Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Shvo's Catalyst in Chemoenzymatic Dynamic Kinetic Resolution of Amines - Inner or Outer Sphere Mechanism?

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Experimental Section

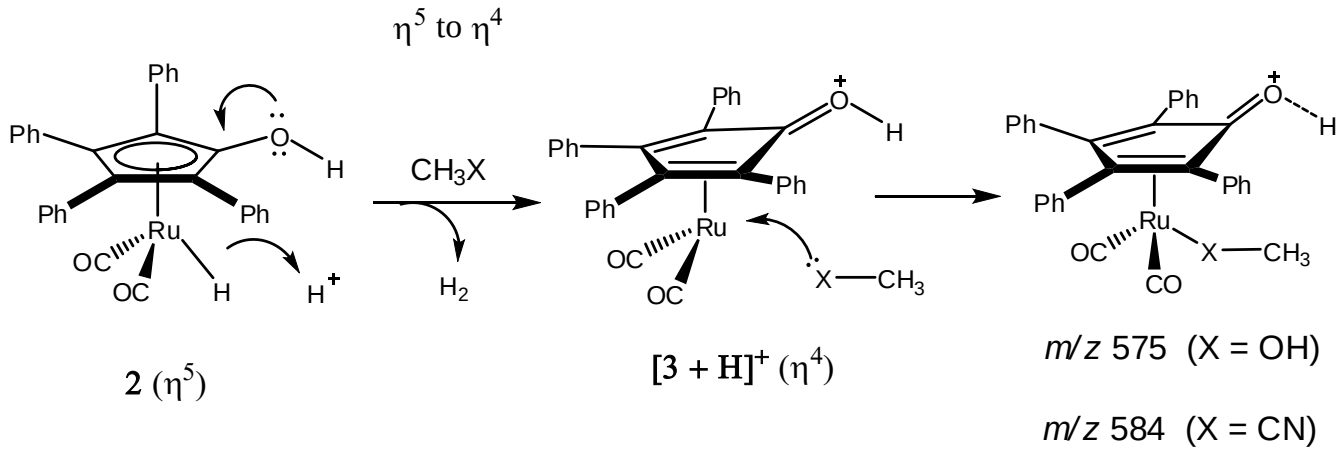
General remarks: All reagents and solvents (HPLC grade) were obtained from commercial sources. Toluene was distilled under nitrogen atmosphere and store with Na^0. Lipase Novozym® 435 was kindly donated by Novozymes Co. Shvo's catalyst was purchased from Sigma-Aldrich.

Mass Spectrometry experiments: ESI mass and tandem mass spectra in the positive ion mode were acquired using a Micromass (Manchester, UK) QTof instrument of ESI-QqTof configuration with 5.000 mass resolution and 50 ppm mass accuracy in the TOF mass analyzer. The following typical operating conditions were used: 3.5 kV capillary voltage, 8V cone voltage and dessolvation gas temperature of 100 ^{0}C. Tandem ESI-MS/MS were collected after 5 - 10 eV collision induced dissociation (CID) of mass-selected ions with argon. Selection was performed by Q1 using a unitary *m/z* window, and collisions were performed in the hexapole collision cell, followed by mass analysis of product ions by the high-resolution orthogonal reflectron TOF analyzer.

Thermal dissociation of Shvo's catalyst: a solution containing Shvo's catalyst **1** (0.02 mmol) in toluene (10 mL) was stirred at 70 °C for 60 min. Aliquots were withdrawn from reaction solution in determined time intervals and diluted with methanol and acidified with formic acid (0.1%) prior to each MS analysis.

DKR reaction of phenylethylamine: the one-pot chemoenzymatic DKR was performed with (±)1-phenylethylamine **6** (0.50 mmol), **1** (0.02 mmol), lipase Novozym® 435 (20 mg), isopropenyl acetate (2,00 mmol) in toluene (10 mL) at 70 °C under magnetic stirring for 120 min. Aliquots were withdrawn from reaction solution in determined time intervals and diluted with methanol and acidified with formic acid (0.1%) prior to each MS analysis.

Trapping experiment: (±)-phenylethylamine **6** (0.50 mmol), benzylamine **8** (0.05mol) and **1** (0.02 mmol) were dissolved in toluene (10 mL) at 70 °C and this mixture was stirred under magnetic stirring for 120 minutes. Aliquots were withdrawn from reaction solution in determined time intervals and diluted with methanol and acidified with formic acid (0.1%) prior to each MS analysis.



