Electronic Supplementary Material (ESI) for RSC Advances.


Supporting Information

# NOVEL SALENCO(III) PHOTOINITIATORS AND THEIR APPLICATION FOR CYCLOADDITION OF CARBON DIOXIDE

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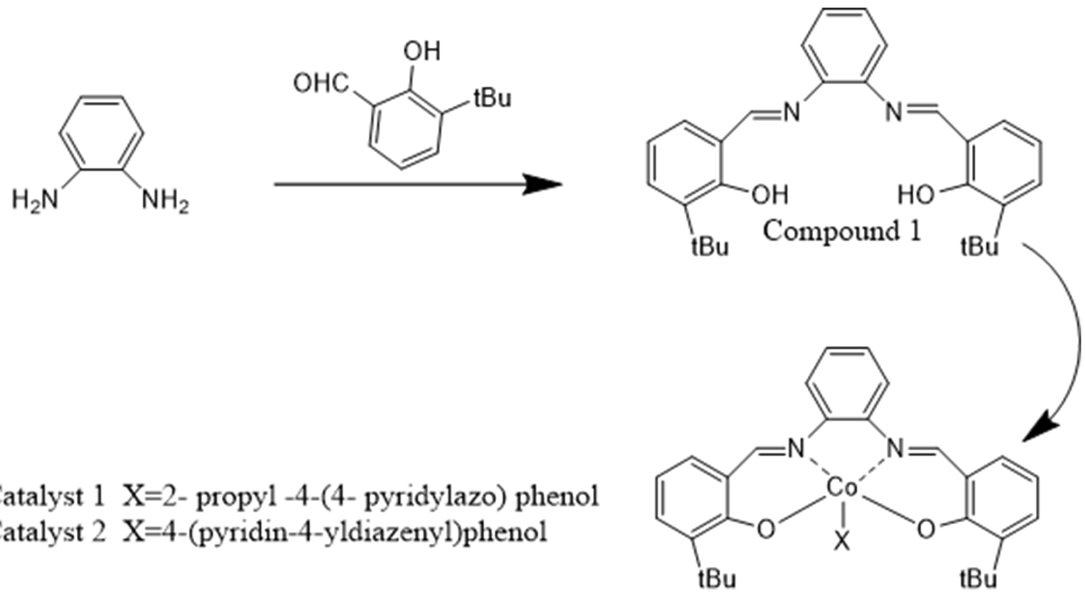
## General information:

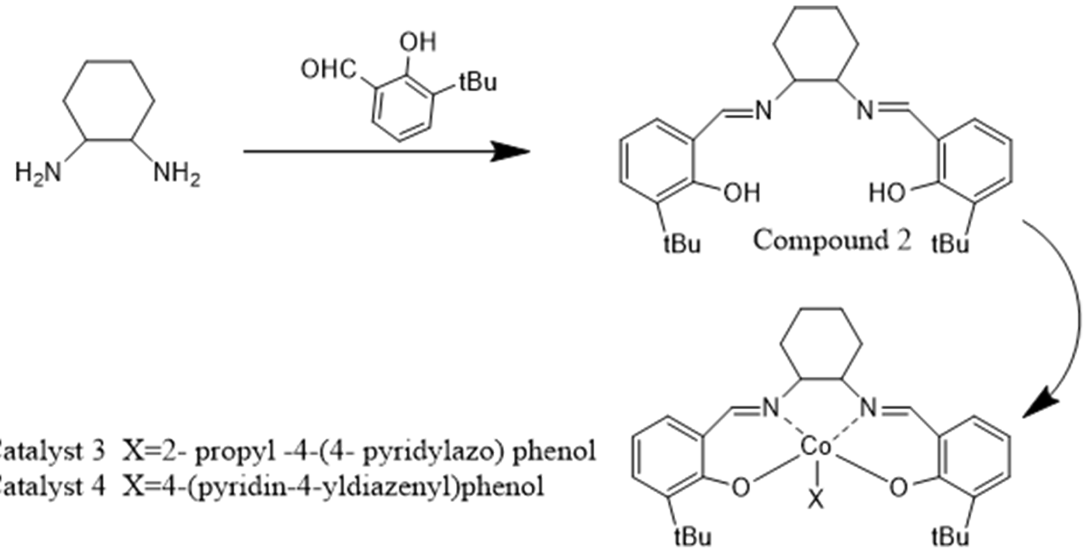
All reactions are protected by the passage of $N_2$, except for specific reactions that require the passage of $O_2$. All reagents purchased were analytically pure (AR) with a purity of 99.0% or higher. All reagents used for the reaction and polymerization were distilled with calcium hydride and placed inside the dry (1,2-dichloroethane, propylene oxide, CH3CN). The $^1$H-NMR was recorded on a nuclear magnetic resonance (NMR) spectrometer (avanceii, 400MHz). Samples were dissolved in $CDCl_3$ or $CD_3SOCD_3$. The ultraviolet visible absorption spectrum was recorded on Shimadzu UV-3600 spectrophotometer.

