

Supplementary Materials for

**A Ru-complex tethered to a N-Rich Covalent Triazine Framework for Tandem Aerobic Oxidation–  
Knoevenagel Condensation Reactions**

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Table S1. Various control experiments to obtain insights into the reaction mechanism for the oxidation of benzyl alcohol.

Figure S1. Proposed mechanism for bipy-CTF-catalyzed aerobic oxidation of benzyl alcohol.

Figure S2. The GC-MS spectra of the  $\alpha$ ,  $\beta$ -unsaturated nitriles.

## 1. Mechanistic studies

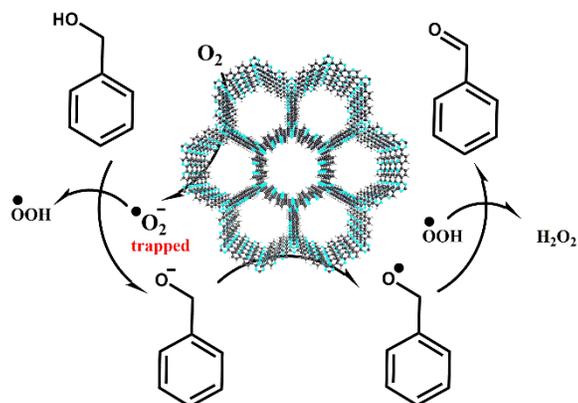
To obtain an insight of the function of the bipy-CTF material in oxidation catalysis, a set of control experiments was performed (Table S1). In this regard, a control experiment was performed using the pristine bipy-CTF material. A conversion of 39% was obtained using the pristine bipy-CTF as the catalyst in the presence of Cs<sub>2</sub>CO<sub>3</sub> as the base. (Table S1, entry 1). To obtain more insight into the role of the base, the influence of different bases was investigated. The obtained results are outlined in Table S1 below. As can be observed, the reaction without any basic additive resulted in no conversion of benzyl alcohol (Table S1, entry 2). However, the addition of a variety of bases, such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and Cs<sub>2</sub>CO<sub>3</sub>, improved the catalytic activity, with the highest activity obtained using Cs<sub>2</sub>CO<sub>3</sub>. In general, carboxylates with bigger counter cations are more dissociated in aprotic solvents and consequently more reactive. Similar trend is observed for the Ru<sup>III</sup>@bipy-CTF catalyst (Table 2, entries 1-4 of the manuscript). We believe that the applied base can facilitate the deprotonation of benzyl alcohol and boosts the catalytic activity. The conversion of benzyl alcohol towards benzaldehyde dramatically lowered to 3% under Ar atmosphere, proving the essential role of oxygen as the oxidant (Table S1, entry 5). Another control experiment was done using *p*-benzoquinone (Table S1, entry 7). The addition of *p*-benzoquinone as superoxide (<sup>•</sup>O<sub>2</sub><sup>-</sup>) scavenger into the reaction system containing bipy-CTF as the catalyst completely suppressed the oxidation of benzyl alcohol (conversion < 1%). This observation indicates that bipy-CTF activates molecular oxygen to superoxide, which acts as oxidant species in the catalytic cycle.

**Table S1.** Various control experiments to obtain insights into the reaction mechanism for the oxidation of benzyl alcohol.

Entry	Catalyst	base	Conversion (%)
1	bipy-CTF	Cs <sub>2</sub> CO <sub>3</sub>	39
2	bipy-CTF	No base	3
3	bipy-CTF	K <sub>2</sub> CO <sub>3</sub>	18
4	bipy-CTF	Na <sub>2</sub> CO <sub>3</sub>	10
5 <sup>a</sup>	bipy-CTF	Cs <sub>2</sub> CO <sub>3</sub>	3
6 <sup>b</sup>	bipy-CTF	Cs <sub>2</sub> CO <sub>3</sub>	14
7 <sup>c</sup>	bipy-CTF	Cs <sub>2</sub> CO <sub>3</sub>	<1

Reaction conditions: 17 mg bipy-CTF, 0.33 mmol benzyl alcohol, 0.4 mmol base, 500 μl toluene, O<sub>2</sub>, 100 °C, 12 h. <sup>a</sup>Under Ar atmosphere. <sup>b</sup>Reaction was done at 50 °C. <sup>c</sup>*p*-benzoquinone (0.33 mmol) was added.

