Supporting Information

A highly stable polyoxovanadate-based Cu(I)–MOF for the carboxylative cyclization of CO_2 with propargylic alcohols at room temperature

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1. Crystallographic Data and Structure Refinements

Table S1. Crystallographic data and structure refinement of V-Cu-MOF

Name	V-Cu-MOF
Empirical formula	$C_{24}H_{20}Cu_2N_8O_6V_2$
Formula weight	745.45
Temperature (K)	293
Wave length (Å)	0.71073
Crystal system	triclinic
Space group	P-1
a (Å)	11.6196(4)
b (Å)	12.0604(5)
c (Å)	12.2162(4)
α (deg)	63.651(2)
β (deg)	75.955(2)
γ (deg)	61.239(2)
Volume ($Å^3$)	1343.91(9)
Z, Dcalc (Mg/m^3)	2, 1.842
Absorption coefficient (mm^{-1})	2.292
F (000)	746.9
Crystal size (mm^3)	0.22 × 0.21 × 0.20
θ range (deg)	5.36 to 51.48
index range (deg)	$-14 \le h \le 14$, $-14 \le k \le 14$, $-14 \le l \le 14$
Reflections collected / unique	23387 / 5117 [Rint = 0.0459]
Data / restraints / parameters	5117 / 7 / 379
Goodness-of-fit on F^2	1.072
R1, wR_2 ($I > 2\sigma(I)$)	0.0292, 0.0606
R1, wR_2 (all data)	0.0458, 0.0681
Largest diff. peak and hole (e $Å^{-3}$)	0.53, -0.49

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ · $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$

2. BVS Results

Table S2. BVS results for the vanadium ions and copper ions in V-Cu-MOF.

Metal site	BVS cacl.	Assigned O.S.
V1	5.125	5
V2	5.132	5
Cu1	1.079	1
Cu2	0.991	1

3. XPS Spectra of V and Cu in V-Cu-MOF

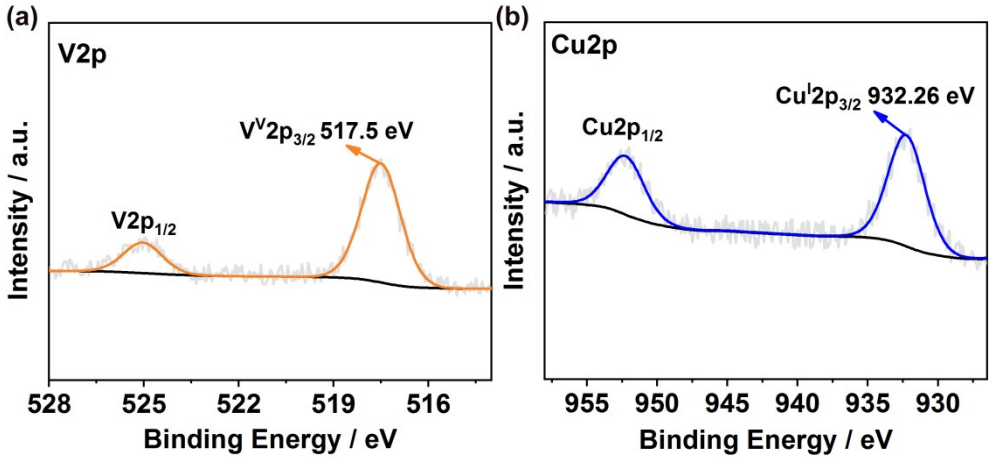


Fig. S1. XPS spectra of V (a) and Cu (b) in V-Cu-MOF.

4. PXRD Patterns of V-Cu-MOF

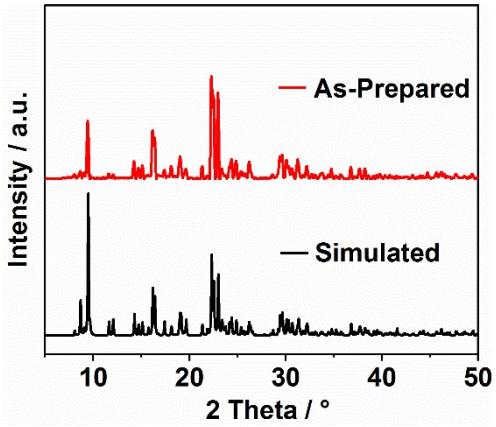


Fig. S2. The PXRD patterns of V-Cu-MOF.