**Scheme S1** Synthesis route of Compound 1, [C1] and [C2]




Catalyst 1 X=2- propyl -4-(4- pyridylazo) phenol
Catalyst 2 X=4-(pyridin-4-yldiazenyl)phenol

**Scheme S2** Synthesis route of Compound 2, [C3] and [C4]




Catalyst 3 X=2- propyl -4-(4- pyridylazo) phenol
Catalyst 4 X=4-(pyridin-4-yldiazenyl)phenol

**Fig S1** (a) is the $^{1}$H-NMR of compound 1; (b) is the ESI-MS mass spectrum of compound 1

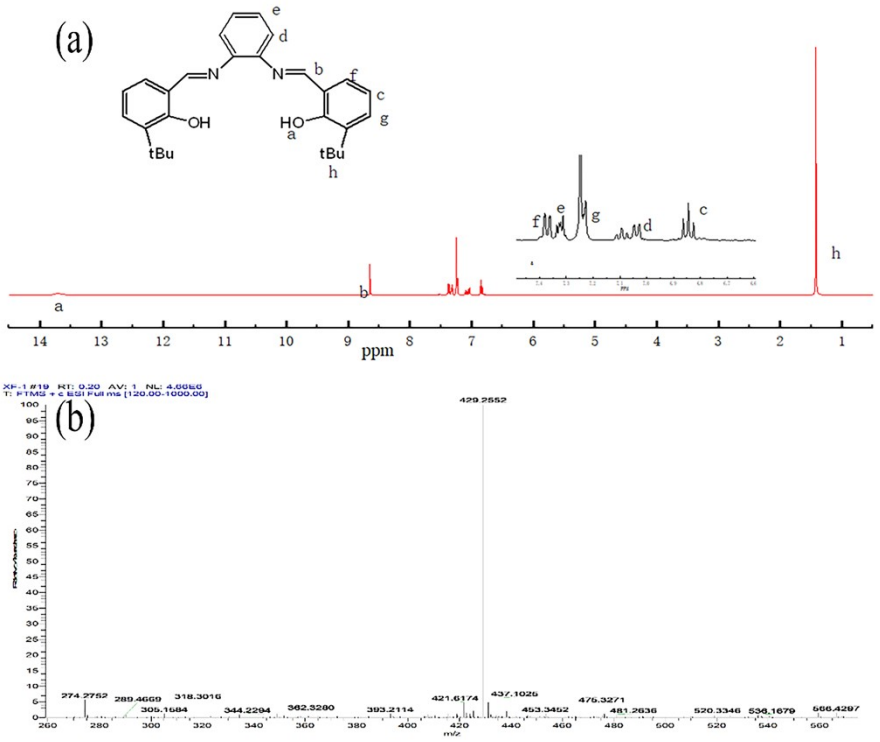



**Fig S2.** Infrared spectrum of compound 1

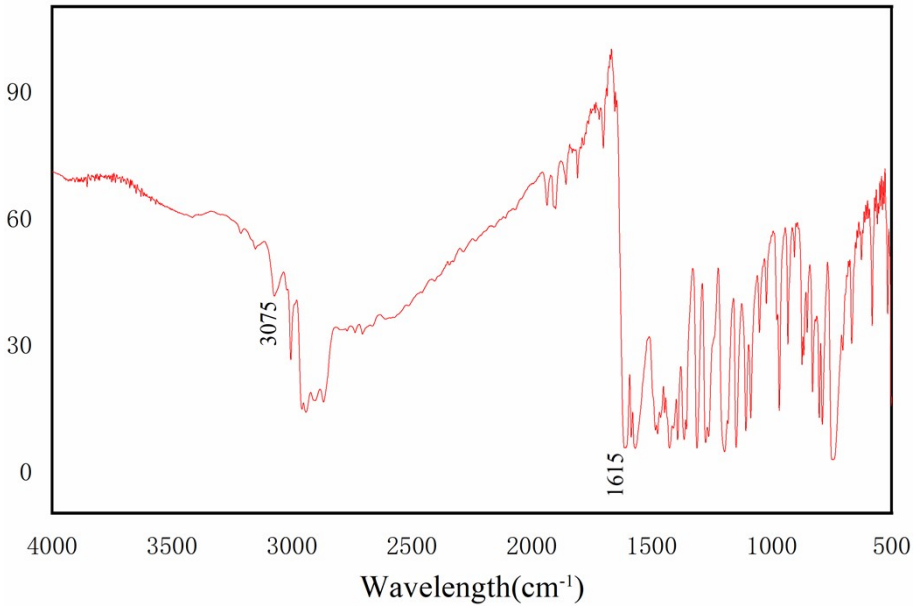


**Fig S3** (a) is the $^{1}$H-NMR of compound 2; (b) is the ESI-MS mass spectrum of compound 2

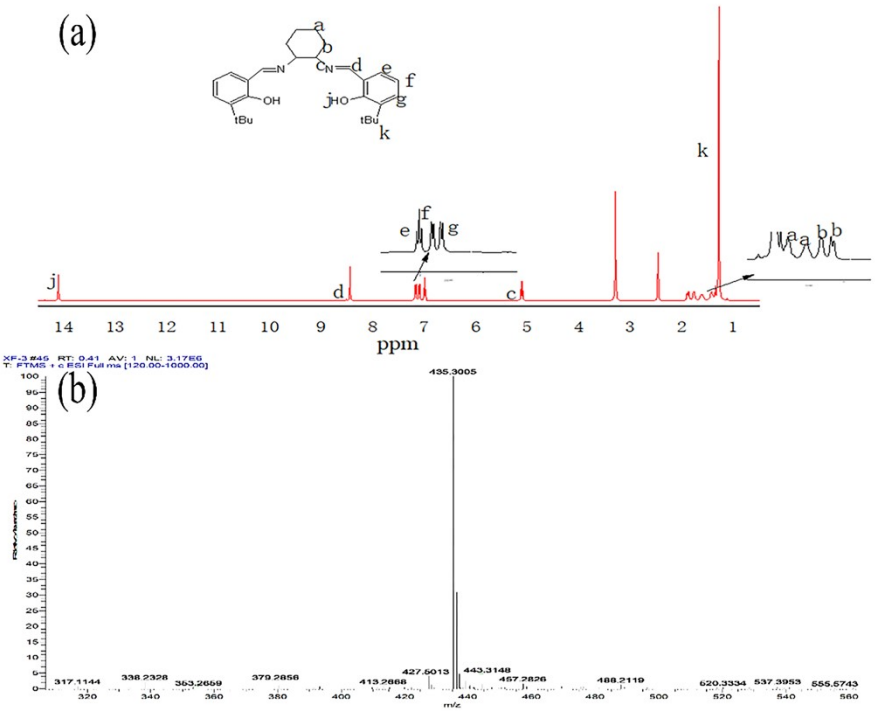



**Fig S4.** Infrared spectrum of compound 2

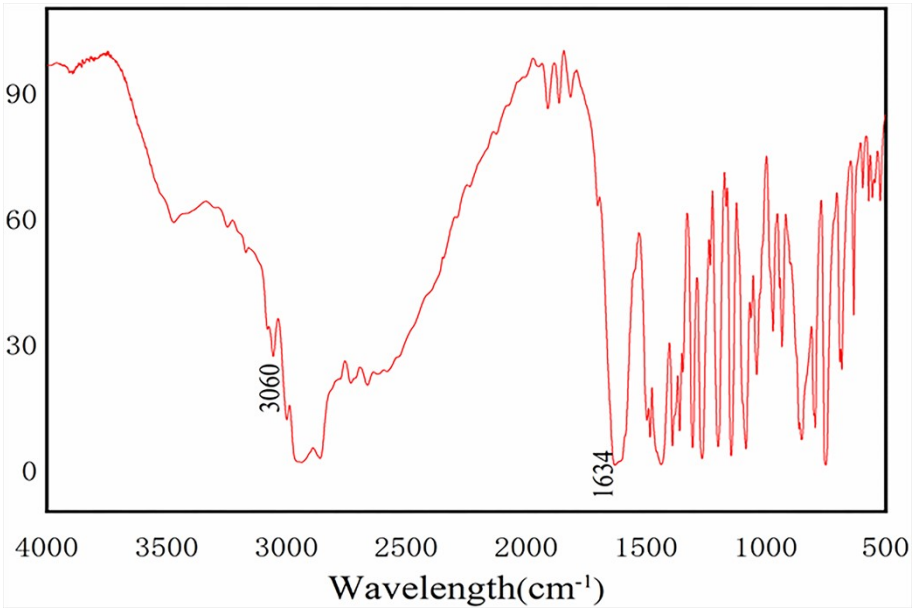


