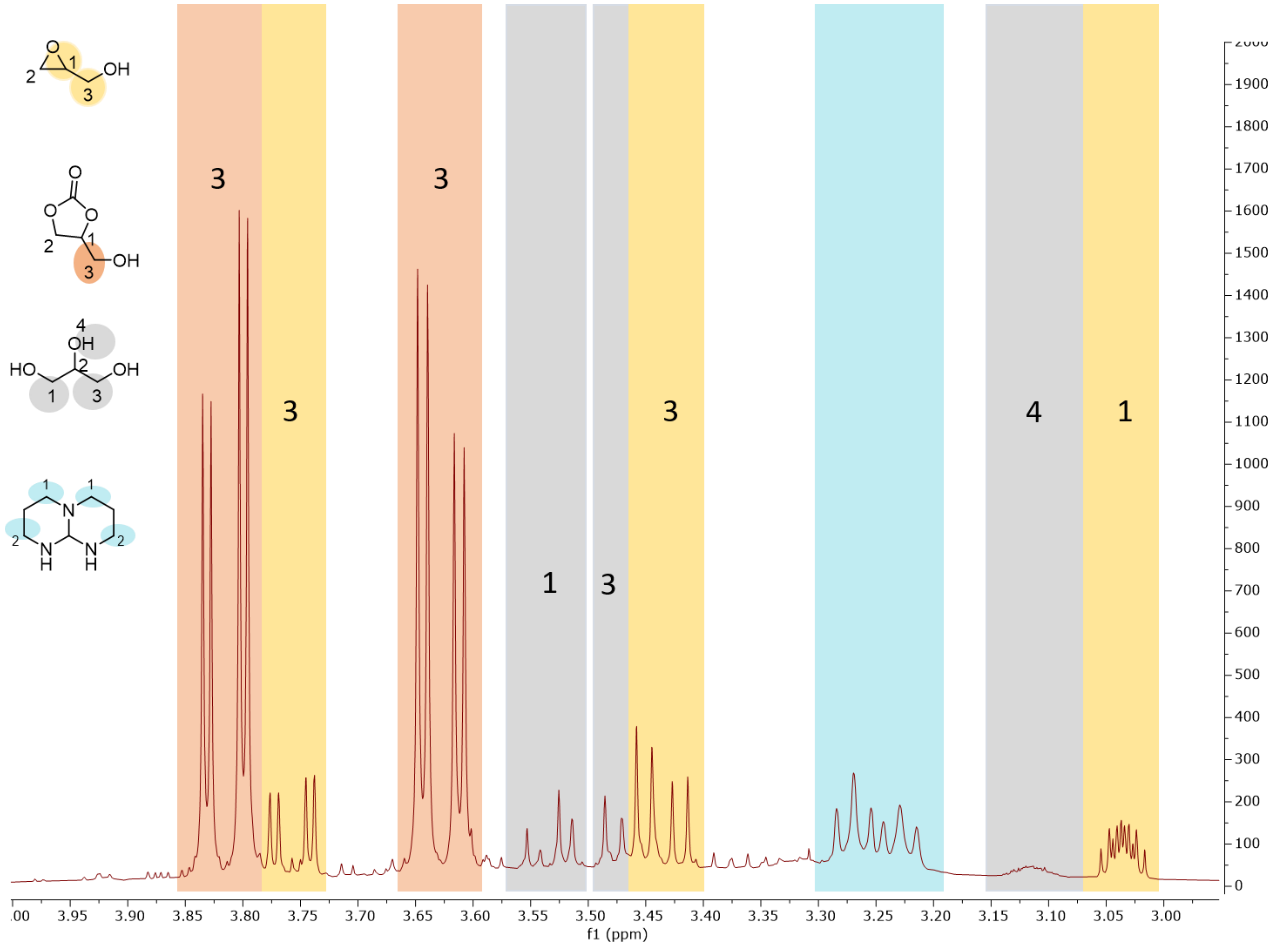


Figure S5.20 Partial ^{1}H NMR spectrum (400 MHz - CD$_3$CN) of a typical crude obtained after reaction (100 °C, 10 bar of counter-pressure, 15 mL$_N$ min^{-1} of CO$_2$ and 14 min residence time) from 3 to 4 ppm.

Unassigned signals come from impurities present in reagent bottle and, therefore and do not affect the mass balance quantification.

5.9 Computational Studies

5.9.1 Mechanistic background from the literature

The coupling of epoxides with CO$_2$ toward cyclic carbonates commonly follows 2 main strategies: (a) the most conventional strategy that relies on binary catalytic systems composed of a Lewis acid (or hydrogen bond donor) and an external nucleophile (Figure S5.21a) and (b) an alternative pathway, which proceeds through direct substrate activation (Figure S5.21b). Both methods rely on the interplay of several elementary steps. The conventional strategy (a) successively sees: (i) a preliminary activation of the epoxide by coordination or hydrogen bonding, followed with (ii) a ring opening via the external nucleophile to yield a stabilized (LA or H bond) alkoxide, (iii) subsequent fixation of CO$_2$ and finally (iv) intramolecular cyclization toward the cyclic carbonate.[5] The alternative pathway (b) combines (i) preliminary intermolecular carbonation of the hydroxyl group of **2** to yield the hemiester of carbonic acid via a proton shuttle and (ii) a subsequent intramolecular nucleophilic addition to form **3**.[6] Noteworthy, the second mechanism critically depends on the availability of a hydroxyl group in the vicinity of the oxirane moiety.[7]Both mechanisms can compete depending on the reaction conditions and additives.[8]

For instance, Kleij reported an Al(III)-metal based Lewis acid featuring an aminotriphenolate ligand for the carbonation of **2** (Figure S5.21c).[8] In the presence of an external nucleophile, both paths (a) and (b) were triggered, while in its absence, only mechanism (b) prevailed. Relying on advanced kinetic studies and computations, the authors demonstrated that the mechanism was triggered through the Al-coordination of the β-hydroxyl group of **2** prior to its deprotonation toward an alkoxide intermediate. The latter would eventually lead to a stepwise CO_2 fixation and epoxide opening, followed by a rate determining intramolecular cyclization toward **3**. The authors emphasized the critical role of water, leading to a significant reduction of the activation barrier ($\Delta G^{\ddagger}$) from 46.2 kcal mol^{-1} to 24.6 kcal mol^{-1}. The effect of water was argued to arise from a combination of factors, mainly stabilizing the alkoxide prior CO_2 capture, favoring the formation of hemiester and activating the epoxide through hydrogen bonding (Figure S5.21c). The authors concluded that the CO_2 fixation and subsequent intramolecular cyclization resulted in a concerted mechanism in the presence of water. Experimentally, **3** was obtained in 32% and 62% (50 °C, 4 h, 10 bar CO_2) under anhydrous and wet conditions, respectively.[9] In another report, D'Elia and Kleij studied sodium citrate as an ambivalent catalyst, emphasizing the synergistic combination of both basicity and hydrogen bond acceptance.[10] The carbonation of **2** proceeded under smooth conditions (60 °C, 1 atm CO_2, 24 h), yet the mechanism appeared to be strongly **1** substrate dependent. No conversion was observed with either **ECH** or styrene oxide under the same conditions, which supported a proton shuttle mechanism mediated by β-hydroxyl group of **2** (Figure S5.21d) leading to substrate activation.[10] The methodology was next extended to more challenging substrates such as bicyclic β-hydroxyl epoxides with control of the relative stereoselectivity.[11–15]

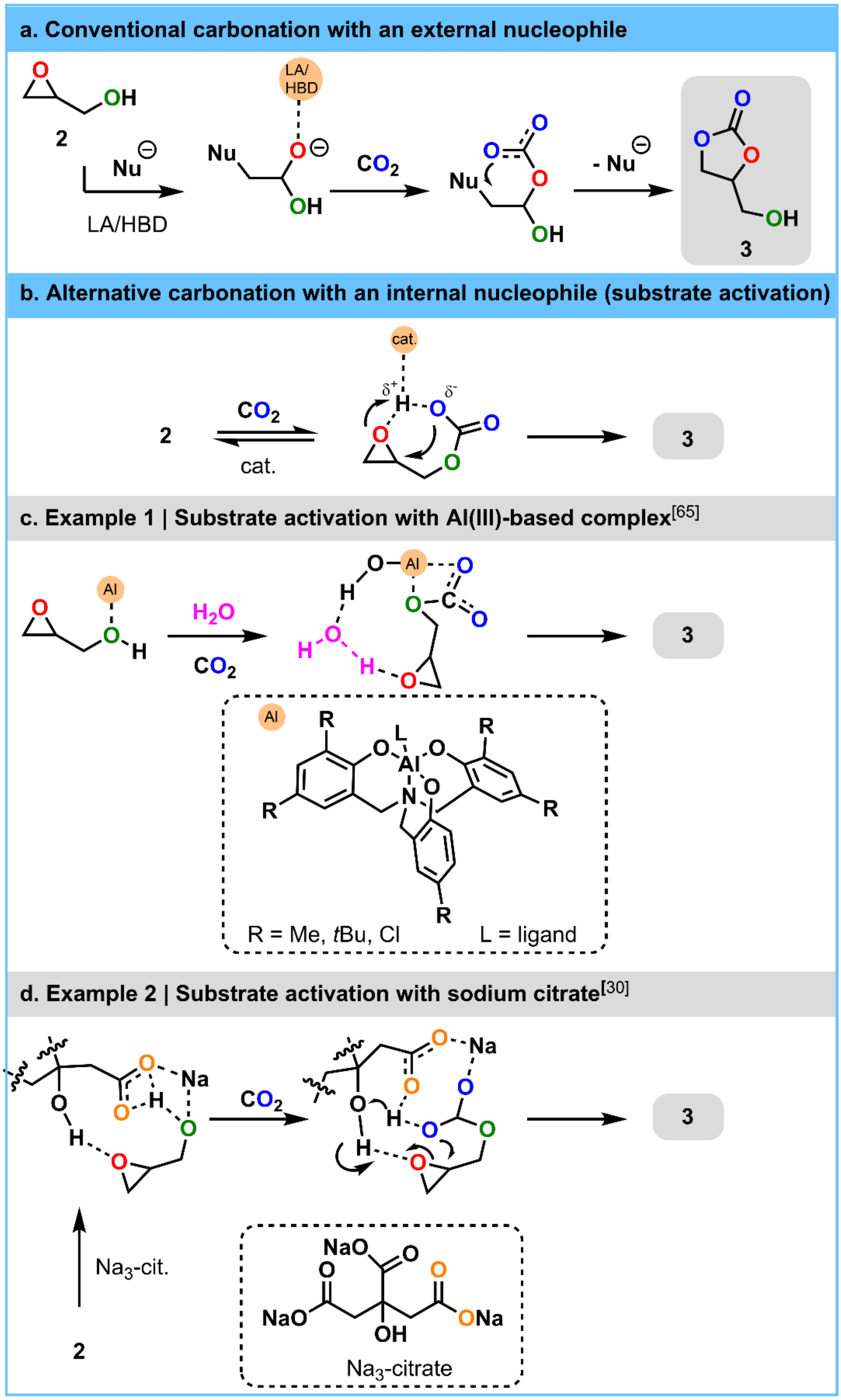


Figure S5.21 Common mechanisms for the carbonation of 2 from the prior art. (**a**). Conventional carbonation relying on the use of a Lewis acid or hydrogen bond donor combined to an external nucleophile;[5] (**b**). Alternative carbonation based on the internal nucleophilic addition of the carbonated intermediate of 2;[6] (**c**). Alternative carbonation catalyzed by Al(III)-based complex (Lewis acid);[9] (**d**). Alternative carbonation with an organic salt derived from Bronsted acid.[10]