5. FTIR Spectrum of V-Cu-MOF

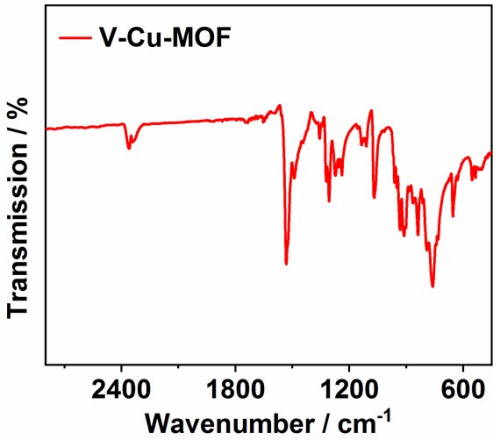


Fig. S3. The FTIR spectrum of V-Cu-MOF.

6. TGA Curve of V-Cu-MOF

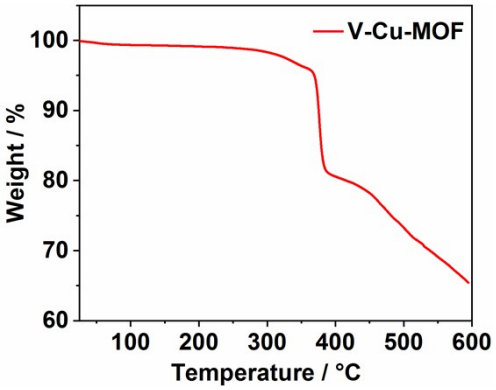


Fig. S4. The TGA curve of V-Cu-MOF.

7. The FTIR Spectra of V-Cu-MOF after Immersing in Various Solvents and pH Solutions

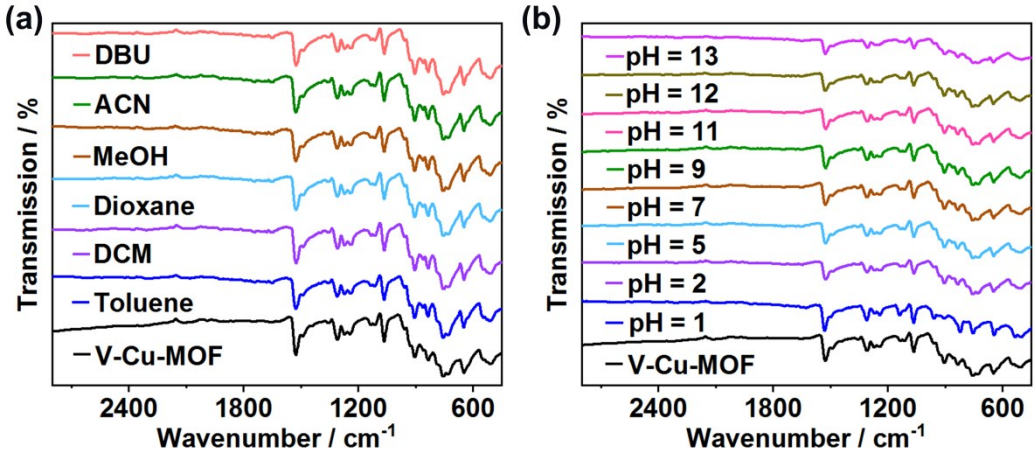


Fig. S5. (a) The FTIR spectra of V-Cu-MOF after immersing in various solvents for 7 days; (b) The FTIR spectra of V-Cu-MOF after immersing in different pH solutions for 12 hours.