Scheme S1. Proposed pathway for fast convertion of 2 **to** 3 **in acidic media.**

ESI(+)-MS and ESI(+)-MS/MS data

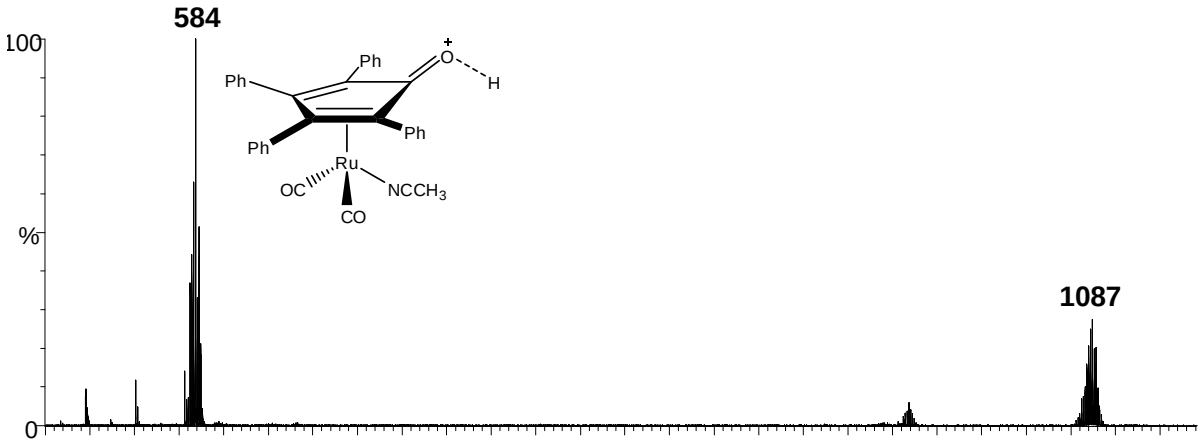


Figure S1. ESI(+)-MS of a toluene solution of the Shvo's catalyst **1** after 20 min from dilution with acetonitrile.

