Novel Copper(II)-Lanthanum(III) Metal Organic Framework as Selective Catalyst for the Aerobic Oxidation of Benzylic Hydrocarbons and Cycloalkenes.

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Supplementary Material

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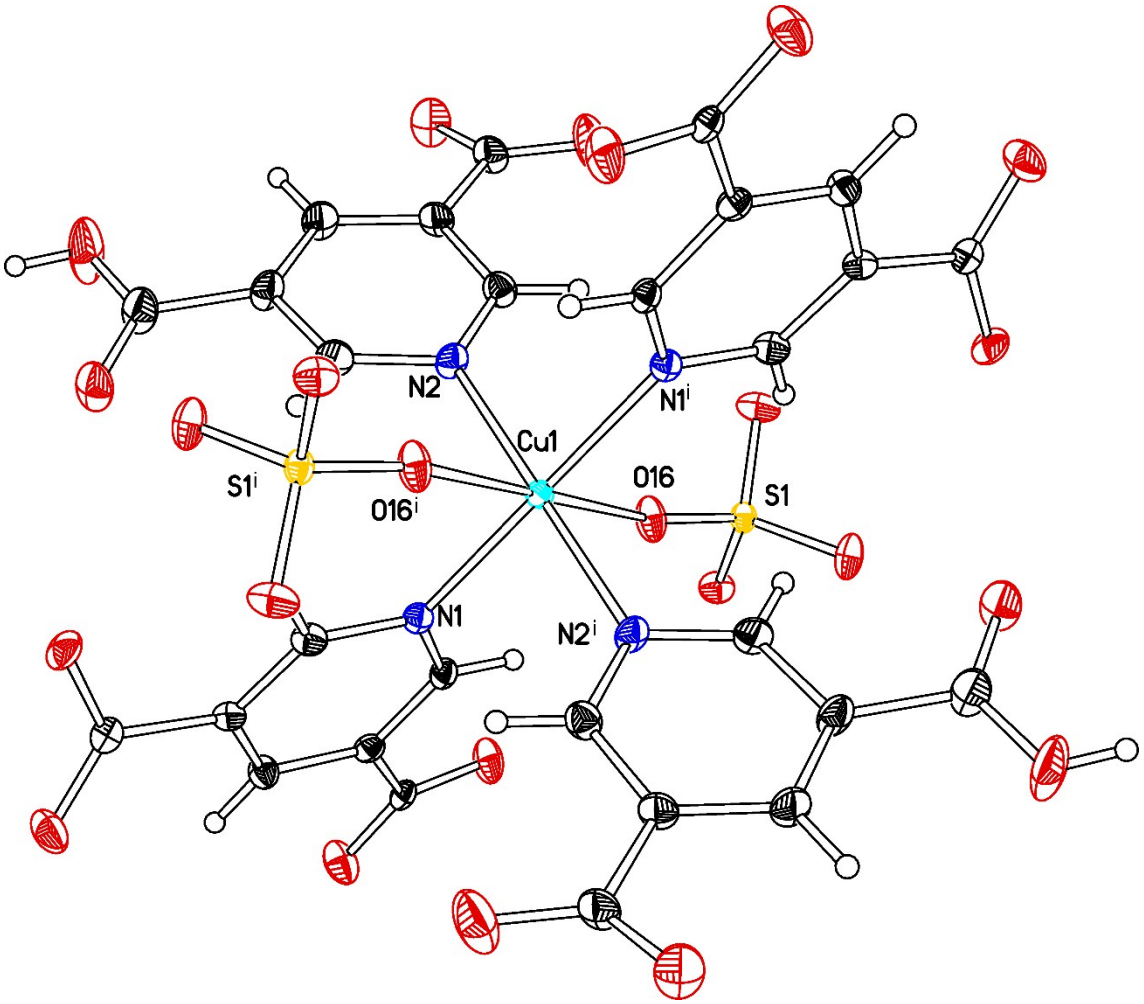

Figure S1. Molecular structure diagram for the coordination sphere of copper (II). Displacement ellipsoids drawn at the 50% level of probability, while hydrogen atoms are drawn as spheres of arbitrary radii. Symmetry Equivalents: (i): -x,-y,1-z; (ii):1-x, 1-y, 2-z; (iii): x, 1+y, z; (iv): 1+x, 1+y, z; (v): 1-x, 2-y, 2-z; (vi): x-1, y, z; (vii): -x, 1-y, 1-z; (viii): x, y-1, z; (ix): x-1, y-1, z; (x): x+1, y, z. Legend: Cyan: Cu; green: La; yellow: S; red: O; grey: C; light blue: N; white: H.