8. BET Analysis of V-Cu-MOF

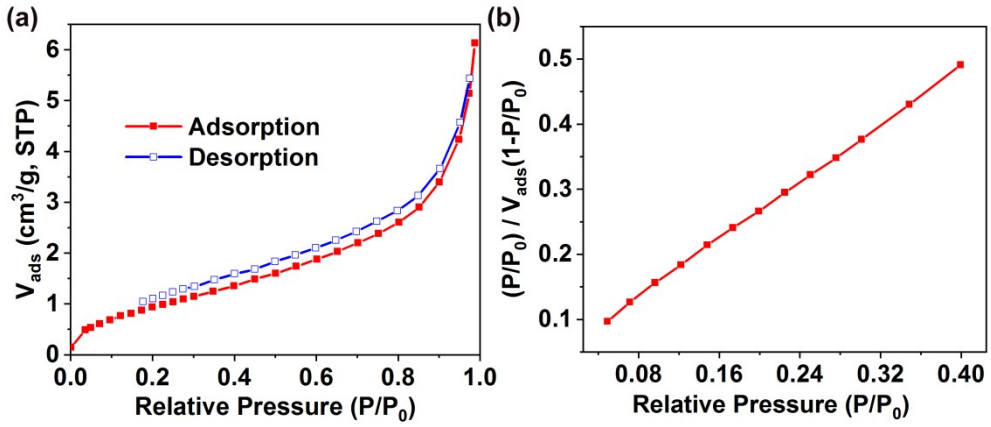
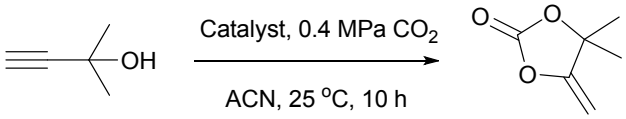


Fig. S6. BET analysis of V-Cu-MOF. The N_2 absorption / desorption isotherms were measured at 77K (P_0 = 101 kPa).

9. Control Experiments of the Cyclization of 1a with CO_2

Table S3. Control experiments of the cyclization of **1a** with CO_2[a].



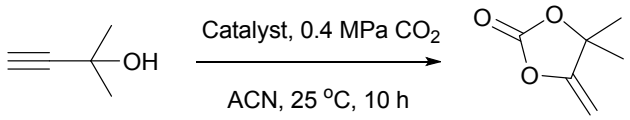
1a **2a**

Entry	Catalyst	Yield (%)[b]
1	$Cu(NO_3)_2{\cdot}3H_2O$	—
2	$NaVO_3$	—
3	bib	—
4	$Cu(NO_3)_2{\cdot}3H_2O$ + $NaVO_3$ + bib	—
5	V-Cu-MOF	—
6	DBU	< 1
7	V-Cu-MOF + TEA	< 1
8	V-Cu-MOF + DIPEA	< 1
9	V-Cu-MOF + DBU	99

[a] Reaction conditions: **1a** (1 mmol), catalyst (0.025mmol, 2.5% mol), 0.4 MPa CO_2, 25 ºC, 10 hours.
[b] Yield was determined by GC and mesitylene as internal standard. Note: the amount of catalyst TEA, DIPEA and DBU added are 0.2 mmol.

10. Comparison of the V-Cu-MOF with the Previously Reported Heterogeneous Catalyst

Table S4. Comparison of the V-Cu-MOF with the previously reported heterogeneous catalyst.

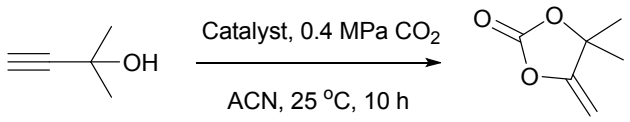


1a **2a**

Entry	Catalyst	Additive	T/ ºC	P_{CO2}/ MPa	t/ hour	Yield/%	Ref.
1	AgNPs/SMR	DBU (1.0 eq.)	25	0.1	10	Run1, 91	[1]
2	PAzo-POP-Ag	DBU (1.0 eq.)	25	1.0	18	Run1, 95	[2]
3	MOF-SO_3Ag	DBU (0.1 eq.)	25	0.1	24	Run1, 99	[3]
4	CNT-NHC-Ag	—	80	3.0	24	Run1, >99	[4]
5	GN-NH-Ag	—	80	3.0	24	Run1, 99	[4]
6	CNT-NHC-Cu	—	80	3.0	24	Run1, 87	[4]
7	GN-NH-Cu	—	80	3.0	24	Run1, 86	[4]
8	{Cu_4I_4}-In	TEA (0.14 eq.)	50	0.5	10	Run1, 99	[5]
9	Ag-TCPE	PPh_3 (0.025 eq.)	50	0.5	20	Run1, >99 Run5, 90	[6]
10	TMOF-3-Ag	DBU (0.1 eq.)	25	0.1	6	Run1, >99 Run3, 89	[7]
11	Ag/POP@g-C_3N_4	DBU (0.5 eq.)	25	1.0	12	Run1, 96 Run5, 88	[8]
12	{Cu_4I_4}-Dy_2	DBU (1.0 eq.)	25	0.1	5	Run1, 95 Run4, 68	[9]
13	V-Cu-MOF	DBU (0.2 eq.)	25	0.4	10	Run1, 99 Run10, 97	This work

