Supporting Information

Continuous Flow Asymmetric Cyclopropanation Reactions Using Cu(I) Complexes of Pc-L* Ligands Supported on Silica as Catalysts with Carbon Dioxide as Carrier.

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PART I

PART II

General. NMR spectra were recorded on Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. Metal loadings are determined by ICP-OES using a Thermo X Series II apparatus. 15 mg of each sample are mineralized by adding 3 mL of 37% HCl, 1 mL of concentrated HNO_3, 1 mL of 98% H_2SO_4. HPLC analyses were performed on a Hewlett-Packard 1050 instrument equipped with DAI-CEL CHIRALCEL, IB, OJ and AD chiral columns. Infrared spectra were recorded on a BIO-RAD FTS-7 spectrophotometer. CO-DRIFT spectra of the samples were recorded using a FTS-60A spectrophotometer equipped with a homemade reaction chamber. After purging the apparatus with ultra-pure He, spectra of the samples were recorded at RT in He and CO flow, before and after catalysis. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. All starting materials (α-methylstryrene, ethyldiazoacetate (EDA),[1] 2,4-dinitrotoluene, styrene, 4-chlorostyrene, 1,1-diphenylethylene, methyl-2-furoate, 1-octene and 1,2-dichloroethane) were purchased from Aldrich and used without further treatment. Solvents for the analytical HPLC were purchased from Sigma-Aldrich, and used as received. Davisil LC150 (Grace Davison, 35-70 micron) and Aerosil 380 (Evonik) are commercially available. MCM-41 was synthesized as already reported.[2] CO_2 (99.9995%) was purchased from BOC gases. Unless otherwise specified, all the reactions were carried out in air atmosphere. The synthesis and characterization of copper(I)(**Pc-L***) complexes **1**[3] and **2**[4] were previously reported. The water and air sensitive catalysts **1/D**, **1/A**, **1/M** and **2/D** were synthesized as already reported[5] and they were handled in a dry-box, model "Labstar 50" (MBraun, Germany).

The collected analytical data for *cis* and *trans* ethyl-2-methyl-2-phenylcyclopropanecarboxylate,[6] *cis* and *trans* ethyl-2-phenylcyclopropanecarboxylate,[7] *cis* and *trans* ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate,[8] ethyl-2,2-diphenylcyclopropanecarboxylate,[6] dimethyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate[9] and *cis* and *trans* ethyl-2-hexylcyclopropanecarboxylate[10] are in agreement with those reported in the literature. The absolute configurations of the product cyclopropanes were assigned based on literature data.

Materials.

Davisil L150 (Grace Davison, 35-70 micron): pore diameter 13.3 nm; pore volume 1.1 mL/g; surface area 279 m^2/g.

Aerosil 380 (Evonik): surface area 262 m^2/g.

MCM-41 (6170): pore diameter 3.6 nm; pore volume 0.73 mL/g; surface area 967 m^2/g.

Activation of all silicas was performed in a Schlenk flask at 300 °C for 2-3 h in air, subsequently in high vacuum (at least 10^{-5} mbar) overnight at 300 °C.

Grafting of [Cu^{I}(Pc-L*)]CF_3SO_3 complex, 1, on silica. Altough the general synthesis of these products has already been reported by us,[4] we here report the exact reagent amuonts used in the present work.

Synthesis of 1/D. $[Cu(OTf)]_2 \cdot (C_6H_6)$ (0.140 g, 0.277 mmol) was added to a $C_2H_4Cl_2$ (28 mL) solution of **1** (0.371 g, 0.555 mmol). The resulting colorless solution was stirred for 1 h., then added to activated Davisil B (3.5 g). The mixture was stirred at RT for 4 h under inert atmosphere, filtered, the solid washed with $C_2H_4Cl_2$ (3 x 10 mL) and dried overnight to yield the immobilized copper(I) complex **1/D**. A copper loading of 0.84 % was determined by ICP-OES.

Synthesis of 1/A. $[Cu(OTf)]_2 \cdot (C_6H_6)$ (0.0411 g, 0.0816 mmol) was added to a $C_2H_4Cl_2$ (8.2 mL) solution of **1** (0.109 g, 0.163 mmol). The resulting colorless solution was stirred for 1 h., then added to activated Aerosil (1.0 g) The mixture was stirred at RT for 4 h under inert atmosphere, filtered, the solid washed with $C_2H_4Cl_2$ (3 x 10 mL) and dried overnight to yield the immobilized copper(I) complex **1/A**. A copper loading of 0.812 % was determined by ICP-OES.

Synthesis of 1/M. $[Cu(OTf)]_2 \cdot (C_6H_6)$ (0.0568 g, 0.113 mmol) was added to a $C_2H_4Cl_2$ (11 mL) solution of **1** (0.151 g, 0.226 mmol). The resulting colorless solution was stirred for 1 h., then added to activated MCM-41 (1.4 g). The mixture was stirred at RT for 4 h under inert atmosphere, filtered, washed with $C_2H_4Cl_2$ (3 x 10 mL) and dried overnight to yield the immobilized copper(I) complex **1/M**. A copper loading of 0.85 % was determined by ICP-OES.

Synthesis of 2/D. Complex **2** (0.410 g, 0.470 mmol) was dissolved in CH_2Cl_2 (40 mL). The resulting colourless solution was added to activated Davisil LC150 (3.0 g), the mixture was stirred at RT for 4 h under inert atmosphere, filtered, the solid washed with CH_2Cl_2 (3 x 10 mL) and dried overnight to yield the immobilized copper(I) complex **2/D**.

Tables of all collected samples S1-S4.

Table S1a. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 3, run 1).[a]

Catalyst (g)	Cu (mmol)
0.4274	0.0565

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
1	218	99	65.2	58:42	38	18
2	249	99	65.7	57:43	39	16
3	280	99	65.4	57:43	36	14
4	300	99	64.8	57:43	31	13
5	328	99	64.3	55:45	29	11
6	354	99	65.0	56:44	26	12
7	381	90,6	73.5	54:46	38	18

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.17 mol/L in DCE at room temperature. Flow 0.2 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S1b. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 3, run 2).[a]

Catalyst (g)	Cu (mmol)
0.4274	0.0565

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
1	226	39,2	61.2	49:51	29	15
2	256	33,1	62.4	48:52	28	15
3	287	24,9	63.7	46:54	26	14
4	322	14,7	65.5	44:56	24	11
5	352	nd	nd	nd	24	12
6	378	4,2	67.3	45:55	20	16
7	399	3,8	67.3	nd	14	13

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.17 mol/L in DCE at room temperature. Flow 0.2 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S1c. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 4, run 1).[a]

Catalyst (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
0.4022	0.0532	1	180	99	54.9	70:30	54	24
		2	212	99	54.7	62:38	40	23
		3	243	99	54.4	61:39	36	21
		4	273	99	57.3	60:40	34	22
		5	303	99	56.5	58:42	30	21
		6	334	99	59.9	56:44	29	23
		7	364	99	59.6	55:45	32	29
		8	394	99	61.6	54:46	31	24

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.085 mol/L in DCE at room temperature. Flow 0.2 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S1d. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 5, run 1).[a]

Cat. (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *trans* (1*R*,2*R*)	Cu leaching Cu[c] (ppb)	Cu leaching Cu lost (%)
0.4068	0.0538	1	487	99	57.6	61:39	30	28		
		2	517	99	56.8	61:39	28	26	1143	0.67
		3	547	99	57.1	60:40	19	27		
		4	578	99	58.1	58:42	22	27		
		5	608	99	52.5	71:29	24	20		
		6	638	99	58.7	57:43	26	25	3788	1.86
		7	668	99	57.5	57:43	n.d	n.d		

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.17 mol/L in DCE at room temperature. Flow 0.1 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S1e. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 6, run 1).[a]

Catalyst (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
0.4081	0.0539	1	92	99	48.7	77:23	39	26
		2	122	99	53.4	67:33	36	24
		3	153	99	59.2	64:38	46	26
		4	183	99	65.8	57:43	55	32
		5	213	99	70.6	57:43	68	32
		6	244	nd	nd	nd	67	33
		7	274	99	71.2	58:42	68	33
		8	304	99	65.4	59:41	68	30
		9	335	99	57.9	62:38	63	29
		10	346	99	52.3	65:35	67	28