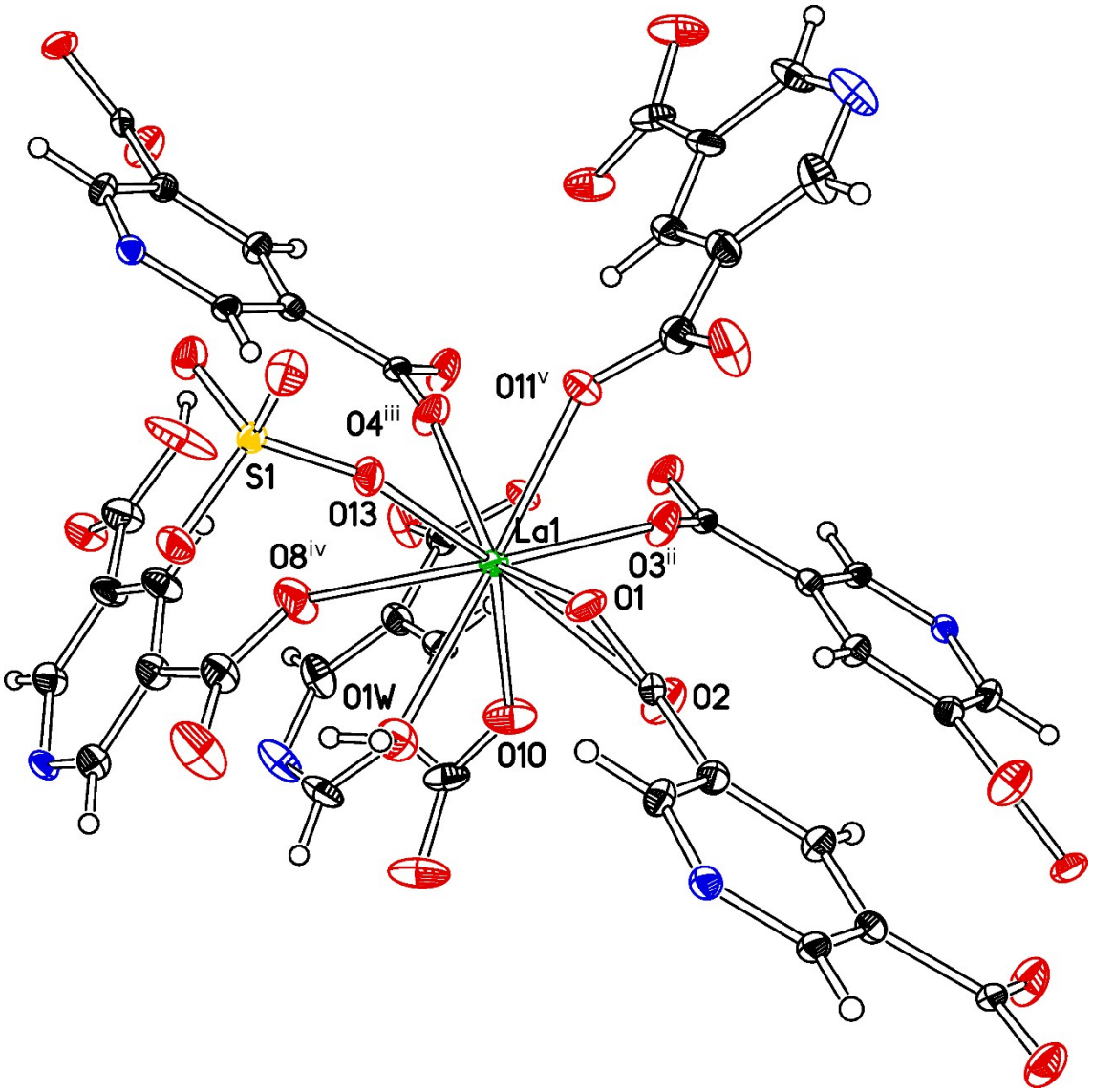

Figure S2. Molecular structure diagram for the coordination sphere of lanthanum (III) (La1). Displacement ellipsoids drawn at the 50% level of probability, while hydrogen atoms are drawn as spheres of arbitrary radii. Symmetry Equivalents: (i): -x,-y,1-z; (ii):1-x, 1-y, 2-z; (iii): x, 1+y, z; (iv): 1+x, 1+y, z; (v): 1-x, 2-y, 2-z; (vi): x-1, y, z; (vii): -x, 1-y, 1-z; (viii): x, y-1, z; (ix): x-1, y-1, z; (x): x+1, y, z. Legend: Cyan: Cu; green: La; yellow: S; red: O; grey: C; light blue: N; white: H.