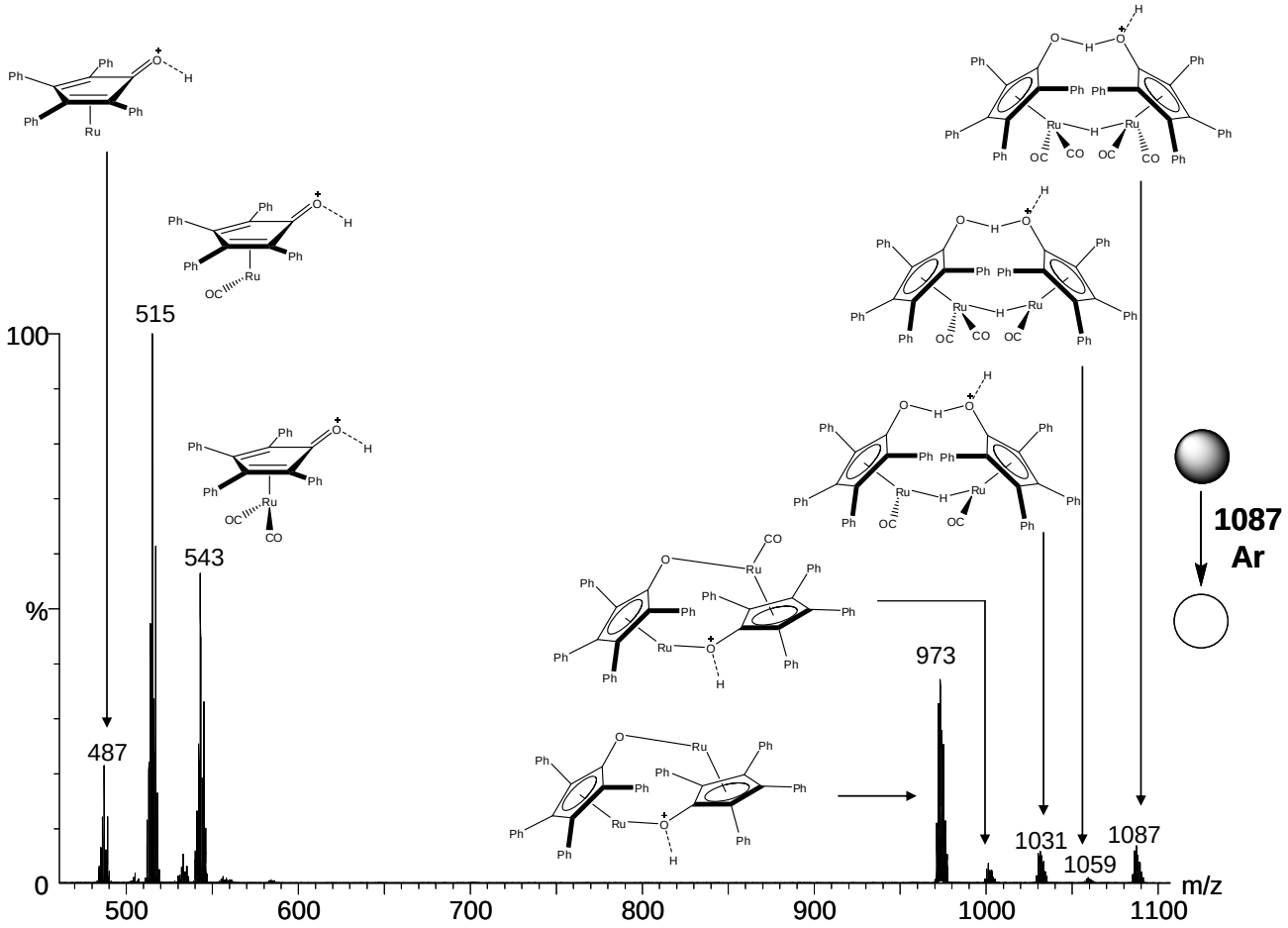


Figure S2. ESI-MS/MS of *m/z* 1087 of Shvo catalyst **1**.

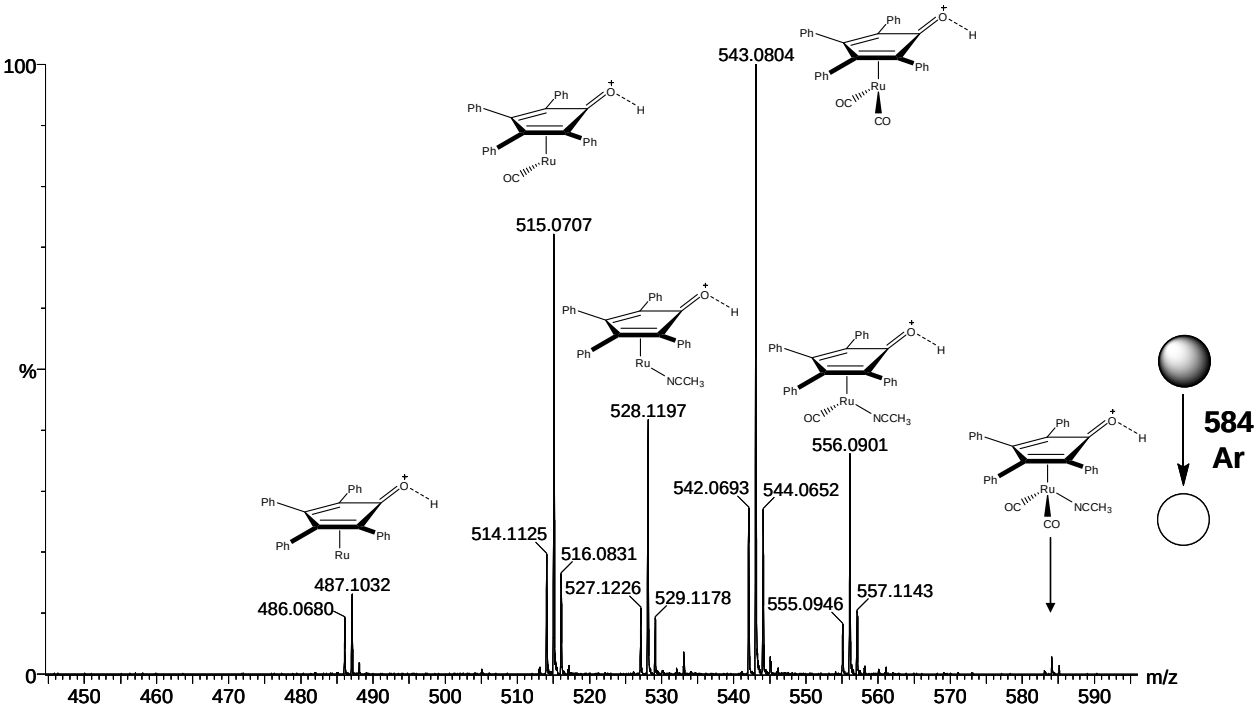


Figure S3. ESI-MS/MS of *m/z* 584 .

