A Diagonal Approach to Chemical Recycling of Carbon Dioxide: Organocatalytic Transformation for the Reductive Functionalization of CO_2

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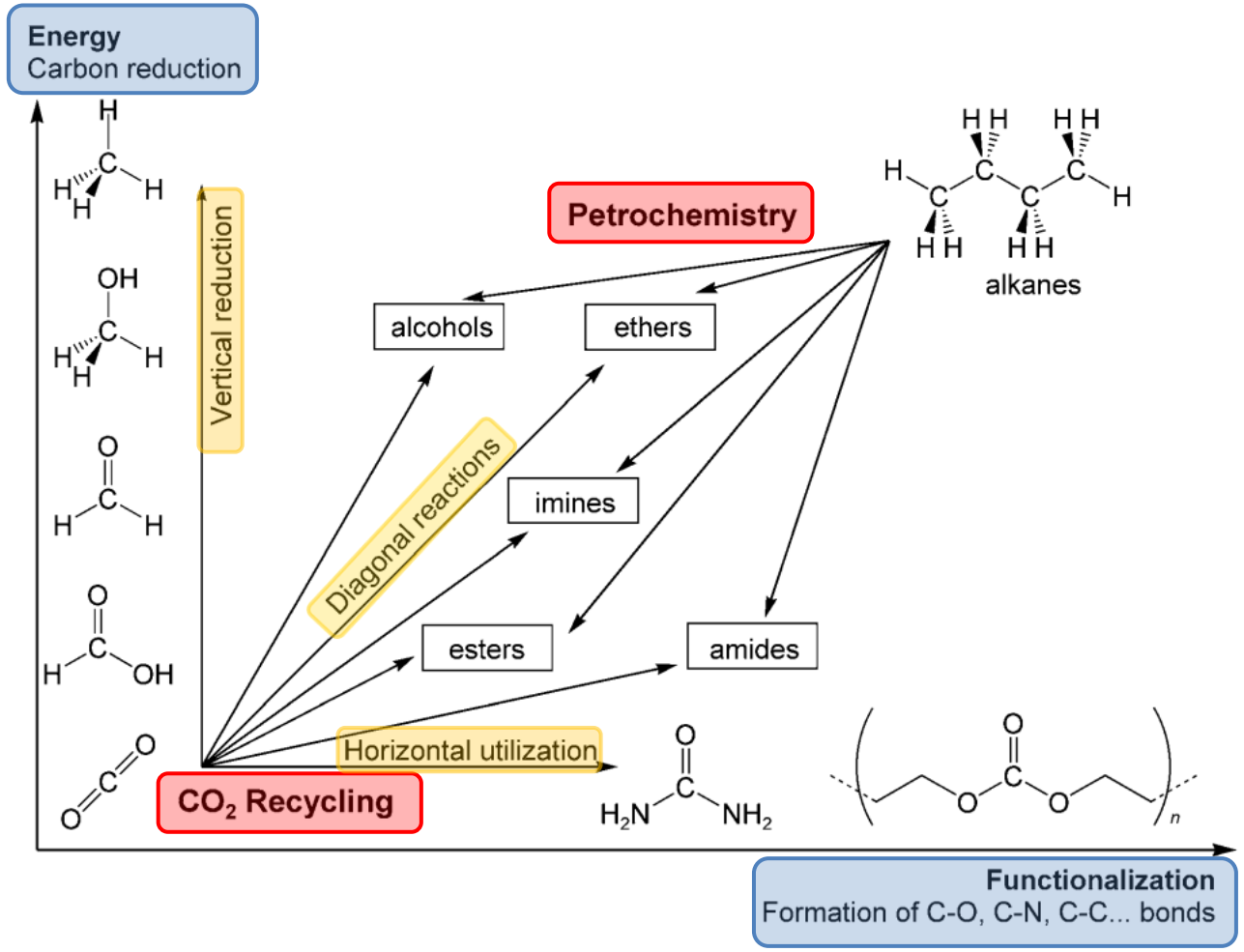
Approaches to recycling transformations of CO_2

