Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Synthesis of five- and six-membered heterocycles by dimethyl carbonate with catalytic amount of nitrogen bicyclic bases

Fabio Aricò, Serena Evaristo and Pietro Tundo

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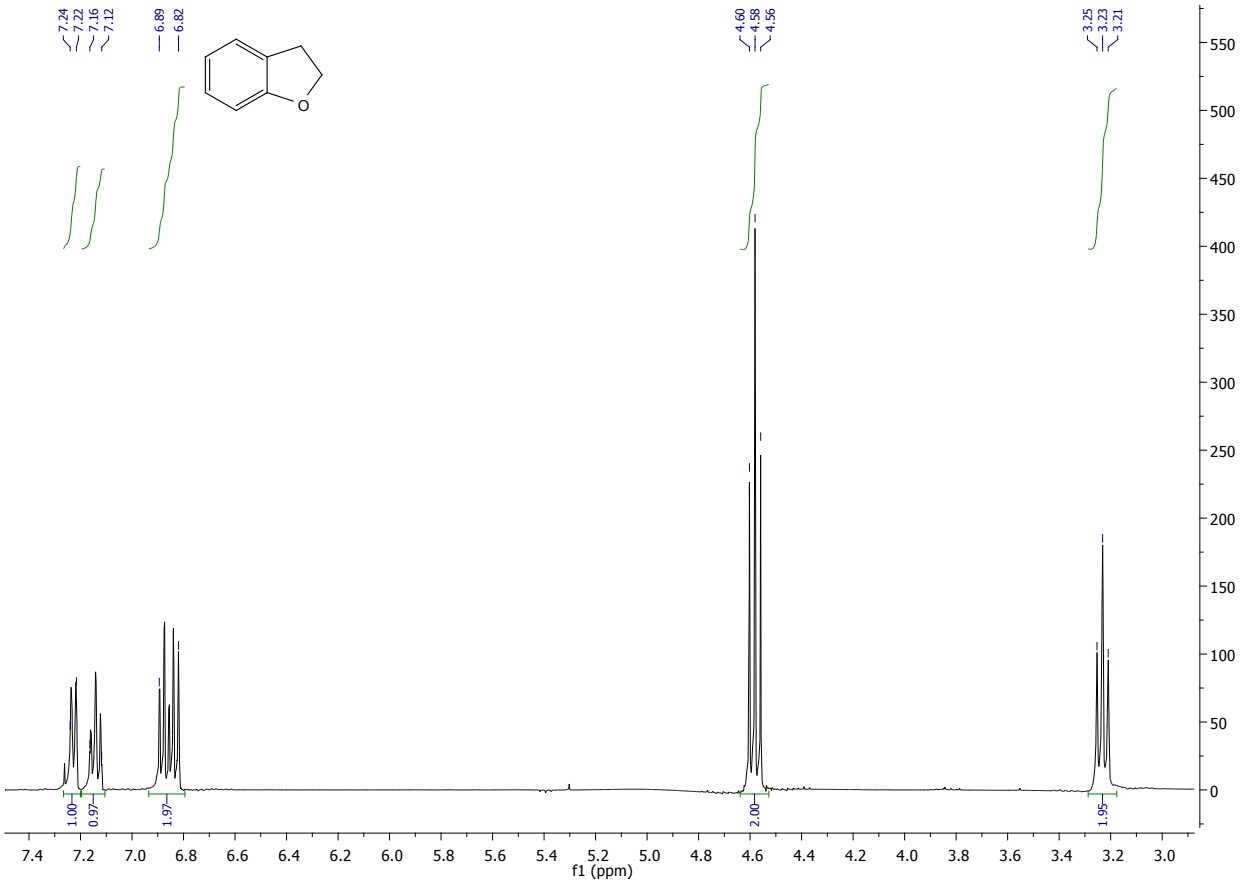
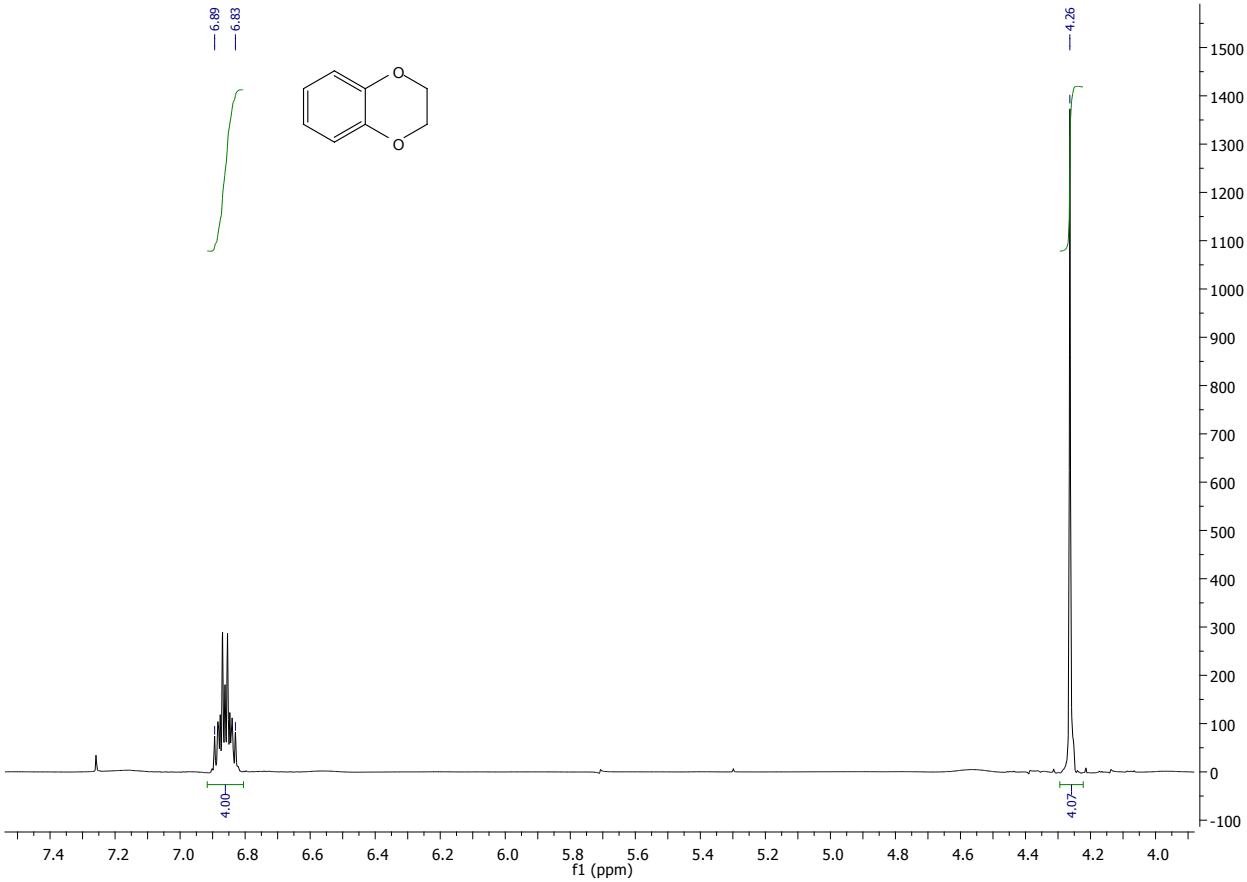
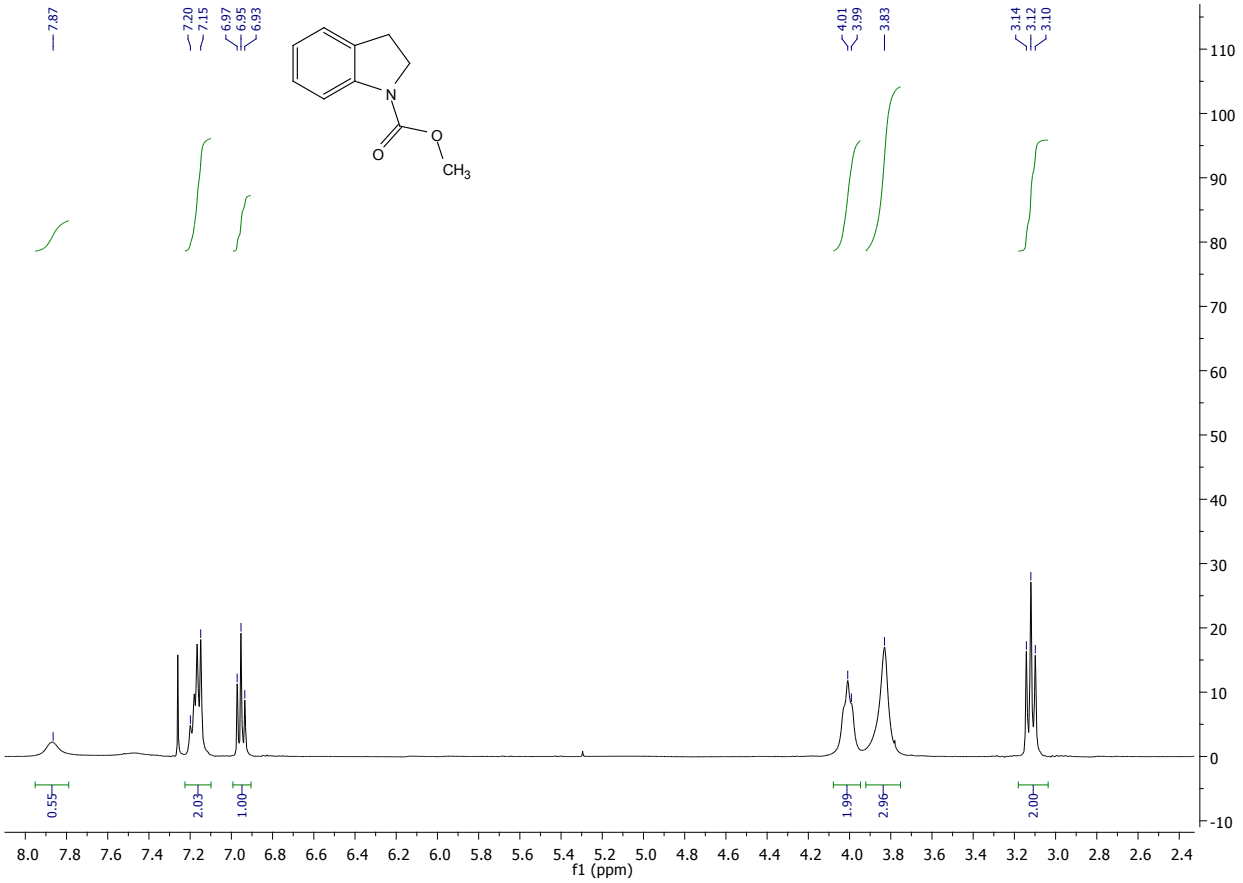
^{1}H NMR spectrum of 2,3-dihydrobenzofuran **1**