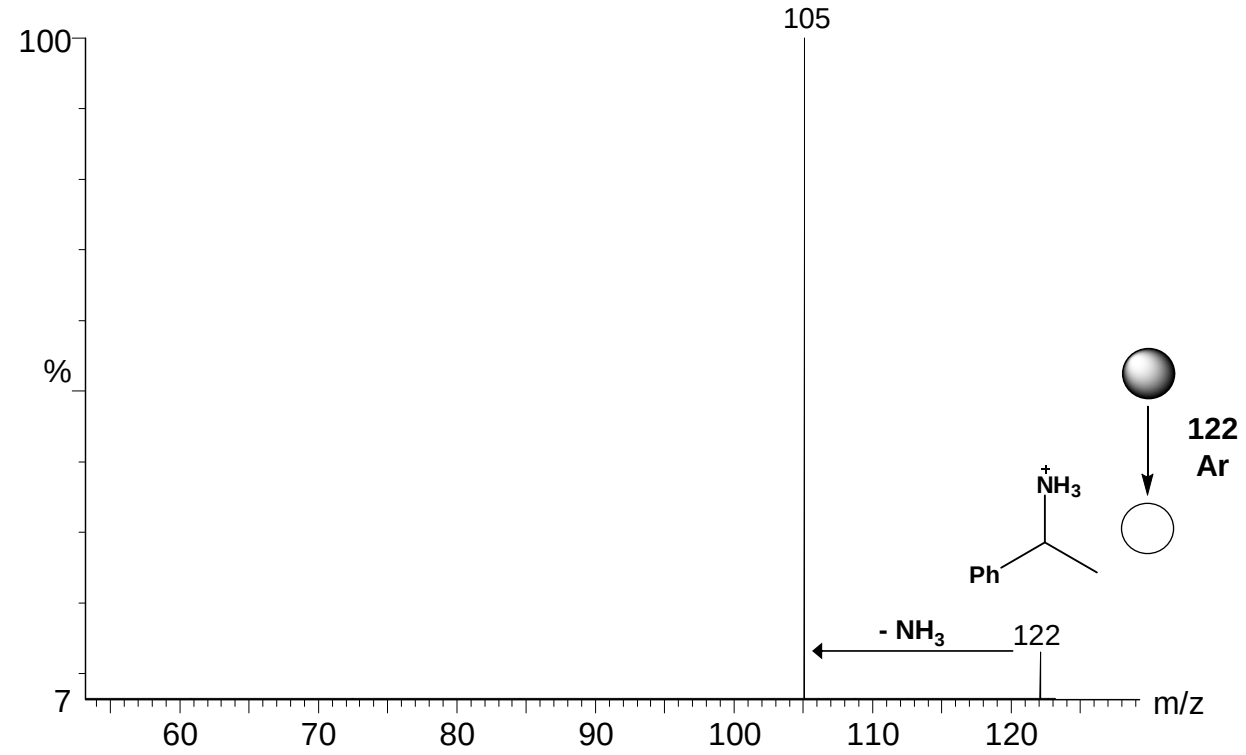


Figure S4. ESI-MS/MS of *m/z* 122 of DKR of (±)1-phenylethylamine **6**.