11. Control Experiments of Determining the Catalytic Active Sites in V-Cu-MOF

Table S5. Control experiments of determining the catalytic active sites in V-Cu-MOF[a].



1a **2a**

Entry	Catalyst	Yield (%)[b]
1	bib	< 1
2	$[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$	< 1
3	CuI	99
4	V-Cu-MOF	99

[a] Reaction conditions: **1a** (1 mmol), catalyst (0.025mmol, 2.5% mol), 0.4 MPa CO_2, DBU (0.2 mmol), 25 ºC, 10 hours. [b] Yield was determined by GC and mesitylene as internal standard.

12. PXRD Patterns of $[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$

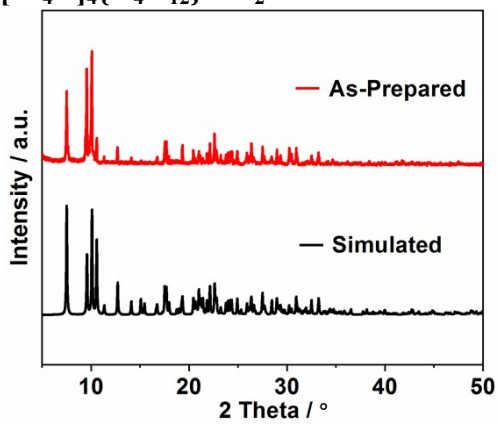
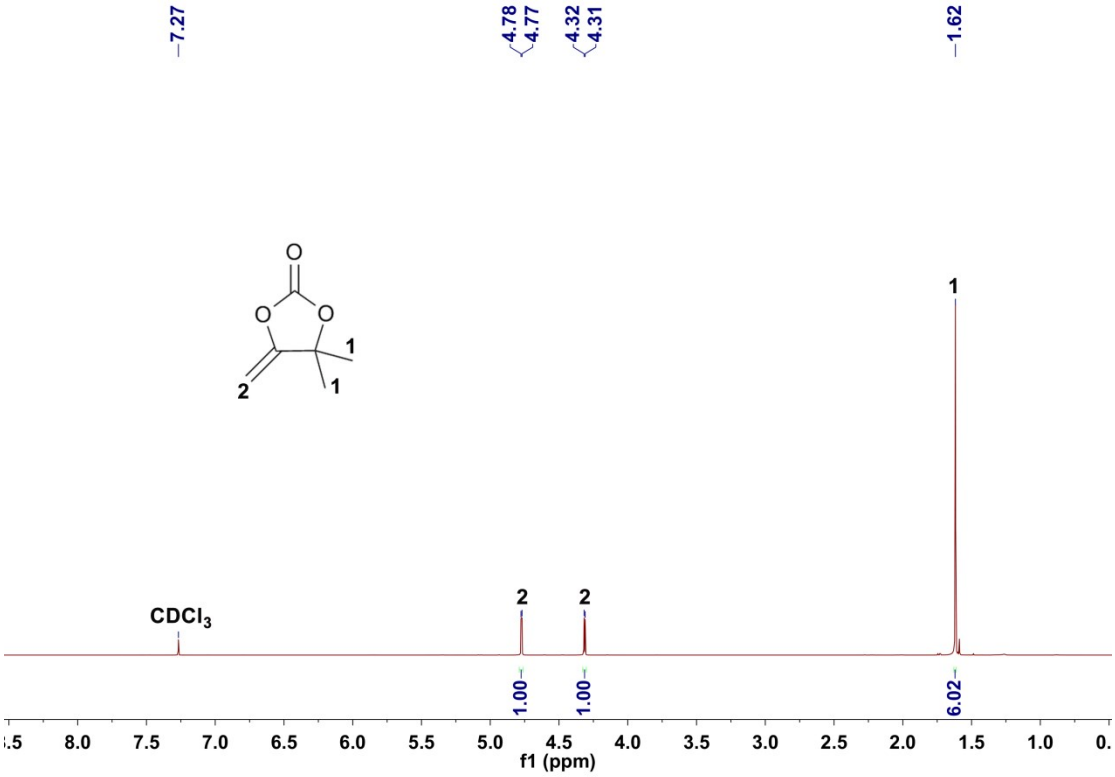
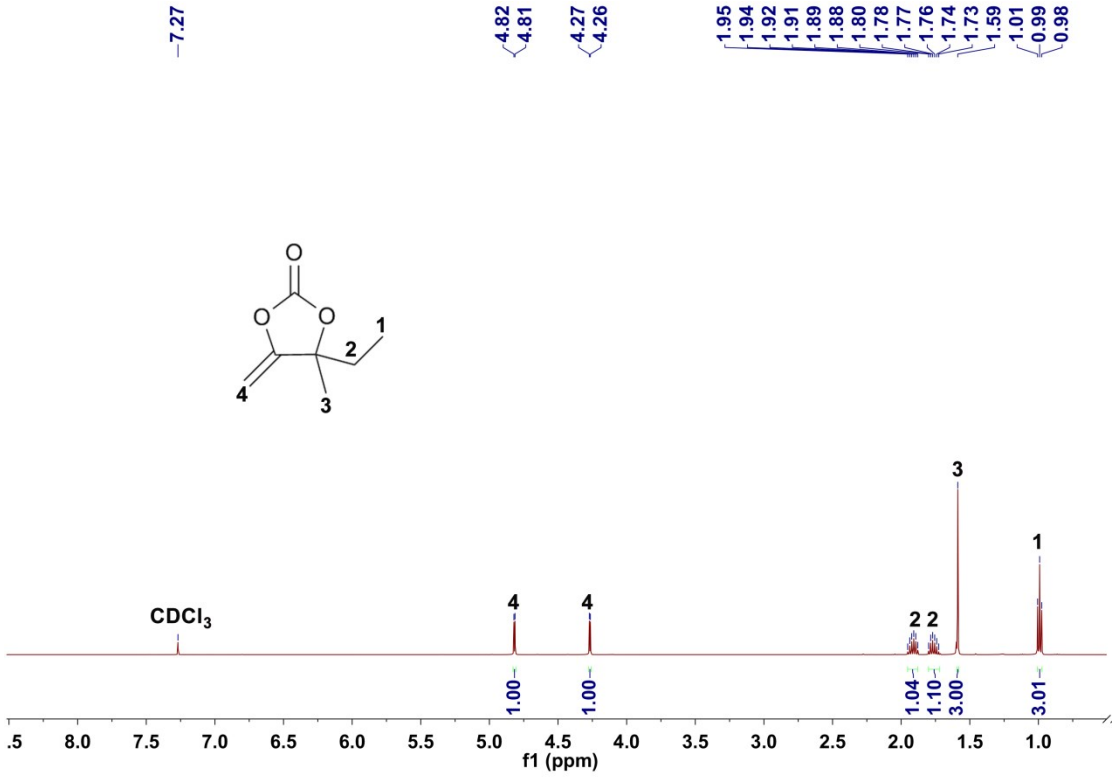


Fig. S7. The PXRD patterns of $[Et_4N]_4\{V_4O_{12}\}\cdot 2H_2O$.