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.17 mol/L in DCE at room temperature. Flow 0.5 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S1f. Cyclopropanation with α-methylstyrene and EDA with **1/D**. (Data referred to Table 2, entry 6, run 2).[a]

Catalyst (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
0.4081	0.0539	1	30	99	58.6	54:46	55	30
		2	60	78	55.6	54:46	46	30
		3	91	59	52.6	56:44	12	nd
		4	121	11	nd	nd	nd	nd

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5. [EDA] = 0.17 mol/L in DCE at room temperature. Flow 0.5 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S2a. Cyclopropanation with α-methylstyrene and EDA with **1/D** under CO_2. (Data referred to Table 3, entry 1, run 1).[a]

Cat. (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *trans* (1*R*,2*R*)	Cu leaching Cu[c] (ppb)	Cu leaching Cu lost (%)
0.4003	0.0529	1	191	99	61.2	63:37	39	33		
		2	222	99	64.6	60:40	37	32		
		3	254	99	65.7	66:34	37	32		
		4	285	99	66.7	68:32	37	33		
		5	317	99	67.1	66:34	36	34	4.3	0.0016
		6	347	99	67.5	69:31	33	41		
		7	377	99	67.8	71:29	32	42		
		8	407	99	66.7	67:33	38	29		
		9	438	99	66.1	70:30	36	33		
		10	468	99	64.4	66:34	38	31		

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S2b. Cyclopropanation with α-methylstyrene and EDA with **1/D** under CO_2. (Data referred to Table 3, entry 1, run 2).[a]

Catalyst (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
0.4003	0.0529	1	30	99	64.7	68:32	44	25
		2	91	99	66.0	70:30	43	27
		3	129	99	66.3	66:34	45	23
		4	159	99	65.1	69:31	42	28

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S2c. Cyclopropanation with α-methylstyrene and EDA with **1/D** under CO_2. (Data referred to Table 3, entry 2, run 1).[a]

Catalyst (g)	Cu (mmol)	Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
0.3943	0.0521	1	147	99	48.9	64:36	36	20
		2	178	99	45.3	64:36	42	22
		3	208	99	45.4	65:35	40	26
		4	239	99	44.6	64:36	43	28
		5	270	99	44.4	62:38	41	25
		6	300	99	44.9	63:37	39	25
		7	330	99	45.2	62:38	31	26
		8	361	99	46.1	61:39	39	27
		9	391	99	45.8	60:40	37	26
		10	422	99	46.8	60:40	36	26
		11	452	99	46.6	61:39	38	25
		12	483	99	47.3	60:40	38	25
		13	513	99	48.1	59:39	35	25
		14	543	99	49.0	60:40	38	25

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:2; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S2d. Cyclopropanation with α-methylstyrene and EDA with **1/D** under CO_2. (Data referred to Table 3, entry 3, run 1).[a]

Catalyst (g)	Cu (mmol)
0.3393	0.0448

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
1	148	99	67.2	63:37	36	26
2	179	99	74.5	70:30	37	27
3	210	99	75.3	69:31	37	27
4	240	99	77.1	69:31	32	31
5	270	99	77.6	70:30	36	30
6	301	99	73.8	79:21	36	28
7	331	99	73.1	83:17	29	29
8	362	99	73.2	79:21	45	25
9	393	99	64.4	90:10	41	23
10	512	99	75.8	70:30	38	26
11	543	nd	nd	nd	nd	nd
12	573	99	70.9	69:31	38	27
13	603	99	69.2	72:28	32	28

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:10; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S2e. Cyclopropanation with α-methylstyrene and EDA with **1/M** under CO_2. (Data referred to Table 3, entry 4, run 1).[a]

Cat. (g)	Cu (mmol)
0.4044	0.0541

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *trans* (1*R*,2*R*)	Cu leaching Cu[c] (ppb)	Cu leaching Cu lost (%)
1	131	99	87.6	58:42	29	32		
2	162	99	87.4	58:42	41	35		
3	192	99	87.5	59:41	41	32	10.8	0.0074
4	223	99	87.3	60:40	42	26		
5	255	99	87.6	60:40	42	28		
6	285	99	87.5	59:41	41	29		
7	316	99	87.5	59:41	40	28	7.18	0.0041
8	346	99	87.9	58:42	42	25		
9	378	99	88.5	58:42	42	29		
10	408	99	88.5	58:42	42	29		
11	439	99	88.5	57:43	42	29		
12	470	99	88.5	59:41	34	30		

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S2f. Cyclopropanation with α-methylstyrene and EDA with **1/A** under CO_2. (Data referred to Table 3, entry 4, run 1).[a]

Catalyst (g)	Cu (mmol)
0.4229	0.0540

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*R*,2*S*)	*ee* (%)[b] *Trans* (1*R*,2*R*)
1	137	99	66.3	58:42	34	26
2	228	99	71.7	58:42	24	28
3	290	99	69.1	58:42	34	18
4	351	99	72.6	59:41	33	23
5	412	99	73.1	53:47	40	17
6	472	99	80.7	54:46	38	15

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75).

Table S3a. Cyclopropanation with α-methylstyrene and EDA with **2/D** under CO_2. (Data referred to Table 4, entry 1, run 1).[a]

Cat. (g)	Cu (mmol)
0.4157	0.0430

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*S*,2*R*)	*ee* (%)[b] *trans* (1*S*,2*S*)	Cu leaching Cu[c] (ppb)	Cu leaching Cu lost (%)
1	92	99	67.3	59:41	57	67		
2	122	99	65.1	57:43	60	70		
3	153	99	66.0	58:42	59	70		
4	183	99	66.1	59:41	60	67		
5	273	99	66.1	57:43	63	70		
6	336	99	69.6	57:43	59	68		
7	366	99	67.8	57:43	56	67	3.2	0.0022
8	397	99	69.2	57:43	58	68		
9	427	99	69.7	55:45	58	69		
10	457	99	71.0	56:44	57	69		
11	488	99	72.4	55:45	56	66		
12	518	99	72.3	58:42	57	66		

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK IB (*n*-hexane/*i*-PrOH = 99.25:0.75). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S4a. Cyclopropanation with styrene and EDA by **2/D** under CO_2. (Data referred to Table 5, entry 1, run 1).[a]

Cat. (g)	Cu (mmol)
0.4022	0.0416

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*S*,2*R*)	*ee* (%)[b] *trans* (1*S*,2*S*)	Cu[c] (ppb)
1	185	99	61.1	33:67	58	55	
2	245	99	63.5	33:67	63	57	10.2
3	306	99	65.2	32:68	60	56	
4	360	99	65.8	31:69	59	56	
5	427	99	66.6	31:69	63	55	
6	487	99	66.9	36:64	65	53	
7	547	99	69.1	30:70	65	54	

[a] Reactions were performed with EDA/styrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK OJ (*n*-hexane/*i*-PrOH = 98:2). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S4b. Cyclopropanation with 4-chlorostyrene and EDA by **2/D** under CO_2. (Data referred to Table 5, entry 2, run 1).[a]

Cat. (g)	Cu (mmol)
0.4020	0.0416

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (1*S*,2*R*)	*ee* (%)[b] *trans* (1*S*,2*S*)	Cu[c] (ppb)
1	121	99	54.6	56:44	44	69	
2	182	99	77.5	48:52	41	71	
3	242	99	81.9	47:53	44	69	24.9
4	302	99	84.2	46:54	42	72	
5	518	99	85.1	46:54	44	75	
6	582	99	83.2	46:54	44	73	

[a] Reactions were performed with EDA/4-chlorostyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK OJ (*n*-hexane/*i*-PrOH = 99:1). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S4c. Cyclopropanation with 1,1-diphenylethylene and EDA by **2/D** under CO_2. (Data referred to Table 5, entry 3, run 1).[a]

Cat. (g)	Cu (mmol)
0.3969	0.0410

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] (1*S*)	Cu[c] (ppb)
1	143	n.d.	n.d.	-	n.d.	
2	203	99	45.5	-	62	
3	264	99	51.0	-	62	
4	324	99	49.1	-	72	
5	384	99	48.0	-	64	
6	445	99	53.1	-	66	17.3
7	505	99	57.5	-	67	
8	565	99	57.9	-	64	

[a] Reactions were performed with EDA/1,1-diphenylethylene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK AD (*n*-hexane/*i*-PrOH = 99.66:0.33). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S4d. Cyclopropanation with methyl-2-furoate and EDA by **2/D** under CO_2. (Data referred to Table 5, entry 4, run 1).[a]

Cat. (g)	Cu (mmol)
0.4064	0.0420

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis*	*ee* (%)[b] *trans* (1*R*,5*R*,6*R*)	Cu leaching Cu[c] (ppb)	Cu leaching Cu lost (%)
1	178	99	30.1	<1:>99	-	68		
2	239	99	35.1	<1:>99	-	67		
3	300	99	34.3	<1:>99	-	68		
4	362	99	34.7	<1:>99	-	66		
5	422	99	34.5	<1:>99	-	66	122.5	0.0905
6	482	99	32.5	<1:>99	-	66		
7	542	99	30.3	<1:>99	-	65	39.8	

[a] Reactions were performed with EDA/methyl-2-furoate ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK OJ (*n*-hexane/*i*-PrOH = 90:10). [c] Although ultra-pure acids have been used for the mineralization process, ppb amounts of copper have also been found in blank test analyses.