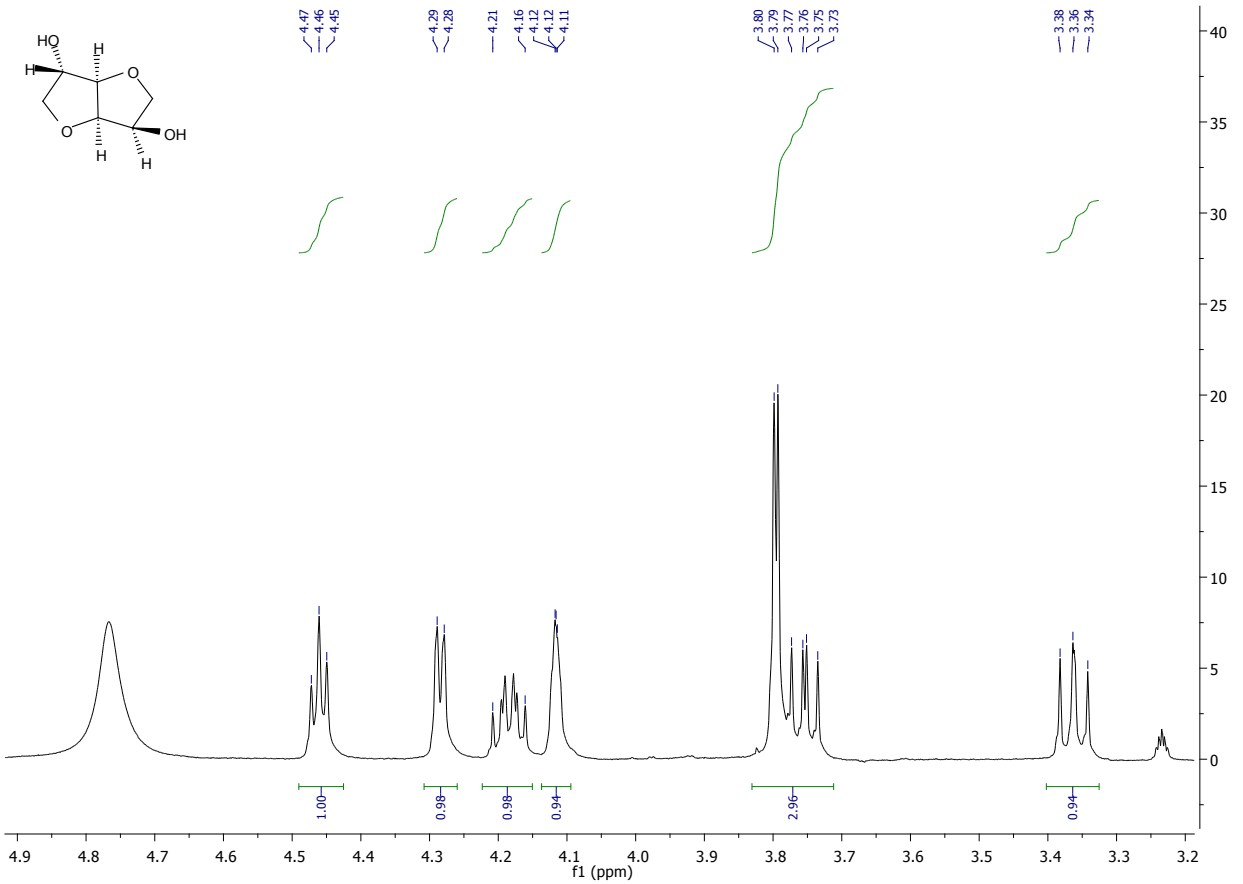
^{1}H NMR spectrum of 2,3-dihydrobenzo[b][1,4]dioxine **5**



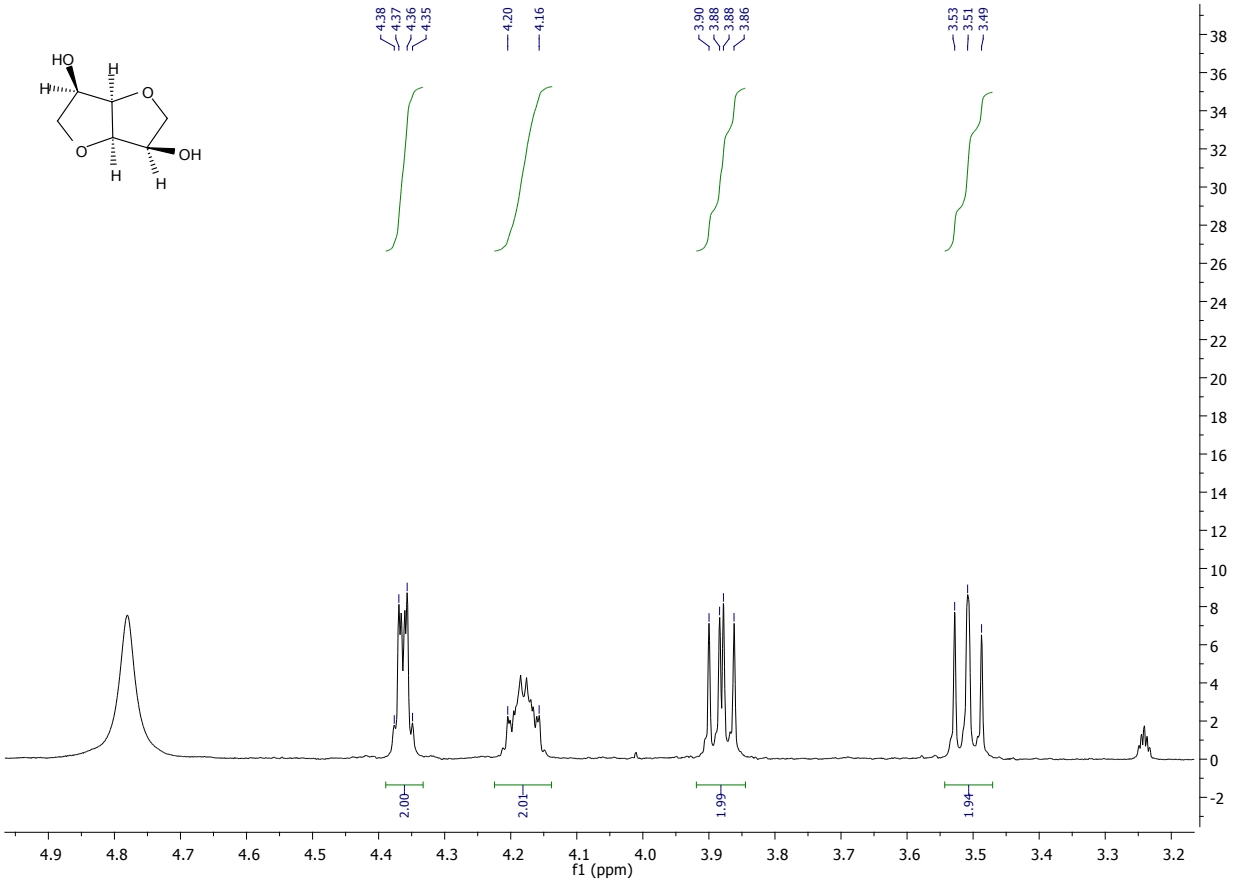
^{1}H NMR spectrum of *N*-carboxymethyl indoline **7**



