Electronic Supplementary Information for:

Unveiling Reactive Metal Sites in a Pd Pincer MOF: Insights into Lewis Acid and Pore Selective Catalysis

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solution.



Figure S2. PXRD patterns of 1–PdI (black), 1–PdBF₄ (red), and 1–PdBF₄ post catalysis (blue) (Cu K α radiation, λ = 1.54 Å).





Figure S4. N₂ adsorption isotherms (77 K) for **1-PdI** (black) and **1-PdBF**₄ (red) after desolvation at 150 °C and $\sim 10^{-4}$ torr for 12 h.



Figure S5. DFT differential pore volume plots for **1-PdI** (black) and **1-PdBF**₄ (red) obtained from the respective N_2 adsorption isotherms (77 K).



S6



Figure S8. ${}^{31}P{}^{1}H$ NMR spectrum (3/1 CF₃CO₂H/C₆D₆) of **1–PdBF₄** before (top) and after treatment with water (bottom).





Figure S11. ¹H NMR spectrum of the intramolecular amination of 2 with $1-PdBF_4$ (5 mol %) (0.012 mmol hexamethylbenzene internal standard).







Figure S13. ¹H NMR spectrum of the intramolecular amination of **2** with **1–PdBF**₄ (0.5 mol %) (0.008) mmol hexamethylbenzene internal standard).



Figure S14. ¹H NMR spectrum of the intramolecular amination of **2** with **1–PdTFA** (5 mol %) (0.006 mmol hexamethylbenzene internal standard).



Figure S15. ¹H NMR spectrum of the intramolecular amination of **2** with **1–PdX** (5 mol %) (0.006 mmol hexamethylbenzene internal standard).



Figure S16. ¹H NMR spectrum of the intramolecular amination of **2** with **1–PdI** (5 mol %) (0.007 mmol hexamethylbenzene internal standard).



Figure S17. ¹H NMR spectrum of the intramolecular amination of **2** with '**Bu**₄L–PdBF₄ (5 mol %) (0.014 mmol hexamethylbenzene internal standard).



Figure S18. Experimental data collected during the cyclization of **2** in the presence of 5 mol % **1– PdBF**₄ using pristine material (black circles) and recycled material (red circles) modeled using a linear regression or single term exponential fit.



Figure S19. ¹H NMR spectrum of the intramolecular amination of 4 with '**Bu**₄L–PdTFA (5 mol %) (0.016 mmol hexamethylbenzene internal standard).



Figure S20. ¹H NMR spectrum of the intramolecular amination of **4** with **1–PdTFA** (5 mol %) (0.006 mmol hexamethylbenzene internal standard).



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
2-ethnylaniline	3.052	<1000	0.59	0
indole	4.219	24527992	0.59	44
quinoline	5.423	10819471	0.21	55
Hexamethylbenzene	10.792	28231557	1.00	

Figure S21. GC-FID trace of the intramolecular amination of **4** with ^{*t*}**Bu**₄**L**–**PdBF**₄ (5 mol %) (0.030 mmol hexamethylbenzene internal standard).



Figure S22. G	C-FID ti	race of the	intramolecular	amination	of 4 v	with 1	1–PdBF ₄ (5	mol 9	%) (0.21
mmol hexameth	nylbenze	ene internal	standard).						

5453485

1.00

Hexamethylbenzene

10.792



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
Isopulegol	6.982	12274411	1.98	65
Citronellal	7.173	<1000	1.98	0
Other diastereomers	7.197 - 7.827	5796339	1.98	31
Hexamethylbenzene	13.314	2644595	1.00	_

Figure S23. GC-FID trace of the carbonyl-ene cyclization of **8** with **1–PdBF**₄ (10 mol %) (0.013 mmol hexamethylbenzene internal standard). All observed products are racemic.



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
Isopulegol	6.982	12958840	1.98	63
Citronellal	7.173	<1000	1.98	0
Other diastereomers	7.197 - 7.827	5911925	1.98	29
Hexamethylbenzene	13.314	7697094	1.00	

Figure S24. GC-FID trace of the carbonyl-ene cyclization of 8 with $1-PdBF_4$ (10 mol %) on the third run (0.039 mmol hexamethylbenzene internal standard). All observed products are racemic.



