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CHEMISTRY

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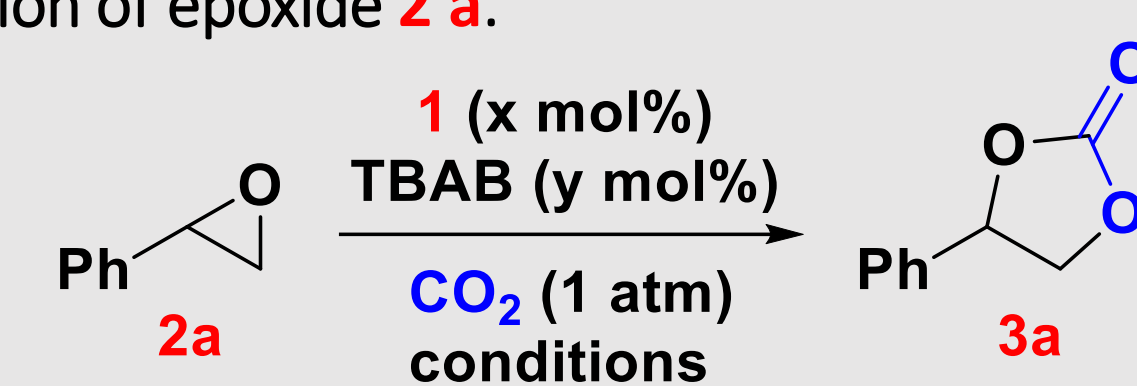
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Most significant Results:

What we did (in short!):

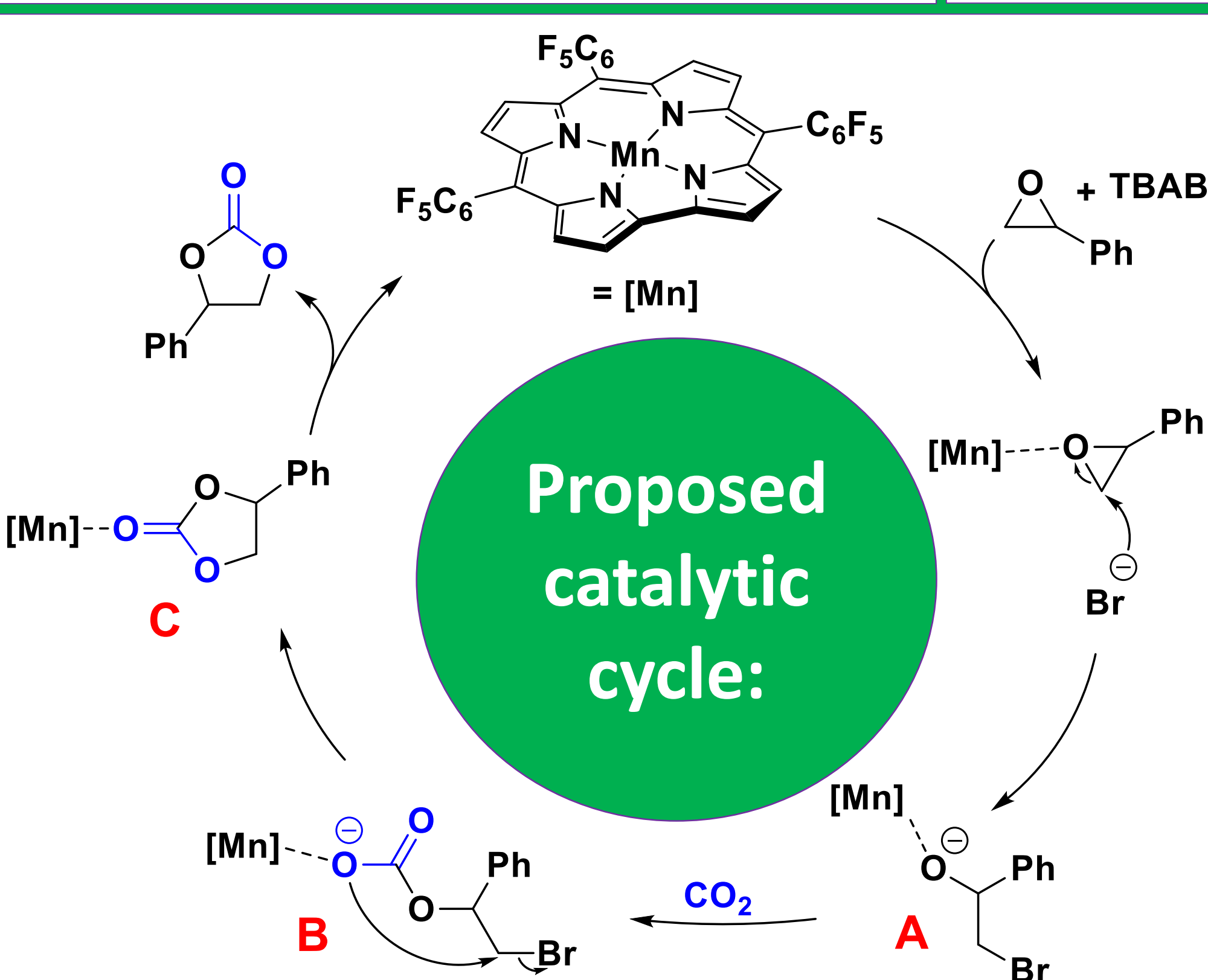
We have investigated the cooperative catalytic activity of several metal corrole complexes in combination with tetrabutylammonium- bromide (TBAB) for the reaction of epoxides with CO₂ to cyclic carbonates. It was found that the use of just 0.05 mol % of a manganese(III)corrole with 2 mol % TBAB exhibits excellent catalytic activity even at room-temperature with just 1 atmosphere of CO₂ [1]. Various catalysts for this reaction have been developed, including metal complexes (e.g., metal-salen complexes and metalloporphyrins) [2-4] and organocatalysts (e.g., quaternary onium salts or N-heterocyclic carbenes) [5-6].