So far, many experimental and theoretical investigations have shown the applicability of N-doped carbon-based materials for adsorption and activation of molecular O<sub>2</sub>.<sup>1-2</sup> Based on our observations and previous reports,<sup>3-4</sup> we propose that the oxygen activation occurs on the surface of bipy-CTF and the generated superoxide reacts with benzyl alcohol to generate PhCH<sub>2</sub>O<sup>-</sup> and subsequently PhCH<sub>2</sub>O<sup>•</sup> and benzaldehyde. Although the exact mechanism on the aerobic oxidation using [Ru(acac)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> complex has been remained unknown in the previous reports, it can be expected that the generated PhCH<sub>2</sub>O<sup>-</sup> on the surface of bipy-CTF reacts with the Ru centers in the reaction system. The obtained results thus corroborate each other, unveiling the promotional impact of bipy-CTF in activating oxygen and benzyl alcohol in our reaction system. A reaction mechanism is proposed based on the obtained results and previous studies<sup>3-4</sup>, as shown in Figure S1.



**Figure S1.** Proposed mechanism for bipy-CTF-catalyzed aerobic oxidation of benzyl alcohol.

## 2. Catalytic reactions

Conversion, yield and selectivity are calculated through equations S1, S2 and S3 respectively. Dodecane was used as the internal standard. The conversion, yield and selectivity are calculated based on the observed peak area using a TRACE GC × GC (Thermo, Interscience) coupled to a TEMPUS TOFMS detector (Thermo, Interscience). The pure starting material (alcohols) and products ( $\alpha$ ,  $\beta$ -unsaturated nitriles) were injected to the GC as the reference peaks.