5.9.2 COMPUTATIONAL METHODS

DFT computations were performed using the Gaussian 16 (Revision C.01)[16] software package. Geometry optimizations were carried out at the B3LYP-D3/6-31+G* level of theory. The SMD method was used to model solvent effects using the built-in parameters for 2-butanone (MEK, ε = 18.246). All possible stationary points were localized at the B3LYP-GD3BJ/6-31+G* level of theory. Stationary points were characterized by frequencies computations (local minima with only real frequencies and transition states with one imaginary frequency) and a systematic attempt to locate the lowest energy form was made. Transition states were verified by following the intrinsic reaction coordinates (IRC). Electronic energies were computed at the M08HX/6-311++G** level whereas solvation and thermal energies were computed at the B3LYP-GD3BJ/6-31+G* level and corrected by concentration, temperature and quasi-harmonic factors at 413.15 K using the GoodVibes Python script.[17]

5.9.3 CALCULATION OF KINETIC PARAMETERS

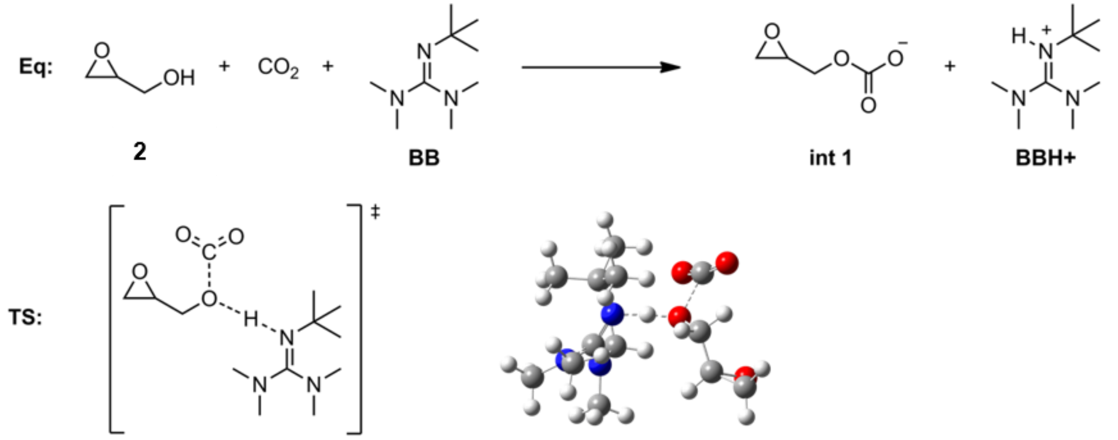
The kinetics constants (k) are calculated from the free enthalpy of activation ($\Delta G^{\ddagger}$) using Eyring's equation:

$$k(T) = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

Symbol – quantity (value) [unit]: k – kinetic constant [$\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$]; k_B – Boltzmann's constant (1.381×10^{-23} $\text{J}\cdot\text{K}^{-1}$); T – reaction temperature (413.15 K); h – Planck's constant (6.626×10^{-34} $\text{J}\cdot\text{s}$); $\Delta G^{\ddagger}$ – the free enthalpy of activation [$\text{J}\cdot\text{mol}^{-1}$]; R – the gas constant (8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

5.9.4 CARTESIAN COORDINATES AND ENERGIES FOR REPRESENTATIVE TRANSITION STATES

Table S5.5 Transition state: **BB + 2 + CO_2** (carbonation step)



Coordinates of the TS (atom, X, Y, Z)	Energies
C 1.56676900 0.48944300 -0.32476600	$\Delta_r H_m$ = -17.2 kcal mol^{-1}
N 0.85241700 -0.55719400 0.03875900	$\Delta_r S_m$ = 4.6 cal mol^{-1} K^{-1}
N 2.68586400 0.95167500 0.32507200	$\Delta_r G_m$ = -6.3 kcal mol^{-1}
N 1.17602300 1.20069600 -1.42492800	
C 3.84988600 1.45363700 -0.39023500	$\Delta H_m^{\ddagger}$ = -19.9 kcal mol^{-1}
H 3.98438500 2.53424600 -0.24471200	$\Delta S_m^{\ddagger}$ = -64.7 cal mol^{-1} K^{-1}
H 4.74771400 0.94340200 -0.01639900	$\Delta G_m^{\ddagger}$ = 6.8 kcal mol^{-1}
H 3.75326200 1.24826600 -1.45735800	
C 2.74677700 1.06955900 1.77268500	
H 1.76465200 0.87905600 2.20390000	
H 3.47461000 0.37825000 2.21752000	
H 3.04859900 2.09345200 2.03264400	

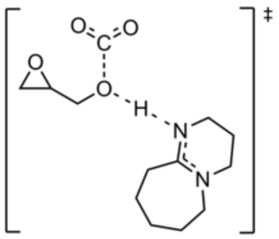
C 0.38620200 0.59736200 -2.49065600	
H -0.67872200 0.82942300 -2.38216300	
H 0.74512100 0.98463700 -3.45214200	
H 0.50377900 -0.48580500 -2.46809300	
C 1.30915500 2.65063800 -1.50470700	
H 1.99637900 2.94472500 -2.30833600	
H 0.32570600 3.09021800 -1.71455100	
H 1.67356000 3.05207500 -0.55866400	
C 1.35600700 -1.81279300 0.64861300	
C 2.86138600 -2.04185100 0.43654500	
H 3.48499300 -1.34407800 0.99777100	
H 3.11495600 -3.05492100 0.77019800	
H 3.12411500 -1.96338700 -0.62496100	
C 0.60003400 -2.94628400 -0.07593600	
H 0.91238400 -3.92149400 0.31557700	
H -0.48011100 -2.85121000 0.07200600	
H 0.80313500 -2.92262200 -1.15236700	
C 1.00383100 -1.89273800 2.14531800	
H -0.06720300 -1.71823100 2.29701600	
H 1.24135900 -2.89155100 2.53117800	
H 1.55993100 -1.16413500 2.74007500	
C -2.72468400 -1.76938000 -1.04620800	
O -3.48555700 -2.05303200 -0.18081600	
O -2.21716700 -1.82965300 -2.11554800	
C -2.42760600 1.75711900 0.87702800	
C -3.43660600 2.39453100 1.73044700	
O -3.74108200 2.07292500 0.35580200	
H -1.63925400 2.38496500 0.45737500	
H -3.36959800 3.45948200 1.95159000	
H -3.97115500 1.79490600 2.46752100	
C -2.07283600 0.29805900 1.01996200	
H -1.29462400 0.21378600 1.79811000	
H -2.95419700 -0.25633400 1.37298700	
O -1.61429400 -0.24794400 -0.19334000	
H -0.44899100 -0.44554900 -0.13537700	
Kinetic parameters	k (413 K) = 2.2 10^{9} L^{2} mol^{-2} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 8.3 10^{-8} s

Table S5.6 Transition state: **DBU + 2 + CO$_2$** (carbonation step)

Eq:

2 **DBU** **int 1** **DBUH+**

TS:

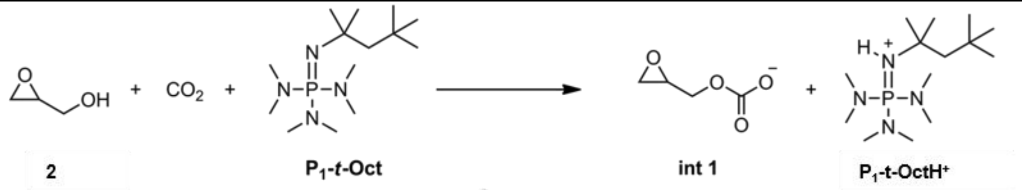


Coordinates of the TS (atom, X, Y, Z)	Energies
C -3.68848500 -0.23687700 -0.62224600	$\Delta_r H_m$ = -12.0 kcal mol^{-1}
C -4.03277000 1.02880300 0.17110900	$\Delta_r S_m$ = 53.4 cal mol^{-1} K^{-1}
C -1.23036900 -0.42523000 -0.39463300	$\Delta_r G_m$ = -1.9 kcal mol^{-1}
C -3.20471500 2.25154600 -0.23820400	

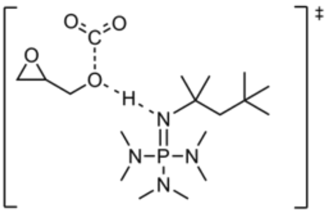
C -1.09779400 0.95214000 -1.00066300 C -1.68617400 2.07654000 -0.12241100 H -3.59773500 -0.00550700 -1.68990800 H -3.90624100 0.81820000 1.24222500 H -3.44744800 2.50326800 -1.28142900 H -1.57321900 0.97043900 -1.98997200 H -4.49342500 -0.96956900 -0.52652300 H -5.09630600 1.25119500 0.01230800 H -3.51111400 3.11291100 0.37004300 H -0.03241100 1.13340800 -1.15313300 H -1.20185800 3.01315700 -0.42136400 H -1.40272900 1.90270500 0.92472100 N -2.46861400 -0.91458800 -0.15997200 C -2.66600400 -2.15673400 0.60492500 H -2.90473900 -2.97300200 -0.09021500 H -3.53360600 -2.00998300 1.25629500 C -0.19412200 -2.37848900 0.54133800 H -0.21448100 -3.15543800 -0.23638800 H 0.72480800 -2.52354400 1.11945300 C -1.42974700 -2.49211100 1.42843600 H -1.52612000 -3.50198400 1.84040100 H -1.34134000 -1.79157800 2.26840800 N -0.12704300 -1.05929900 -0.08355600 C 3.30031100 -1.81853500 -0.57445500 O 2.80179500 -2.34044400 -1.52083600 O 4.09739700 -1.73752500 0.30713000 C 2.90155800 2.04007500 0.19222500 C 2.64736800 3.25510100 0.97382600 O 1.85223400 2.95794200 -0.19469800 H 3.74720200 2.03741400 -0.49742600 H 3.31118800 4.11342000 0.87504200 H 2.11057900 3.18206600 1.91977800 C 2.47472700 0.68337500 0.68483200 H 3.28861700 0.25710800 1.28998300 H 1.59079000 0.78760300 1.33201500 O 2.18805100 -0.18589000 -0.39490600 H 1.10068400 -0.56535500 -0.29762300	$\Delta H_m^{\ddagger}$ = -17.7 kcal mol^{-1} $\Delta S_m^{\ddagger}$ = -62.0 cal mol^{-1} K^{-1} $\Delta G_m^{\ddagger}$ = 7.9 kcal mol^{-1}
Kinetic parameters	k (413 K) = 5.42 10^7 L^2 mol^{-2} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 3.41 10^{-7} s

Table S5.7 Transition state: **P₁-*t*-Oct + 2 + CO₂** (carbonation step)

Eq:



TS:



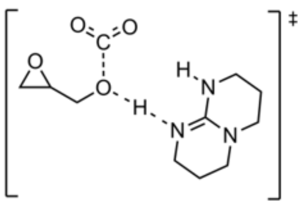
Coordinates of the TS (atom, X, Y, Z)	Energies
C -1.19735600 2.81044200 1.37150900	$\Delta_r H_m = -18.6$ kcal mol^{-1}
O -1.25107400 2.19961100 2.39390000	$\Delta_r S_m = 54.3$ cal mol^{-1} K^{-1}
O -1.57412700 3.66980500 0.63335100	$\Delta_r G_m = -8.9$ kcal mol^{-1}
C 1.63794100 3.81407600 -0.36986800	
C 2.62705300 4.31725300 -1.32848600	$\Delta H_m^{\ddagger} = -27.7$ kcal mol^{-1}
O 3.04737400 3.54295500 -0.18387700	$\Delta S_m^{\ddagger} = -67.2$ cal mol^{-1} K^{-1}
H 1.23481300 4.51155200 0.36493800	$\Delta G_m^{\ddagger} = 0.1$ kcal s mol^{-1}
H 2.91874500 5.36663000 -1.30860900	
H 2.74825000 3.81305600 -2.28744400	
C 0.74220800 2.65428600 -0.71199400	
H -0.11950100 3.04460300 -1.27301100	
H 1.27776900 1.94884000 -1.35955800	
O 0.30626600 1.98282900 0.45731400	
H 0.13078100 0.86062100 0.25259400	
P 1.23206700 -1.40575200 0.14335700	
N -0.05427100 -0.47090400 -0.04602600	
N 2.48108600 -0.54122600 0.85451700	
N 1.85370000 -2.05801500 -1.27094000	
N 1.01572700 -2.71518000 1.17321000	
C 2.24635800 0.03247800 2.18002900	
H 3.17156900 -0.03330400 2.76740600	
H 1.93135500 1.08119100 2.11836400	
H 1.46723700 -0.52878400 2.70302700	
C 3.57380600 0.08180300 0.11479900	
H 3.33853400 1.10287200 -0.21211000	
H 4.44944600 0.12921200 0.77494800	
H 3.84276700 -0.52776500 -0.74911800	
C -0.15112900 -2.85084800 2.03631700	
H -0.55421800 -3.87070700 1.97676200	
H 0.11834700 -2.64561000 3.08321100	
H -0.92572000 -2.14747000 1.74150200	
C 2.19315400 -3.41475100 1.68920100	
H 3.04726800 -3.29529800 1.02113400	
H 2.47473000 -3.02972900 2.68053300	
H 1.97205200 -4.48573200 1.78127500	
C 1.98657100 -3.48060200 -1.55946600	
H 3.03712600 -3.74868200 -1.74071100	
H 1.60232500 -4.08289700 -0.73733500	
H 1.40835900 -3.72876000 -2.46082800	
C 2.02281200 -1.20761800 -2.44622700	
H 3.03137200 -1.33218000 -2.86289200	

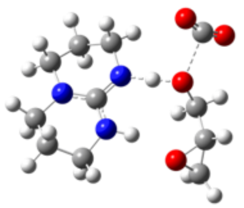
H 1.29233900 -1.47448400 -3.22357700 H 1.88276600 -0.15545100 -2.19354200 C -1.32083900 -0.76148800 -0.79268400 C -2.47461400 -0.50865300 0.22714700 H -2.47203200 -1.36976400 0.90577500 H -2.16982300 0.34805200 0.83533100 C -3.96281800 -0.25784000 -0.16089500 C -1.37600100 0.19552400 -1.99496000 H -2.24842600 -0.01035600 -2.62282000 H -1.42702800 1.23832800 -1.67297600 H -0.48048200 0.07026200 -2.61061900 C -1.36393800 -2.20593900 -1.32121900 H -2.30559600 -2.39420200 -1.84033400 H -0.55418700 -2.38696600 -2.03318000 H -1.27883600 -2.93594600 -0.50949700 C -4.19212000 1.15157700 -0.74086200 H -3.75447900 1.91952600 -0.09125600 H -3.76378800 1.27124900 -1.73903400 H -5.26873800 1.35354800 -0.81927500 C -4.75156300 -0.34063300 1.16463400 H -5.81478500 -0.12371600 0.99911000 H -4.67579800 -1.34142700 1.60920000 H -4.37010200 0.38259300 1.89723300 C -4.54734900 -1.30527800 -1.12278200 H -4.10352500 -1.24269500 -2.12183100 H -4.39774400 -2.32427300 -0.74477700 H -5.62841300 -1.14671900 -1.23437300	
Kinetic parameters	k (413 K) = 7.57 10^{12} L mol^{-1} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 2.45 10^{-11}s

Table S5.8 Transition state: **TBD + 2 + CO₂** (carbonation step)

Eq:

TS:





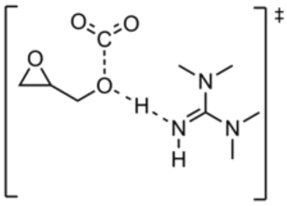
Coordinates of the TS (atom, X, Y, Z)	Energies
C -3.18594300 1.85320400 -0.60228400 O -2.62918800 2.33858700 -1.52823800 O -3.98554700 1.74821100 0.26705300 C -2.52663400 -2.19325000 0.15761800 C -2.05775600 -3.32391500 0.96629400 O -1.26474700 -2.84656000 -0.14710200 H -3.28918300 -2.37825800 -0.59956400 H -2.48828100 -4.31367500 0.82236400 H -1.62120500 -3.13562400 1.94652400 C -2.42437200 -0.77116800 0.64791700 H -3.39808600 -0.47471900 1.06770200 H -1.68506100 -0.72349200 1.46590600 O -2.06574600 0.09920200 -0.39804400 H -0.94490900 0.44292000 -0.21788000	$\Delta_r H_m$ = -15.7 kcal mol^{-1} $\Delta_r S_m$ = 56.4 cal mol^{-1} K^{-1} $\Delta_r G_m$ = -6.8 kcal mol^{-1} $\Delta H_m^{‡}$ = -21.9 kcal mol^{-1} $\Delta S_m^{‡}$ = -62.4 cal mol^{-1} K^{-1} $\Delta G_m^{‡}$ = 3.9 kcal mol^{-1}

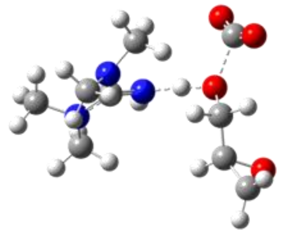
C	0.37667200	2.29300400	0.35639600	
C	1.33735800	0.12817000	-0.08293100	
C	2.83529300	1.99930900	0.48623000	
C	1.61717200	2.57352000	1.19685600	
H	0.42449400	2.87136700	-0.57915000	
C	3.80689900	-0.20554200	-0.10211600	
H	3.70436600	1.99279100	1.15342000	
H	1.75351100	3.65002800	1.34558800	
C	3.53416900	-1.47106200	-0.90319200	
C	2.28075900	-2.14255600	-0.36142600	
H	4.55792100	0.41331200	-0.60586300	
H	3.38728400	-1.22460000	-1.96171100	
H	2.45087800	-2.48652300	0.67077600	
H	4.39555600	-2.14202900	-0.82555100	
H	2.00190600	-3.01107000	-0.96422400	
H	4.20109000	-0.45876000	0.89283700	
H	3.09579200	2.60707600	-0.39172800	
H	1.50724400	2.10658400	2.18389700	
H	-0.53195000	2.60724200	0.88140500	
N	1.18116400	-1.18599600	-0.42475400	
H	0.24496200	-1.57154500	-0.31145600	
N	0.25291200	0.86852500	0.06689800	
N	2.59932300	0.61392500	0.06088200	
Kinetic parameters				k (413 K) = 7.9 10^{10} $L^2 mol^{-2} s^{-1}$ $t_{1/2}$ (413 K, 0.09 M) = 2.4 10^{-9} s

Table S5.9 Transition state: **TMG + 2 + CO₂** (carbonation step)

Eq:

TS:





Coordinates of the TS (atom, X, Y, Z)				Energies
C	2.24259800	2.11355100	-0.60129200	$\Delta_r H_m$ = -9.2 kcal mol^{-1}
O	2.97576000	2.24393000	0.33790800	$\Delta_r S_m$ = 54.4 cal mol^{-1} K^{-1}
O	1.72031300	2.57952000	-1.57320000	$\Delta_r G_m$ = 0.4 $kcalmol^{-1}$
C	2.08219800	-1.88254600	0.22742400	
C	2.95930500	-2.76658400	1.00355600	$\Delta H_m^‡$ = -14.5 kcal mol^{-1}
O	3.35336300	-2.31186900	-0.30925600	$\Delta S_m^‡$ = -61.7 cal mol^{-1} K^{-1}
H	1.22572800	-2.32624000	-0.28176100	$\Delta G_m^‡$ = 11.0 kcal mol^{-1}
H	2.73058600	-3.82931800	1.07478100	
H	3.54609700	-2.35391000	1.82412700	
C	1.94727000	-0.42475000	0.57731900	
H	1.15757200	-0.31103400	1.33587700	
H	2.88292900	-0.05261800	1.00408400	
O	1.64257300	0.35372900	-0.57534500	
H	0.51860500	0.29168200	-0.80314100	
C	-1.82058300	0.05281500	-0.26462200	
N	-0.79316300	0.07343500	-1.08963300	
H	-0.96879500	-0.39027800	-1.97670100	

N -2.90872000 -0.76270100 -0.44505900 N -1.82177100 0.85646100 0.84098700 C -0.91680200 1.99443200 0.93015200 H -1.40527800 2.78068200 1.51611200 H 0.02432800 1.72878600 1.42995000 H -0.69710900 2.37732000 -0.06635900 C -2.38675300 0.42810100 2.11785500 H -3.15031300 1.13369800 2.46652800 H -2.83021500 -0.56341400 2.02851200 H -1.58698100 0.38396700 2.86924000 C -2.83322300 -1.86639300 -1.39425700 H -3.60674500 -2.59521900 -1.13490900 H -3.00450600 -1.53589600 -2.43005800 H -1.85987100 -2.35907200 -1.33113200 C -4.26967900 -0.30214800 -0.16380400 H -4.25263600 0.67383400 0.32017100 H -4.82543900 -0.20971700 -1.10672100 H -4.79442900 -1.01495900 0.48249000	
Kinetic parameters	k (413 K) = 1.3 10^{7} L^{2} mol^{-2} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 1.4 10^{-5} s