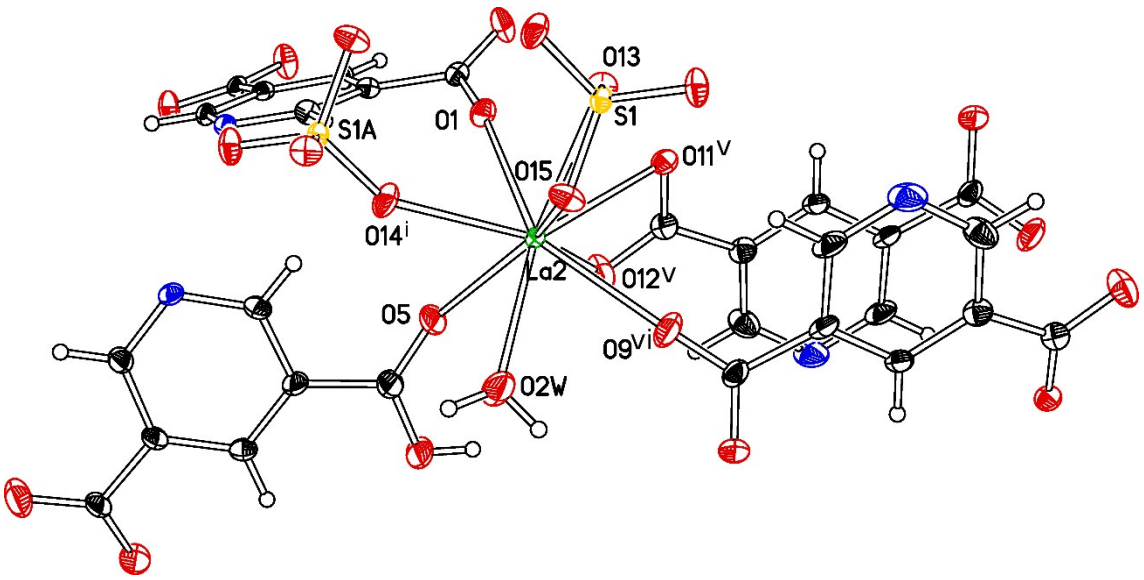

Figure S3. Molecular structure diagram for the coordination sphere of lanthanum (III) (La2). Displacement ellipsoids drawn at the 50% level of probability, while hydrogen atoms are drawn as spheres of arbitrary radii. Symmetry Equivalents: (i): -x,-y,1-z; (ii):1-x, 1-y, 2-z; (iii): x, 1+y, z; (iv): 1+x, 1+y, z; (v): 1-x, 2-y, 2-z; (vi): x-1, y, z; (vii): -x, 1-y, 1-z; (viii): x, y-1, z; (ix): x-1, y-1, z; (x): x+1, y, z. Legend: Cyan: Cu; green: La; yellow: S; red: O; grey: C; light blue: N; white: H.

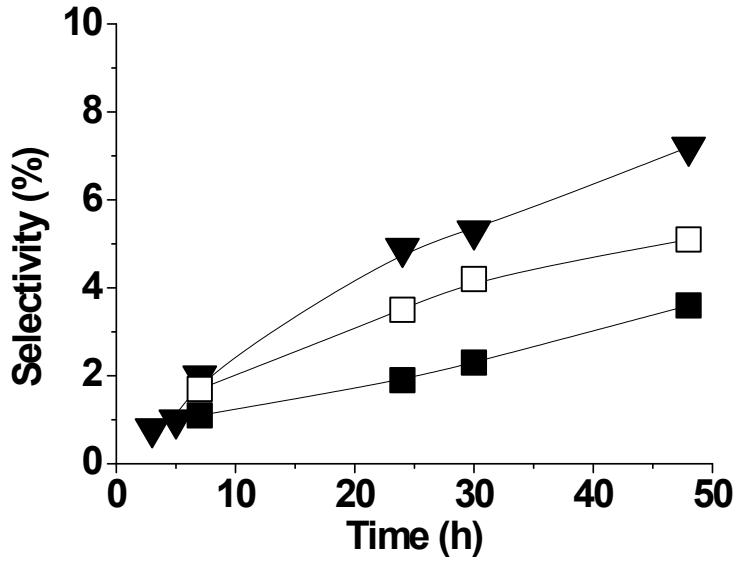

Figure S4. Time selectivity plot for minor products observed during the aerobic oxidation of indane using CuLa-MOF as catalyst during four consecutive uses. Reaction conditions: Catalyst (20 mg, 0.5 mol % Cu), substrate (20 mmol), 120 ºC, O_2 atmosphere. Legend:1,3-indanediol (▼), 3-hydroxy-indanone (□), 1,3-indanedione (■).