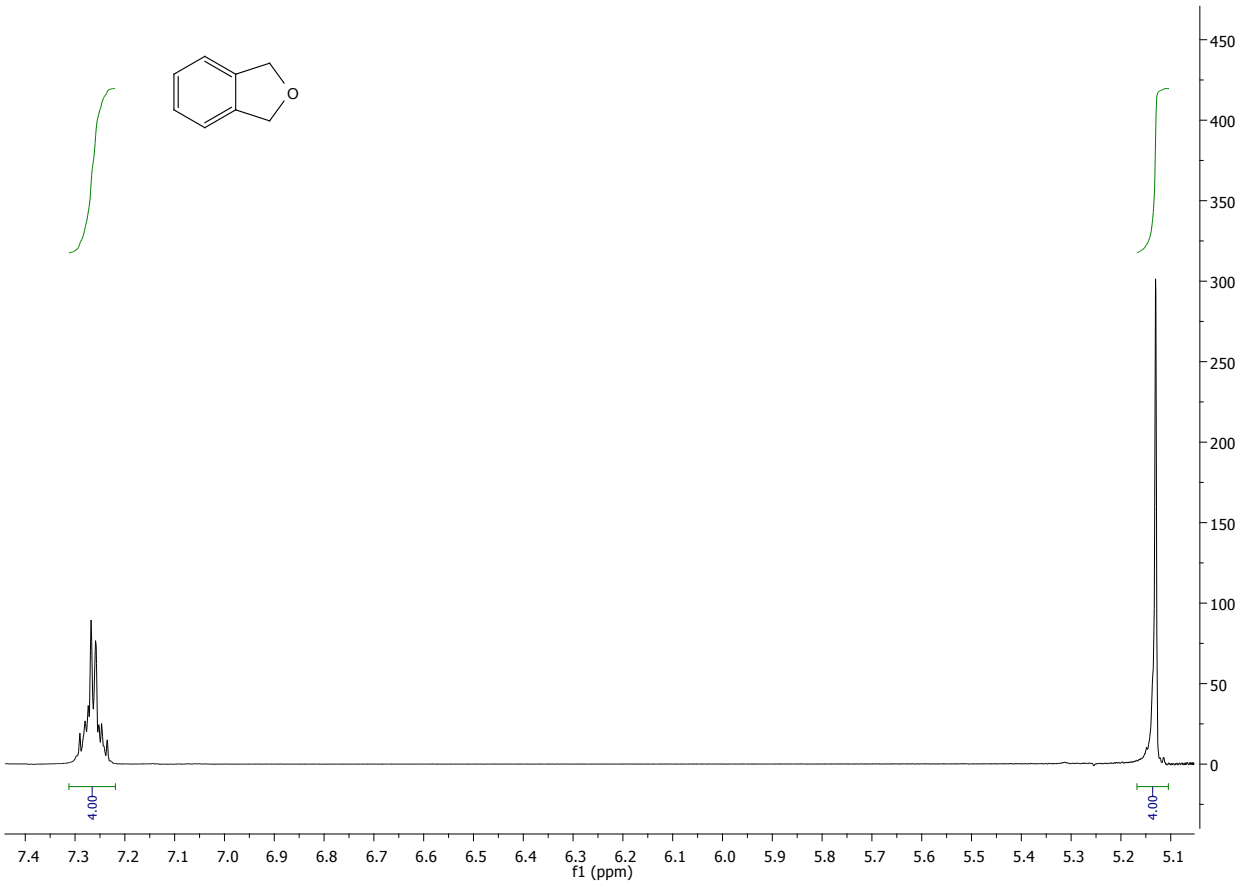
^{1}H NMR spectrum of isosorbide **8**



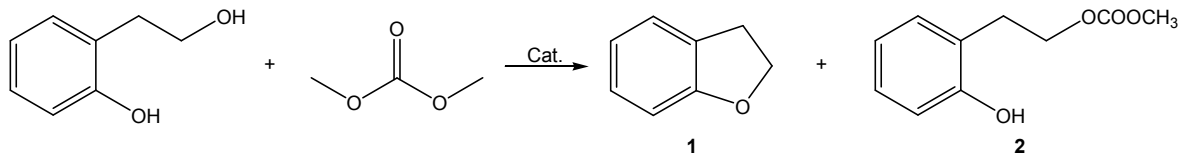
^{1}H NMR spectrum of isomannide **9**



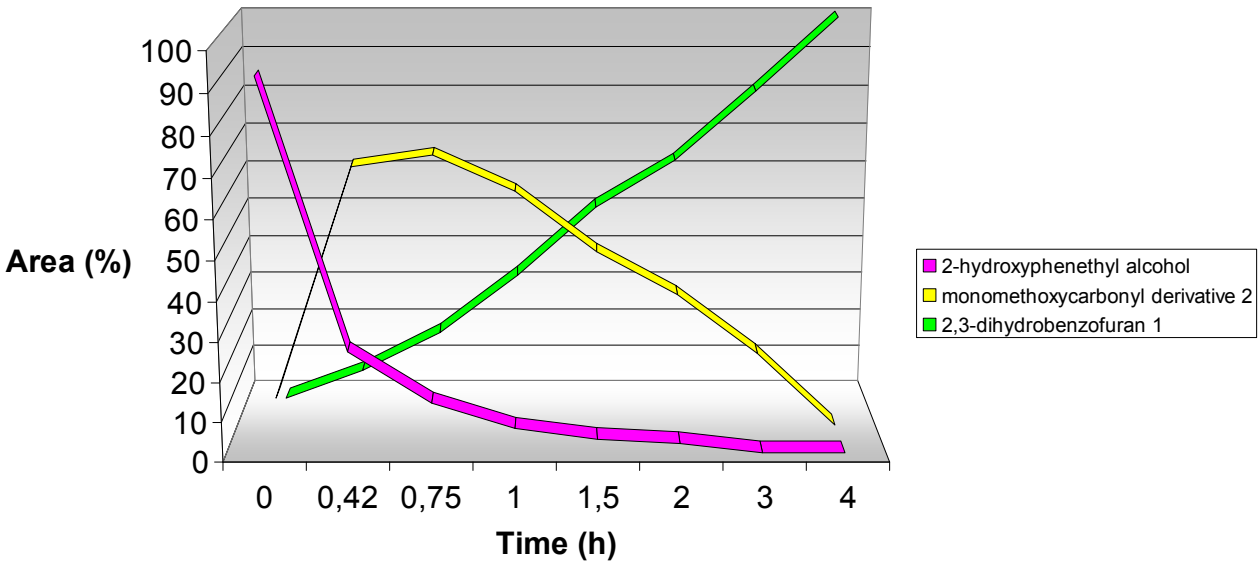
^{1}H NMR spectrum of phtalan **3**



Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzofuran **1** with DBU calculated by HPLC.[a]



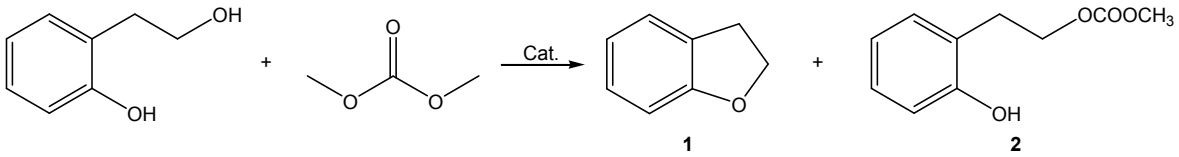
[a] Reaction conditions: 2-hydroxyphenethyl alcohol (1.00 eq. mol), DMC (4.00 eq. mol), catalyst (0.25 eq. mol), 90 °C.