Table S4e. Cyclopropanation with 1-octene and EDA by **2/D** under CO_2. (Data referred to Table 5, entry 5, run 1).[a]

Cat. (g)	Cu (mmol)
0.4097	0.0424

Entry	time (min)	conversion (%)	selectivity (%)	*cis:trans*	*ee* (%)[b] *cis* (n.d)	*ee* (%)[b] *trans* (n.d.)	Cu[c] (ppb)
1	154	99	68.0	48:52	72	39	
2	237	99	70.6	47:53	72	42	8.1
3	298	99	70.4	47:53	71	41	
4	357	99	71.0	48:52	63	39	
5	417	99	72.6	49:51	64	41	
6	477	99	74.8	49:51	63	39	

[a] Reactions were performed with EDA/1-octene ratio = 1:10; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] Determined by chiral HPLC equipped with DAICEL CHIRALPAK OJ (*n*-hexane/*i*-PrOH = 99.9:0.1).

Table S5. Reaction between with α-methylstyrene and EDA in the presence of bare Davisil under CO_2. [a]

Silica (g)	Entry	time (min)	conversion (%)	selectivity in fum + mal(%)[b]	*mal:fum*
0.4112	1	245	49	68.1	2:1
	2	305	51	65.7	2:1
	3	366	50	63.1	2:1
	4	427	49	64.6	2: 1
	5	486	42	72.1	2:1

[a] Reactions were performed with EDA/α-methylstyrene ratio = 1:5; T = 40°C, P_{CO2} = 130 bar, flow CO_2 = 0.5 mL/min, flow HPLC = 0.02 mL/min. [b] The selectivity in this case is reported as the sum of maleate and fumarate, which are the major reaction products. Traces of cyclopropane products (*cis*/*trans* ratio ca. 3:2) were also detected in the reaction mixture.

Figure S1. Chemoselectivity (%) *vs* time of stream (minutes) of the cyclopropanation reaction of different alkenes catalysed by **2/D**.

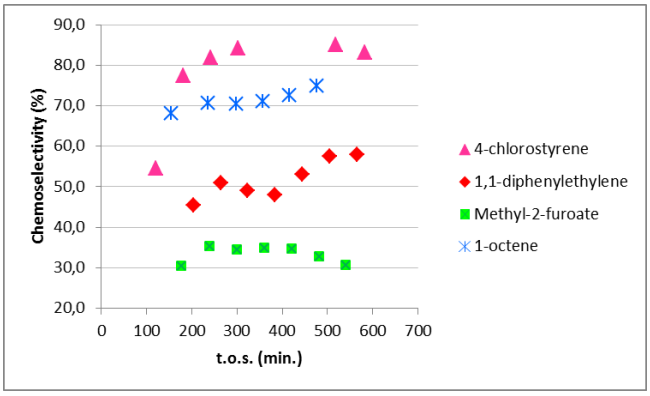


Figure S2. DRIFT spectra showing the comparison of supported catalyst **2/D** and free complex **2** in KBr.

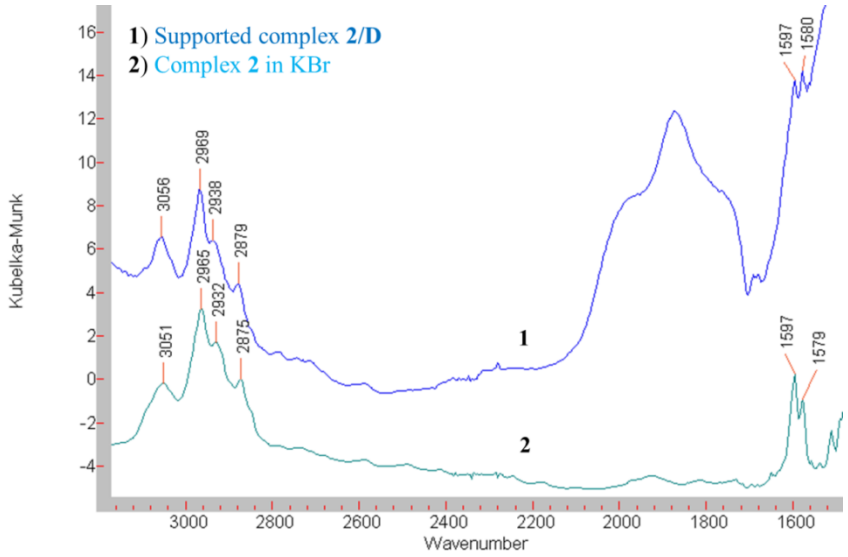


Figure S3. CO-DRIFT spectra showing the comparison of catalyst **2/D** pre- and post-catalysis with 4-chlorostyrene and α-methylstyrene and EDA after treatment under CO atmosphere. While the copper catalyst adsorb CO, the material after catalysis does not.

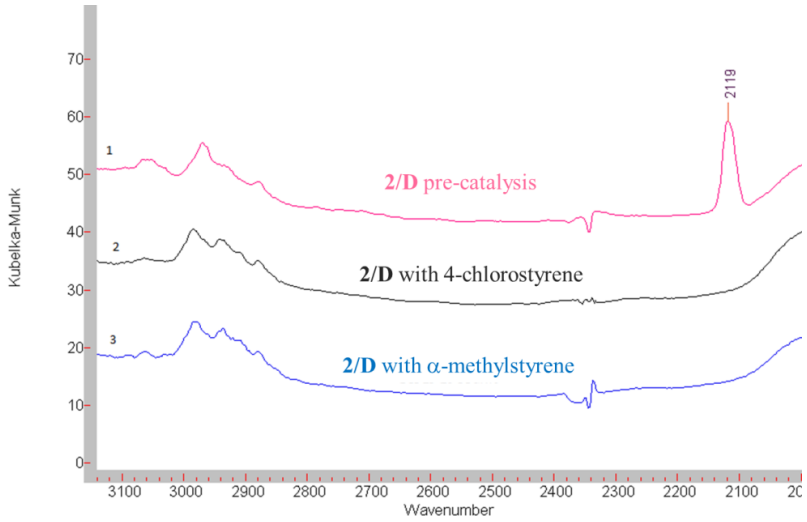


Figure S4. DRIFT spectra showing the comparison of catalyst **2/D** pre- and post-catalysis with different alkenes and EDA.

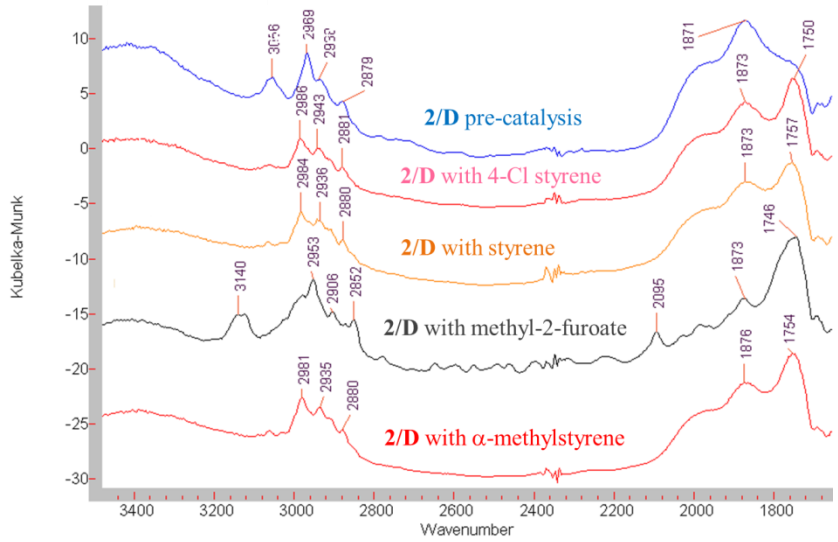


Figure S5. Spectra in 1,2-DCE of catalyst **2** with ethyl-fumarate, showing the interaction of this molecule with the catalyst.

