

## Controlling the Selectivity in Ethenolysis of Cyclic Olefins with Ru-Based Metathesis Catalysts via Ancillary NHC Ligands: A Structure Activity Study

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Cross-metathesis reaction between cyclic olefins and ethylene (ethenolysis) yields valuable terminal dienes.<sup>1</sup> While ethenolysis of ethyl oleate with Grubbs-type Ru metathesis catalysts has been widely studied<sup>2</sup> there currently are only a few reports on ethenolysis of cyclic olefins with Ru catalysts,<sup>3</sup> presumably due to the high activity of Grubbs-type initiators in the ring opening metathesis polymerization. Supporting ligands can greatly influence the selectivity of Ru catalysts.<sup>4</sup> For instance, ruthenium metathesis catalysts with unsymmetrical N-trifluoromethyl NHC ligands display an unusually high selectivity (80–90%) for terminal olefins in ethenolysis of ethyl oleate.<sup>5</sup> In the present work we tested 28 isostructural Ru metathesis catalysts featuring various NHC ligands in ethenolysis of *cis*-cyclooctene as a model substrate. Our study identified the dissymmetry of the NHC ligand as a key structural feature for improving the chemoselectivity to the terminal diene from 12% for the benchmark second-generation Grubbs catalyst up to 53% for the catalyst containing an unconventional CF<sub>3</sub>-functionalized NHC ligand. To rationalize the experimental results, a computational study was conducted that explained the observed dependence via the univariate correlations of activity to electronic and steric properties of the ligand. The optimal catalyst compared favorably to the Grubbs 2<sup>nd</sup> generation catalyst in ethenolysis of other cyclic olefins including functionalized norbornenes.

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