



Supporting Information

Exovinylene Cyclic Carbonates: Multifaceted CO₂-Based Building Blocks for Modern Chemistry and Polymer Science

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Catalysts for α CCs synthesis

3.1. Homogeneous single activation catalysts

3.1.1 Organic bases

Table S1. Catalytic performances of selected organic bases for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol in neat conditions (results plotted in Figure 1)

Catalyst	Loading (mol%)	T (°C)	P (bar)	Conv (%)	Yield DMACC (%)	Duration (h)	Ref
PPh₃	8	140	50	100	78	20	27, 28
PBu₃	5	100	100	100	99	15	29
NEt₃	100	30	10		0	10	30
TBD	10	100	50	91	21	24	31
MTBD	1	60	30	100	52	8	32

3.1.2 Lewis base-CO₂ adducts

Table S2. Catalytic performances of selected Lewis base-CO₂ adducts for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol in neat conditions (results plotted in Figure 2)

Catalyst	Loading (mol%)	T (°C)	P (bar)	Conv (%)	Yield DMACC (%)	Duration (h)	Ref
NHC-CO₂ (catalyst 9a)	5	60	45	100	99	15	33
CDC-CO₂ (catalyst 10d)	5	80	20	100	94	12	34
NHO-CO₂ (catalyst 11d)	5	60	20	100	96	3	35
AFIB-CO₂ (catalyst 12d)	2	60	20	100	97	5	36
DBN-CO₂ (catalyst 13a)	5	60	20	100	91	2	37

3.1.3 Ionic liquids

Table S3. Catalytic performances of selected Ionic Liquids for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol in neat conditions – Influence of the cations (results plotted in Figure 3a)

Catalyst	Loading (mol%)	T (°C)	P (bar)	Conv (%)	Yield DMACC (%)	Duration (h)	Ref
[nBu ₄ N][OAc]	5	80	50	100	93	6	42
[nBu ₄ P][OAc]	5	80	50	100	10	6	42
[DBUH][OAc]	5	80	50	100	0	6	42
[BMIm][OAc]	5	80	50	100	16	6	42

Table S4. Catalytic performances of selected Ionic Liquids for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol in neat conditions – Influence of the anions (results plotted in Figure 3b)

Catalyst	Loading (mol%)	Temp (°C)	P (bar)	Conv (%)	Yield DMACC (%)	Duration (h)	Ref
[nBu ₄ N][OPh]	5	80	50	100	89	1	42
[nBu ₄ N][Im]	5	80	50	100	93	6	42
[nBu ₄ N][CN]	5	80	30	100	84	6	22
[nBu ₄ N][F]	5	100	50	100	10	24	31

3.2. Dual activation by Ag- and Cu-based catalysts

Table S5. Catalytic performances of dual catalytic systems for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol in neat conditions – Influence of the metal salt (results plotted in Figure 4a)

Catalyst (Loading mol%)	Metal (Loading mol%)	T (°C)	P (bar)	Conv (%)	Yield DMACC (%)	Duration (h)	Ref
[nBu ₄ N][OPh] (5)	AgOAc (5)	40	15	100	38	1	54
[nBu ₄ N][OPh] (5)	AgI (5)	40	15	100	99	1	54
[nBu ₄ N][OPh] (5)	Ag ₂ CO ₃ (5)	40	15	100	70	1	54
[nBu ₄ N][OPh] (5)	CuI (5)	40	15	81	81	1	54

Table S6. Catalytic performances of dual catalytic systems for the carboxylative coupling of CO₂ with 2-methyl-3-butyn-2-ol – Influence of the additive (results plotted in Figure 4b)

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