**Fig S5** (a) is the $^{1}$H-NMR of [C1]; (b) is the ESI-MS mass spectrum of [C1]

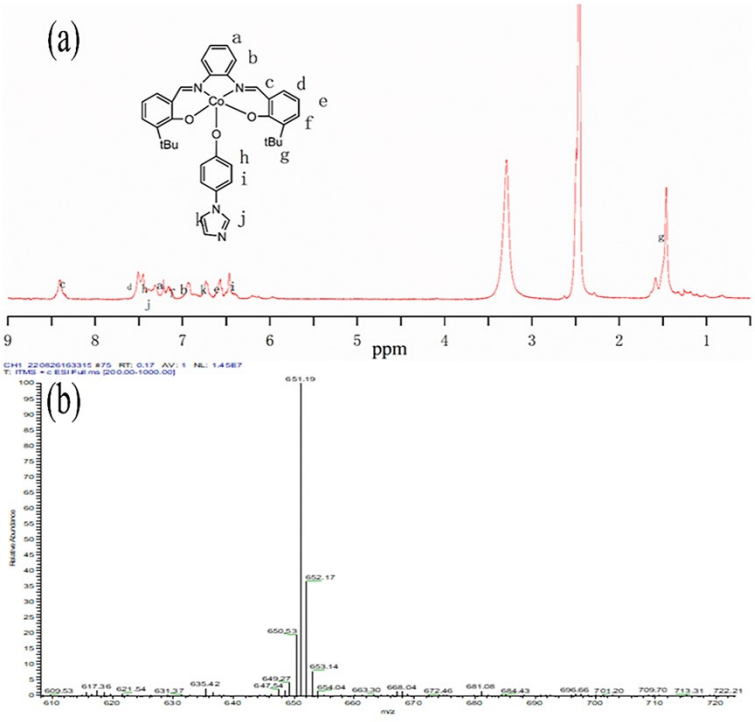



**Fig S6** (a) is the $^{1}$H-NMR of [C2]; (b) is the ESI-MS mass spectrum of [C2]

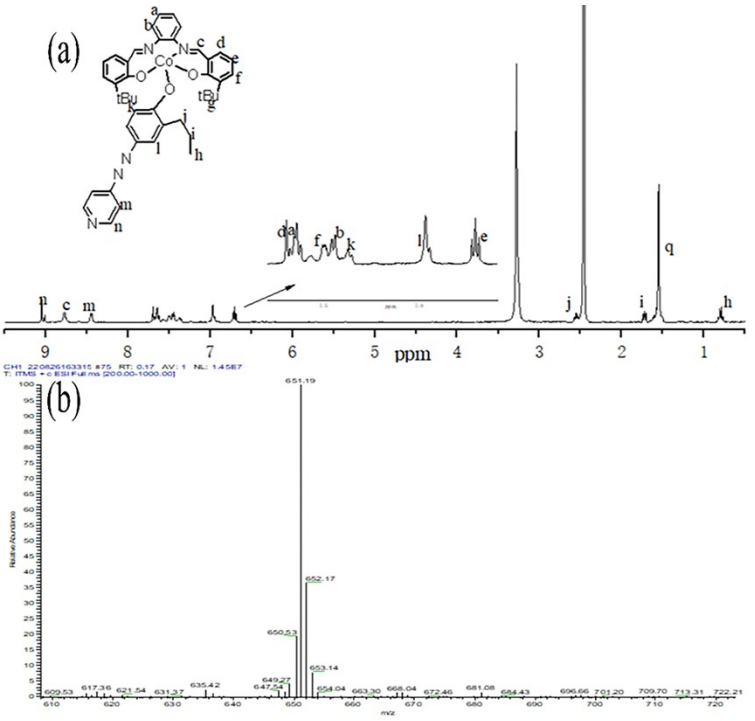


**Fig S7.** Infrared spectrum of [C1] and [C2]

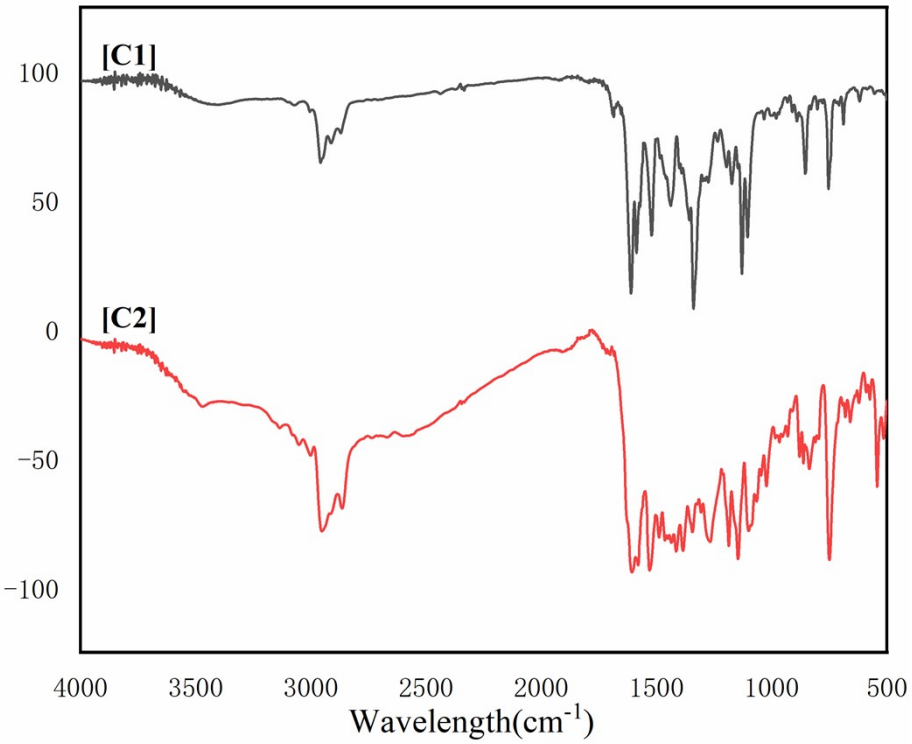