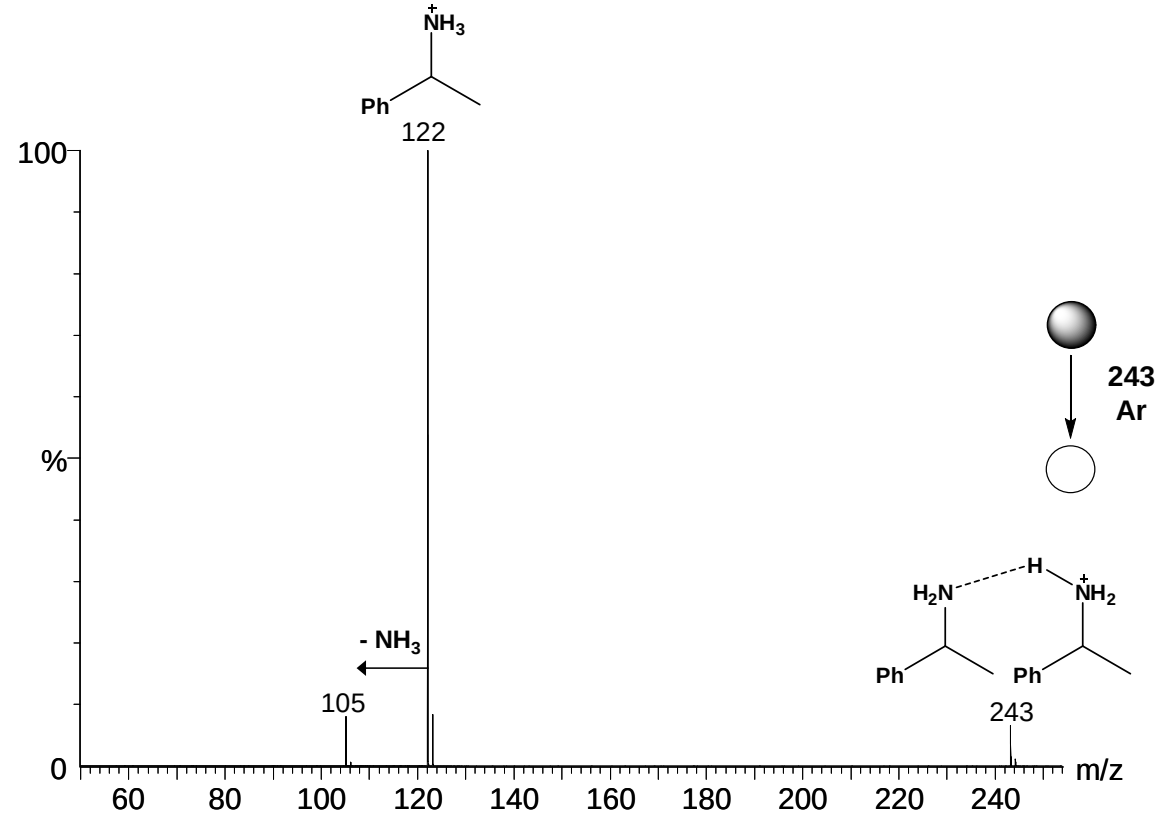


Figure S5. ESI-MS/MS of *m/z* 243 of DKR of (±)1-phenylethylamine **6**.