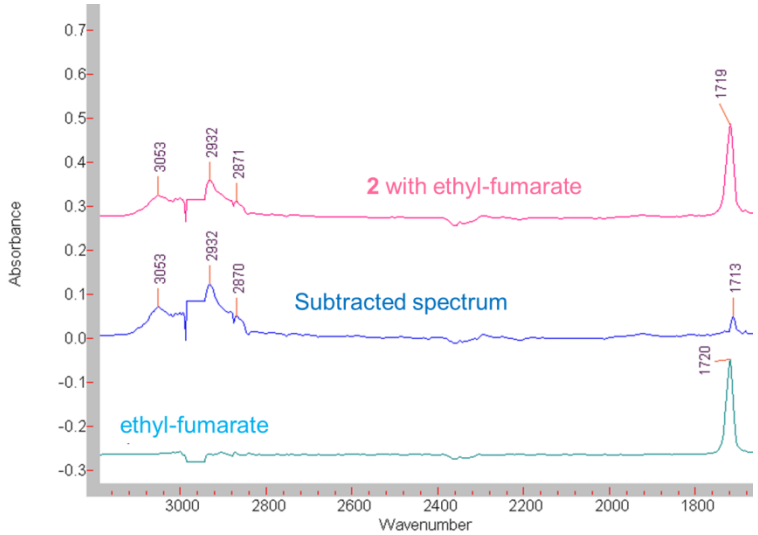
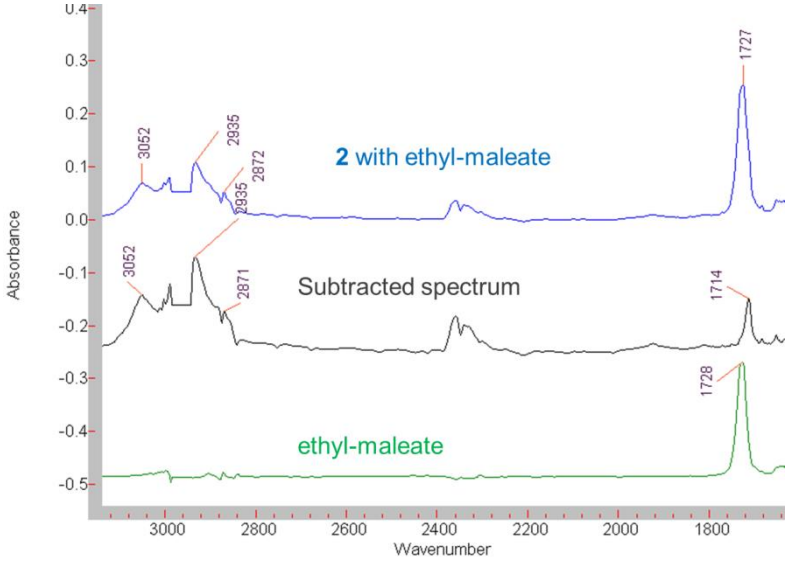
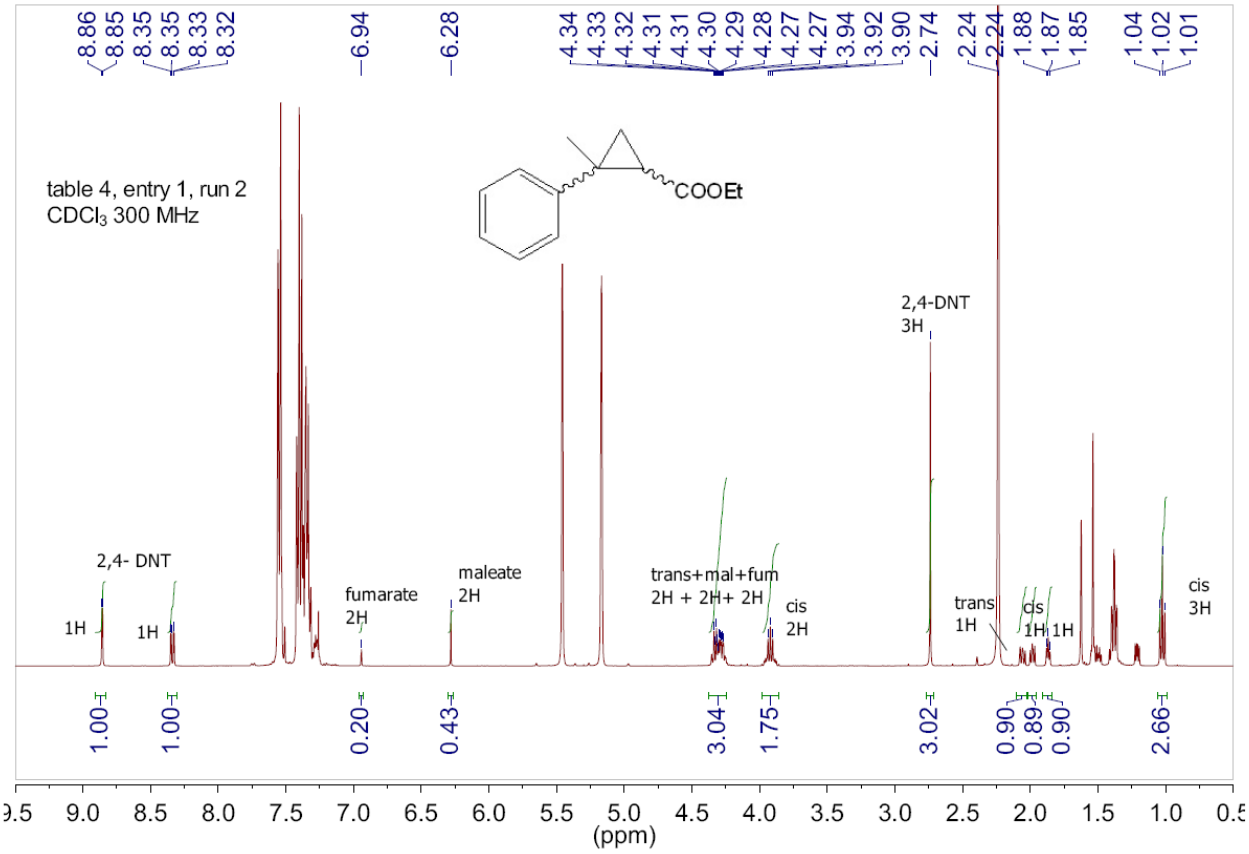
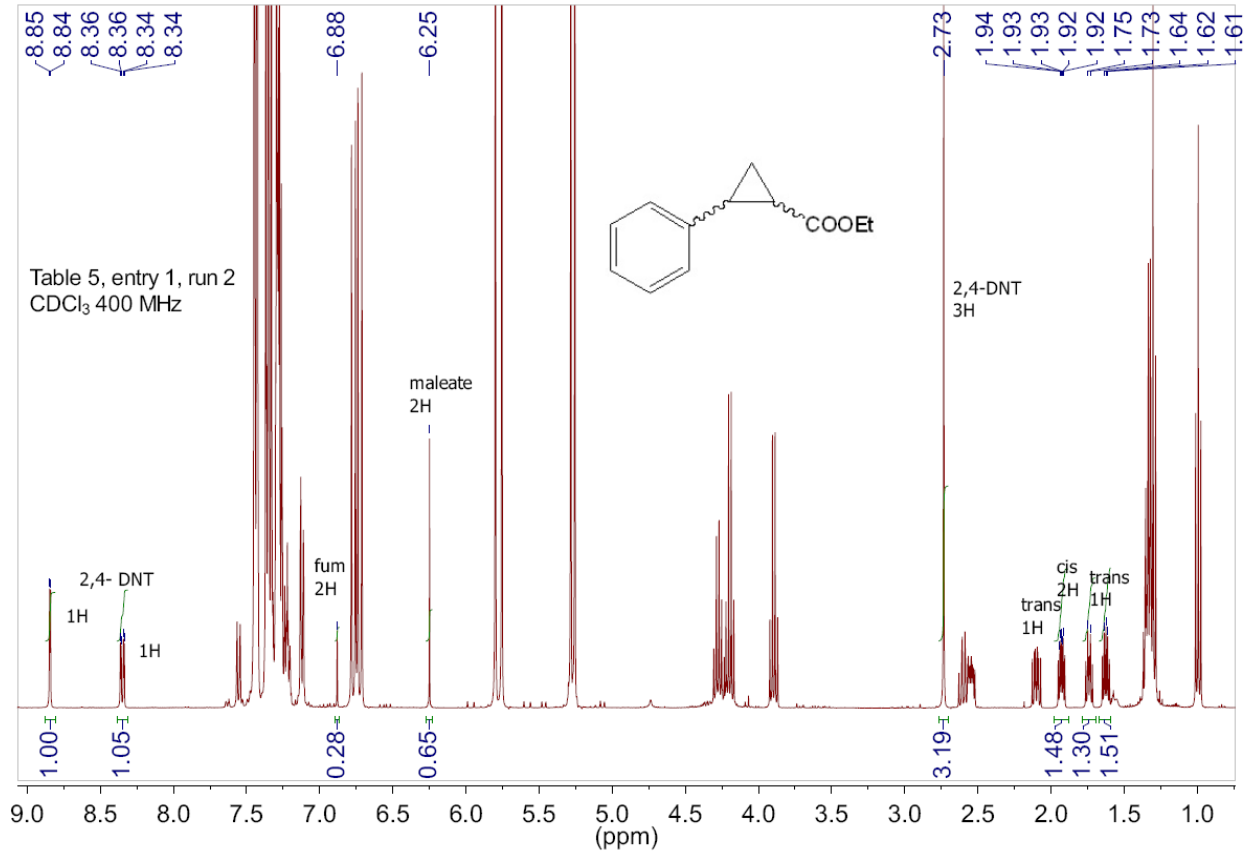