**Fig S8** (a) is the $^{1}$H-NMR of [C3]; (b) is the ESI-MS mass spectrum of [C3]

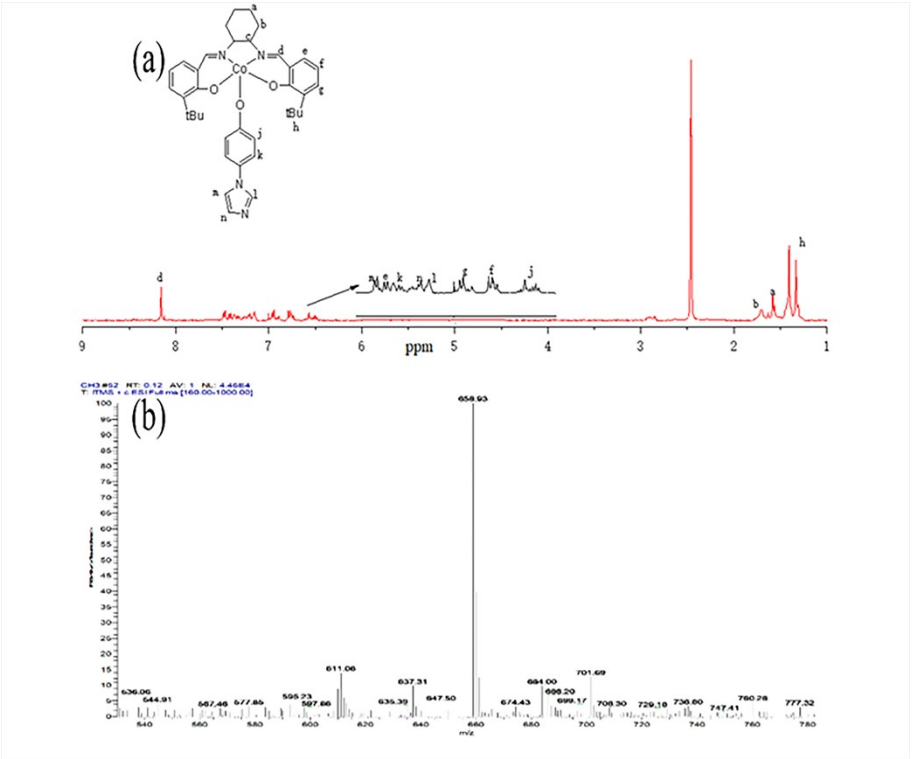


**Fig S9** (a) is the $^{1}$H-NMR of [C4]; (b) is the ESI-MS mass spectrum of [C4]

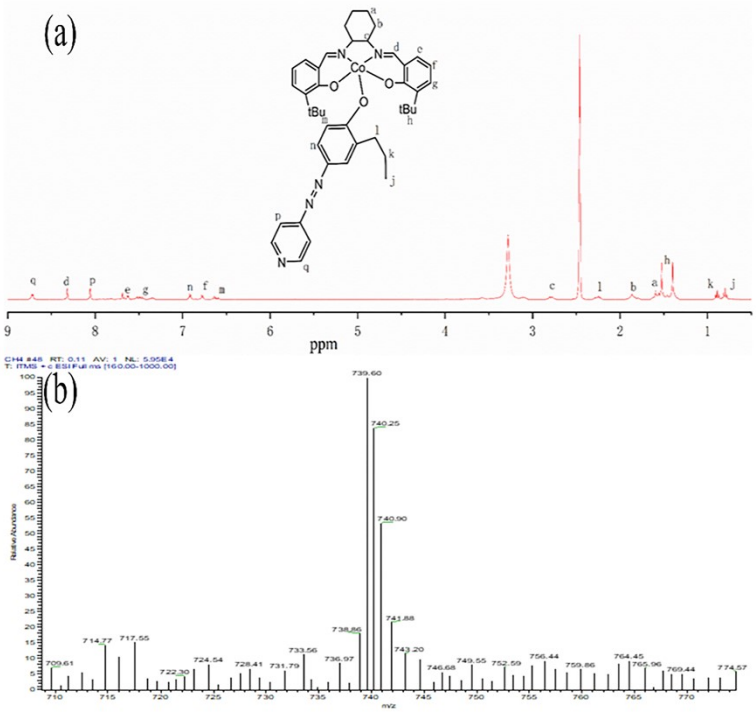



**Fig S10.** Infrared spectrum of [C3] and [C4]

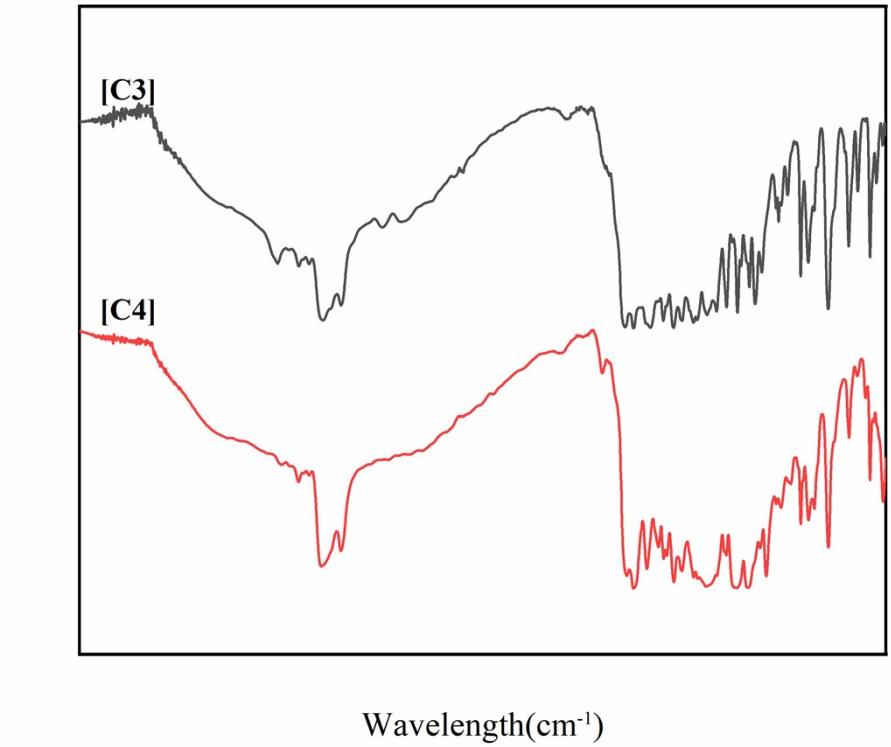