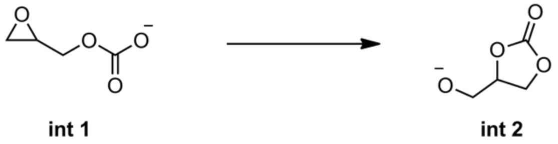
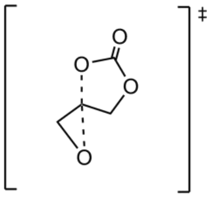
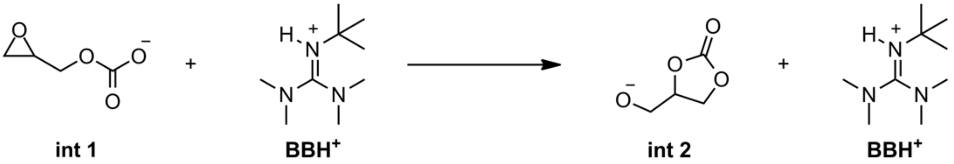
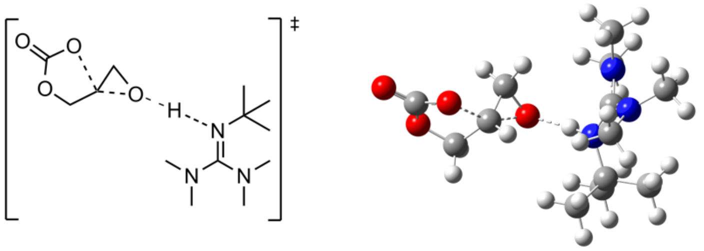
Table S5.10 Transition state: intramolecular cyclization	
Eq:  **TS:**  	
Coordinates of the TS (atom, X, Y, Z)	Energies
C -0.95450700 -0.15020700 0.52684900 C -1.71821700 -0.76213700 -0.56968500 O -2.75175100 0.08188900 -0.17958700 H -1.24559100 -0.44841100 1.52404700 H -1.90519900 -1.84421400 -0.45518600 H -1.30495900 -0.57693900 -1.57823900 C -0.31112500 1.19766200 0.31954600 H -0.92601700 1.82850900 -0.32236700 H -0.13822900 1.70320500 1.27669800 O 0.95448600 1.03352700 -0.35145800 C 1.56803500 -0.16176100 -0.01211600 O 0.83515100 -0.93685300 0.70384500 O 2.71397400 -0.35399900 -0.42686500	$\Delta_r H_m$ = -1.6 kcal mol^{-1} $\Delta_r S_m$ = 21.0 cal mol^{-1} K^{-1} $\Delta_r G_m$ = 10.2 kcal mol^{-1} $\Delta H_m^{\ddagger}$ = 25.3 kcal mol^{-1} $\Delta S_m^{\ddagger}$ = -90.0 cal mol^{-1} K^{-1} $\Delta G_m^{\ddagger}$ = 23.6 kcal mol^{-1}
Kinetic parameters	k (413 K) = 2.7 10^{-3} s^{-1} $t_{1/2}$ (413 K, 1.8 M) = 260.7 s

Table S5.11 Transition state: intramolecular cyclization assisted by **BB**

Eq:



TS:

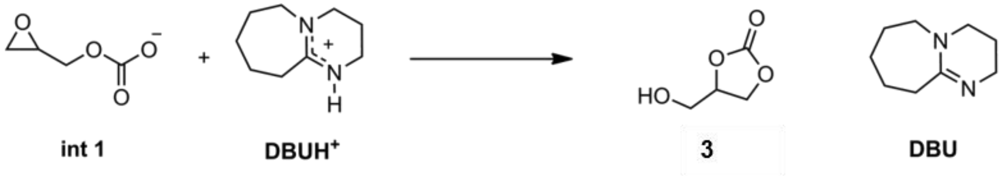


Coordinates of the TS (atom, X, Y, Z)				Energies
C	-2.19899500	0.21796000	0.10419700	$\Delta_r H_m$ = -7.4 kcal mol^{-1}
C	-1.80782200	-0.70880300	1.16668600	$\Delta_r S_m$ = 48.3 cal mol^{-1} K^{-1}
O	-1.08338700	0.41279800	1.61494900	$\Delta_r G_m$ = -5.2 kcal mol^{-1}
H	-1.46406400	0.40955300	-0.66390300	
H	-1.20342000	-1.57154100	0.85281000	$\Delta H_m^{\ddagger}$ = 5.8 kcal mol^{-1}
H	-2.61102800	-1.03558600	1.84163700	$\Delta S_m^{\ddagger}$ = -90.0 cal mol^{-1} K^{-1}
C	-3.32794600	1.19227100	0.31661900	$\Delta G_m^{\ddagger}$ = 23.6 kcal mol^{-1}
H	-3.28834900	1.62041800	1.31877900	
H	-3.28519600	1.99671600	-0.42686000	
O	-4.59181100	0.51688800	0.20958300	
C	-4.56809000	-0.49129300	-0.75173200	
O	-3.40549900	-0.72168700	-1.23477200	
O	-5.64248300	-1.04053700	-1.01329100	
C	1.92999200	-0.60917000	0.01566200	
N	1.30868800	0.55418300	0.24317100	
N	2.63590600	-0.84476900	-1.11665200	
N	1.82395500	-1.59389000	0.93588100	
C	3.85683000	-1.64457800	-1.12045600	
H	3.70653400	-2.60772800	-1.62276700	
H	4.63299900	-1.08844400	-1.65932800	
H	4.19745600	-1.81785800	-0.09922100	
C	2.18535500	-0.38565500	-2.42619300	
H	1.17644000	0.01732800	-2.35294500	
H	2.85430000	0.37638000	-2.84159000	
H	2.17359400	-1.24454300	-3.10823800	
C	1.61001600	-1.31696100	2.35507700	
H	0.56368300	-1.47564300	2.63629000	
H	2.24356700	-1.99538000	2.93683900	
H	1.88629800	-0.28693800	2.58068700	
C	1.77941300	-3.00708000	0.56454800	
H	2.69212900	-3.52863600	0.87512000	
H	0.92331200	-3.47059900	1.06652500	
H	1.65033400	-3.11066700	-0.51294300	
C	1.79358000	1.94929800	0.02323000	
C	3.29504300	2.00211400	-0.27708500	
H	3.55320700	1.57121300	-1.24609000	
H	3.60563800	3.05256400	-0.28964800	
H	3.87311300	1.48999200	0.50010900	
C	1.52731600	2.68148400	1.35211000	
H	1.81588800	3.73421800	1.26068000	
H	0.46577800	2.63607100	1.61811400	
H	2.10759000	2.23184600	2.16592700	
C	0.98249000	2.62628400	-1.09262100	

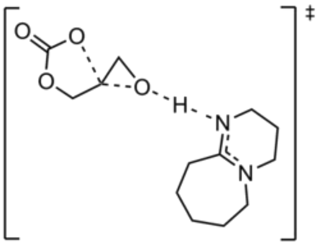
H -0.09096000 2.55844900 -0.88331200 H 1.25080500 3.68726300 -1.15346400 H 1.17580800 2.17302300 -2.06831700 H 0.45704800 0.49493700 0.84630100	
Kinetic parameters	k (413 K) = 2.8 L.mol^{-1}.s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 4.0 s

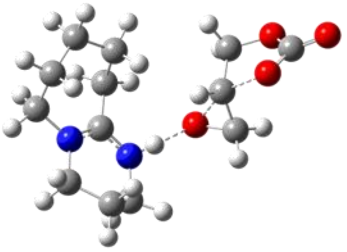
Table S5.12 Transition state: unimolecular cyclization assisted by **DBU**

Eq:



TS:



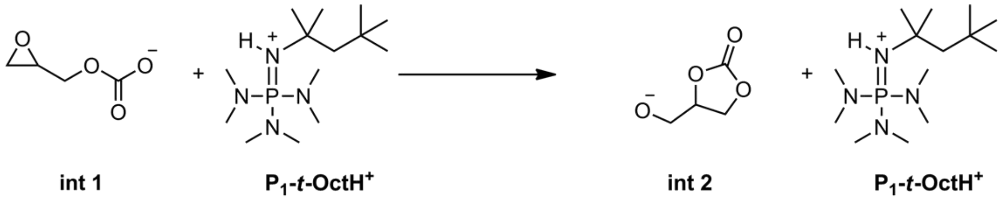


Coordinates of the TS (atom, X, Y, Z)	Energies
C -2.11460300 -0.39711600 0.19092400 C -2.25144800 -1.82010900 0.49554900 O -1.29840000 -1.48036200 1.48246000 H -1.23990600 -0.10364600 -0.37079800 H -1.90207400 -2.51514300 -0.27897500 H -3.22196700 -2.14251400 0.89431600 C -2.88536500 0.63702000 0.96898600 H -2.88950800 0.39849500 2.03317000 H -2.44776500 1.63046500 0.81848500 O -4.25866400 0.65637100 0.55025700 C -4.39501200 0.43213500 -0.81996300 O -3.30752000 0.09668300 -1.40254100 O -5.52582000 0.57019400 -1.29682100 H 0.27872300 -1.49727800 0.94980800 C 3.82255600 1.13625500 0.09008600 C 3.20395600 2.26743500 -0.73782800 C 1.88828800 -0.29580200 0.57968300 C 2.00327800 2.94104400 -0.06408900 C 1.19916000 0.86345700 1.24934100 C 0.83785200 2.00492800 0.27462700 H 3.90959800 1.42760800 1.14220500 H 2.92330400 1.87109900 -1.72317300 H 2.34741200 3.42022900 0.86412400 H 1.84047500 1.24837800 2.05206000 H 4.83019400 0.91300500 -0.26507800 H 3.98311000 3.02160300 -0.90662800 H 1.63359200 3.74491500 -0.71339100 H 0.29333400 0.47689300 1.71990400 H 0.04087500 2.59312400 0.74404100 H 0.41263500 1.57796300 -0.64289300 N 3.07648500 -0.13309000 0.00010200 C 3.70471600 -1.21438300 -0.78510100 H 4.46788500 -1.69848600 -0.16329000 H 4.20787300 -0.74597900 -1.63493700 C 1.78892100 -2.64908100 -0.09874400	Δ_rH_m = -21.5 kcal mol^{-1} Δ_rS_m = -7.2 cal mol^{-1} K^{-1} Δ_rG_m =-9.6 kcal mol^{-1} $\Delta H_m^{\ddagger}$ = 5.2 kcal mol^{-1} $\Delta S_m^{\ddagger}$ = -43.8 cal mol^{-1} K^{-1} $\Delta G_m^{\ddagger}$ = 23.2 kcal mol^{-1}

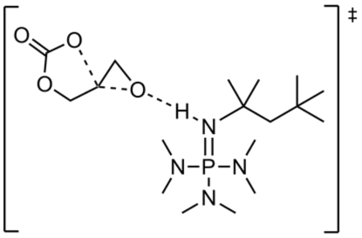
H 2.36470500 -3.23712000 0.62692200	
H 0.94180900 -3.25431500 -0.43050700	
C 2.66804300 -2.22059800 -1.26670400	
H 3.17720800 -3.08655500 -1.69961200	
H 2.04501500 -1.76689200 -2.04654100	
N 1.25275300 -1.45691600 0.55751800	
Kinetic parameters	k (413 K) = 4.4 L mol^{-1} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 2.5 s

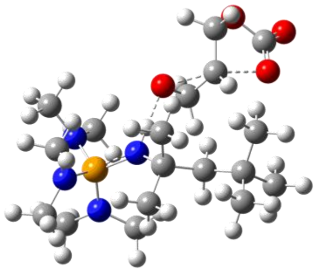
Table S5.13 Transition state: unimolecular cyclization assisted by **P₁-*t*-Oct**

Eq:



TS:



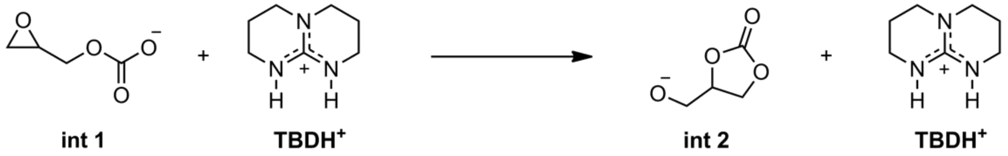


Coordinates of the TS (atom, X, Y, Z)	Energies
C 3.06049000 -0.66527300 -0.46013800	$\Delta_r H_m$ = -6.0 kcal mol^{-1}
C 2.07966900 -1.37048200 0.36280200	$\Delta_r S_m$ = -8.1 calmol^{-1} K^{-1}
O 1.30923100 -1.26358500 -0.81060000	$\Delta_r G_m$ = -2.62 kcal mol^{-1}
H 2.90712600 0.39370500 -0.59801300	
H 1.69499600 -0.81732800 1.23148000	$\Delta H_m^{\ddagger}$ = 6.1 kcal mol^{-1}
H 2.34328000 -2.39704200 0.65434400	$\Delta S_m^{\ddagger}$ = -30.7 cal mol^{-1} K^{-1}
C 3.93841500 -1.42434600 -1.42025700	$\Delta G_m^{\ddagger}$ = 18.8 kcal mol^{-1}
H 3.36835100 -2.19360400 -1.94250000	
H 4.38720600 -0.74136300 -2.15075100	
O 4.98357200 -2.10419100 -0.70595600	
C 5.44039200 -1.36504000 0.38422200	
O 4.74857400 -0.31743700 0.62861100	
O 6.42984000 -1.80235300 0.98017400	
H -0.16129900 -0.39009200 -0.50014500	
P -2.31734400 -0.80658000 0.09429100	
N -1.04299500 0.13680000 -0.29855500	
N -1.94144300 -2.40988900 -0.16200700	
N -3.65396000 -0.39937200 -0.79418200	
N -2.72850000 -0.72620300 1.69878700	
C -0.92053700 -3.04143500 0.68354600	
H -1.25055500 -4.05496900 0.94130000	
H 0.03988700 -3.09239000 0.16018800	
H -0.78497400 -2.47424000 1.60729800	
C -2.12953000 -3.07176200 -1.45259400	
H -1.30848000 -2.86401600 -2.15303700	
H -2.16858500 -4.15197400 -1.27542500	
H -3.07611900 -2.77350600 -1.90428800	
C -1.96739300 0.01129200 2.70194500	
H -2.62669600 0.69045100 3.25711300	
H -1.50771200 -0.69018900 3.41157100	
H -1.17715800 0.59069000 2.23134100	
C -3.64150400 -1.72223600 2.26704300	

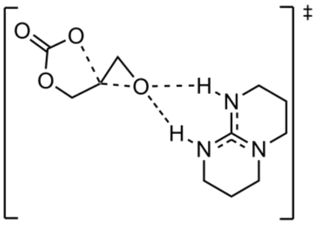
H -4.19029000 -2.24667700 1.48353100 H -3.08102400 -2.46294400 2.85356900 H -4.36303900 -1.22459400 2.92607500 C -4.96103700 -0.08539200 -0.22177600 H -5.68335400 -0.88963400 -0.41537800 H -4.88540400 0.07920100 0.85242600 H -5.33500700 0.83748400 -0.68219300 C -3.59975200 -0.27764300 -2.25146600 H -4.32286200 -0.95961400 -2.71646800 H -3.84773600 0.74946700 -2.54942000 H -2.60522800 -0.51578000 -2.62931200 C -0.90572800 1.62041500 -0.51652000 C 0.28327400 2.05541200 0.39211900 H -0.09046700 2.01447100 1.42143600 H 1.04418900 1.27237000 0.31590300 C 1.04560000 3.40744700 0.24768700 C -0.62589000 1.83113500 -2.01036700 H -0.54564500 2.89651000 -2.24370200 H 0.30415700 1.33749700 -2.31040200 H -1.44271400 1.41652400 -2.60672400 C -2.20362300 2.33958700 -0.12888100 H -2.08779100 3.41402900 -0.27267300 H -3.03988400 2.01268100 -0.75030900 H -2.46253000 2.16873000 0.92121400 C 1.99470800 3.43083400 -0.96640100 H 2.65877000 2.55810400 -0.96681000 H 1.46162500 3.45011600 -1.91991300 H 2.62699800 4.32741600 -0.92597600 C 1.92011300 3.51746200 1.51596800 H 2.54332700 4.41994000 1.48011100 H 1.30133100 3.56924900 2.42107400 H 2.58747300 2.65131500 1.61280400 C 0.12917200 4.64062100 0.19375000 H -0.44562600 4.68540500 -0.73730600 H -0.57514700 4.65573600 1.03454700 H 0.73426500 5.55517300 0.24883500	
Kinetic parameters	k (413 K) = 8.0 L mol^{-1} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 1.4 s

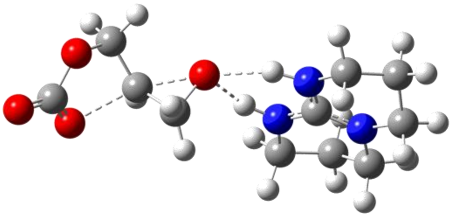
Table S5.14 Transition state: unimolecular cyclization assisted by **TBD**

Eq:



TS:





Coordinates of the TS (atom, X, Y, Z)			
C	2.65123200	0.43293900	-0.42484300
C	1.78141100	-0.19611600	0.56448000
O	0.98154500	-0.33505400	-0.59765700
H	2.41249700	1.44494600	-0.71727700
H	1.36678700	0.45792400	1.34208000
H	2.13261200	-1.14252900	0.99330300
C	3.58721100	-0.39576300	-1.26557900
H	3.07946000	-1.28113900	-1.65130100
H	3.97090600	0.19861600	-2.10281300
O	4.68555200	-0.86958600	-0.47355800
C	5.11706100	0.08364300	0.45357700
O	4.36593500	1.11316700	0.52726500
O	6.14481600	-0.18467300	1.08454400
H	-0.42351700	0.78120600	-0.48586400
C	-1.83448300	2.40424100	-0.13317700
C	-2.21069800	-0.03883200	-0.08215800
C	-4.05933600	1.46036400	0.47534500
C	-3.33684100	2.51009800	-0.36097000
H	-1.57451100	2.74617900	0.87775600
C	-4.34589300	-1.03316100	0.58818000
H	-5.12200700	1.42908000	0.22137800
H	-3.68982800	3.50649200	-0.07831600
C	-3.87655800	-2.29408300	-0.12792300
C	-2.38735500	-2.50087100	0.11561000
H	-4.31563600	-1.16973300	1.67818500
H	-4.43982600	-3.15492400	0.24472400
H	-1.98774500	-3.29366000	-0.52216300
H	-4.06832800	-2.20049600	-1.20340300
H	-2.20420400	-2.77974300	1.16209100
H	-5.37462400	-0.79090400	0.30796700
H	-3.97450800	1.68914800	1.54689800
H	-3.56488400	2.35598700	-1.42233200
H	-1.28078100	3.01642400	-0.85018200
N	-1.67384000	-1.26669200	-0.20610000
H	-0.66349500	-1.28884200	-0.37516700
N	-1.41517300	1.01659600	-0.31277400
N	-3.51322400	0.12015000	0.21807900

Energies

$\Delta_r H_m$ = -8.9 kcal mol^{-1}
$\Delta_r S_m$ = -10.2 cal mol^{-1} K^{-1}
$\Delta_r G_m$ = -4.7 kcal mol^{-1}

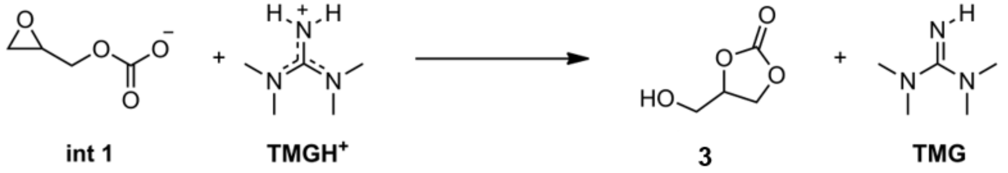
$\Delta H_m^{\ddagger}$ = 6.4 kcal mol^{-1}
$\Delta S_m^{\ddagger}$ = -43.3 cal mol^{-1} K^{-1}
$\Delta G_m^{\ddagger}$ = 24.3 kcal mol^{-1}

Kinetic parameters

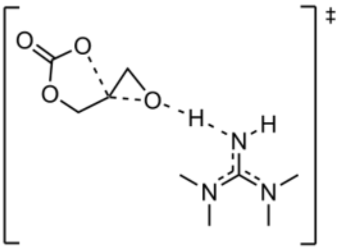
k (413 K) = 1.2 L mol^{-1} s^{-1}
$t_{1/2}$ (413 K, 0.09 M) = 9.5 s

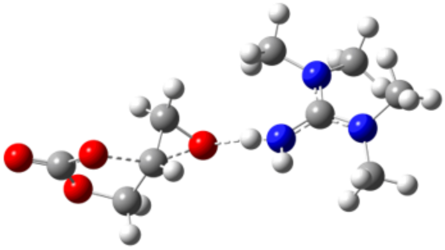
Table S5.15 Transition state: unimolecular cyclization assisted by **TMG**

Eq:



TS:

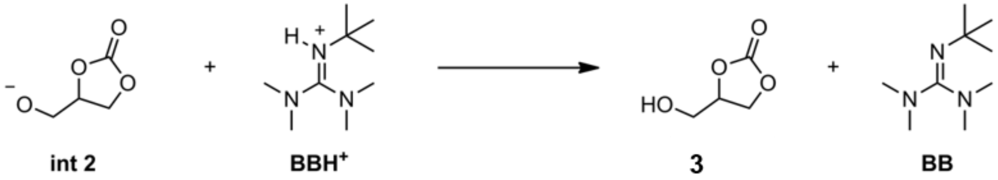




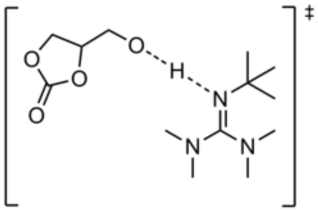
Coordinates of the TS (atom, X, Y, Z)				Energies
C	2.24951600	-0.38494900	0.07828300	$\Delta_r H_m = -15.3$ kcal mol^{-1}
C	1.66209700	0.95107300	-0.00334400	$\Delta_r S_m = -8.2$ cal mol^{-1} K^{-1}
O	0.78117700	0.39429900	0.94833500	$\Delta_r G_m = -11.9$ kcal mol^{-1}
H	1.73606100	-1.17492900	-0.45133000	
H	1.20947300	1.21929400	-0.96695800	$\Delta H_m^{\ddagger} = 7.8$ kcal mol^{-1}
H	2.27855900	1.77703400	0.37492400	$\Delta S_m^{\ddagger} = -41.4$ cal mol^{-1} K^{-1}
C	3.23123300	-0.72703400	1.16841600	$\Delta G_m^{\ddagger} = 24.9$ kcal mol^{-1}
H	2.90154900	-0.32679800	2.12797500	
H	3.35144200	-1.81376900	1.24718700	
O	4.50664400	-0.12758600	0.89289200	
C	4.80449500	-0.13183500	-0.47004200	
O	3.83600600	-0.51468400	-1.21193400	
O	5.93797400	0.23611700	-0.79385000	
H	-0.59585600	-0.21989800	0.26853500	
C	-2.66855600	-0.17336700	-0.09212500	
N	-1.44346800	-0.70420000	-0.12980700	
H	-1.33899600	-1.68023600	-0.37707200	
N	-3.76341900	-0.96704500	-0.09777200	
N	-2.81105200	1.16952200	-0.05872200	
C	-1.72283200	2.05393800	-0.47335600	
H	-2.16645400	2.97661700	-0.85817300	
H	-1.05937700	2.29740200	0.36469200	
H	-1.14128800	1.58532900	-1.26835400	
C	-3.90123600	1.82371900	0.66683100	
H	-4.53223800	2.40464000	-0.01458000	
H	-4.51179000	1.08679700	1.18774000	
H	-3.46678700	2.50279800	1.40975400	
C	-3.66684500	-2.38406700	0.24833100	
H	-4.63541800	-2.70506700	0.64109100	
H	-3.42392500	-2.99815600	-0.62950200	
H	-2.91137200	-2.53742800	1.02166500	
C	-5.00468700	-0.57937400	-0.77233200	
H	-4.88320700	0.37893800	-1.27602600	
H	-5.24431800	-1.33918300	-1.52512300	
H	-5.83399900	-0.51509600	-0.05985600	
Kinetic parameters				k (413 K) = 0.56 L mol^{-1} s^{-1} $t_{1/2}$ (413 K, 0.09 M) = 20 s

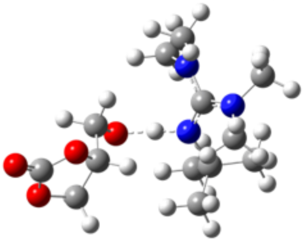
Table S5.16 Transition state: protonation of 3 by **BB**

Eq:



TS:



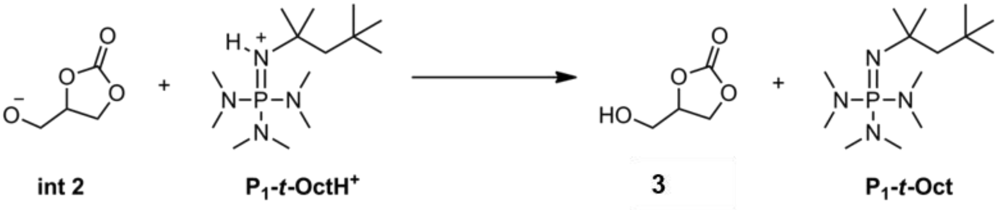


Coordinates of the TS (atom, X, Y, Z)	Energies
C -2.28507200 0.08932100 -0.18569900	$\Delta_r H_m$ = -16.0 kcal mol^{-1}
C -1.70669200 -0.41665700 1.14443900	$\Delta_r S_m$ = -32.8 cal mol^{-1} K^{-1}
O -0.85615500 0.52160100 1.69129400	$\Delta_r G_m$ = -15.4 kcal mol^{-1}
H -1.49221300 0.25665400 -0.91514800	
H -1.21748400 -1.39305400 0.93676400	
H -2.56270700 -0.64436200 1.81440300	
C -3.20003900 1.30482200 -0.03157600	
H -3.05724900 1.81869400 0.91874600	
H -3.13729200 2.01157500 -0.86338400	
O -4.53350800 0.72001000 -0.04588800	
C -4.46707000 -0.52871600 -0.54914700	
O -3.19484000 -0.90424800 -0.76642900	
O -5.43478500 -1.21859700 -0.77937700	
C 1.86659900 -0.59897900 0.04655100	
N 1.29716100 0.55195900 0.36567100	
N 2.50461400 -0.83921800 -1.13979000	
N 1.79974900 -1.62913500 0.93419200	
C 3.71596200 -1.64374300 -1.22238500	
H 3.53606000 -2.60041900 -1.73051300	
H 4.47217100 -1.08839700 -1.79214700	
H 4.10771400 -1.83856900 -0.22314300	
C 1.94959900 -0.41486600 -2.41663700	
H 0.95276700 -0.00076300 -2.27063900	
H 2.58129500 0.33213500 -2.91332900	
H 1.87169600 -1.28941300 -3.07630600	
C 1.64884300 -1.40529500 2.36716400	
H 0.60279100 -1.49623000 2.68029800	
H 2.25185800 -2.15057100 2.89872800	
H 2.00023700 -0.40556900 2.62387100	
C 1.66198100 -3.01777800 0.50636100	
H 2.54931200 -3.60602700 0.77097500	
H 0.79129600 -3.45876400 1.00624600	
H 1.50500600 -3.06889500 -0.57135500	
C 1.75109500 1.92902300 0.04445100	
C 3.20933500 1.99791700 -0.42866800	
H 3.36161300 1.56375600 -1.41816500	
H 3.50868100 3.05116400 -0.48040800	
H 3.87790900 1.49429400 0.27883400	
C 1.63714900 2.70522700 1.37339600	
H 1.89692800 3.75893900 1.21906500	
H 0.61705500 2.64840500 1.76654100	
H 2.31959700 2.28707300 2.12291400	

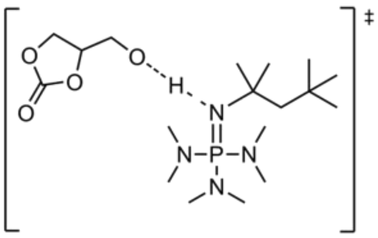
C	0.81075700	2.58285700	-0.98335700	
H	-0.22883900	2.51586500	-0.64425700	
H	1.06405500	3.64342000	-1.09979900	
H	0.88718000	2.10980400	-1.96606500	
H	0.32952200	0.51508400	1.02059900	

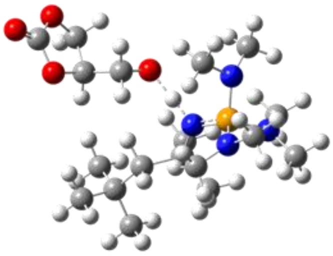
Table S5.17 Transition state: protonation of **3** by **P$_1$-*t*-Oct**

Eq:



TS:



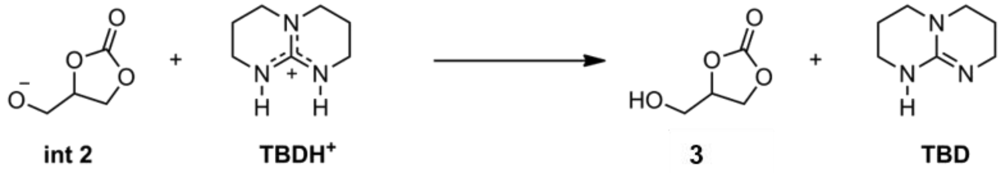


Coordinates of the TS (atom, X, Y, Z)				Energies
C	3.34019900	-0.46793400	-0.28686500	$\Delta_r H_m$ = -14.7 kcal mol^{-1}
C	2.01940100	-1.19972100	-0.02448400	$\Delta_r S_m$ = -82.6 cal mol^{-1} K^{-1}
O	1.14526000	-0.99469800	-1.06980300	$\Delta_r G_m$ = -12.8 kcal mol^{-1}
H	3.18265700	0.60847900	-0.34857500	
H	1.62875200	-0.83757900	0.95022500	
H	2.26658700	-2.27412900	0.13291700	
C	4.11328000	-1.01525100	-1.48727200	
H	3.48521900	-1.60117300	-2.15793200	
H	4.66004000	-0.24931100	-2.04377600	
O	5.09124800	-1.90376800	-0.87549700	
C	5.19085400	-1.61846900	0.43840600	
O	4.28401400	-0.70008500	0.81238400	
O	6.00114000	-2.12545600	1.18149700	
H	-0.00904000	-0.41651200	-0.64641500	
P	-2.23530400	-0.82056900	0.07621800	
N	-0.98976300	0.12917800	-0.30551100	
N	-1.86814500	-2.42969200	-0.22816700	
N	-3.62751200	-0.43995500	-0.76005600	
N	-2.64144000	-0.81589800	1.69541100	
C	-0.81326500	-3.06191700	0.57127700	
H	-1.09341500	-4.10451200	0.76764900	
H	0.14597800	-3.03688700	0.04420000	
H	-0.69821200	-2.54858400	1.52876400	
C	-1.99904900	-3.01054700	-1.56302500	
H	-1.16712700	-2.72858600	-2.22455800	
H	-2.00447700	-4.10159800	-1.46021400	
H	-2.94398800	-2.71538200	-2.02078000	
C	-1.85290400	-0.12895800	2.71119300	
H	-2.50160100	0.49426700	3.34062800	
H	-1.34133900	-0.85988400	3.35419000	
H	-1.10034400	0.50292900	2.24567200	
C	-3.51313700	-1.85781100	2.24067500	
H	-4.08270900	-2.34830800	1.45029600	
H	-2.92148200	-2.62190500	2.76496000	
H	-4.21790900	-1.41256300	2.95414200	

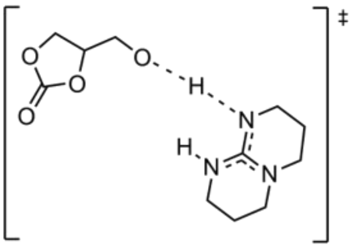
C -4.92170300 -0.16693600 -0.14455100	
H -5.64281800 -0.96897800 -0.35627200	
H -4.82284300 -0.05078900 0.93401800	
H -5.32014800 0.77177400 -0.55162500	
C -3.61578600 -0.24684000 -2.20837600	
H -4.33488800 -0.92321300 -2.68962300	
H -3.89616700 0.78695600 -2.45375800	
H -2.62673400 -0.44145900 -2.62377700	
C -0.91479200 1.62062300 -0.45936400	
C 0.29308300 2.05934400 0.42453400	
H -0.04640700 1.97815200 1.46403600	
H 1.06309700 1.29462000 0.29659200	
C 1.02681000 3.42880800 0.30068900	
C -0.69346400 1.91137100 -1.95116500	
H -0.64590900 2.98809400 -2.13930600	
H 0.23366300 1.44937100 -2.30353700	
H -1.52260300 1.50552900 -2.53692300	
C -2.21245600 2.30229500 0.00041600	
H -2.12492600 3.38513300 -0.10134500	
H -3.06416400 1.98286400 -0.60464600	
H -2.43392900 2.08299600 1.05034600	
C 1.92828600 3.50950100 -0.94739500	
H 2.58411100 2.63313200 -1.01856300	
H 1.35744700 3.57739700 -1.87651500	
H 2.56747500 4.40047000 -0.88913900	
C 1.94894100 3.50944200 1.53728600	
H 2.55393700 4.42487000 1.51288100	
H 1.36602100 3.51410100 2.46735500	
H 2.63519100 2.65324200 1.57522400	
C 0.09143900 4.64851600 0.32581400	
H -0.52282500 4.71335700 -0.57842200	
H -0.57781100 4.62415100 1.19474900	
H 0.68349500 5.57152600 0.38643600	