Figure S6. Spectra in 1,2-DCE of catalyst **2** with ethyl-maleate, showing the interaction of this molecule with the catalyst.



^{1}H NMR and HPLC analysis of selected samples.





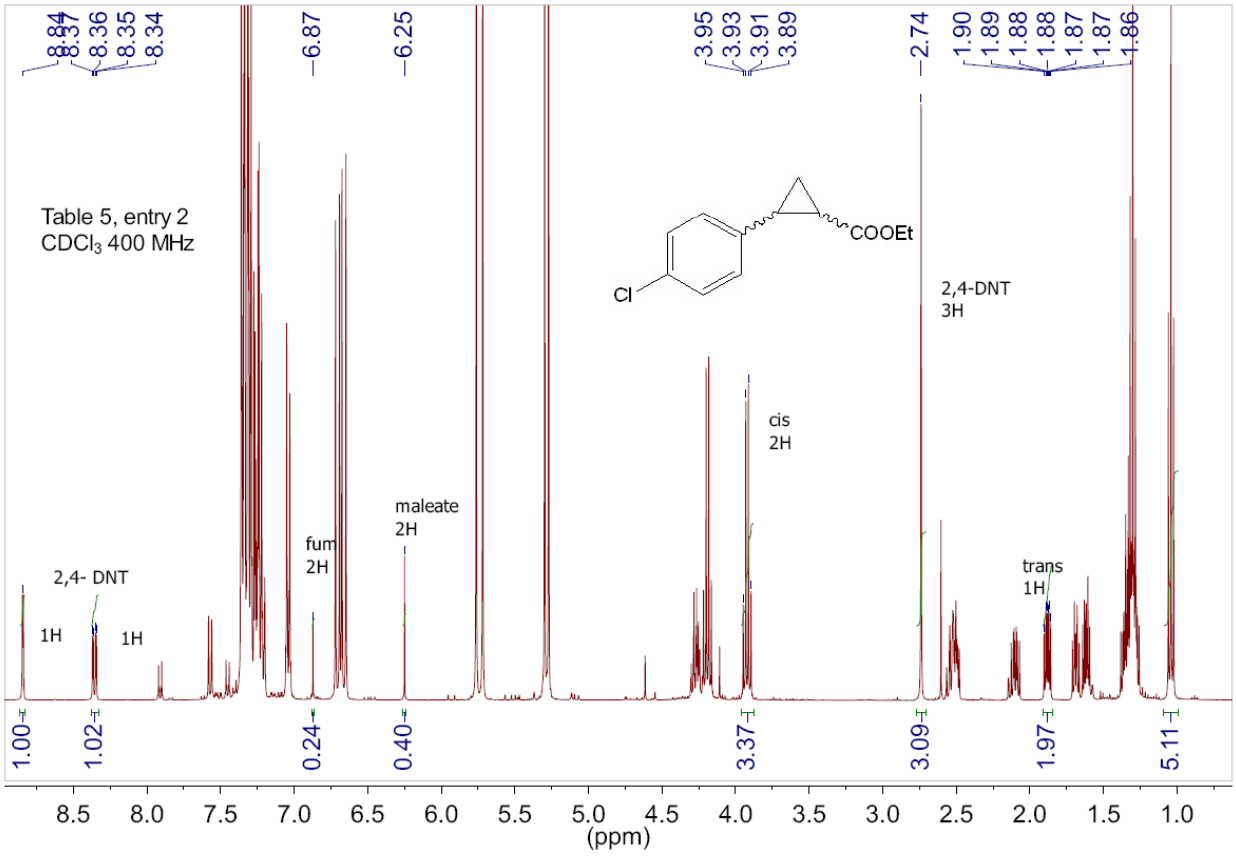


Table 5, entry 2
CDCl3 400 MHz
COOEt
Cl
2,4-DNT
3H
cis
2H
maleate
2H
fum
2H
2,4- DNT
1H
1H
trans
1H
(ppm)