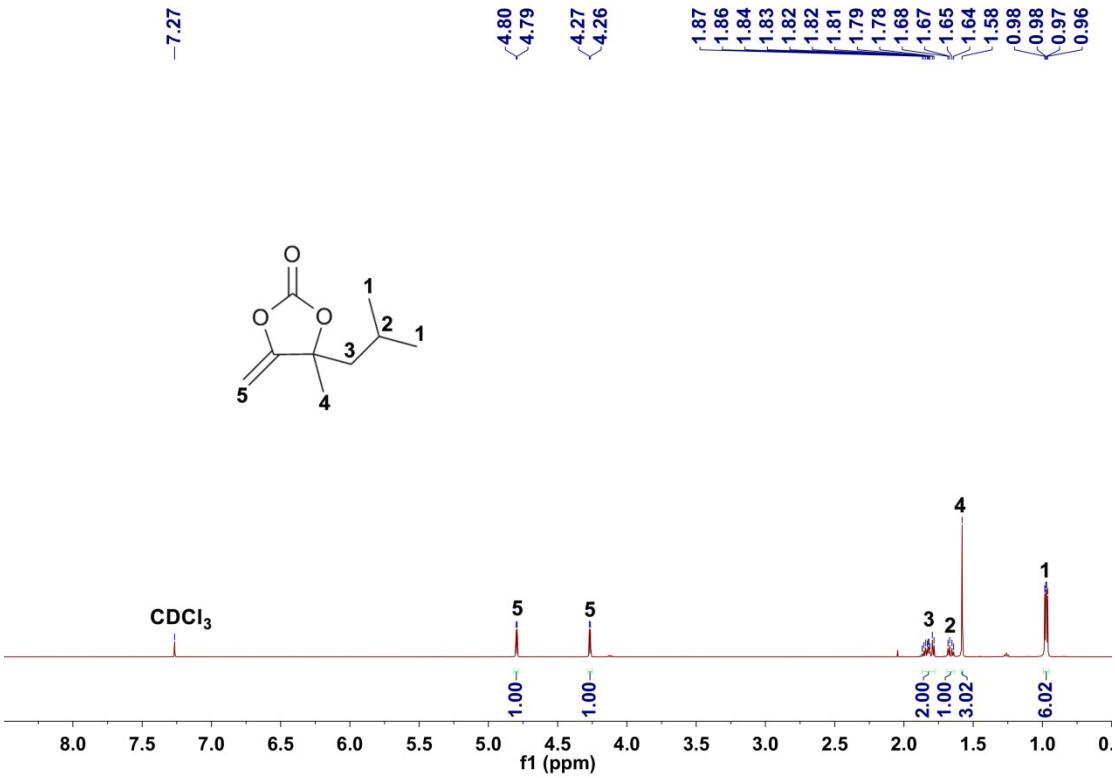
13. ^{1}H-NMR Spectra of α-Alkylidene Cyclic Carbonates



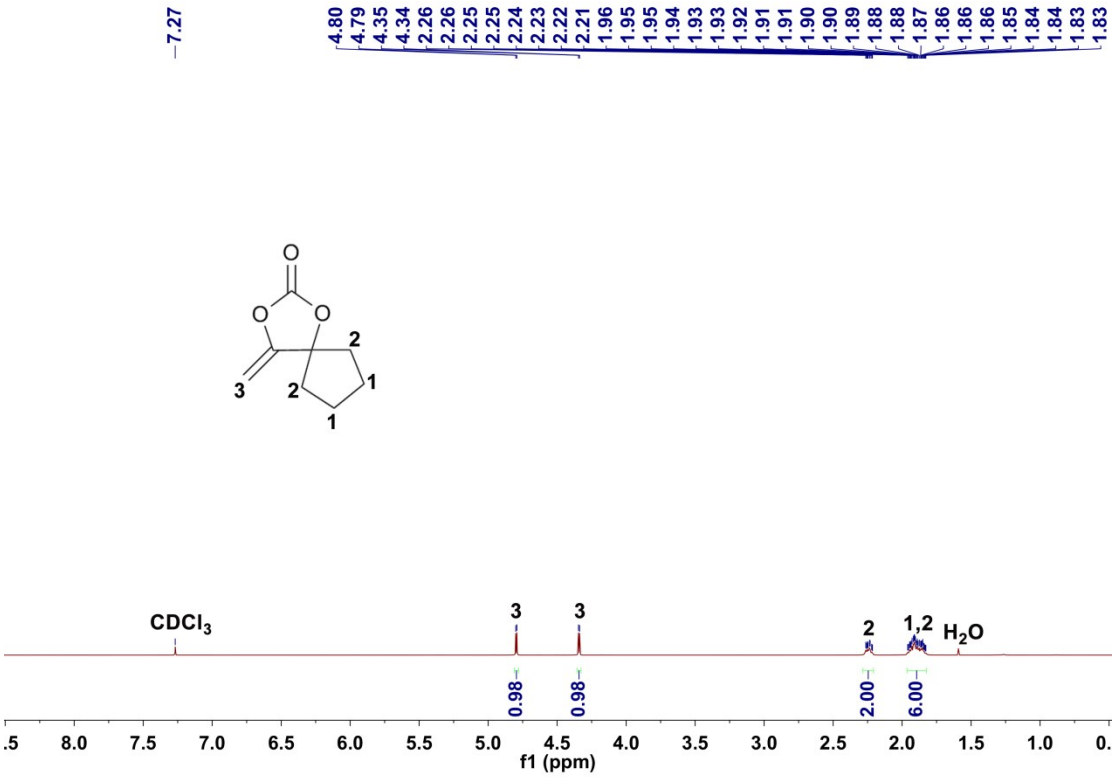
4,4-Dimethyl-5-methylene-[1,3]dioxolan-2-one (2a). Colorless oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.78 (d, J = 5.0 Hz, 1H), 4.32 (d, J = 5.0 Hz, 1H), 1.62 (s, 6H).