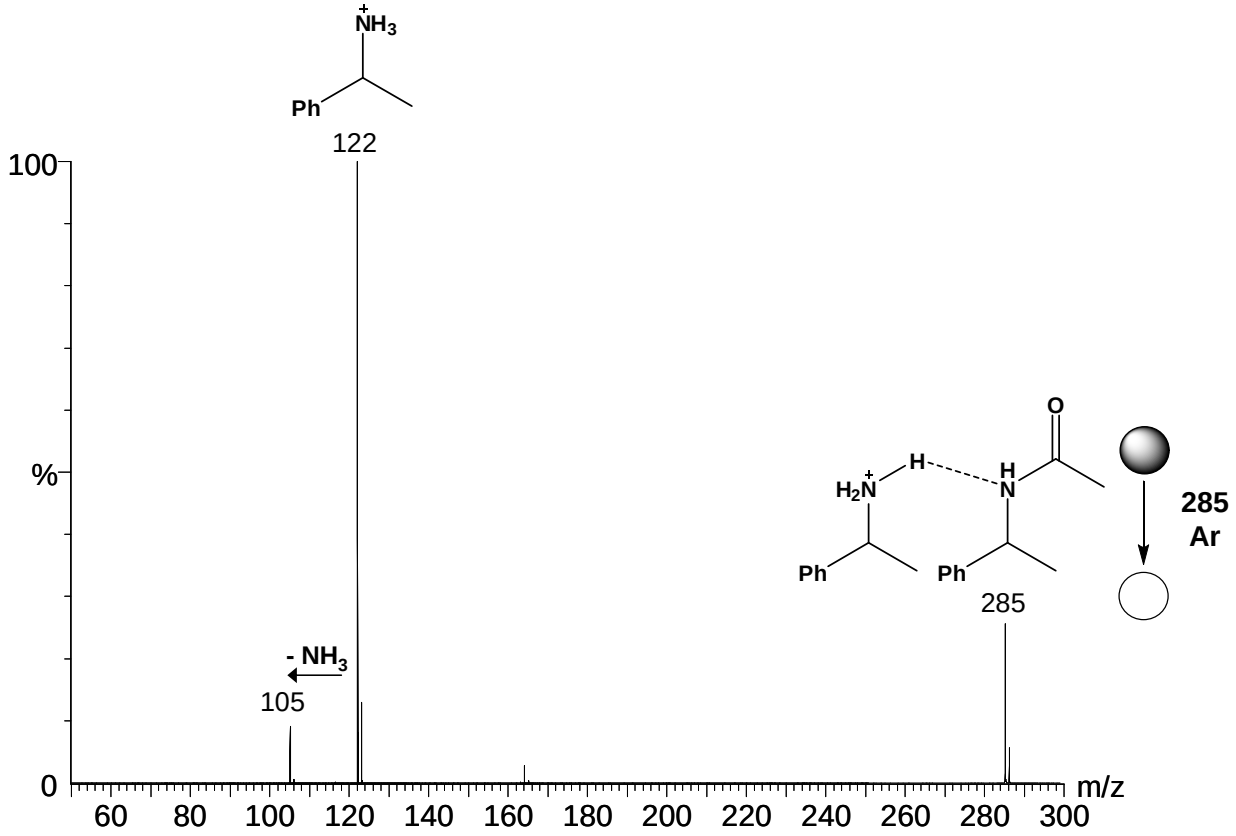


Figure S6. ESI-MS/MS of *m/z* 285 of DKR of (±)1-phenylethylamine **6.**

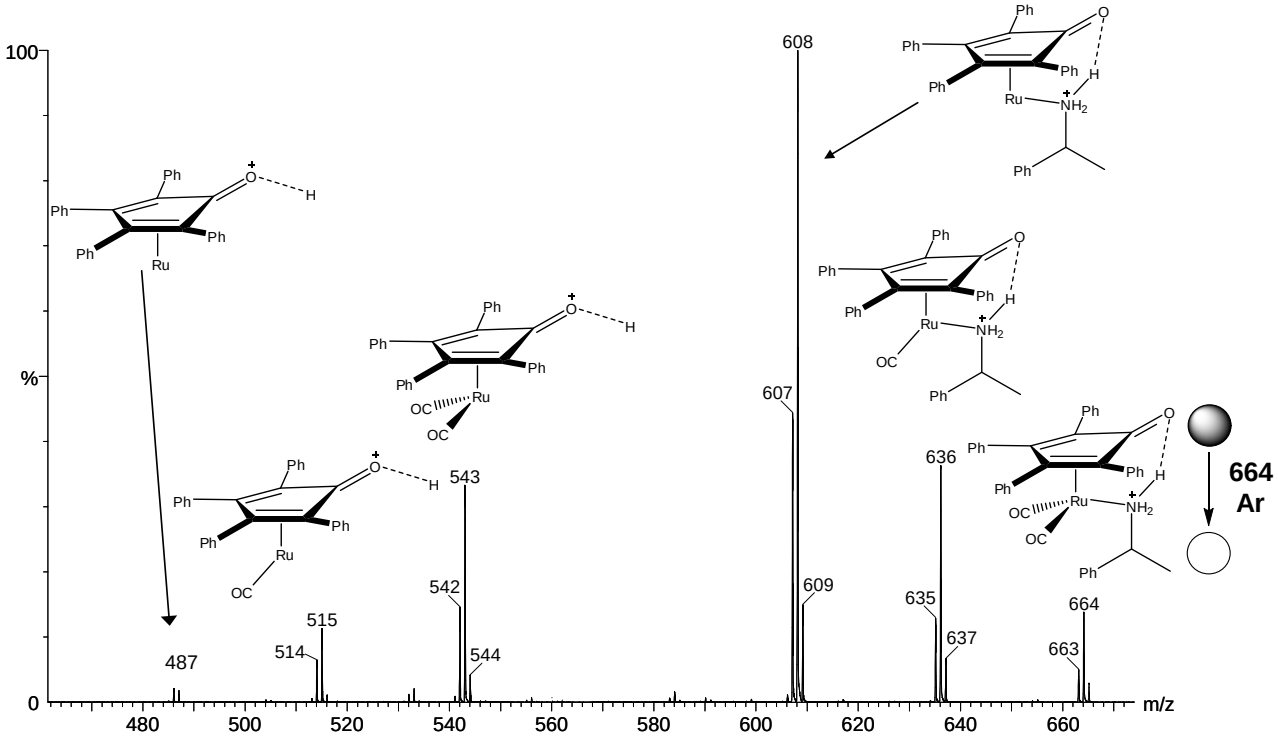