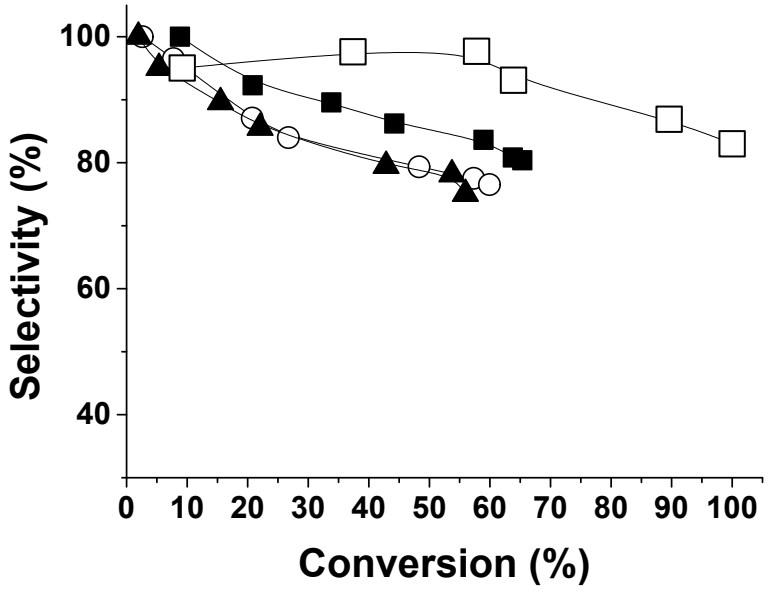

Figure S5. Time selectivity plot for the aerobic oxidation of indane using the heterogeneous CuLa-MOF (□) or different amounts of $Cu(OAc)_2$ corresponding to leaching found after using the catalyst (1.5 ■ , 0.8 ○ or 0.3 ▲ wt%). Note: Selectivity includes hydroperoxide/-ol/-one. Reaction conditions: Catalyst (20 mg, 0.5 mol % Cu), substrate (20 mmol), 120 ºC, O_2 atmosphere.

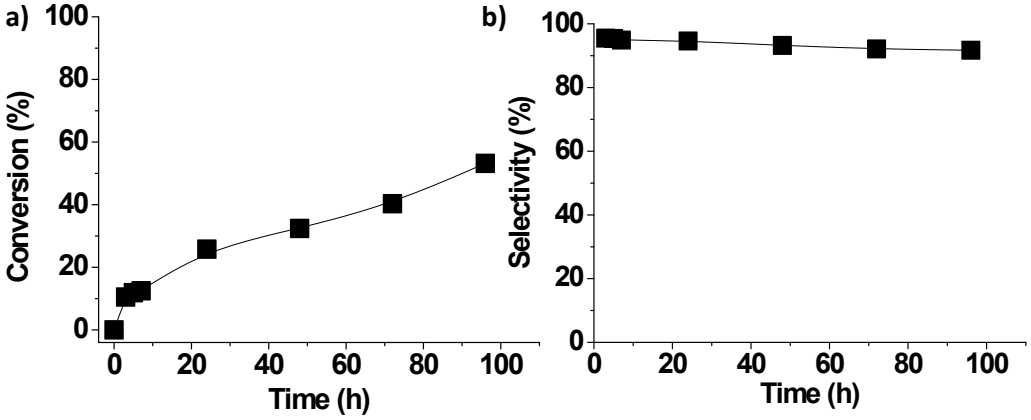

Figure S6. Productivity test for the aerobic oxidation of indane under aerobic conditions using CuLa-MOF as catalyst. Reaction conditions: catalyst (2 mg, 0.0011 mmol), substrate (40 mL, 325 mmol), 120 ºC, O_2 atmosphere (1 atm).