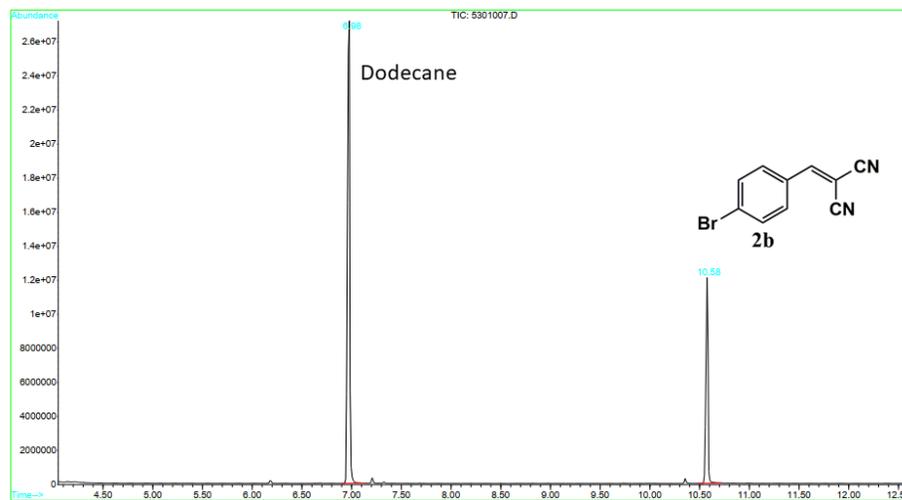
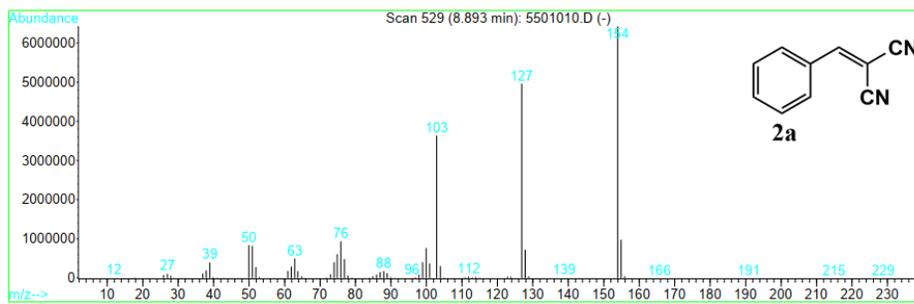
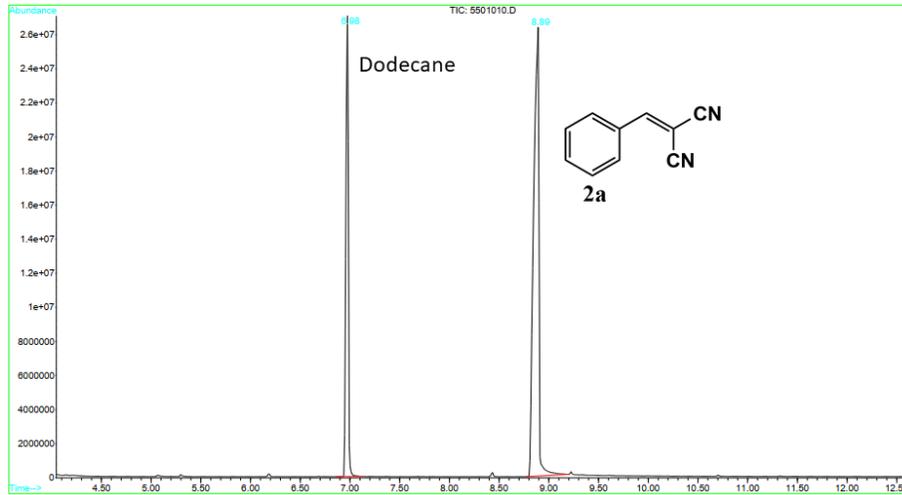
$$(S1) \text{ Conversion} = 1 - \left( \frac{\text{Area of IS1}}{\text{Area of S1}} \times \frac{\text{Area of S2}}{\text{Area of IS2}} \right) \times 100$$