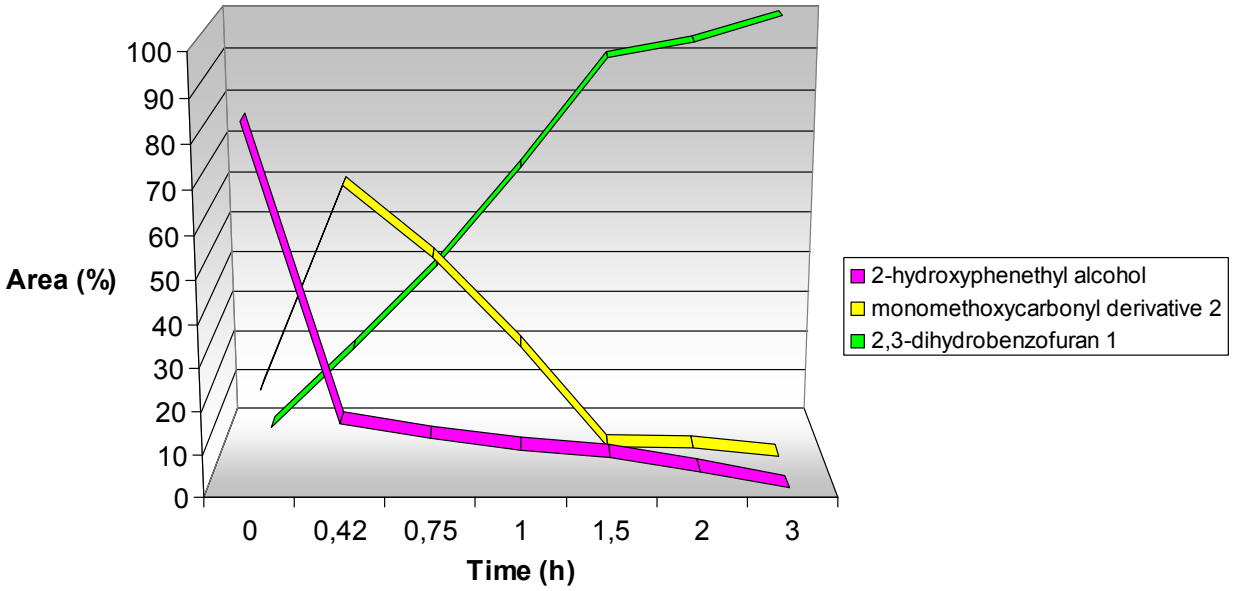
Time (h)	% Area starting material	% Area intermediate 2	% Area cyclic product 1
0.00[b]	92.90	7.10	0.00
0.42	25.80	66.60	7.60
0.75	12.70	69.50	17.80
1.00	6.30	60.40	33.30
1.50	3.60	45.10	51.30
2.00	2.50	34.10	63.40
3.00	0.00	18.70	81.30
4.00	0.00	0.00	100.00

[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzofuran **1** with TBD calculated by HPLC.[a]



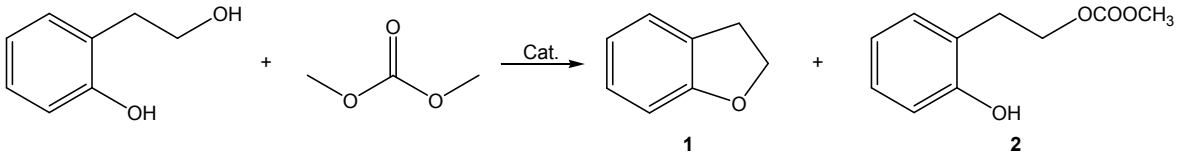
[a] Reaction conditions: 2-hydroxyphenethyl alcohol (1.00 eq. mol), DMC (4.00 eq. mol), catalyst (0.25 eq. mol), 90 °C.



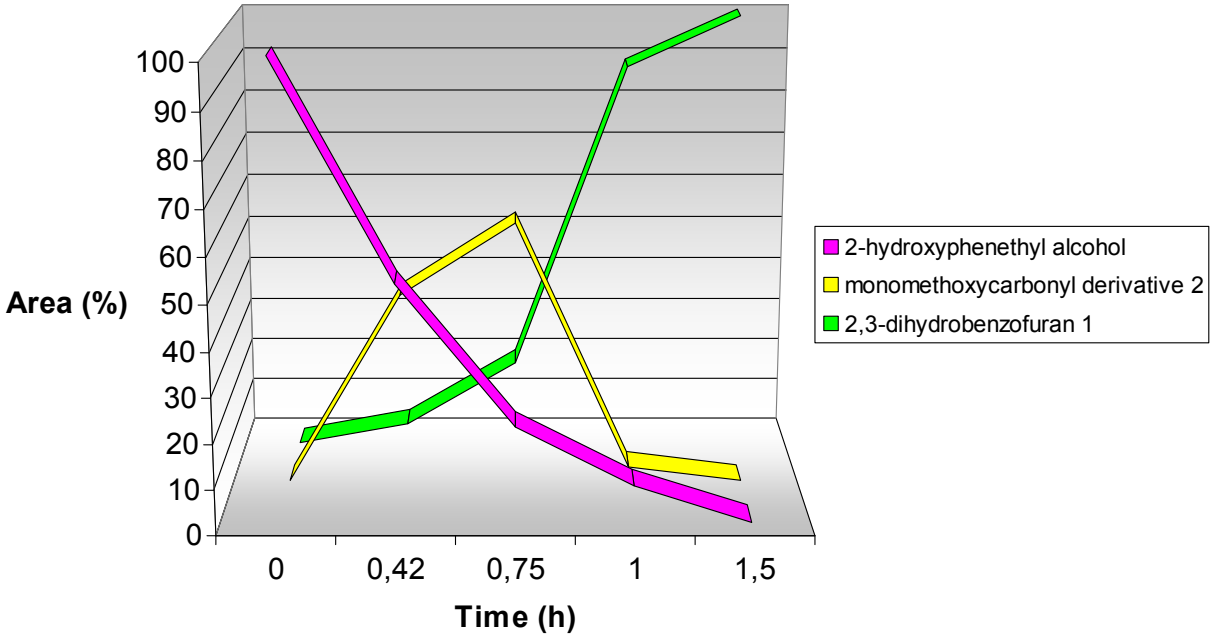
Time (h)	% Area starting material	% Area intermediate 2	% Area cyclic product 1
0.00[b]	83.80	16.20	0.00
0.42	15.30	64.90	19.80
0.75	11.70	47.90	40.40
1.00	9.00	26.70	64.30
1.50	7.30	2.40	90.30
2.00	3.80	2.30	93.90
3.00	0.00	0.00	100.00

[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzofuran **1** with DABCO calculated by HPLC.[a]