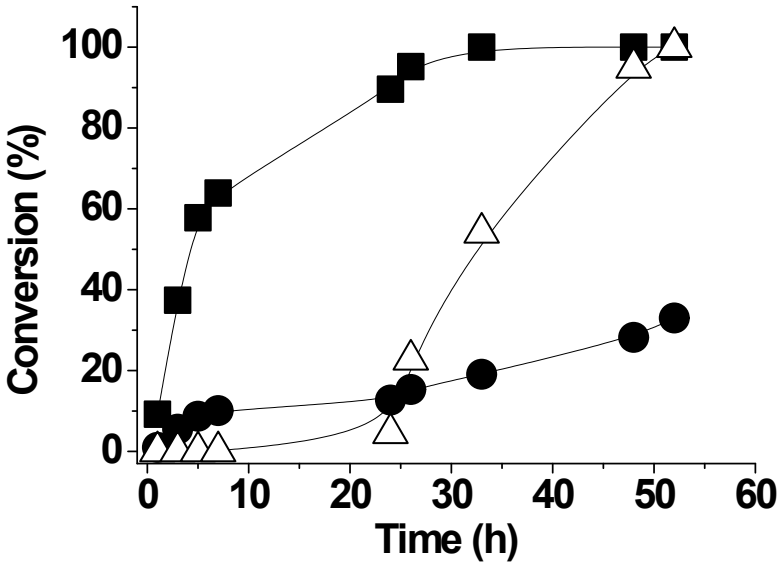

Figure S7. Influence of the reaction atmosphere on the time-conversion plot during the indane reaction in the presence of CuLaPDC. Reaction conditions: Catalyst (20 mg), indane (20 mmol), 120 ºC, atmosphere as indicated (1 atm). Legend: O_2 (■), air (Δ), Ar for 24 h and then O_2 (●).

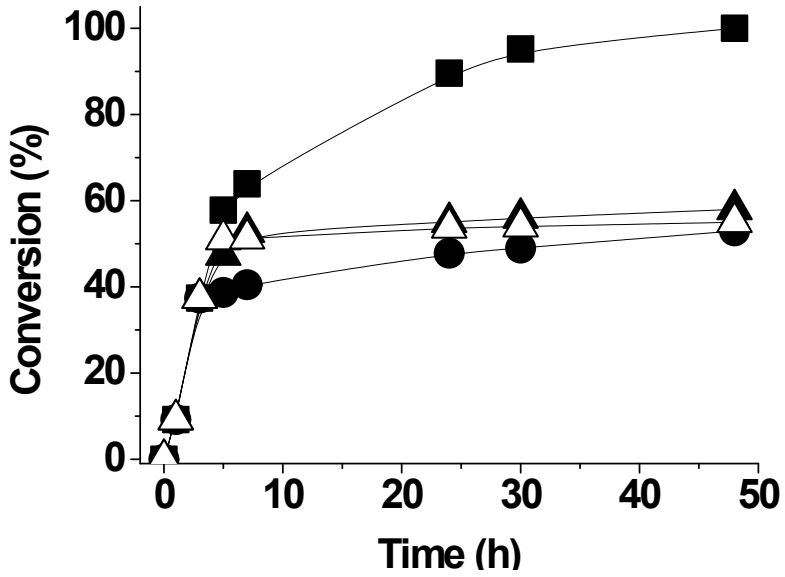

Figure S8. Time conversion plot for the aerobic oxidation of indane using CuLa-MOF in the absence (●) or in the presence of quenchers including benzoic acid (●), DMF (▲) or TEMPO (∆) added at ~ 40 % conversion. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, benzoic acid or DMF (20 mol % respect indane), atmosphere as indicated (1 atm).

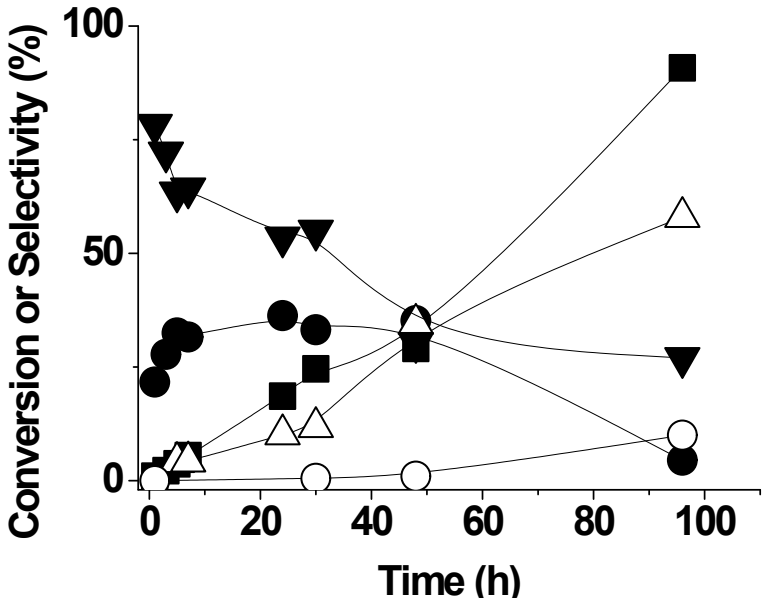

Figure S9. Time conversion (■) and selectivity plots for the aerobic oxidation of *n*-butylbenzene using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (1 atm). Legend: Selectivity to hydroperoxide (▼) alcohol (●) and ketone (Δ) at benzylic positions and benzoic acid (○).