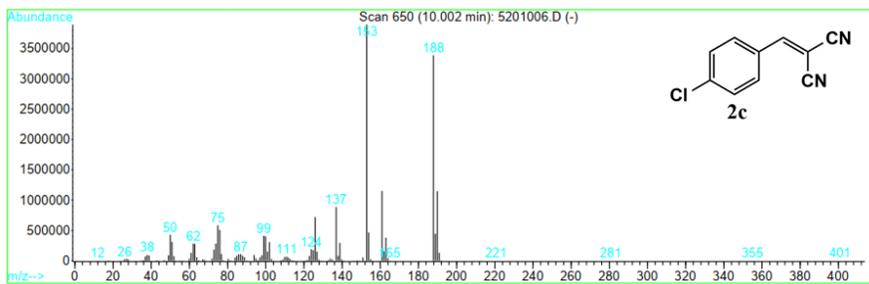
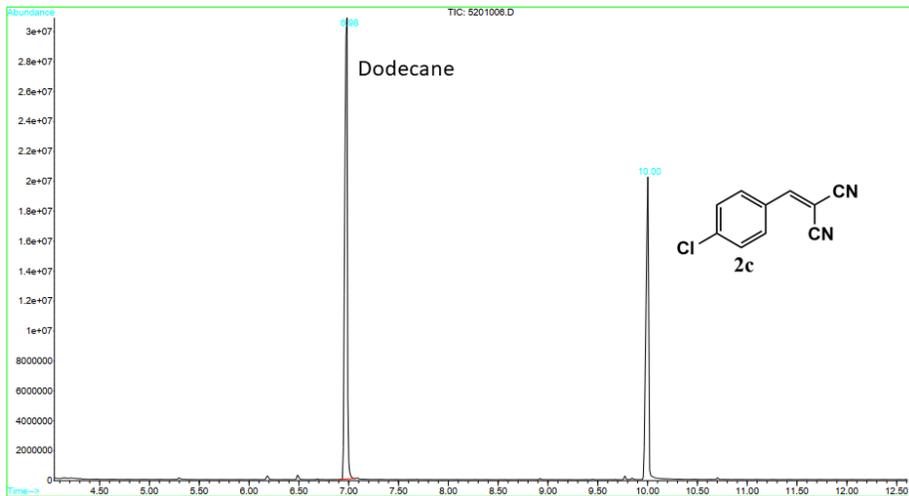
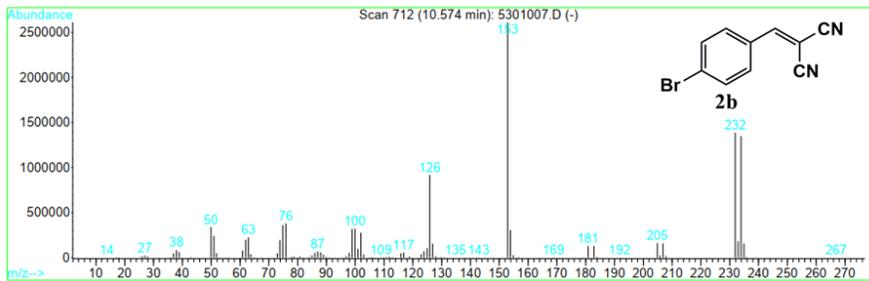
$$(S2) \text{ Yield} = \frac{\text{mmol of S1} - \text{mmol of S2}}{\text{mmol of S1}} \times 100$$