**Fig S11.** $^{1}H$ NMR of the products catalyzed by [C1], [C2], [C3] and [C4] with shading experiments

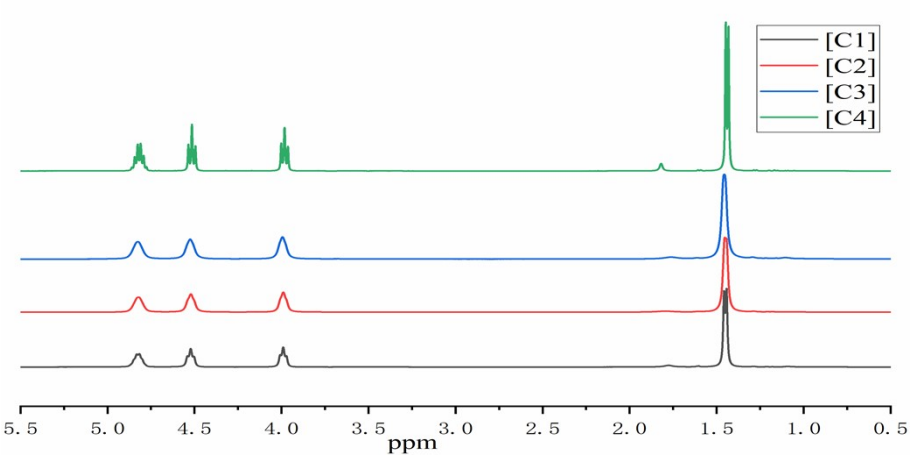



**Fig S12.** $^{1}H$ NMR of the products catalyzed by [C1], [C2], [C3] and [C4] with light experiments.

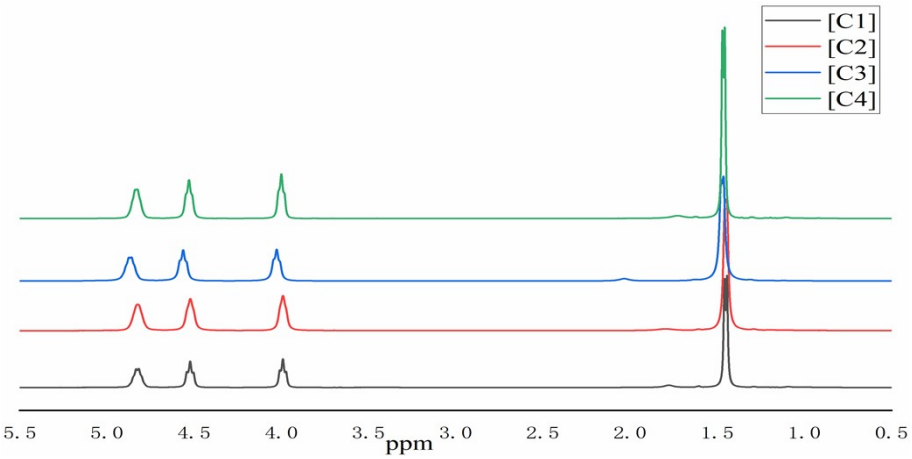



**Fig S13.** The $^{1}H$ NMR of the products for [C4] under different light sources: 0 W, 100 W, 200 W at 60℃, 6 h and 2 MPa $CO_2$