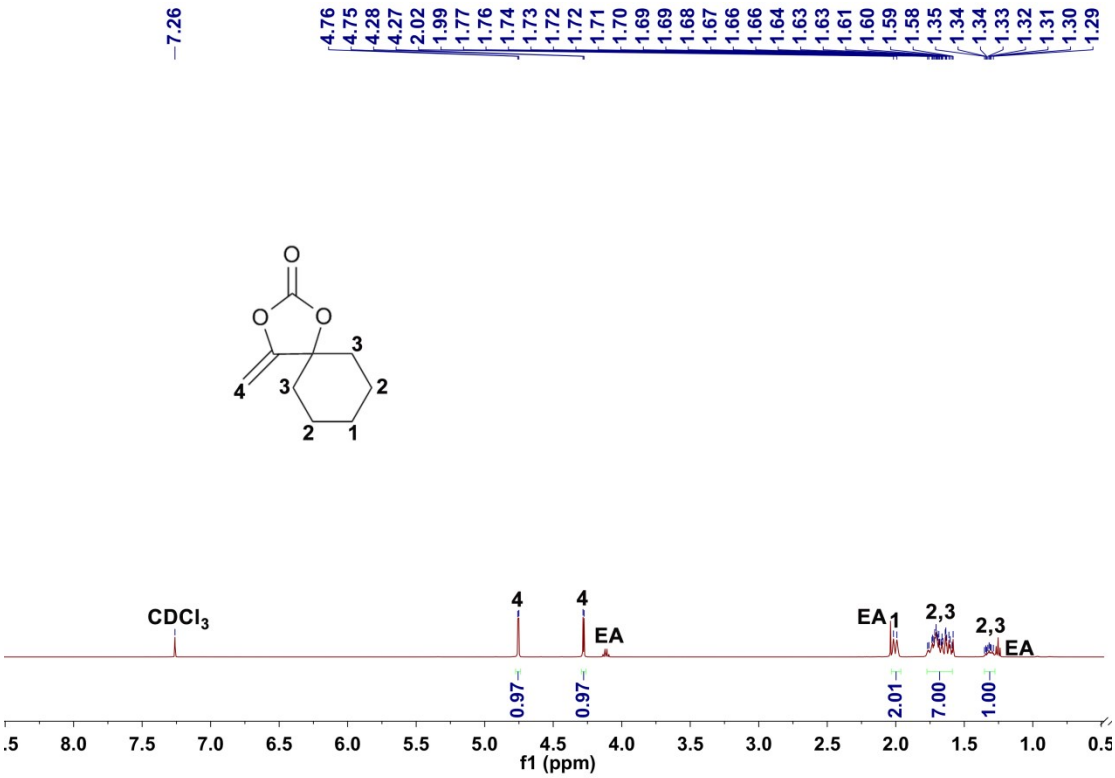
4-Ethyl-4-methyl-5-methylene-[1,3]dioxolan-2-one (2b). Light yellow oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.82 (d, J = 5.0 Hz, 1H), 4.27 (d, J = 5.0 Hz, 1H), 1.95-1.88 (m, 1H), 1.80-1.73 (m, 1H), 1.59 (s, 3H), 0.99 (t, J = 7.4 Hz, 3H).