Table 1. Identification of the optimum catalyst system for the CO₂ fixation of epoxide **2a**.

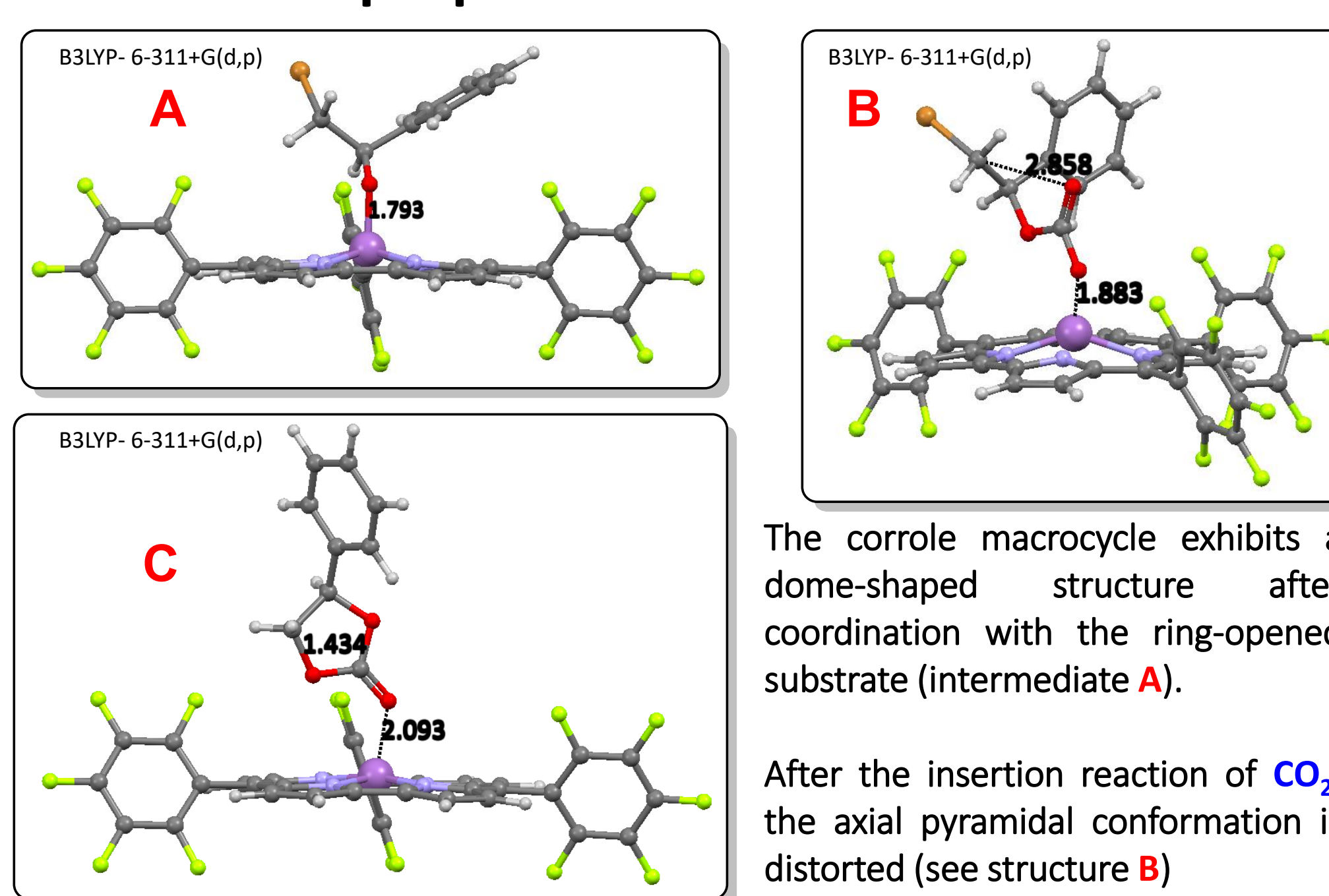


entry ^[a]	1 [mol %]	TBAB [mol %]	T [°C]	t [h]	conv. [%] ^[b]
1	Mn 1a (0.05 %)	1%	60	4	48
2	-	1%	60	4	9
3	Mn 1a (0.05 %)	-	60	4	n.r.
4	Mn 1a (0.05 %)	1%	25	4	8
5	Fe 1b (0.05 %)	1%	60	4	34
6	Co 1c (0.05 %)	1%	60	4	13
7	Cu 1d (0.05 %)	1%	60	4	13
8	Sb 1e (0.05 %)	1%	60	4	12
9	Bi 1f (0.05 %)	1%	60	4	15
10	Mn 1a (0.01 %)	1%	60	4	29