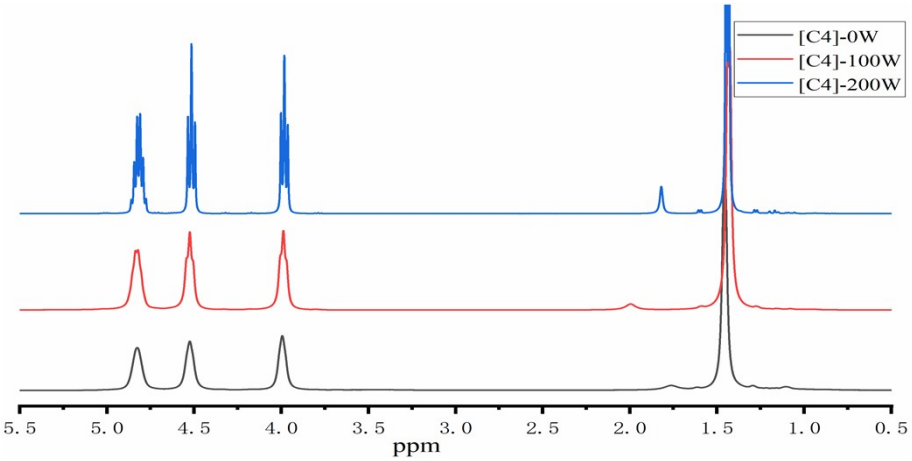


**Fig S14.** The light transmittance of the filter can reach about 90% in the range of 395 nm~421nm.

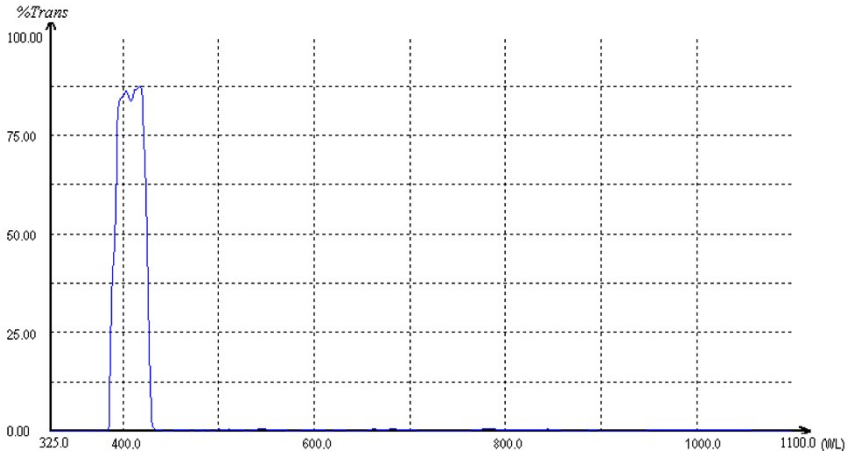



**Fig S15.** The light transmittance of the filter can reach about 90% in the range of433 nm~459 nm.

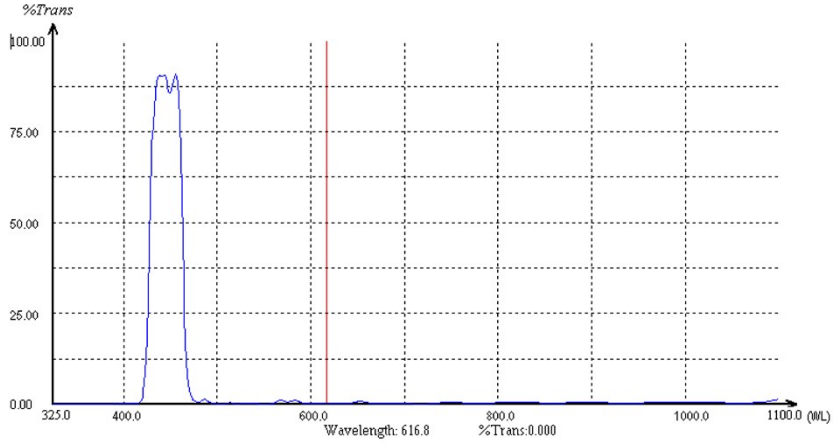



**Fig S16.** The light transmittance of the filter can reach about 90% in the range of 472 nm~505 nm.

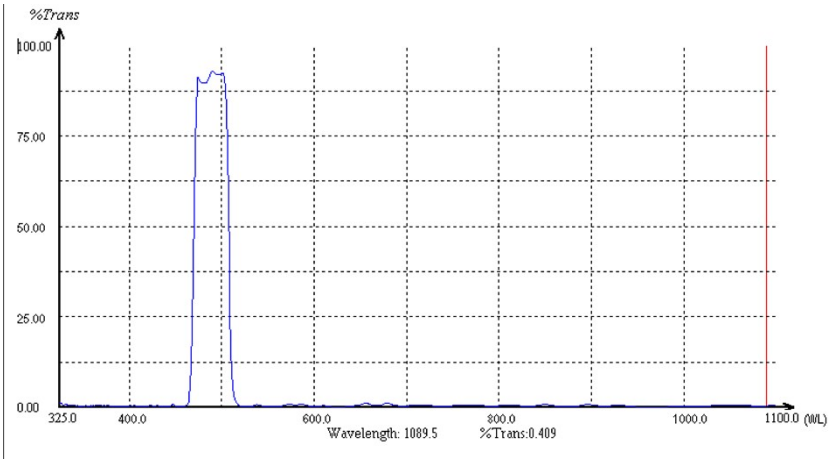



**Fig S17.** The light transmittance of the filter can reach about 90% in the range of 520nm~554nm.

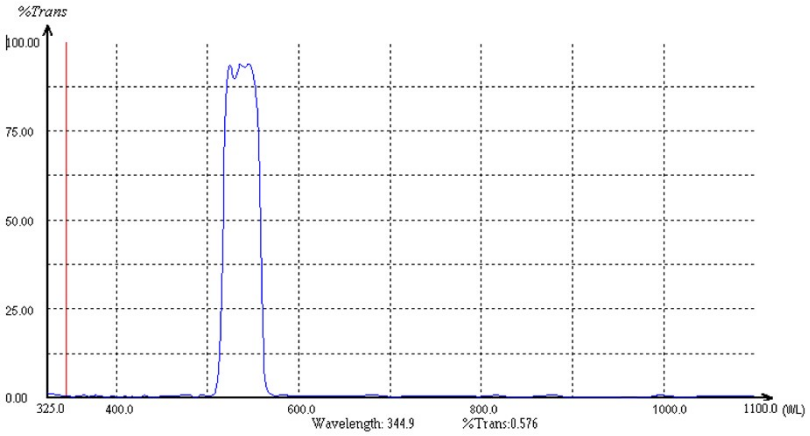



**Fig S18.** The light transmittance of the filter can reach about 90% in the range of 536nm~575nm.

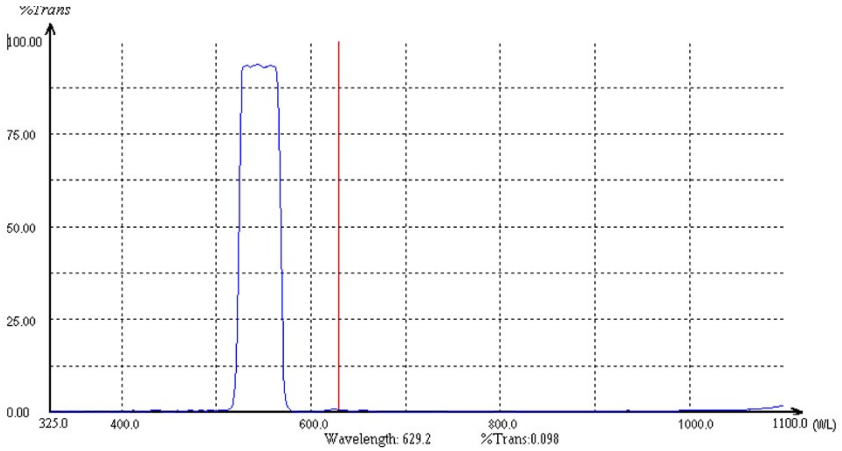



**Table S1** Elemental analysis

| Entry | Sample | C% | H% | N% |
|---|---|---|---|---|
| 1 | Compound 1 | 78.47 | 7.53 | 6.54 |
| 2 | Compound 2 | 77.38 | 8.81 | 6.45 |
| 3 | [C1] | 68.95 | 5.80 | 8.75 |
| 4 | [C2] | 69.31 | 6.11 | 9.65 |
| 5 | [C3] | 68.30 | 6.65 | 8.61 |
| 6 | [C4] | 68.93 | 6.89 | 9.57 |

**Table S2** The result of catalytic copolymerization of $CO_2$ with PO[a]

| Cat | T (℃) | P (MPa) | t (h) | $TOF^{-1}$ | TON |