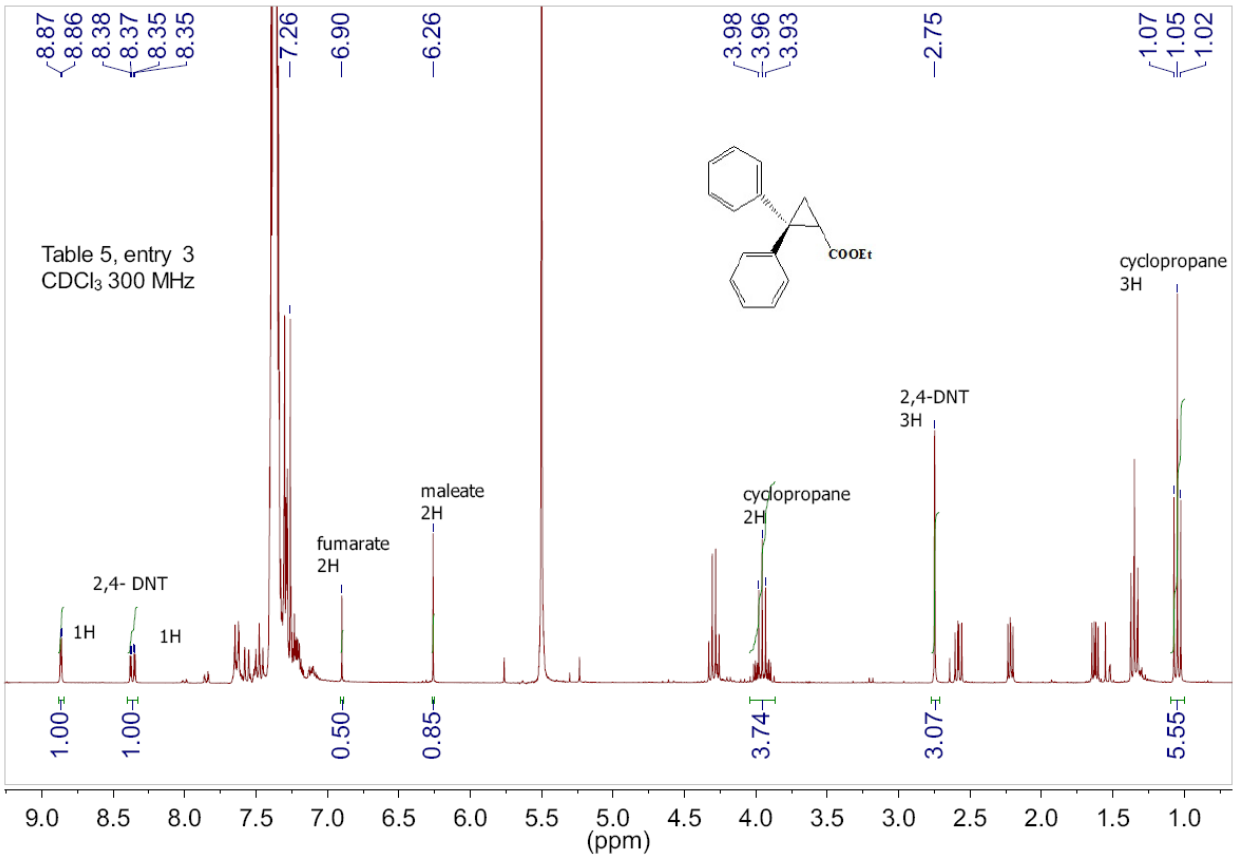
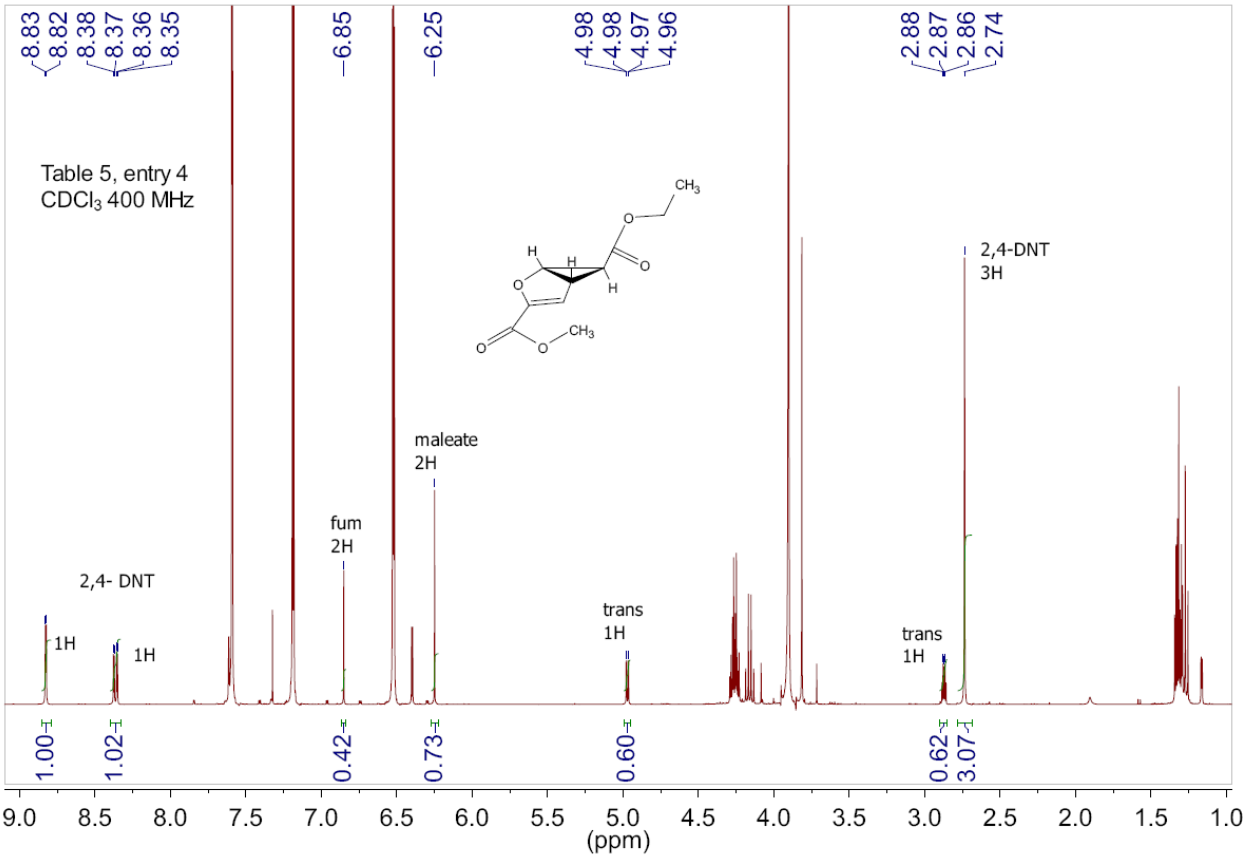
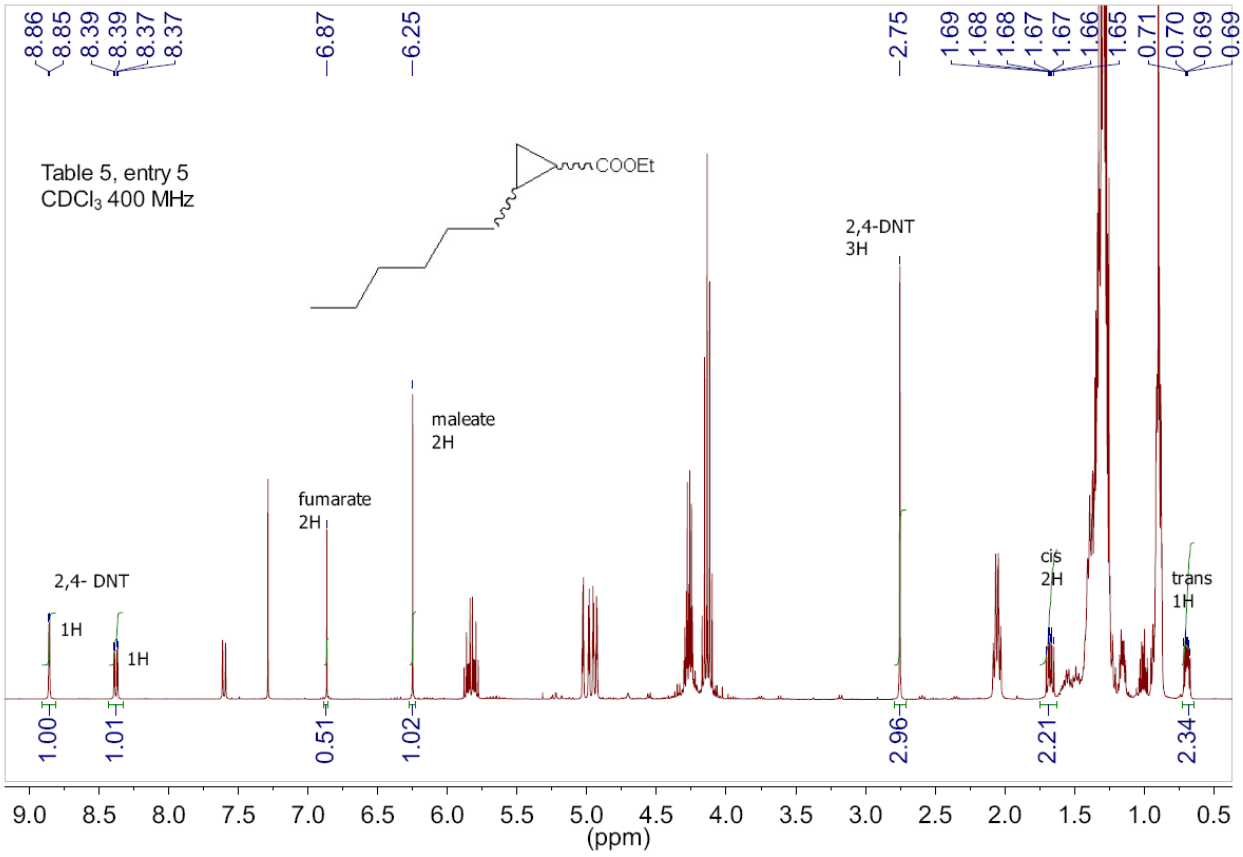
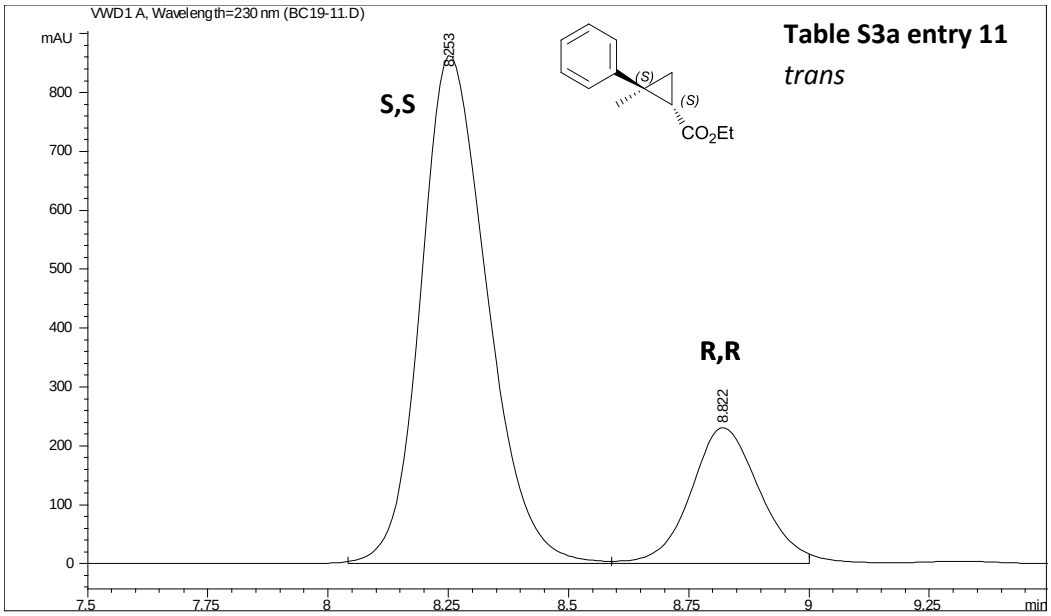