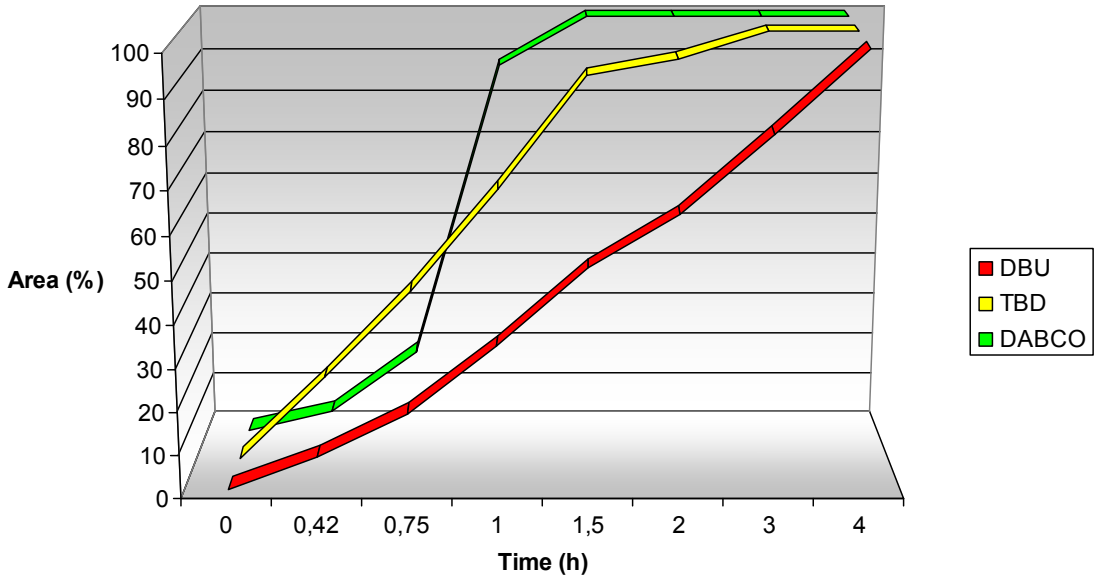
[a] Reaction conditions: 2-hydroxyphenethyl alcohol (1.00 eq. mol), DMC (4.00 eq. mol), catalyst (0.25 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 2	% Area cyclic product 1
0.00[b]	100.00	0.00	0.00
0.42	52.50	42.80	4.70
0.75	21.30	59.10	19.60
1.00	8.20	3.20	88.60
1.50	0.00	0.00	100.00

[b] First sample taken at reflux temperature.

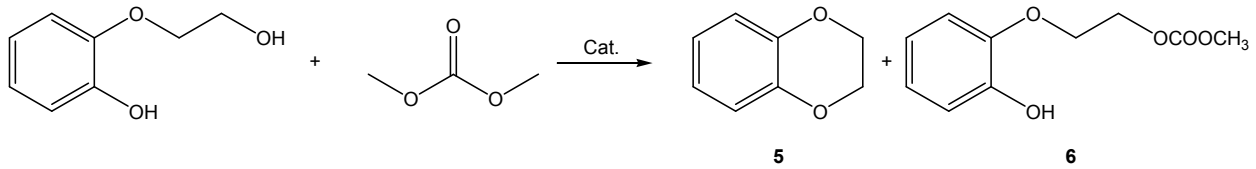
Reaction profiles of the 2,3-dihydrobenzofuran **1** synthesised using respectively DBU, TBD and DABCO as catalysts calculated by HPLC.



Time (h)	% Area (reaction with DBU)	% Area (reaction with TBD)	% Area (reaction with DABCO)
0.00[b]	0.00	0.00	0.00
0.42	7.60	19.80	4.70
0.75	17.80	40.40	19.60
1.00	33.30	64.30	88.60
1.50	51.30	90.30	100.00
2.00	63.40	93.90	100.00
3.00	81.30	100.00	100.00
4.00	100.00	100.00	100.00

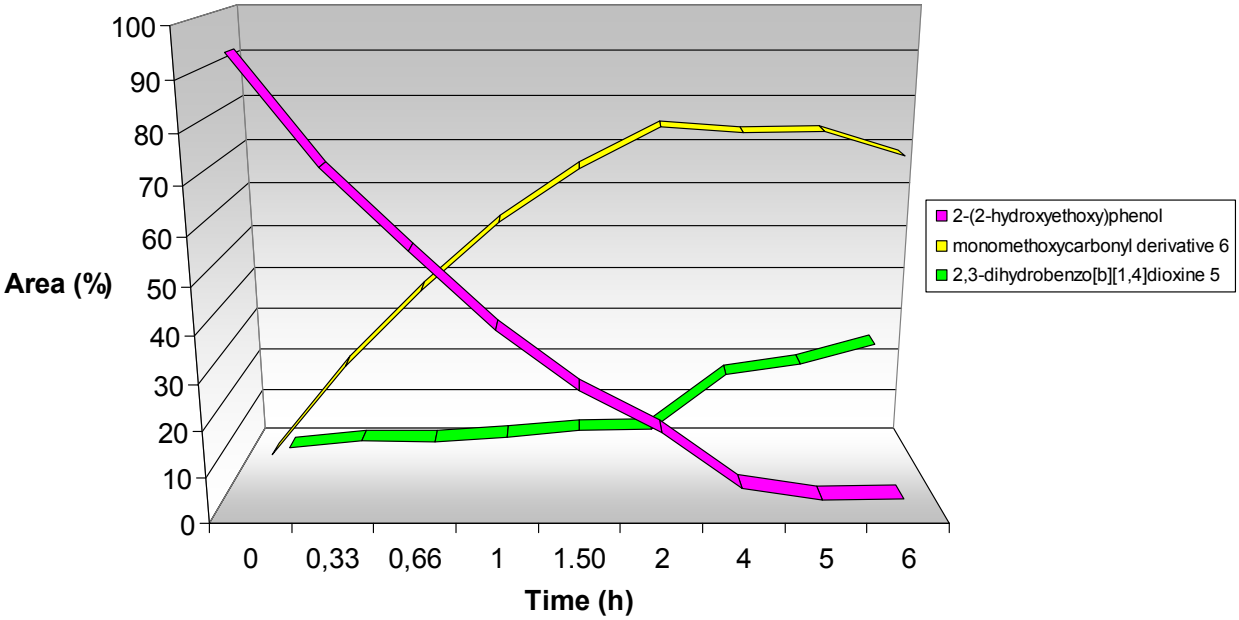
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzo[b][1,4]dioxine **5** with DBU calculated by GC-MS.[a]



5 **6**

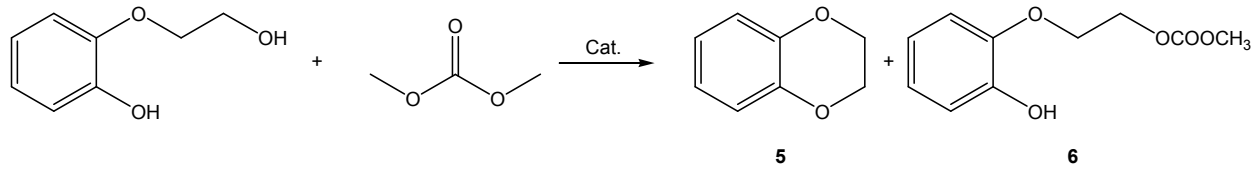
[a] Reaction conditions: 2-(2-hydroxyethoxy)phenol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.10 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 6	% Area cyclic product 5
0.00[b]	94.40	5.60	0.00
0.33	72.50	25.80	1.70
0.66	55.70	42.80	1.50
1.00	39.60	57.60	2.80
1.50	26.80	68.90	4.30
2.00	17.70	77.60	4.70
4.00	5.60	76.50	17.90
5.00	2.90	76.60	20.50
6.00	3.20	71.60	25.20