11	Mn 1a (0.003 %)	1%	60	4	15
12	Mn 1a (0.05 %)	2%	60	4	60 ^[c]
13	Mn 1a (0.05 %)	2%	60	8	>95 ^[d]
14	Mn 1a (0.05 %)	2%	60	8	>95 ^[e]

[a] 4 mmol scale (neat); [b] determined by ¹H NMR of the reaction mixture; [c] less than 15% conv. in the absence of **1a**; [d] the product can be quantitatively isolated after filtration over a short plug of silica; [e] recycled **1a** used.



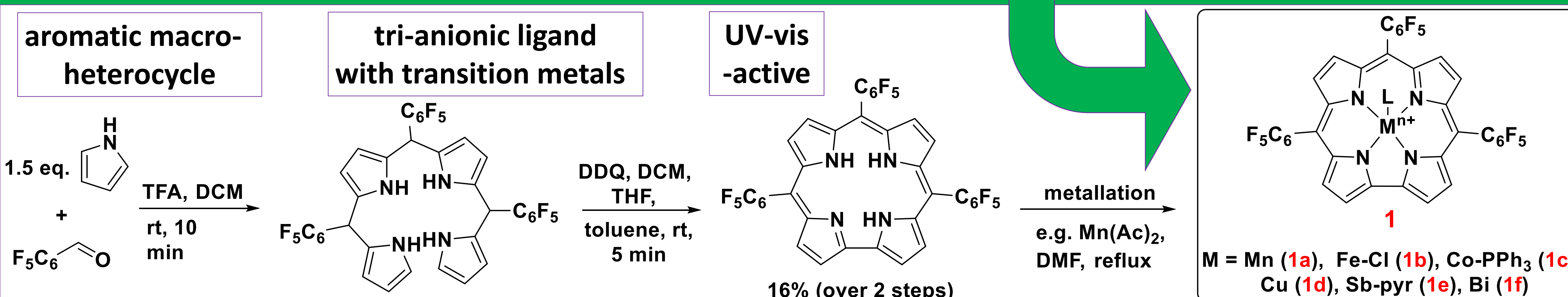
DFT calculated structures of the three main proposed intermediates A-C