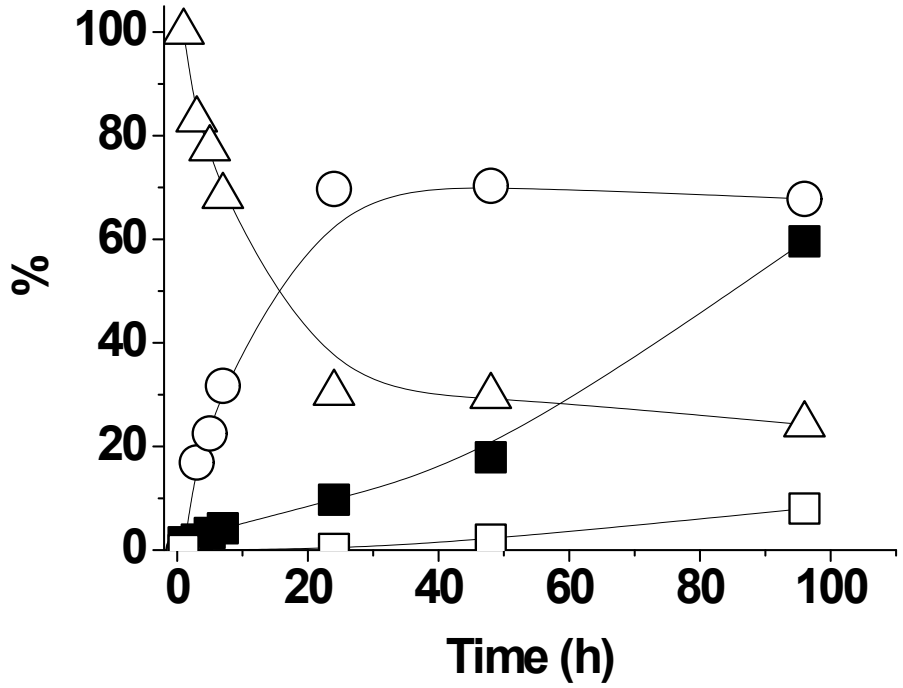

Figure S10. Time conversion (■) and selectivity plots for the aerobic oxidation of isobutylbenzene using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (1 atm). Legend: Selectivity to hydroperoxide (∆) and ketone (○) at benzylic position and benzoic acid (□).

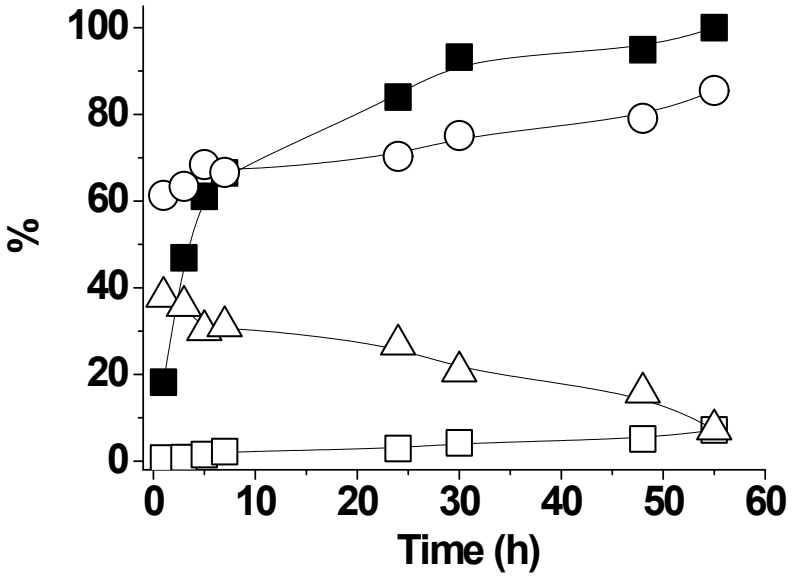

Figure S11. Time conversion (■) and selectivity plots for the aerobic oxidation of cumene using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (1 atm). Legend: Selectivity to hydroperoxide (Δ) and ketone (○) at benzylic position and α-methylstyrene (□).