Figure S7. ESI-MS/MS of *m/z* 664 of DKR of (±)1-phenylethylamine **6.**

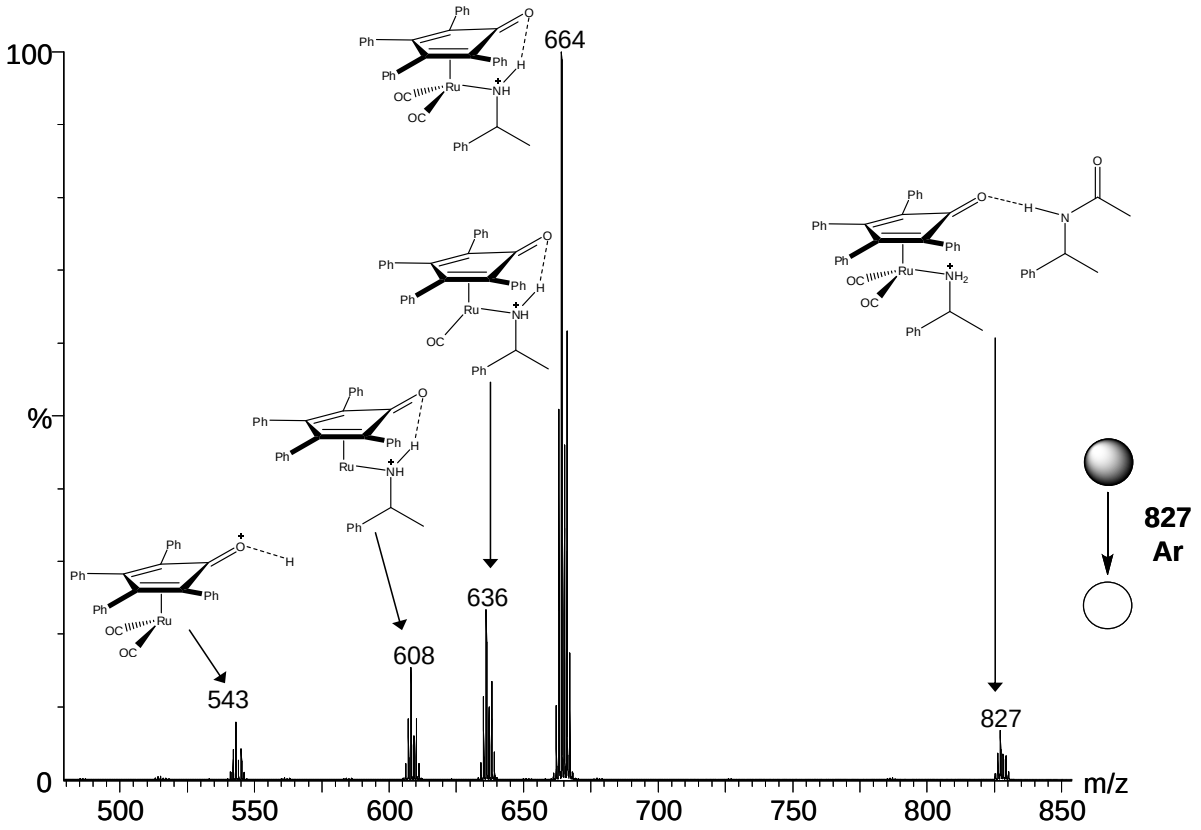


Figure S8. ESI-MS/MS of *m/z* 827 of DKR of (±)1-phenylethylamine **6**.