CO_2 recycling ⟶ Reduce dependence on petrochemicals

CO_2 nontoxic, abundant C1 building block



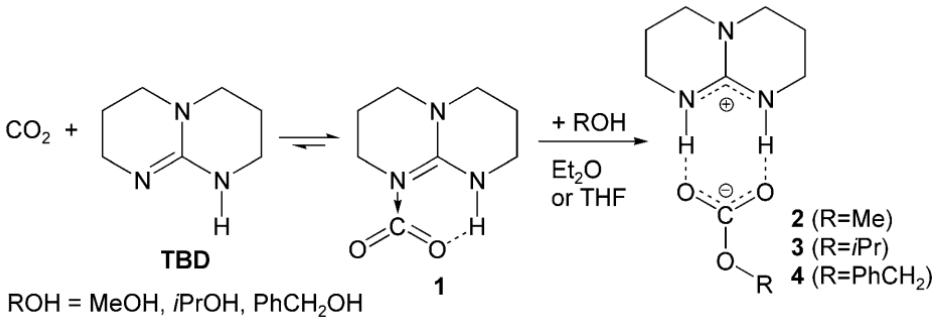
Organocatalytic synthesis of formamides from CO_2

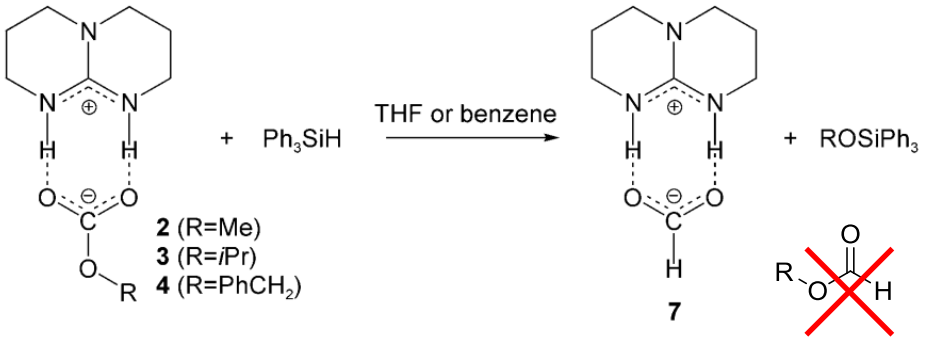
Idea: develop a new reductive functionalization of CO_2

Functionalization reagent : amine, alcohol

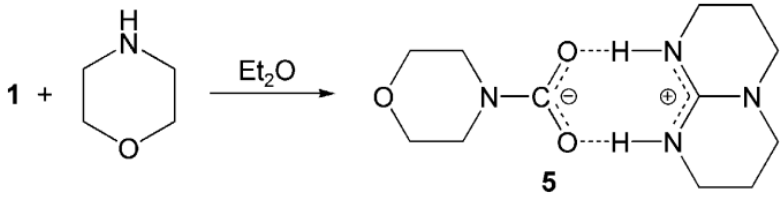
Reducing agent: organosilane (cheap, nontoxic, mild reducing potential)