Scheme 1. Proposed synergistic catalysis mode for the Mn-corrole **1a**- and TBAB-catalyzed CO₂ fixation with epoxides (based on recent studies)[7-12] and calculated molecular structures of the proposed intermediates A-C.

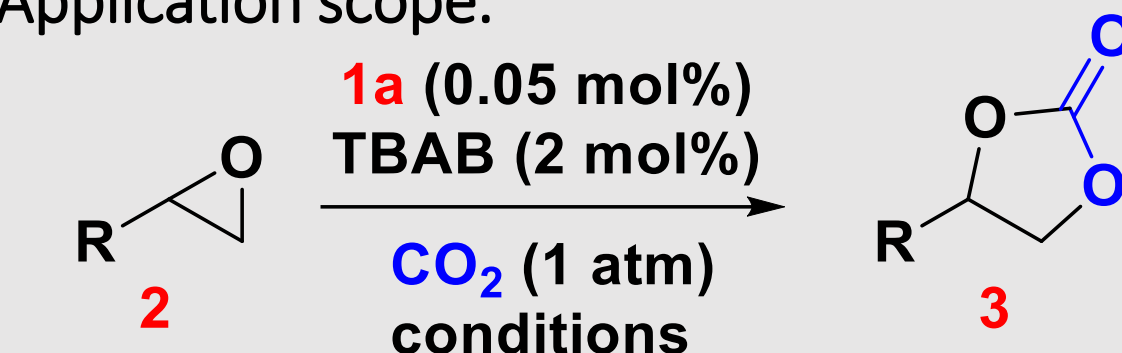
Corrole (Synthesis):

Investigated Metal Corroles:



Scheme 2. The synthesis of 5,10,15-tris(pentafluorophenyl)corrole (TpFPC) according to [12]. (The three C₆F₅-groups in the *meso* positions of the macrocycle withdraw electron density from the 18- π -electron system. A consequence of this effect is the improved stability of such high-valent metal corroles.)

Table 2. Application scope.



entry ^[a]	R	T [°C]	t [h]	conv. [%] ^[b]	yield. [%] ^[c]	TON ^[d]	TOF ^[d] [h ⁻¹]
1	Ph	60	8	>95	94	1880	235
2	Ph	25	8	25	24	480	60
3	4-Cl-C ₆ H ₄	60	8	>98	96	1920	240
4	4-F-C ₆ H ₄	25	8	>98	98	1960	245
5	PhOCH ₂	60	8	>95	94	1880	235
6	Ph ₂ CHOCH ₂	60	8	71	70	1400	175
7	ClCH ₂	60	8	89	88	1760	220
8	vinyl	60	8	>98	93	1860	232
9	but-3-enyl	60	8	>98	98	1960	245
10	but-3-enyl	60	20	>98	98	1960	98
11	Me	25	8	57	55	1100	137
12	Me	25	20	>95	88	1760	88

[a] 4 mmol scale (neat); [b] judged by ¹H NMR of the reaction mixture; [c] isolated yield after filtration over a short plug of silica; [d] based on **1a**. TON=turnover number; TOF=turnover frequency.

See the corrole-ation?

To obtain further mechanistic details, we investigated the time course UV/Vis spectral changes occurring to the catalyst **1a** during the reaction.