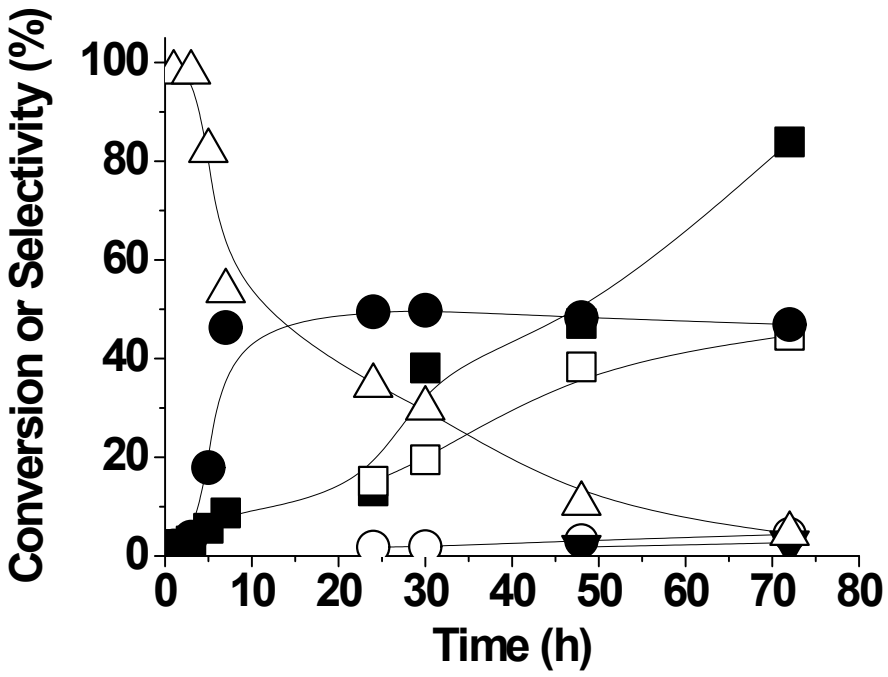

Figure S12. Time conversion (■) and selectivity plots for the aerobic oxidation of secbutylbenzene using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (1 atm). Legend: Selectivity to hydroperoxide (Δ), alcohol (▼) and ketone (●) at benzylic position and to acetophenone (□).

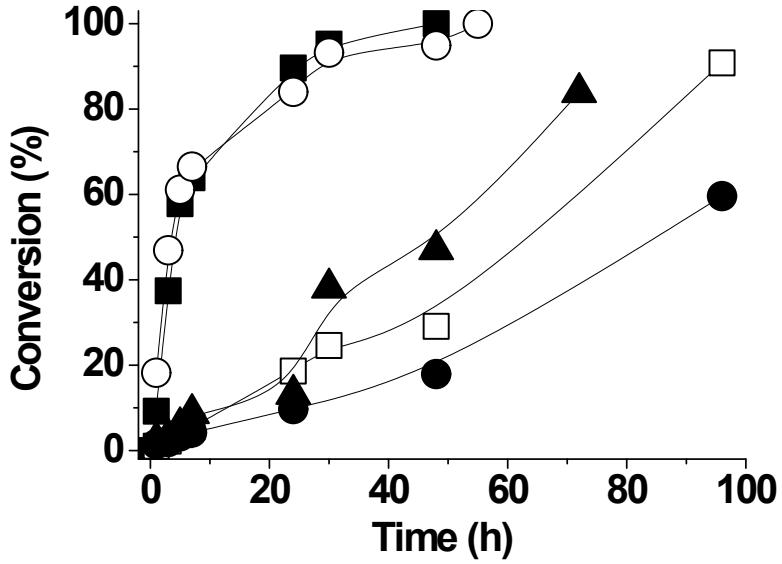

Figure S13. Comparison of the time conversion plot for the aerobic oxidation of cumene (○), indane (■), secbutylbenzene (▲), *n*-butylbenzene (□) and isobutylbenzene (●) using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (1 atm).