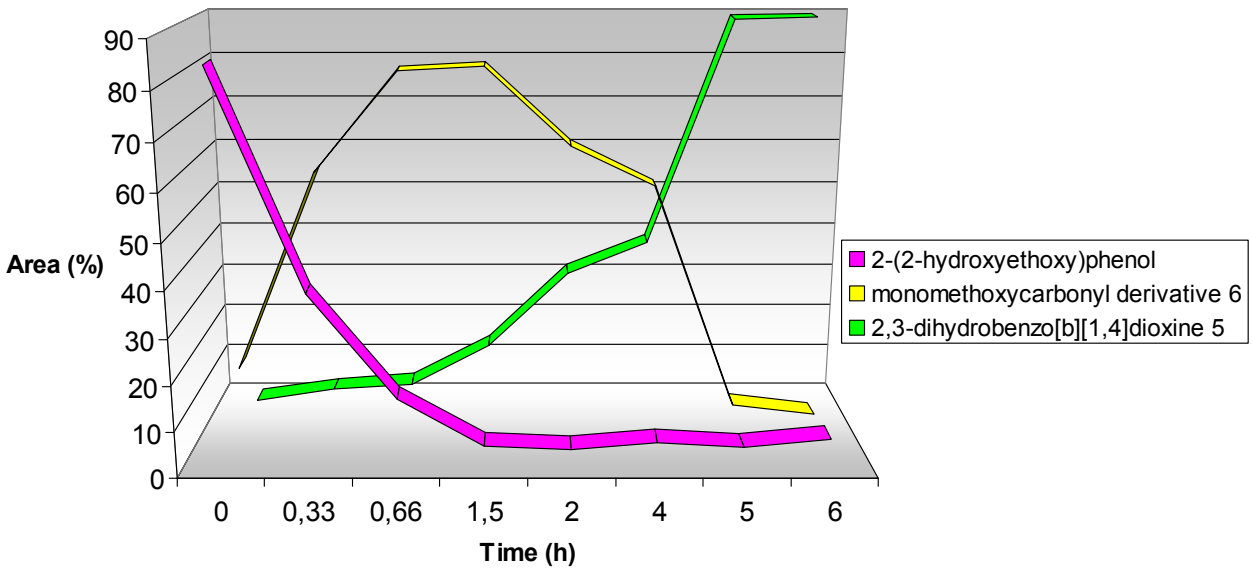
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzo[b][1,4]dioxine **5** with TBD calculated by GC-MS.[a]



5 **6**

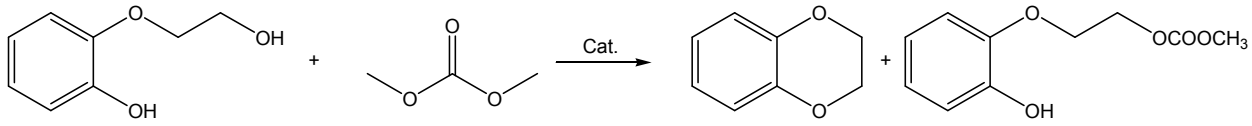
[a] Reaction conditions: 2-(2-hydroxyethoxy)phenol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.10 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 6	% Area cyclic product 5
0.00[b]	84.40	15.00	0.60
0.33	37.90	58.80	3.30
0.66	15.00	80.40	4.60
1.50	4.70	81.40	13.90
2.00	3.90	64.60	31.50
4.00	5.50	55.90	38.60
5.00	4.40	6.50	89.10
6.00	6.20	4.30	89.50

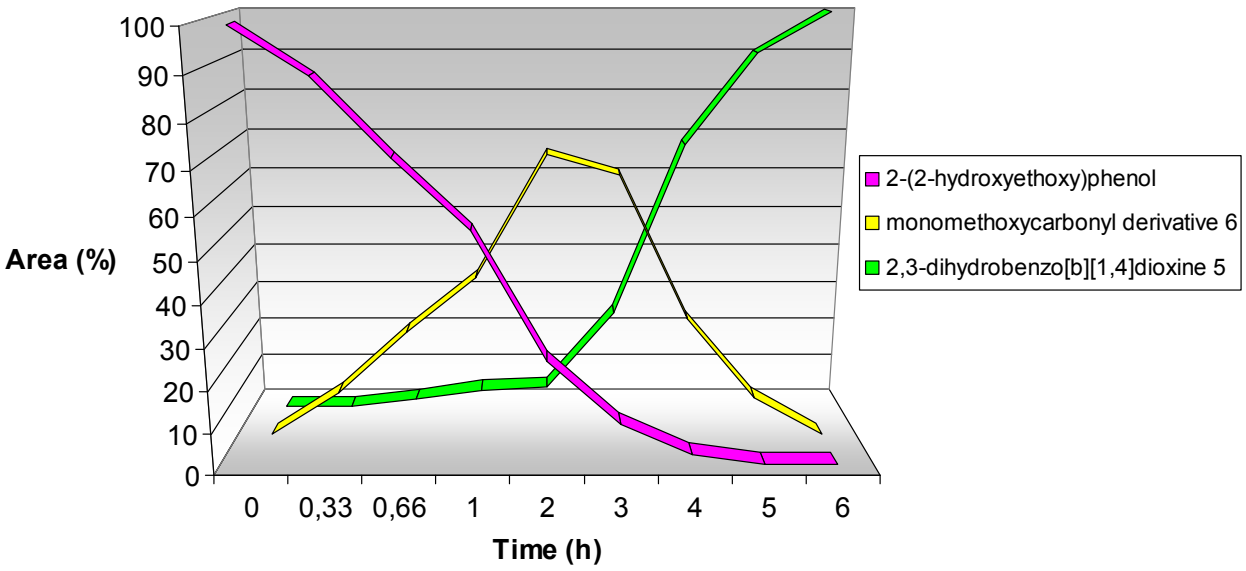
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of 2,3-dihydrobenzo[b][1,4]dioxine **5** with DABCO calculated by GC-MS.[a]



5 **6**

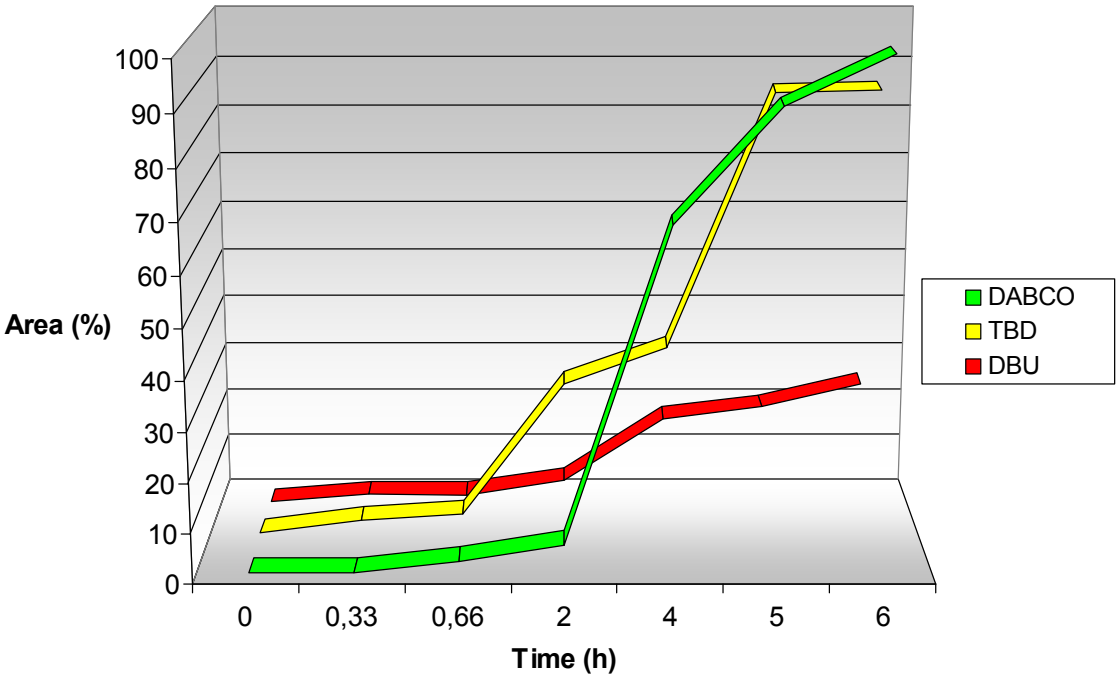
[a] Reaction conditions: 2-(2-hydroxyethoxy)phenol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.10 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 6	% Area cyclic product 5
0.00[b]	100.00	0.00	0.00
0.33	89.20	10.80	0.00
0.66	71.60	26.20	2.20
1.00	55.70	39.70	4.60
2.00	25.30	69.20	5.50
3.00	10.10	64.50	25.40
4.00	2.40	29.40	68.20
5.00	0.00	9.70	90.30
6.00	0.00	0.00	100.00

[b] First sample taken at reflux temperature.

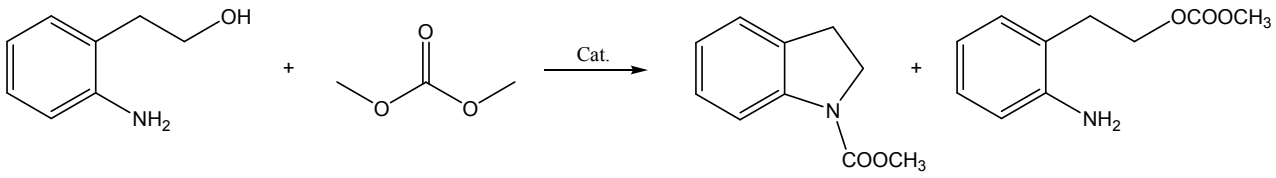
Reaction profiles of the 2,3-dihydrobenzo[b][1,4]dioxine **5** synthesised using respectively DBU, TBD and DABCO as catalysts calculated by GC-MS.