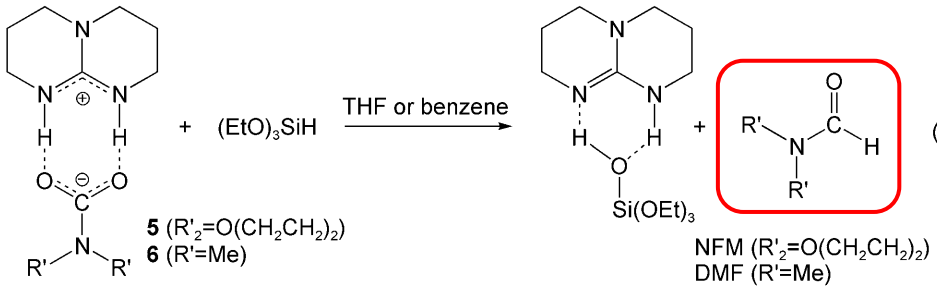
alcohols





Amines





Screening

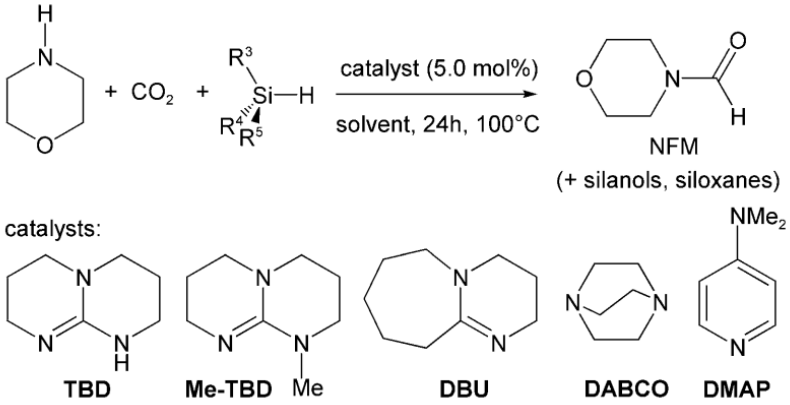
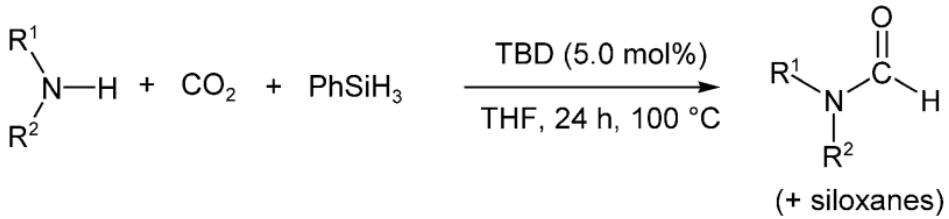


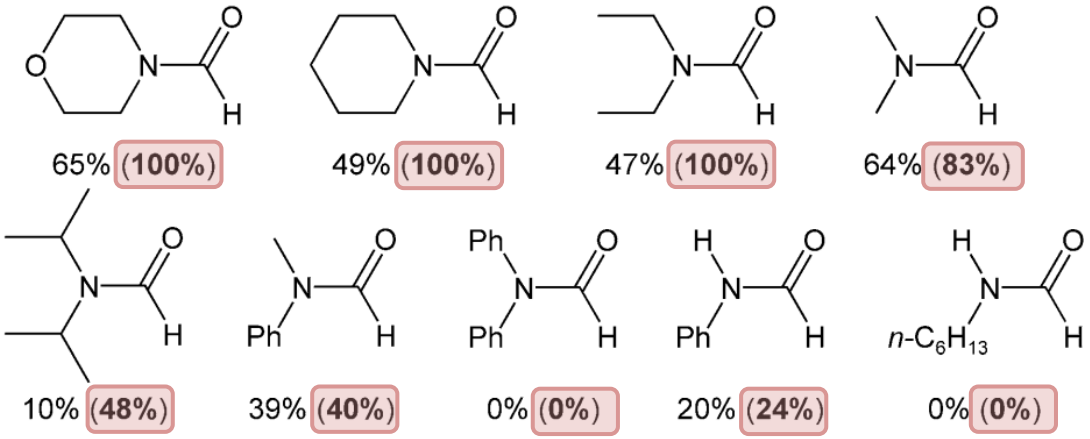
Table 1: Catalytic formylation of morpholine using CO_2 and silanes as shown in Equation (6).

Entry	Silane ($R^3R^4R^5SiH$)	Catalyst	Solvent	Yield [%]
1	$PhSiH_3$ (1 equiv)	TBD	THF	65
2	$PhSiH_3$ (1 equiv)	DBU	THF	20
3	$PhSiH_3$ (1 equiv)	Me-TBD	THF	15
4	$PhSiH_3$ (1 equiv)	DMAP	THF	17
5	$PhSiH_3$ (1 equiv)	DABCO	THF	<5
6	$PhSiH_3$ (1 equiv)	NEt_3	THF	<5
7	$PhSiH_3$ (1 equiv)	none	THF	0
8	$PhSiH_3$ (1 equiv)	TBD	CH_3CN	93
9	$PhSiH_3$ (1 equiv)	TBD	none	100
10	$PhSiH_3$ (1 equiv)	TBD	DMSO	74
11	$PhSiH_3$ (1 equiv)	TBD	C_6H_6	70
12	Ph_2SiH_2 (1.5 equiv)	TBD	THF	33
13	$(EtO)_3SiH$ (3 equiv)	TBD	THF	46
14	Ph_3SiH (3 equiv)	TBD	THF	0