Table 5, entry 3
CDCl3 300 MHz
COOEt
cyclopropane
3H
2,4-DNT
3H
maleate
2H
cyclopropane
2H
fumarate
2H
2,4- DNT
1H
1H
(ppm)

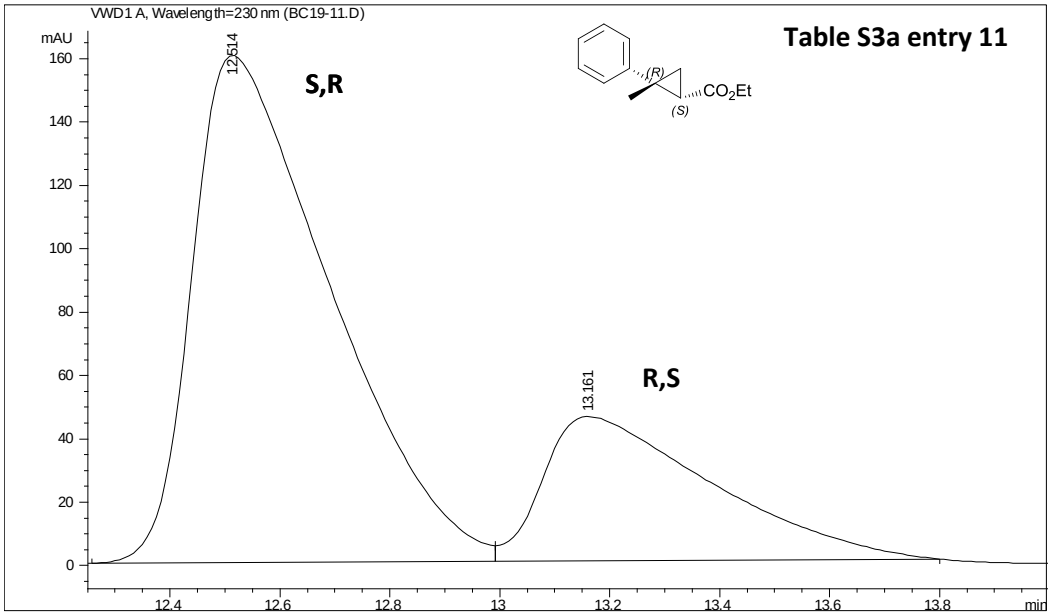

8.83
8.82
8.38
8.37
8.36
8.35
6.85
6.25
4.98
4.98
4.97
4.96
2.88
2.87
2.86
2.74
Table 5, entry 4
CDCl3 400 MHz
2,4-DNT
3H
maleate
2H
fum
2H
2,4- DNT
1H
1H
trans
1H
trans
1H
1.00
1.02
0.42
0.73
0.60
0.62
3.07
(ppm)


8.86
8.85
8.39
8.39
8.37
8.37
6.87
6.25
2.75
1.69
1.68
1.68
1.67
1.67
1.66
1.65
0.71
0.70
0.69
0.69
Table 5, entry 5
CDCl3 400 MHz
COOEt
2,4-DNT
3H
maleate
2H
fumarate
2H
2,4- DNT
1H
1H
cis
2H
trans
1H
1.00
1.01
0.51
1.02
2.96
2.21
2.34
(ppm)



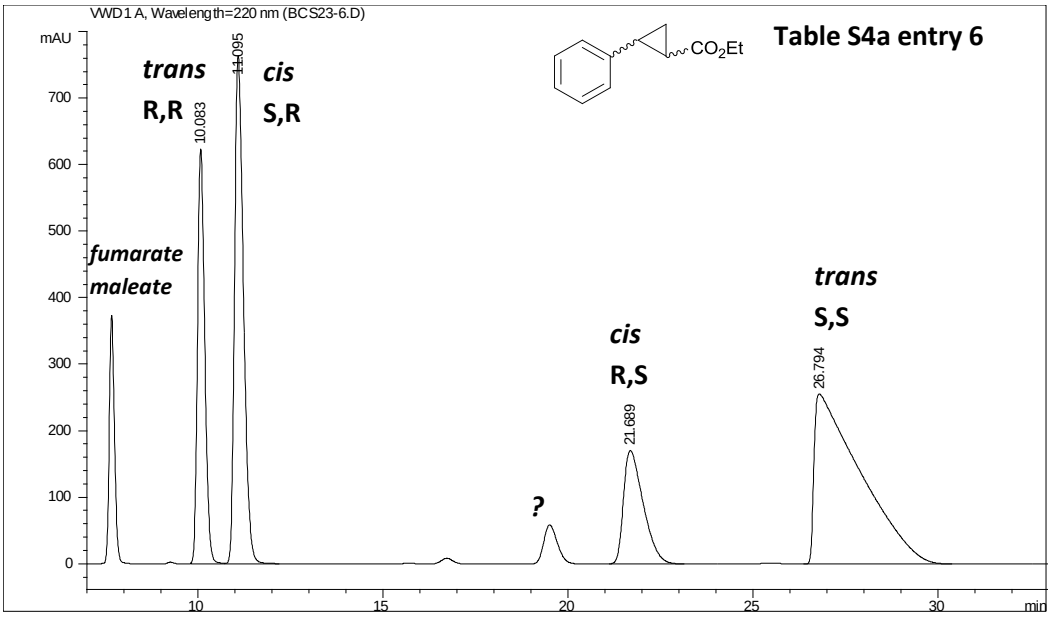
Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.253	BV	0.1465	8188.98730	862.73212	82.8398
2	8.822	VBA	0.1544	1696.34167	230.14224	17.1602



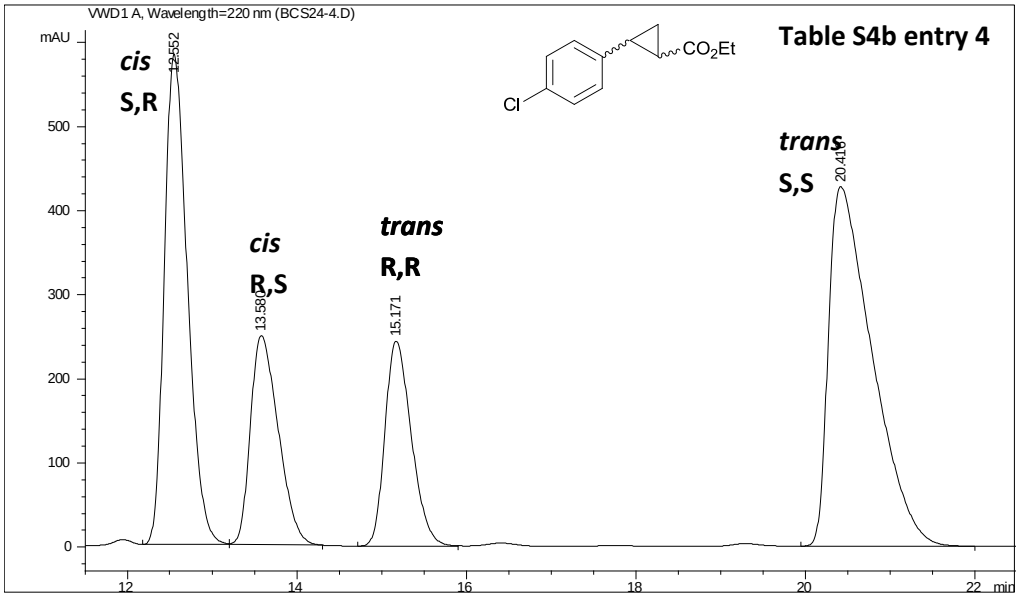
Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.514	PV	0.2607	2803.21631	159.08958	77.9257
2	13.161	VBA	0.6884	794.07599	40.98441	22.0743