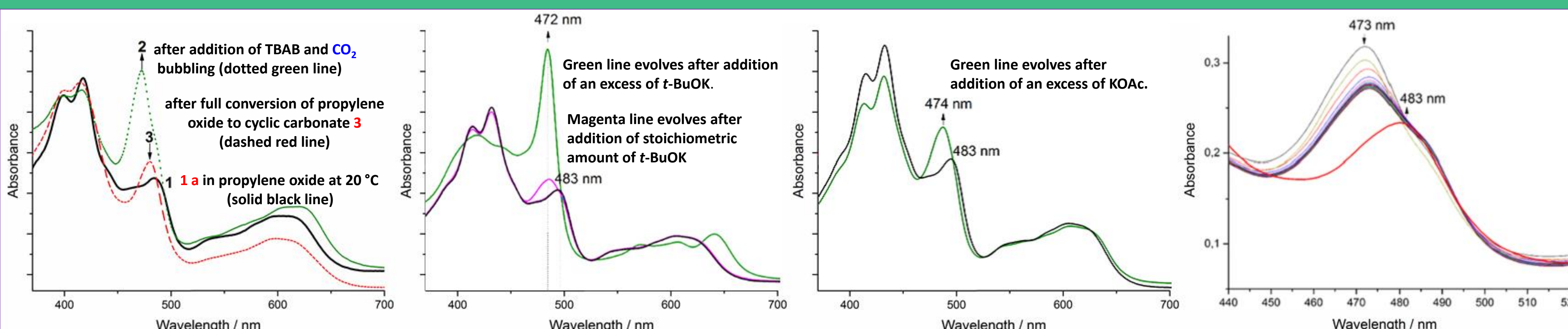


Figure 1. UV/Vis absorption spectra of **1a** during the CO₂ fixation reaction of propylene oxide to 4-methyl-1,3-dioxolan-2-one.

Figure 2. Titration of **1a** (black line) with t-BuOK.

Figure 3. Titration of **1a** (black line) with KOAc (green line).

Figure 4. Section of the time-course UV-vis spectra of the back conversion to **1a**.

Conclusion:

- We have identified that TBAB/Mn^{III}corrole **1a** is the best-suited cooperative catalyst combination so far.
- Reducing the catalyst loading below 0.01 mol % **1a** resulted in a reduced conversion rate.
- Carrying out the reaction with 0.05 mol % **1a** and 2 mol % TBAB led to >95% conversion within just 8h.
- We investigated the time course UV/Vis spectral changes occurring to the catalyst **1a** during the reaction.
- The dramatic changes observed in the time course UV/Vis spectra for **1a** during the reaction could be attributed to the effect of axial binding of the oxygen atom of the ring-opened epoxide **A**, and to the intermediate **B** after CO₂ insertion/fixation.
- We have shown that recycling of the Mn-corrole is possible and makes the Lewis-acidic manganese corrole complex reusable for further transformations.

References & Acknowledgements:

[1] M. Tiffner, S. Gonglach, M. Haas, W. Schöfberger, M. Waser, *Chem. Asian J.* **2017**, *12*, 1048-1051; [2] T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, *48*, 4489-4491; [3] J. A. Castro-Osma, M. North, X. Wu, *Chem. Eur. J.* **2016**, *22*, 2100-2107; [4] X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462-1484; [5] S. Liu, N. Suematsu, K. Maruoka, S. Shirakawa, *Green Chem.* **2016**, *18*, 4611-4615; [6] Y. Toda, Y. Komiyama, A. Kikuchi, H. Suga, *ACS Catal.* **2016**, *6*, 6906-6910; [7] X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang, R. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 3732-3733; [8] X.-B. Lu, Y.-J. Zhang, B. Liang, X. Li, H. Wang, *J. Mol. Catal. A* **2004**, *210*, 31-34; [9] X.-B. Lu, D. J. Darensbourg, *J. Chem. Soc.* **2012**, *41*, 1462-1484; [10] W.-M. Ren, Y. Liu, X.-B. Lu, *J. Org. Chem.* **2014**, *79*, 9771-9777; [11] T. Ema, Y. Miyazaki, J. Shimomishi, C. Maeda, J.-Y. Hasegawa, *J. Am. Chem. Soc.* **2014**, *136*, 15270-15279; [12] F. Faschinger, S. Aichhorn, M. Himmelsbach, W. Schöfberger, *Synthesis* **2014**, *46*, 3085-3096.

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