Scope



yields : in THF **(without solvent)**

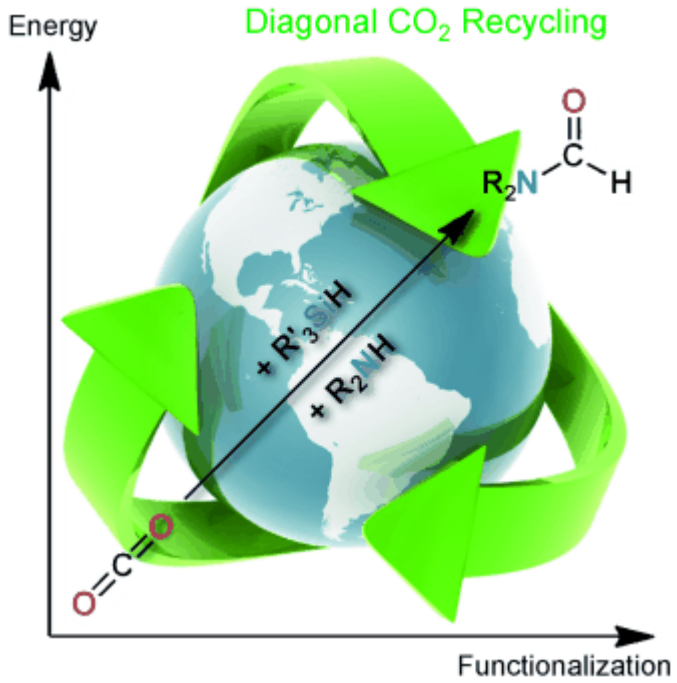


Scheme 2. Organocatalytic reduction of CO_2 to formamides using amines and $PhSiH_3$.

Secondary amines **>** primary amines

Aliphatic amines **>** aromatic amines

conclusion

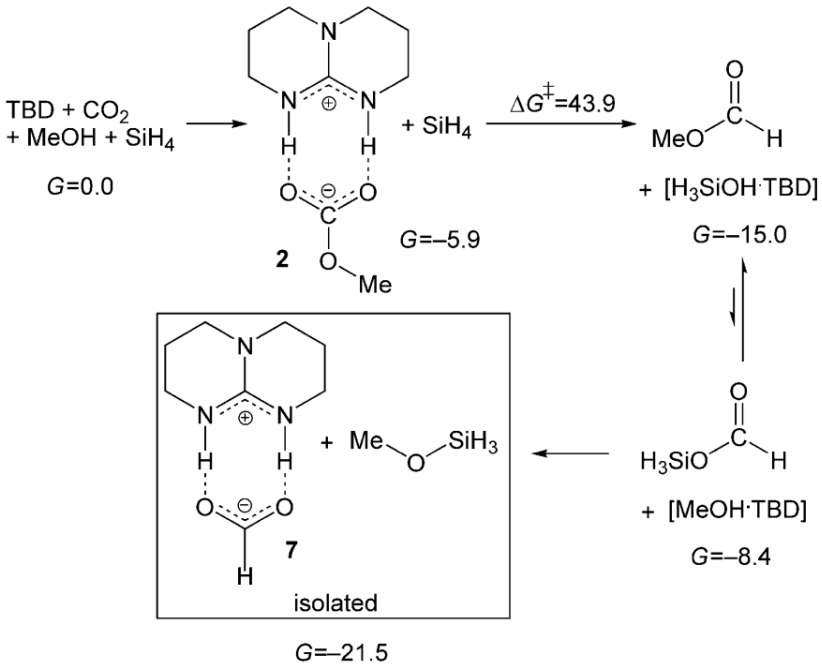


Advantages compared to formylation using CO_2/H_2/amine:

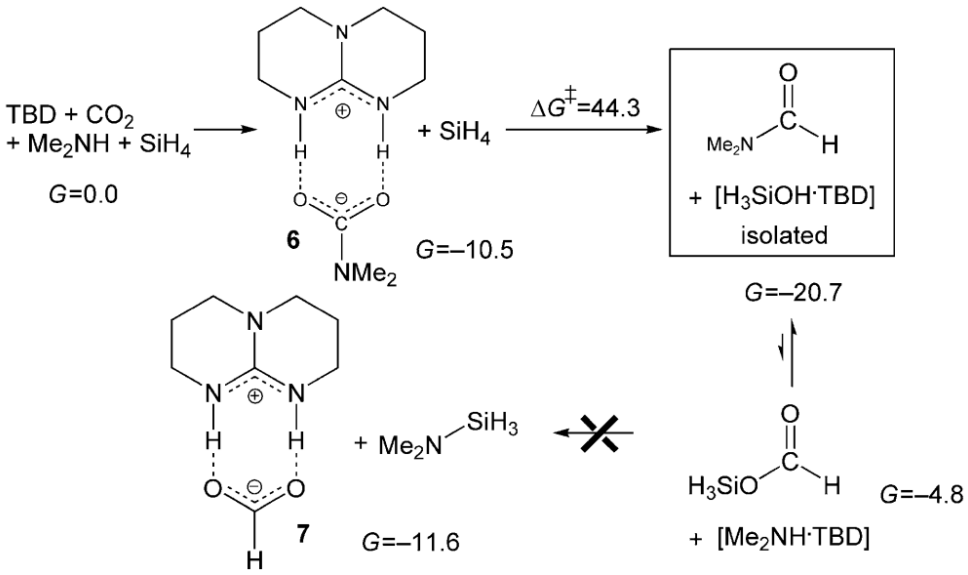
- Organocatalyst **vs** metal catalyst
- Low pressure (<3 bar) **vs** high pressure (100 bar)
- Solvent-free **vs** Organic solvent
- Wide spectrum of amines **vs** limited to Me_2NH, Et_2NH, $PhNH_2$