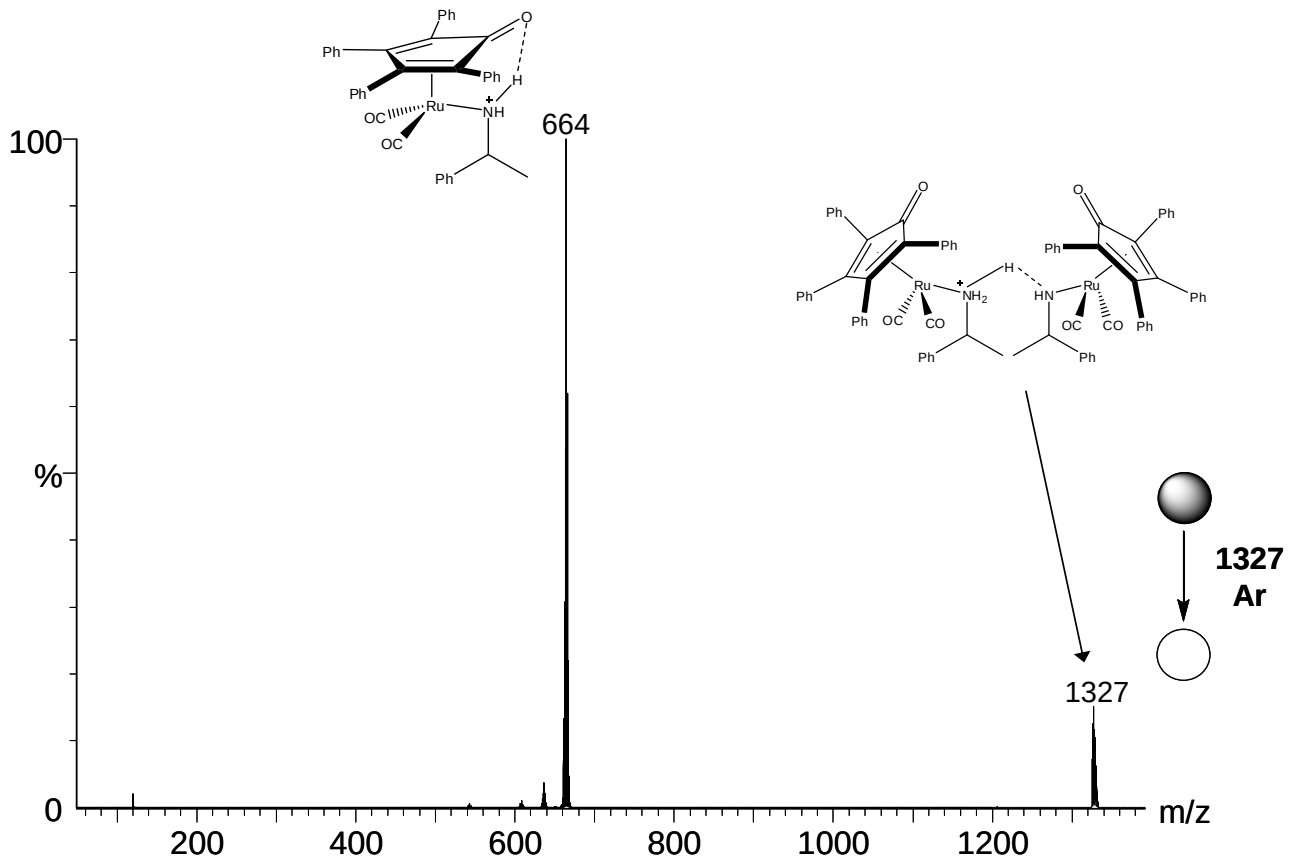


Figure S9. ESI-MS/MS of *m/z* 1327 of DKR of (±)1-phenylethylamine **6**.

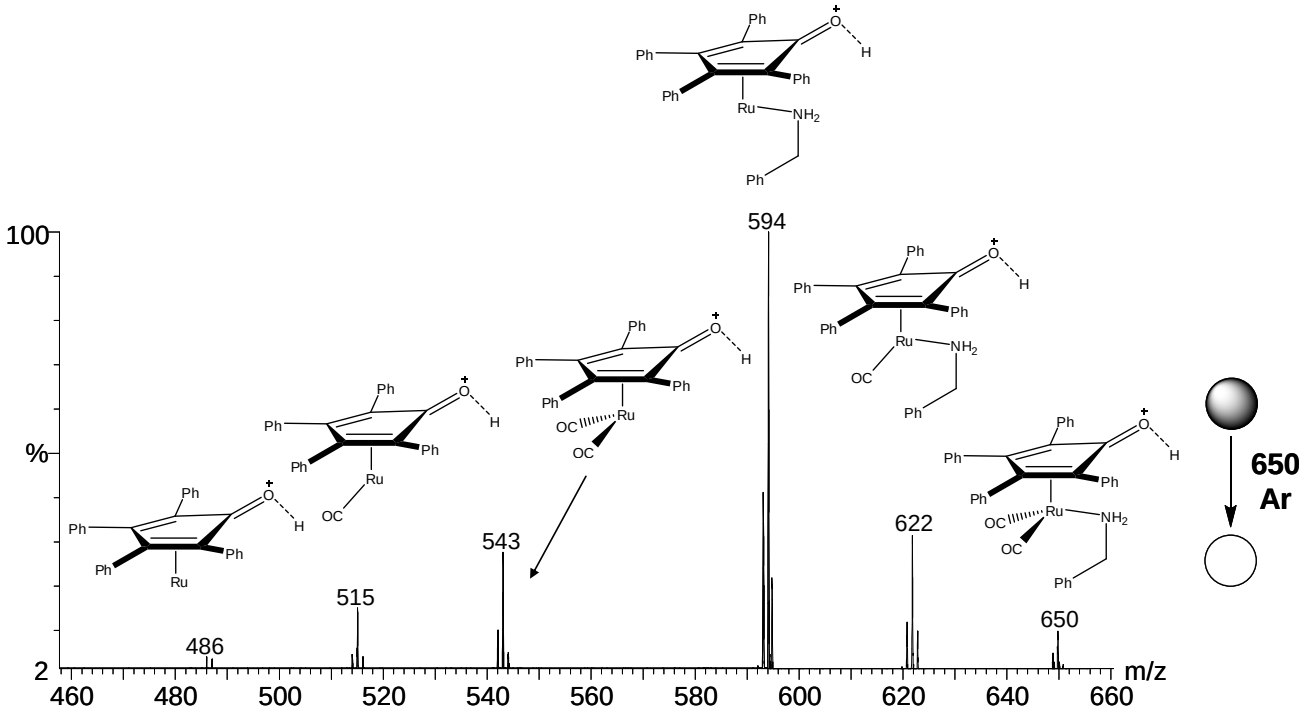


Figure S10. ESI-MS/MS of *m/z* 650 of DKR trap experiment.