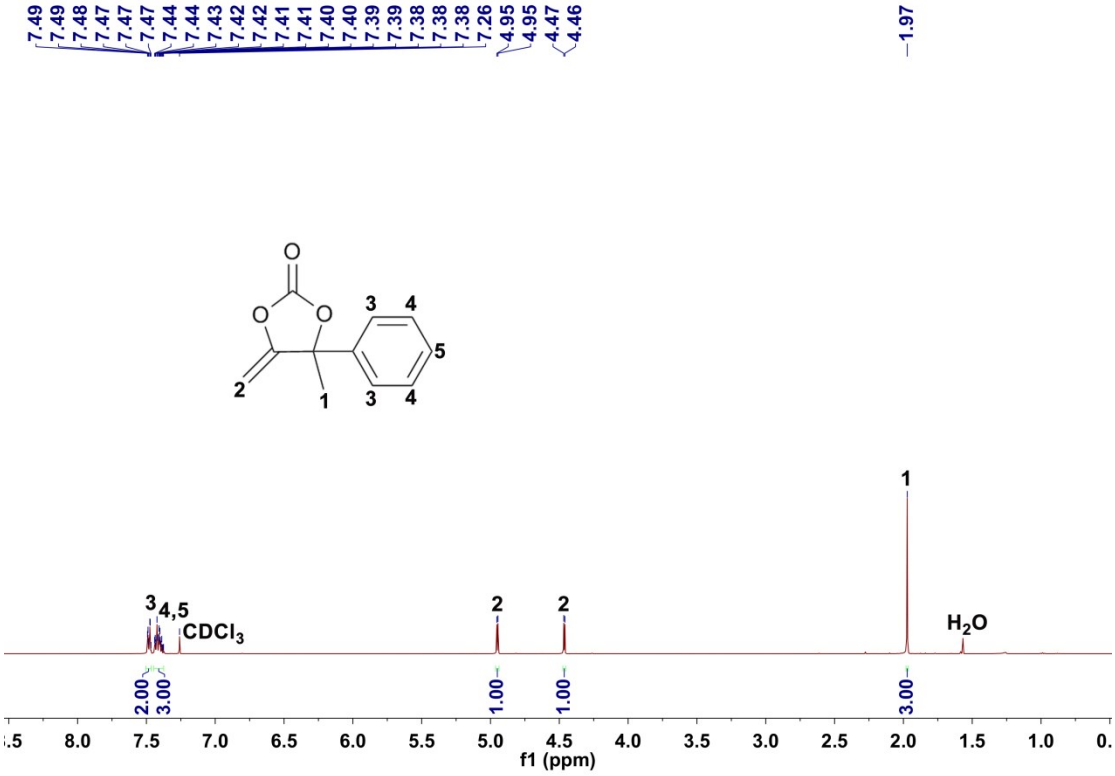
4-Isobutyl-4-methyl-5-methylene-[1,3]dioxolan-2-one (2c). Light yellow oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.80 (d, J = 5.0 Hz, 1H), 4.27 (d, J = 5.0 Hz, 1H), 1.87-1.78 (m, 2H), 1.68-1.64 (m, 1H), 1.58 (s, 3H), 0.98-0.96 (m, 6H).



4-Methylene-1,3-dioxa-spiro[4.4]nonan-2-one (2d) Colorless oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) : 4.80 (d, J = 5.0 Hz, 1H), 4.35 (d, J = 5.0 Hz, 1H), 2.26-2.21 (m, 2H), 1.95-1.83 (m, 6H).



4-Methylene-1,3-dioxa-spiro[4.5]decan-2-one (2e). Colorless oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.76 (d, J = 5.0 Hz, 1H), 4.28 (d, J = 5.0 Hz, 1H), 2.02-1.99 (m, 2H), 1.77-1.58 (m, 7H), 1.35-1.29 (m, 1H). Note: EA = Ethyl acetate, it derives from residual eluent.



4-methyl-5-methylene-4-phenyl-[1,3]dioxolan-2-one (2h). Colorless oil liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.44-7.38 (m, 3H), 4.95 (d, J = 5.0 Hz, 1H), 4.47 (d, J = 5.0 Hz, 1H), 1.97 (s, 3H).

14. References

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