Time (h)	% Area (reaction with DBU)	% Area (reaction with TBD)	% Area (reaction with DABCO)
0.00[b]	0.00	0.60	0.00
0.33	1.70	3.30	0.00
0.66	1.50	4.60	2.20
2.00	4.70	31.50	5.50
4.00	17.90	38.60	68.20
5.00	20.50	89.10	90.30
6.00	25.20	89.50	100.00

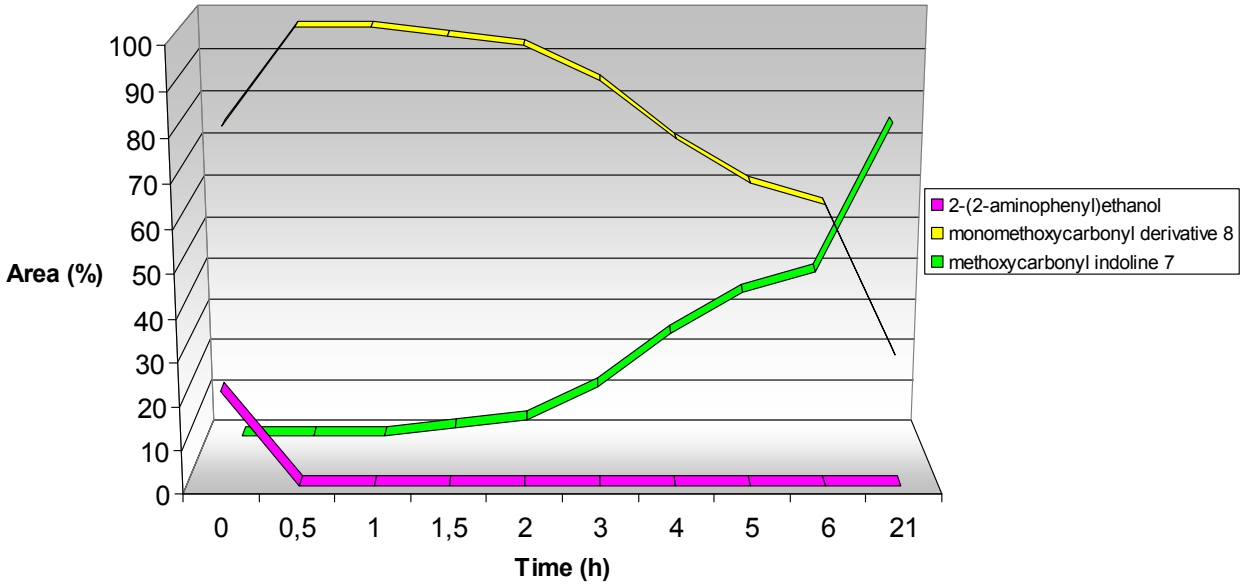
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of methoxycarbonyl indoline **7** with DBU calculated by GC-MS.[a]



7 **8**

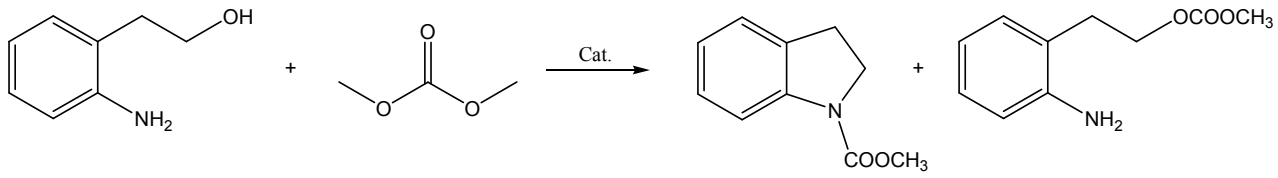
[a] Reaction conditions: 2-(2-aminophenyl)ethanol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.50 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 8	% Area cyclic product 7
0.00[b]	22.0	78.00	0.00
0.50	0.00	100.00	0.00
1.00	0.00	100.00	0.00
1.50	0.00	98.00	2.00
2.00	0.00	96.00	4.00
3.00	0.00	88.00	12.00
4.00	0.00	75.00	25.00
5.00	0.00	65.00	35.00
6.00	0.00	60.00	40.00
21.00	0.00	25.00	75.00

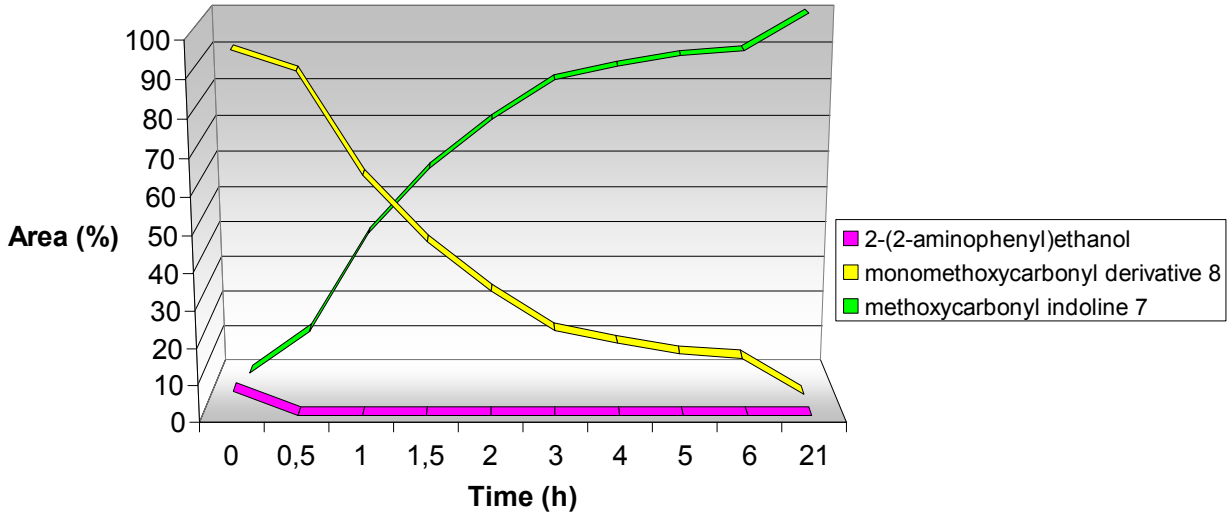
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of methoxycarbonyl indoline **7** with TBD calculated by GC-MS.[a]



7 **8**

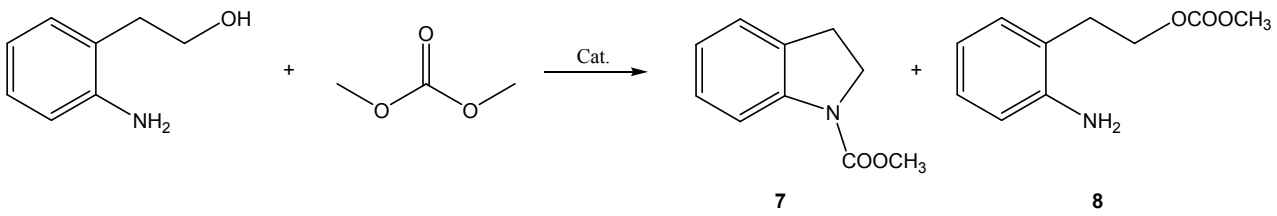
[a] Reaction conditions: 2-(2-aminophenyl)ethanol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.50 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 8	% Area cyclic product 7
0.00[b]	6.60	93.40	0.00
0.50	0.00	87.90	12.10
1.00	0.00	60.20	39.80
1.50	0.00	42.10	57.90
2.00	0.00	28.60	71.40
3.00	0.00	17.80	82.20
4.00	0.00	14.30	85.70
5.00	0.00	11.30	88.70
6.00	0.00	10.10	89.90
21.00	0.00	0.00	100.00