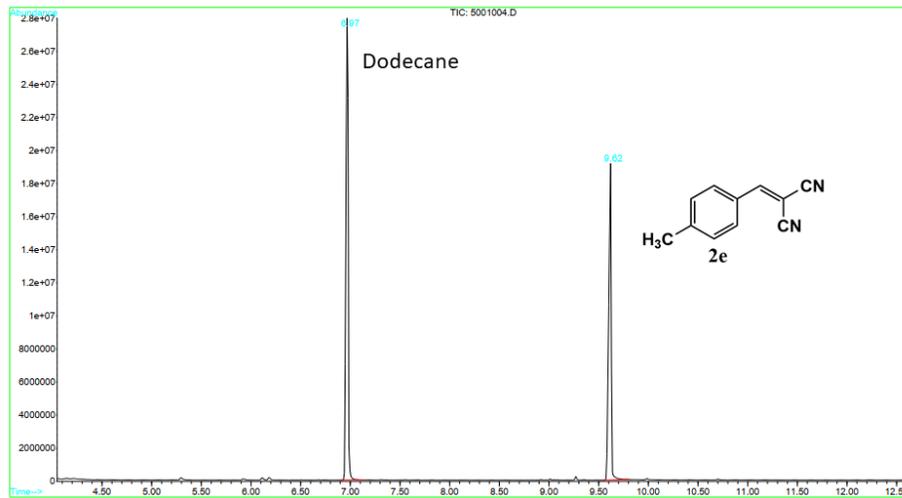
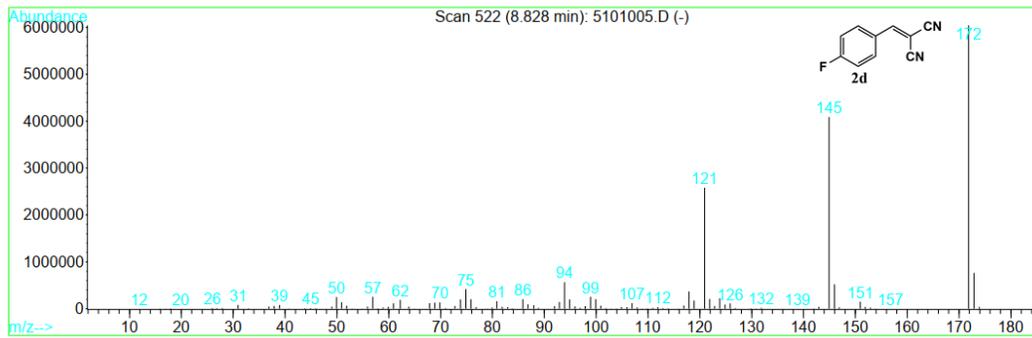
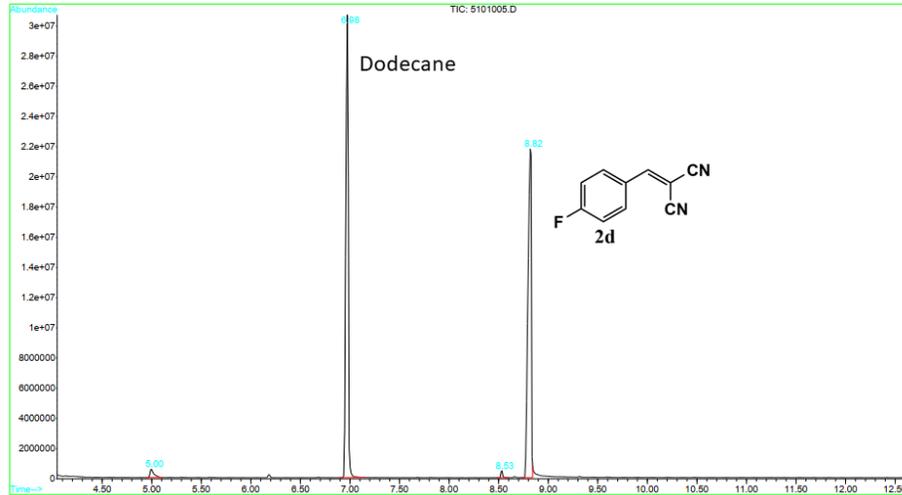
$$(S3) \text{ Selectivity} = \frac{\text{Area of Px}}{\text{Area of all products}} \times 100$$