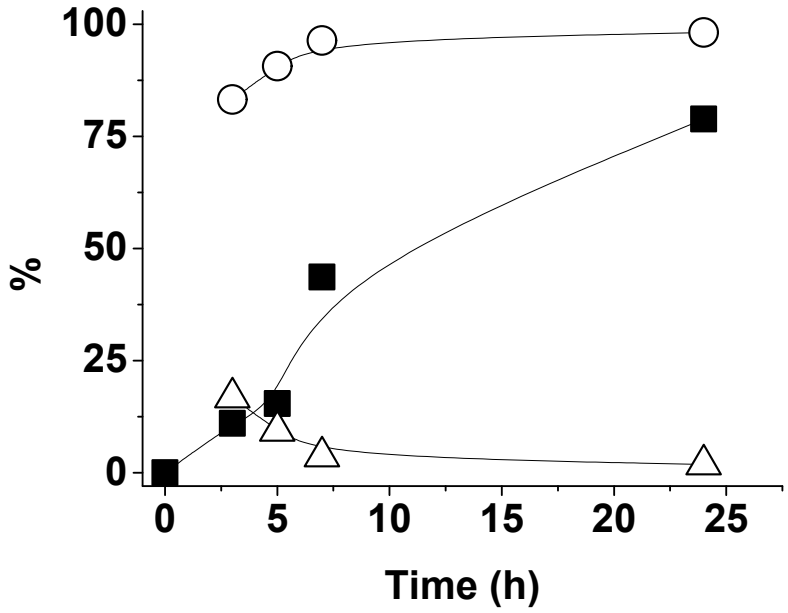

Figure S14. Time conversion (■) and selectivity plots for the aerobic oxidation of cyclooctene using CuLa-MOF as catalyst and under oxygen pressure. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (5 atm). Legend: Selectivity to hydroperoxide (Δ) and epoxide (○).

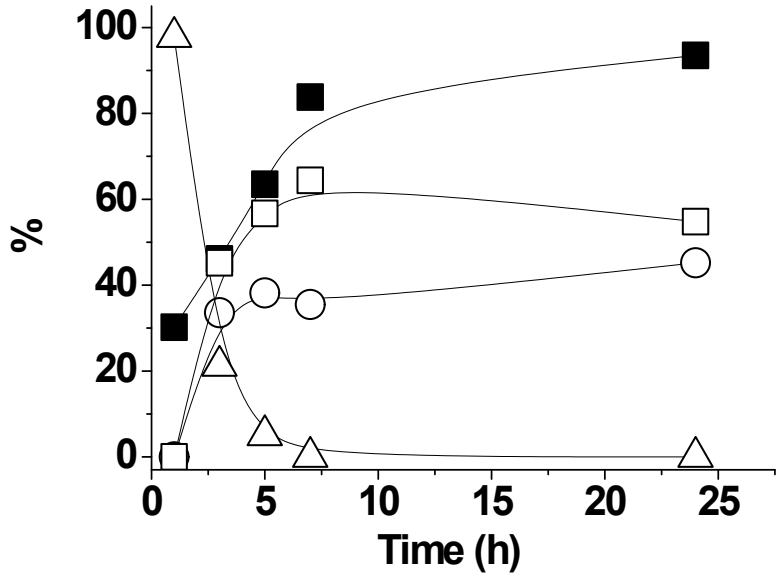

Figure S15. Time conversion (■) and selectivity plots for the aerobic oxidation of cycloheptene using CuLa-MOF as catalyst and under oxygen pressure. Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (5 atm). Legend: Selectivity to epoxide (○), alcohol (Δ) and ketone (□). Note: traces of hydroperoxide were detected.

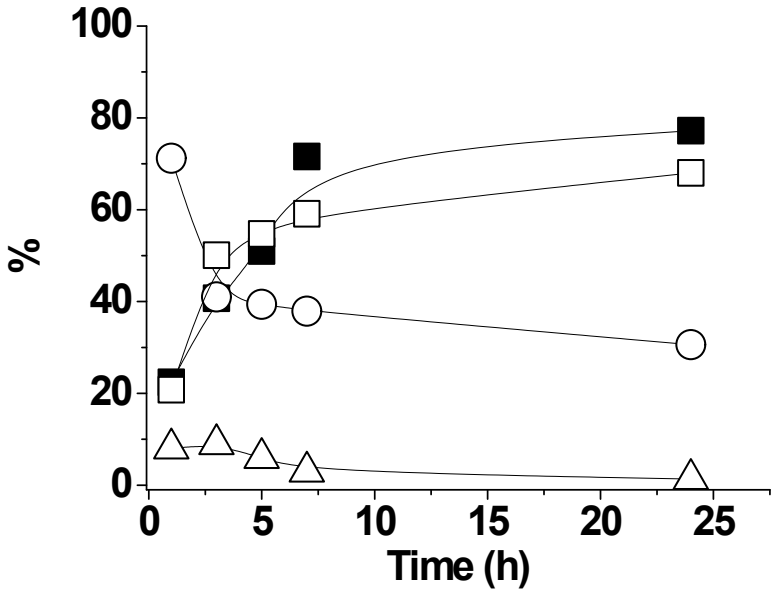

Figure S16. Time conversion (■) and selectivity plots for the aerobic oxidation of cyclohexene using CuLa-MOF as catalyst and under oxygen pressure. Reaction conditi: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), 120 ºC, O_2 atmosphere (5 atm). Legend: Selectivity to epoxide (Δ), alcohol (○) and ketone (□). Note: traces of hydroperoxide were detected.