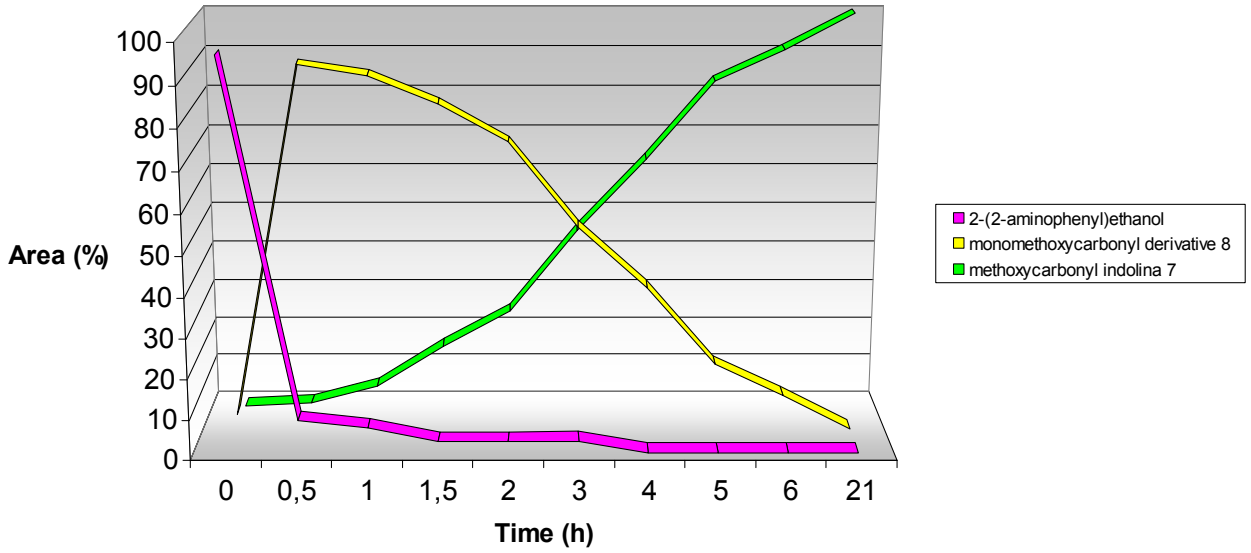
[b] First sample taken at reflux temperature.

Reaction profiles of the starting material, intermediate and cyclic product in the synthesis of methoxycarbonyl indoline **7** with DABCO calculated by GC-MS.[a]



7 **8**

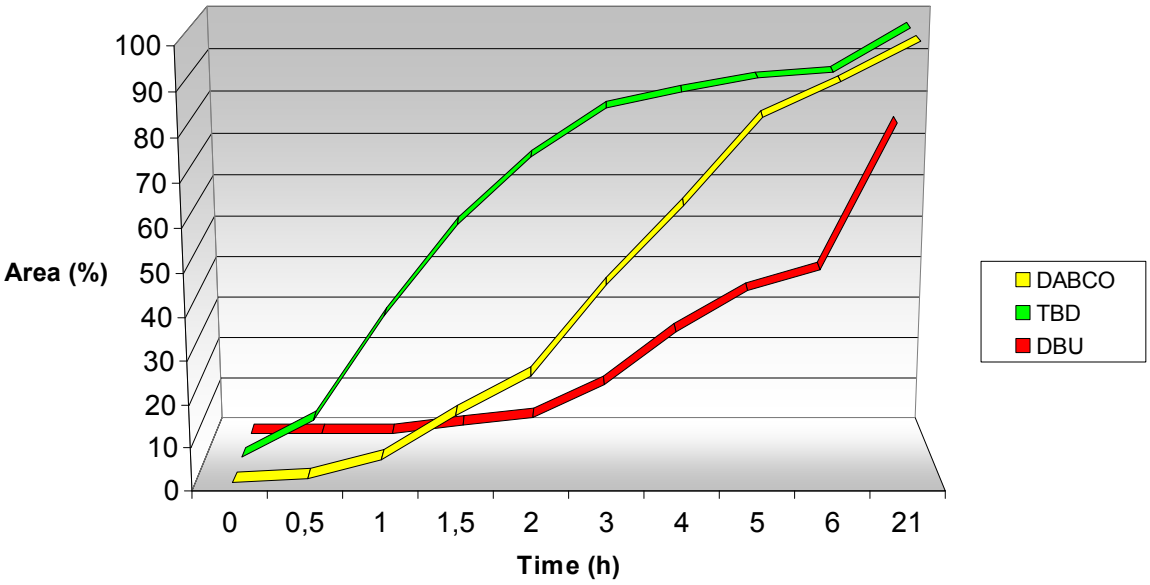
[a] Reaction conditions: 2-(2-aminophenyl)ethanol (1.00 eq. mol), DMC (8.00 eq. mol), catalyst (0.50 eq. mol), 90 °C.



Time (h)	% Area starting material	% Area intermediate 8	% Area cyclic product 7
0.00[b]	96.20	3.80	0.00
0.50	8.10	90.90	1.00
1.00	6.40	88.10	5.50
1.50	2.80	81.30	15.90
2.00	2.80	72.10	25.10
3.00	2.90	51.20	45.90
4.00	0.00	36.10	63.90
5.00	0.00	16.60	83.40
6.00	0.00	8.70	91.30
21.00	0.00	0.00	100.00

[b] First sample taken at reflux temperature.

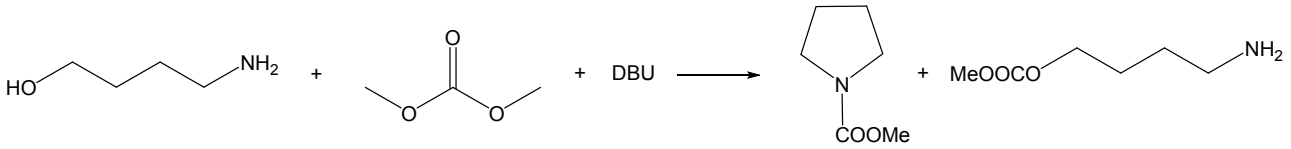
Reaction profiles of the methoxycarbonyl indoline **7** synthesised using respectively DBU, TBD and DABCO as catalysts calculated by GC-MS.



Time (h)	% Area (reaction with DBU)	% Area (reaction with TBD)	% Area (reaction with DABCO)
0.00[b]	0.00	0.00	0.00
0.50	0.00	12.10	1.00
1.00	0.00	39.80	5.50
1.50	2.00	57.90	15.90
2.00	4.00	71.40	25.10
3.00	12.00	82.20	45.90
4.00	25.00	85.70	63.90
5.00	35.00	88.70	83.40
6.00	40.00	89.90	91.30
21.00	75.00	100.00	100.00

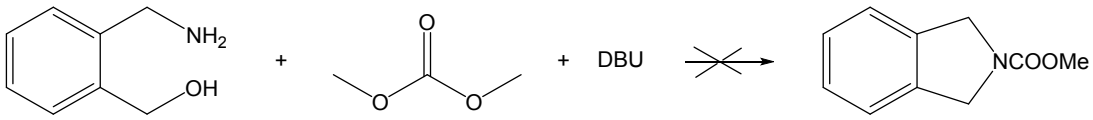
[b] First sample taken at reflux temperature.

Reaction of 4-aminobutan-1-ol with DMC and DBU.



In a vessel equipped with a reflux condenser, 4-aminobutan-1-ol (3.36 mmol, 1.00 mol. eq.), DMC (26.90 mmol, 8.00 mol. eq.) and DBU (3.36 mmol, 1.00 mol. eq.) were heated at reflux while stirring. The progress of the reaction was monitored by TLC. After 24 hours the reaction was stopped, cooled at room temperature and the solvent evaporated. It was recovered the monomethoxycarbonyl derivative in 69% yield (0.34 g, 2.31 mmol) by column chromatography on silica gel using dichloromethane/methanol (95:5) as elution mixture. This is because the cyclic product and the intermediate have the same retention factor on the TLC.

Reaction of 2-(aminomethyl)benzyl alcohol with DMC and DBU.



In a vessel equipped with a reflux condenser, 2-(aminomethyl)benzyl alcohol (1.00 mol. eq.), DMC (8.00 mol. eq.) and DBU (1.00 mol. eq.) were heated at reflux while stirring. The progress of the reaction was monitored by TLC. After 24 hours only starting materials can be observed.