|---|---|---|---|---|---|
| [C4] | 50 | 2 | 6 | 27.52 | 165.1 |
| [C4] | 60 | 2 | 6 | 31.55 | 189.3 |
| [C4] | 70 | 2 | 6 | 33.72 | 202.3 |
| [C4] | 80 | 2 | 6 | 35.43 | 212.6 |
| [C4] | 60 | 1 | 6 | 24.17 | 145 |
| [C4] | 60 | 2 | 6 | 31.55 | 189.3 |
| [C4] | 60 | 3 | 6 | 36.05 | 216.3 |
| [C4] | 60 | 4 | 6 | 37.75 | 226.5 |
| [C4] | 60 | 2 | 0.5 | 172.6 | 86.3 |
| [C4] | 60 | 2 | 2 | 62.7 | 125.4 |
| [C4] | 60 | 2 | 4 | 41.28 | 165.1 |
| [C4] | 60 | 2 | 6 | 31.55 | 189.3 |
| [C4] | 60 | 2 | 8 | 25.71 | 205.7 |
| [C4] | 60 | 2 | 12 | 19.175 | 230.1 |
| [C4] | 60 | 2 | 16 | 14.28 | 228.5 |
| [C4] | 60 | 2 | 20 | 10.77 | 215.3 |

[a.] Reaction conditions: catalyst $3*10^{-5}$ mol; 100 W light source lighting.

**Table S3** Activity of past heterogeneous catalysts in carbon dioxide cycloaddition reactions

| Cat | Epoxide | T (℃) | P (MPa) | TON | CPC (%) | Ref. |
|---|---|---|---|---|---|---|
| 6 | PO | 60 | 2 | 126 | 10 | [1] |
| 6 | CHO | 60 | 2 | 216 | 13 | [1] |
| [C4] | PO | 60 | 2 | 128.4 | 44.3 | This work |
| [C4] | CHO | 60 | 2 | 204.5 | 46.7 | This work |

## References

[1] L. Du, C. Wang, W. Zhu and J. Zhang, *J Chin Chem Soc*, 2020, **67**, 72–79.