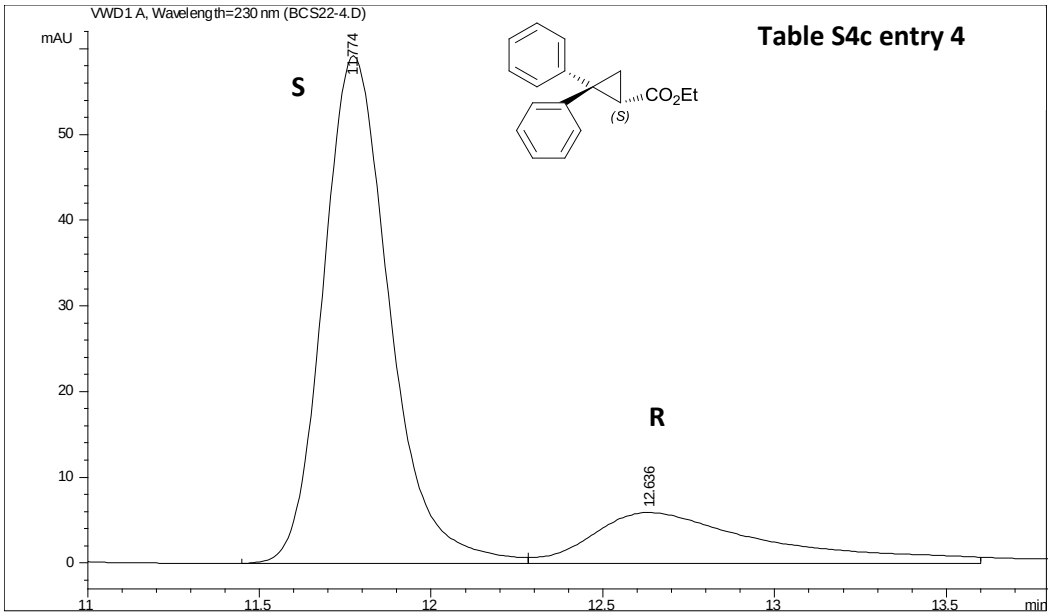
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.083	MM	0.1987	6762.06689	567.23120	15.1572
2	11.095	MM	0.2808	1.28914e4	765.16040	28.8961
3	21.688	MM	0.4086	2695.27832	109.94267	6.0415
4	26.791	BB	1.1475	2.22643e4	255.90244	49.9053



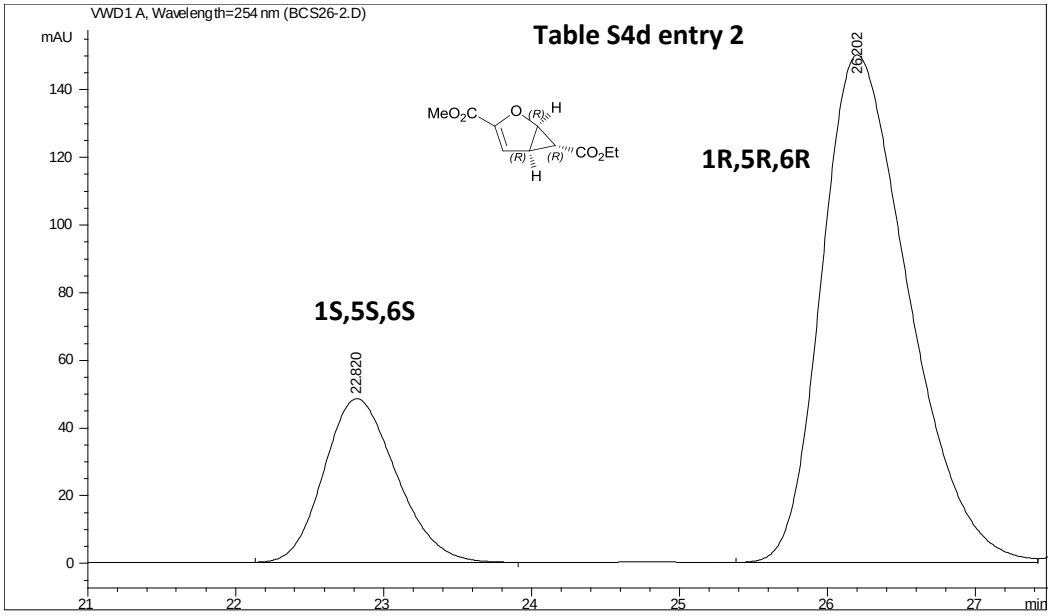
Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height mAU]	Area %
1	12.552	PV	0.2937	1.10495e4	582.71674	33.0939
2	13.580	VBA	0.3095	4541.09814	247.01970	13.6008
3	15.171	BBA	0.2705	2494.49854	243.77048	7.4712
4	20.416	BPA	0.5325	1.53033e4	427.60849	45.8341



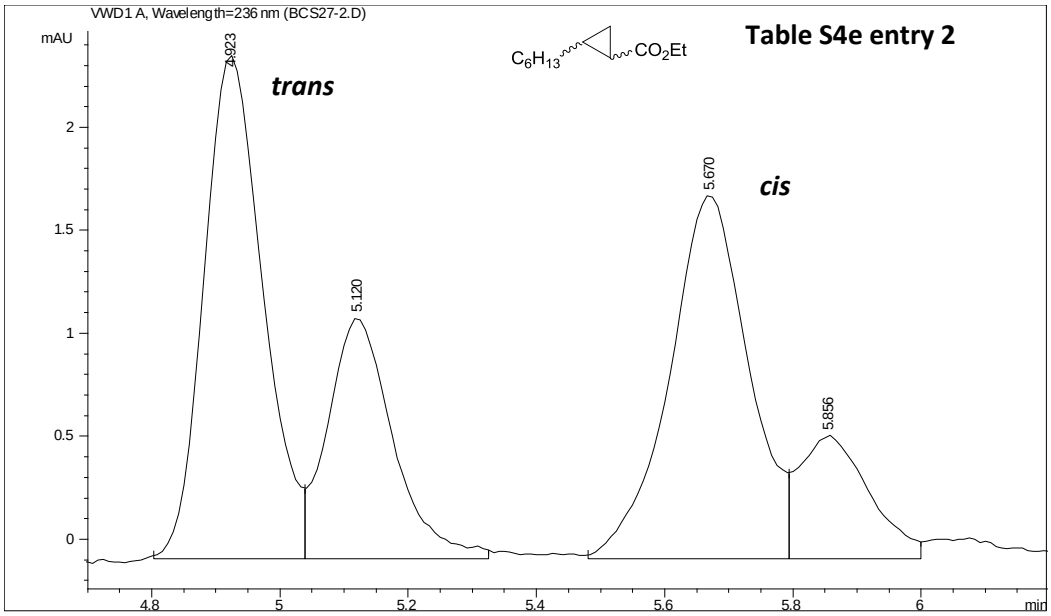
Signal 1: VWD1 A, Wavelength=230 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.774	BV	0.2067	795.80957	59.25520	86.2357
2	12.636	VBA	0.3140	127.02103	5.95084	13.7643



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.820	BBA	0.4114	1195.53821	48.42975	16.3399
2	26.202	BV	0.6283	6121.13330	150.07933	83.6601



Signal 1: VWD1 A, Wavelength=236 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.923	BV	0.1106	16.45330	2.47873	40.4158
2	5.120	VB	0.0923	6.67279	1.20476	16.3910
3	5.670	BV	0.1435	15.15985	1.76023	37.2386
4	5.856	VBA	0.0699	2.42410	5.77861e-1	5.9545

References

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