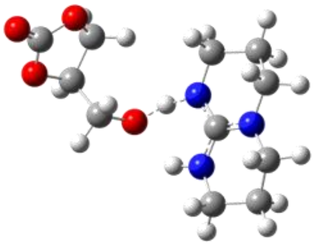
Table S5.18 Transition state: protonation of **3** by **TBD**

Eq:



TS:





Coordinates of the TS (atom, X, Y, Z)	Energies
C -3.05560400 0.82624600 0.81838600	$\Delta_r H_m$ = -17.5 kcal mol^{-1}
C -1.69656700 1.38364200 0.37989500	$\Delta_r S_m$ = -84.6 cal mol^{-1} K^{-1}
O -0.75283000 1.20839700 1.38416700	$\Delta_r G_m$ = -14.9 kcal mol^{-1}
H -3.41569200 1.34494200 1.70790700	
H -1.83796500 2.44891200 0.12581700	
H -1.40732200 0.87062800 -0.56272100	
C -3.08642900 -0.69465600 0.97395200	

H	-2.09855200	-1.13428900	1.10679800
H	-3.76375600	-1.03780300	1.76042400
O	-3.61914600	-1.14455100	-0.30304200
C	-4.23142500	-0.11072300	-0.91520800
O	-4.04714800	1.03806400	-0.23905100
O	-4.86739400	-0.20910600	-1.93940600
H	1.11706000	1.83864800	0.69440900
C	2.95979700	2.27225200	-0.33171000
C	1.94622800	0.07723700	0.22790300
C	4.07256000	0.15269000	-1.01730800
C	4.28976700	1.53396100	-0.41056500
H	2.60119200	2.51662700	-1.34292200
C	2.91358900	-2.01555700	-0.56609100
H	4.98296200	-0.44938100	-0.93961500
H	4.99811800	2.09498100	-1.02843000
C	2.05801200	-2.68481300	0.50338700
C	0.70541900	-1.98313900	0.58427400
H	2.49309900	-2.19458100	-1.56718500
H	1.92529700	-3.74408600	0.25935500
H	0.14267100	-2.32625700	1.45923900
H	2.57005900	-2.62235700	1.47163900
H	0.10370500	-2.22776500	-0.30391600
H	3.93221200	-2.41478900	-0.55648500
H	3.81913100	0.23778900	-2.08491600
H	4.71730000	1.43447300	0.59447500
H	3.05976500	3.20812500	0.22510500
N	0.86757500	-0.53754200	0.68726800
H	-0.00139400	0.22959700	1.08114400
N	1.99686100	1.43147900	0.37155900
N	3.00730300	-0.57374900	-0.31639200

5.10 COPIES OF ^{1}H ,^{13}C NMR SPECTRA

Glycerol (1)

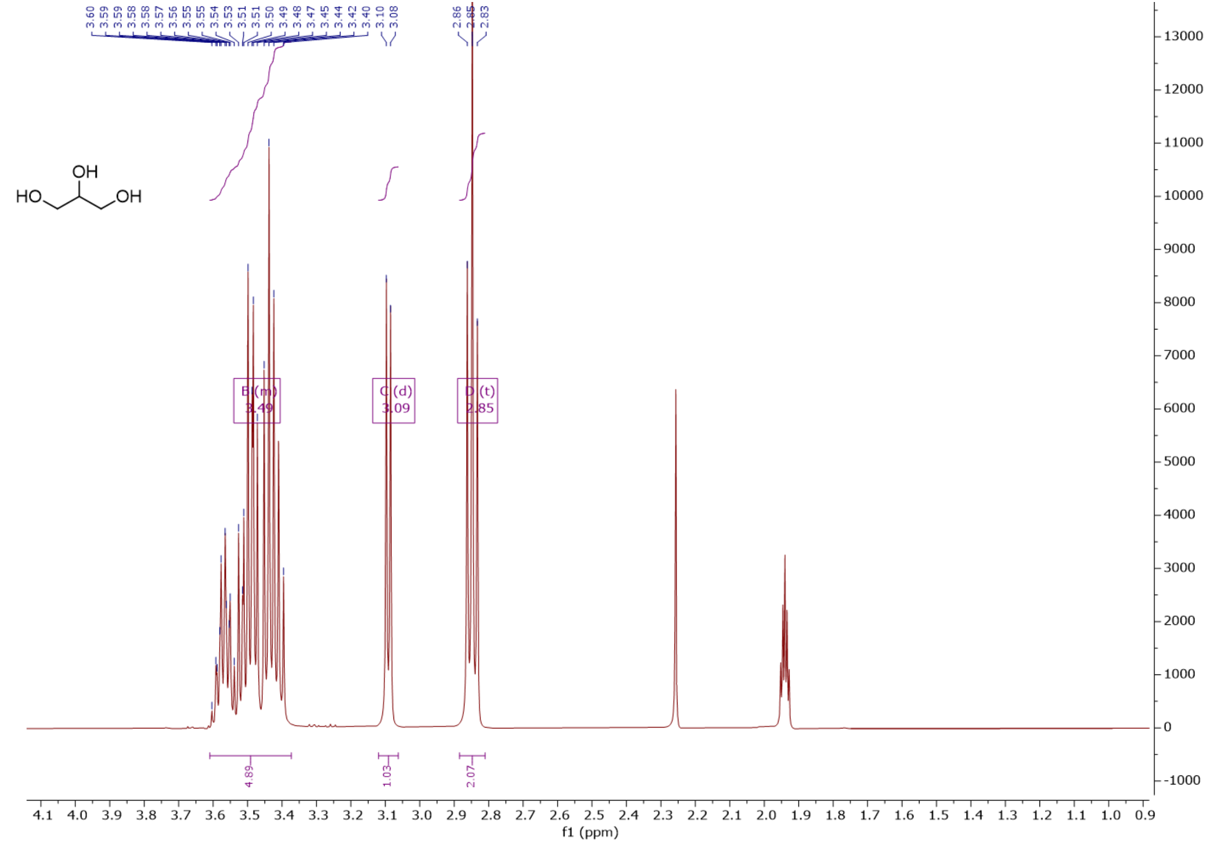


Figure S5.22 ^{1}H NMR spectrum (400 MHz - CD_3CN) of a commercial reference of **1**.

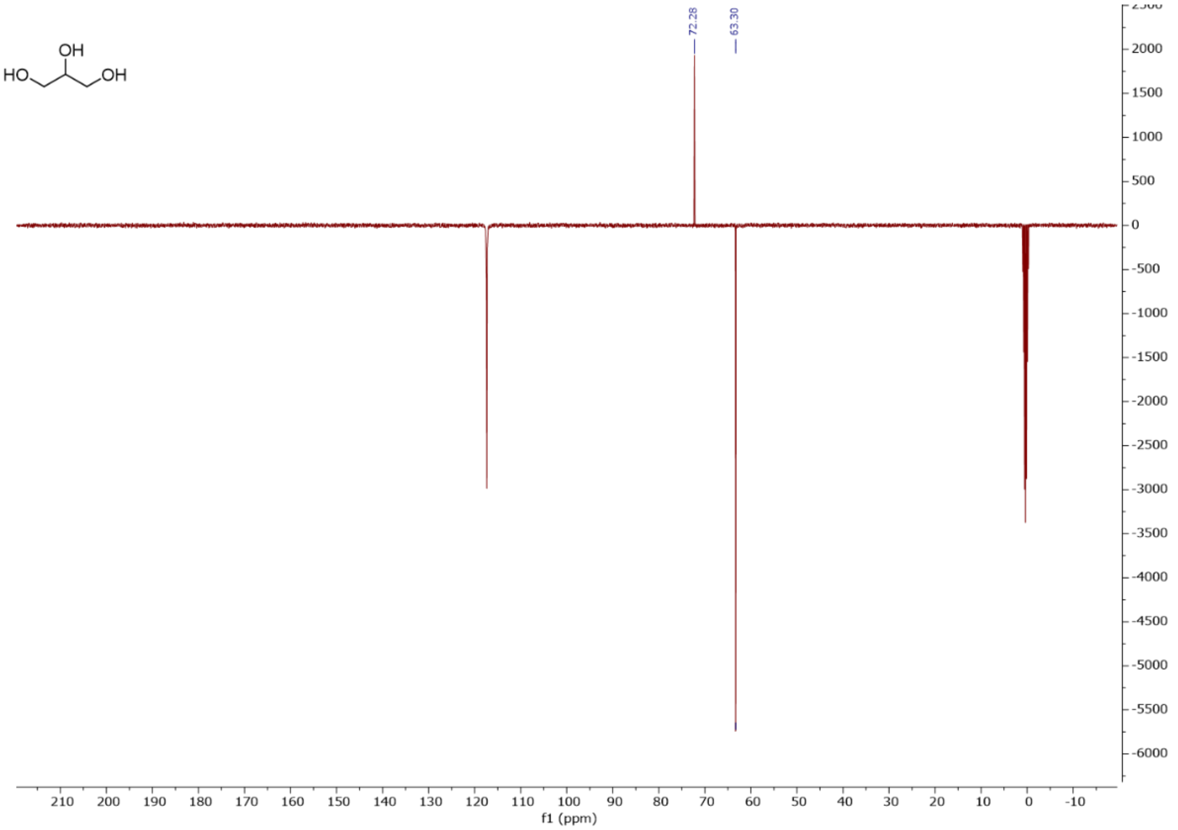


Figure S5.23 ^{13}C APT NMR spectrum (101 MHz - CD_3CN) of a commercial reference of **1**.

Glycidol (2)

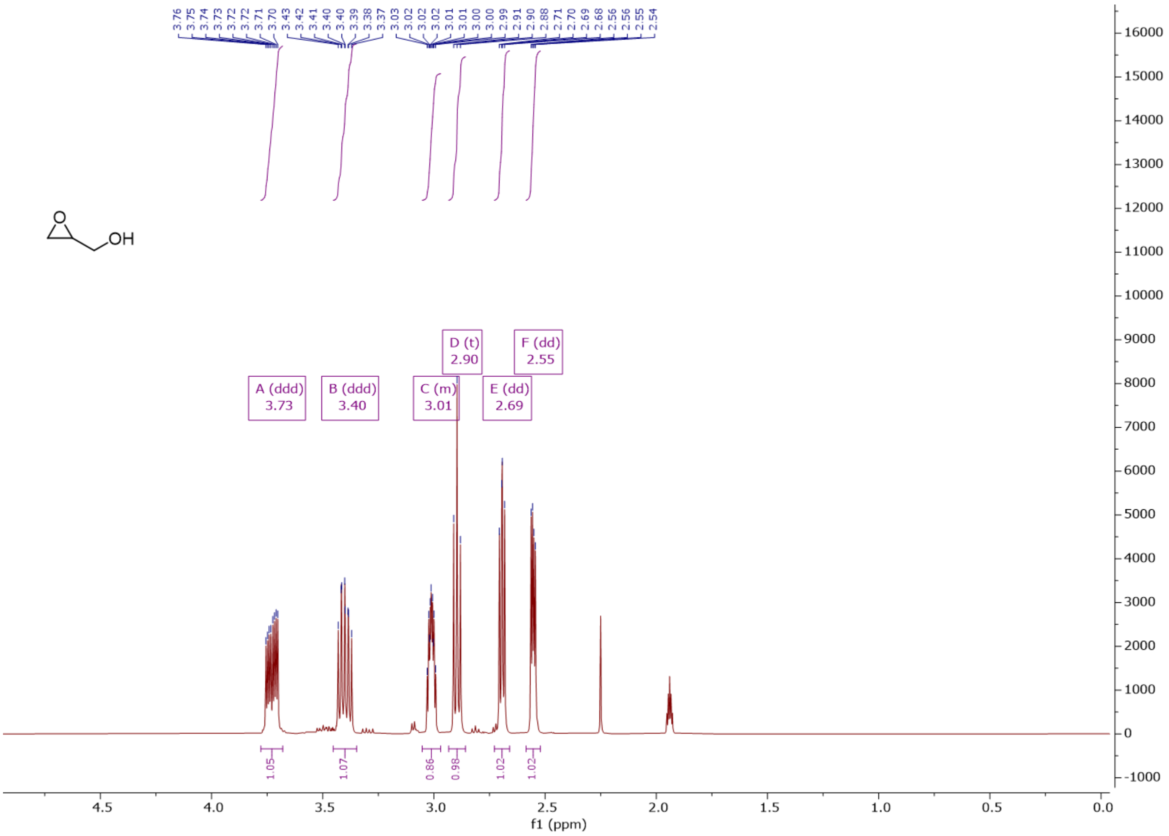


Figure S5.24 ^{1}H NMR spectrum (400 MHz - CD_3CN) of **2**.