Computed pathways

alcohols



Amines



Supporting Figure S1

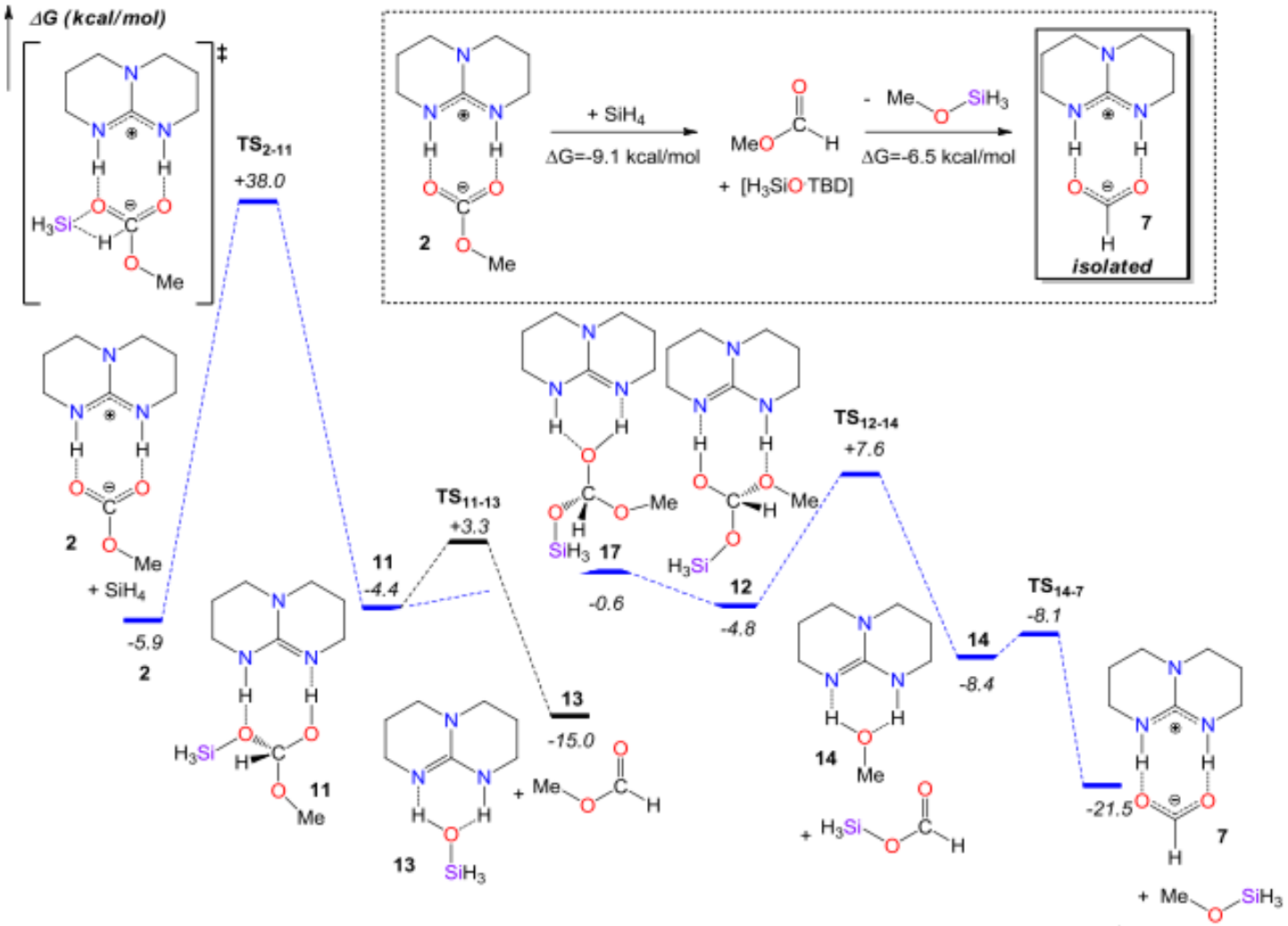
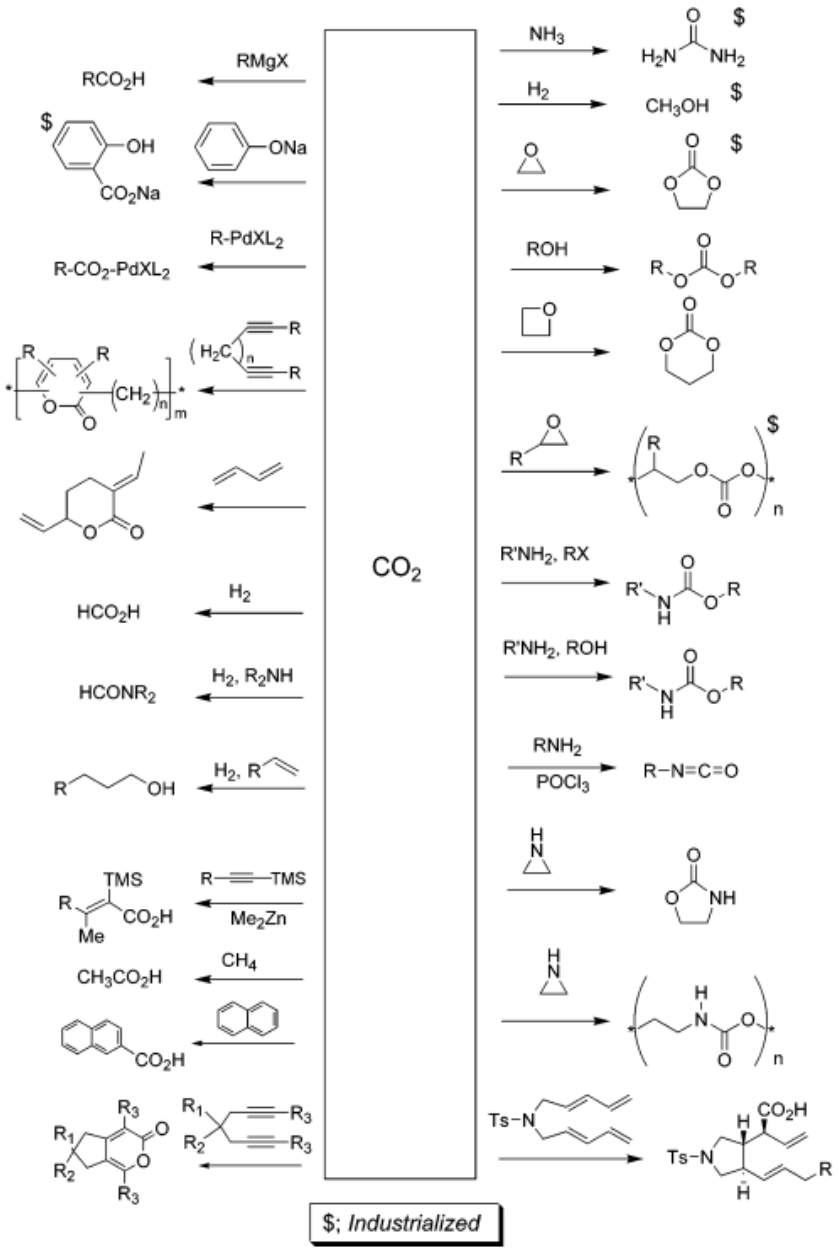


Figure S1 | Computed pathway for the reduction of **2** to formate salt [HCO_2^-][$TBDH^+$]. Gas-

Scheme 5. Transformations of Carbon Dioxide



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