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
Isopulegol	6.982	2,589,013	1.98	16
Citronellal	7.173	13,312,758	1.98	83
Other diastereomers	7.197 - 7.827	<1000	1.98	0
Hexamethylbenzene	13.314	4,223,863	1.00	_

Figure S25. GC-FID trace of the carbonyl-ene cyclization of **8** with **1–PdX** (10 mol %) (0.026 mmol hexamethylbenzene internal standard). All observed products are racemic.



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
Isopulegol	6.982	50898793	1.98	60
Citronellal	7.173	3373824	1.98	4
Other diastereomers	7.197 - 7.827	26094676	1.98	31
Hexamethylbenzene	13.314	3021523	1.00	_

Figure S26. GC-FID trace of the carbonyl-ene cyclization of **8** with **1–PdBF**₄ (0.5 mol %) (0.014 mmol hexamethylbenzene internal standard). All observed products are racemic.



Substrate	Retention Time (min)	Integration (a.u.)	Response Factor	Yield (%)
Isopulegol	6.982	12,736,861	1.98	73
Citronellal	7.173	<1000	1.98	0
Other diastereomers	7.197 - 7.827	4915655	1.98	27
Hexamethylbenzene	13.314	4,572,822	1.00	

Figure S27. GC-FID trace of the carbonyl-ene cyclization of **8** with '**Bu**₄L–PdBF₄ (10 mol %) (0.026 mmol hexamethylbenzene internal standard). All observed products are racemic.



Figure S28. GC-FID trace of the carbonyl-ene cyclization of **8** with '**Bu**₄L–PdBF₄ (0.5 mol %) (0.035 mmol hexamethylbenzene internal standard). All observed products are racemic.



Figure S29. Experimental data collected during the cyclization of 8 (100 mM) in the presence of 0.5 mol % 1–PdBF₄ (black circles) modeled with a single term exponential fit (black line).



Figure S30. Experimental data collected during the cyclization of **8** (200 mM) in the presence of 0.5 mol % **1–PdBF**₄.



Figure S31. ¹H NMR spectrum (3/1 CF₃CO₂H/DMSO-*d*₆) of an activated sample of **1–PdBF**₄ showing the presence of MeCN in a ~1:1 ratio with the H₄[L-PdBF₄]⁺ linkers. The overlayed spectrum was spiked with a small amount of MeCN to confirm the assignment.

Details of hot filtration test and ICP-MS analysis. The catalytic intramolecular hydroamination of **2** was set up as described in the Experimental section with **1-PdBF**₄ (5 mol % Pd) as the catalyst. After 30 min of heating at 95 °C, the hot suspension was quickly filtered inti a clean vial using a 0.45 μ m Teflon syringe filter. A small aliquot was removed for ¹H NMR analysis and the remaining filtrate was quickly sealed and heated back to 95 °C. The filtrate was again analyzed by ¹H NMR spectroscopy after heating for 3.5 h. The results are shown below in Figure S32. ICP-MS analysis was performed at the Trace Element Research Laboratory (Ohio State University) using a Perkin-Elmer Sciex ELAN 6000 ICP-MS spectrometer. The organic volatiles

University) using a Perkin-Elmer Sciex ELAN 6000 ICP-MS spectrometer. The organic volatiles were removed in vacuo from the combined filtrate from the hot filtration test. The resulting solid was digested by heating in a mixture of trace metal grade concentrated $HCl_{(aq)}$ and $HNO_{3(aq)}$ and diluted to a final volume of 100 mL. The concentration of Pd was determined with respect to a blank sample and 50 ppb standard solution and found to be ~200 ppb.



Figure S32. Solvent suppressed ¹H NMR spectra (1,4-dioxane) of filtrate collected from hot filtration test. ¹H NMR shows that the reaction had proceeded to ~ 43 % conversion after 30 min and the filtrate showed only a small increase in substrate conversion (~ 46 %) after continued heating for 3.5 h.