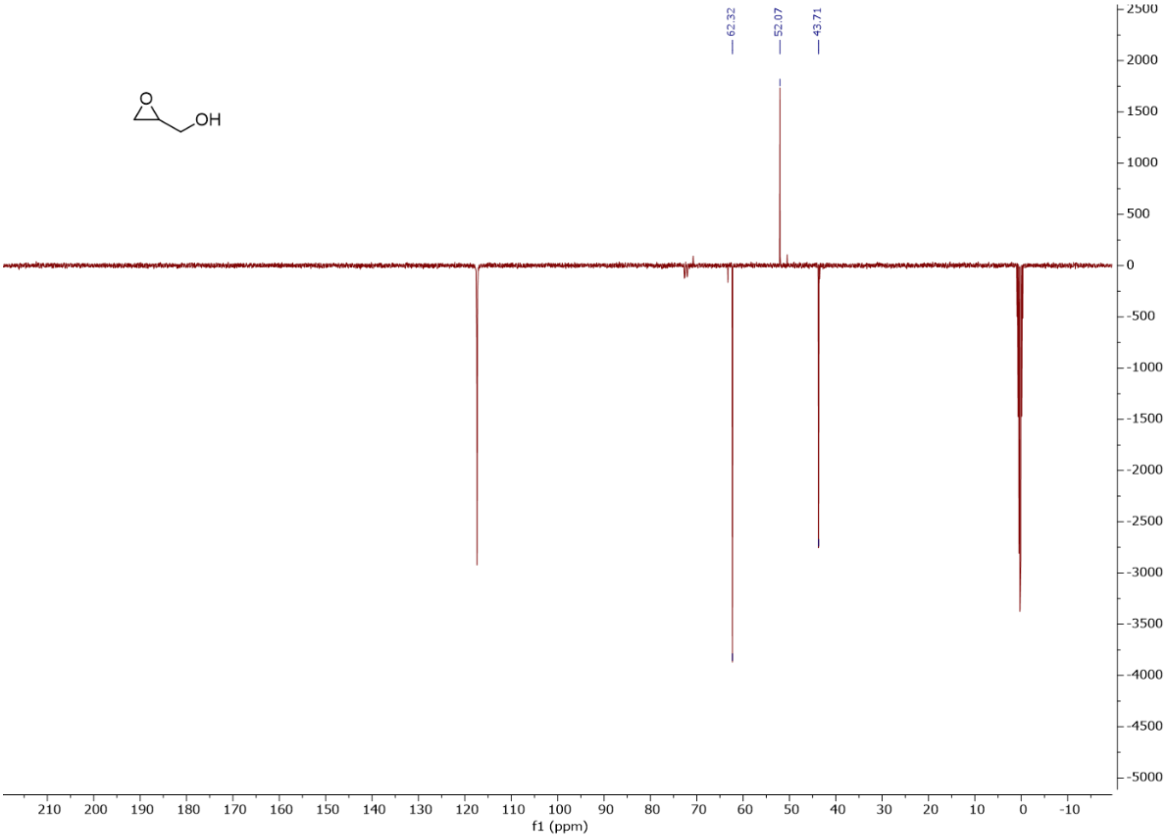


Figure S5.25 ^{13}C APT NMR spectrum (101 MHz - CD_3CN) of **2**.

Glycerol carbonate (3)

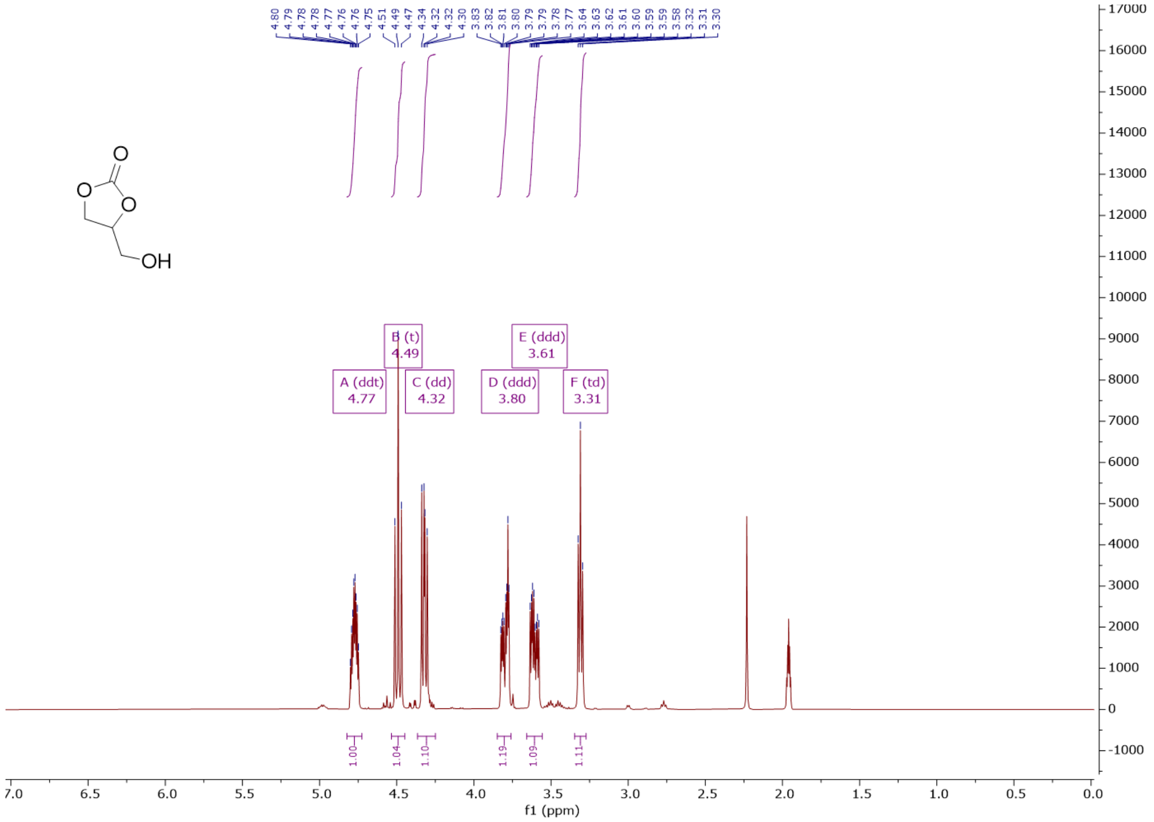


Figure S5.26 ^{1}H NMR spectrum (400 MHz - CD_3CN) of a commercial reference of **3**.

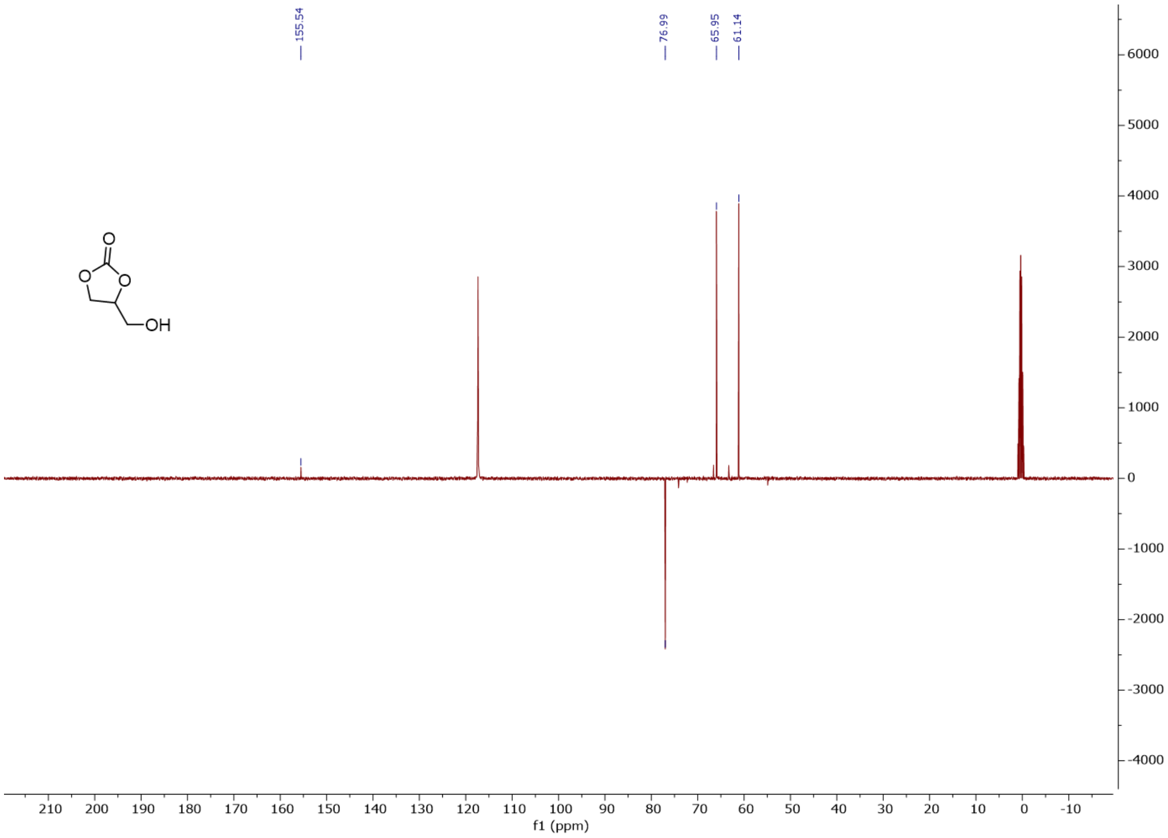


Figure S5.27 ^{13}C APT NMR spectrum (101 MHz - CD_3CN) of a commercial reference of **3**.

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