*IS1= Internal standard at time zero; S1= Substrate at time zero; S2= Substrate at time X; IS2= Internal standard at time X; PX= Product X.*

The GC-MS spectra of the  $\alpha$ ,  $\beta$ -unsaturated nitriles are presented below.







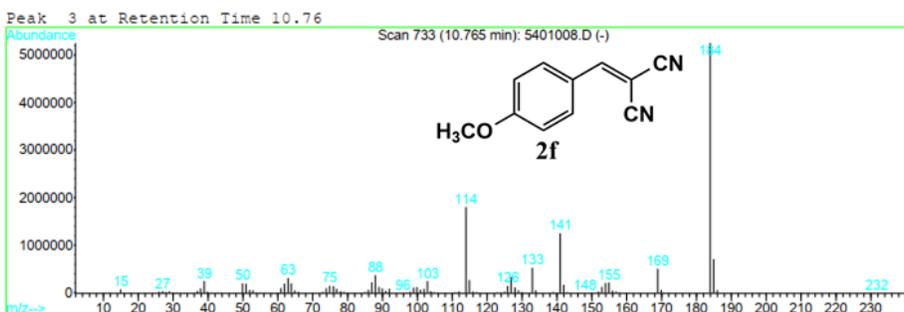
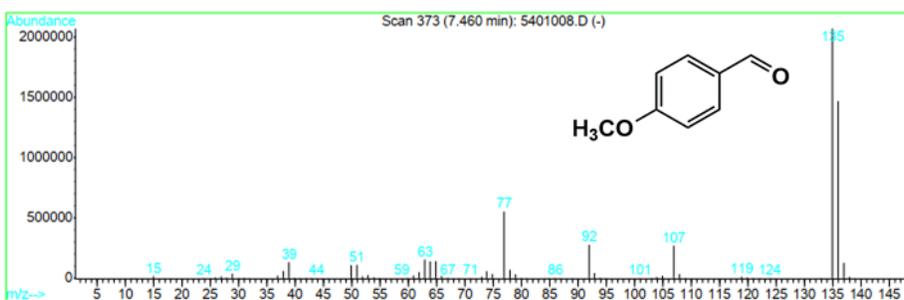
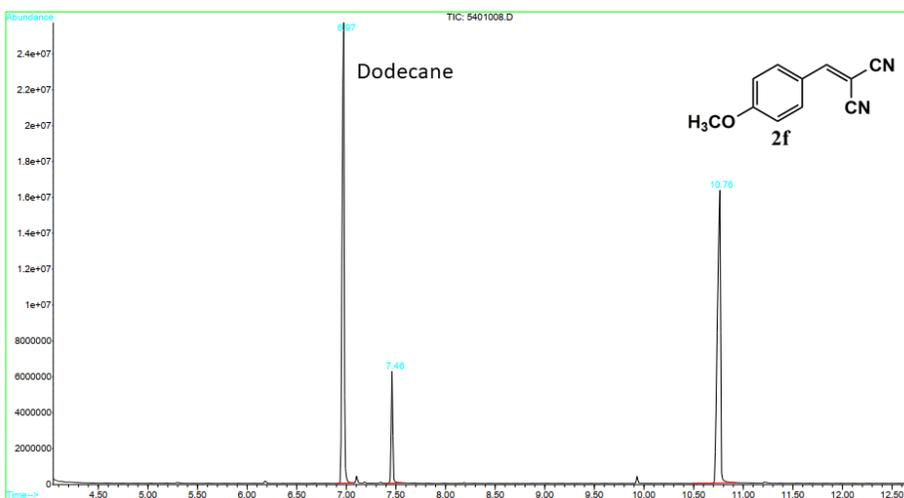
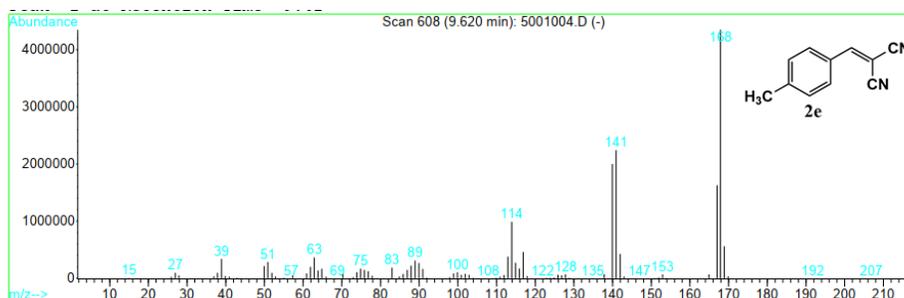


Figure S2. The GC-MS spectra of the  $\alpha$ ,  $\beta$ -unsaturated nitriles.

## References:

[1] Watanabe, H.; Asano, S.; Fujita, S.; Yoshida, H.; Arai, M., Nitrogen-Doped, Metal-Free Activated Carbon Catalysts for Aerobic Oxidation of Alcohols. *Acs Catal* **2015**, *5* (5), 2886-2894.

[2] Eisenberg, D; Slot, T.K; Rothenberg, G.; Understanding oxygen activation on metal- and nitrogen-codoped carbon catalysts. *ACS Catal* **2018**, *8*, 8618–8629.

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[4] Abednatanzi, S.; Derakhshandeh, P. G.; Tack, P.; Muniz-Miranda, F.; Liu, Y. Y.; Everaert, J.; Meledina, M.; Vanden Bussche, F.; Vincze, L.; Stevens, C. V.; Van Speybroeck, V.; Vrielinck, H.; Callens, F.; Leus, K.; Van Der Voort, P., Elucidating the promotional effect of a covalent triazine framework in aerobic oxidation. *Appl Catal B-Environ* **2020**, 269.