Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Surface ligands enhance the catalytic activity of supported Au nanoparticles for the aerobic α-oxidation of amines to amides

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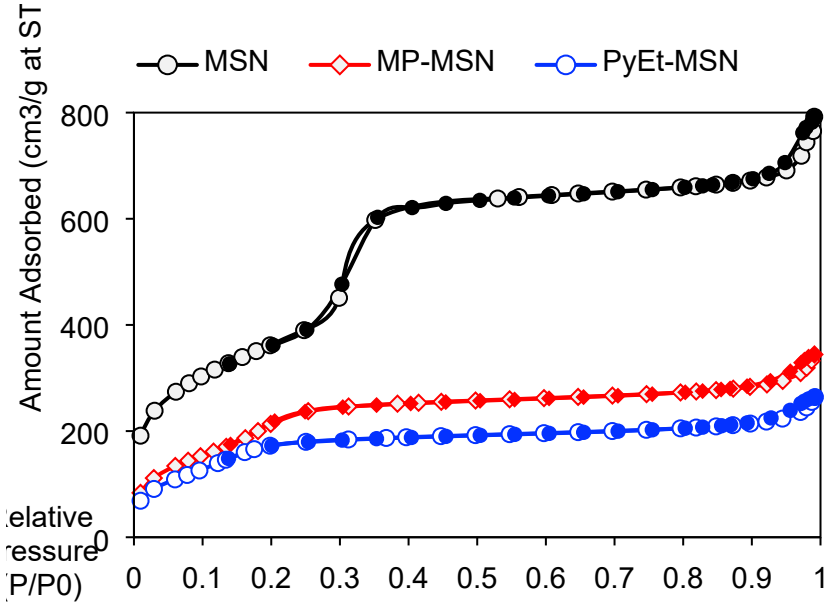
Table S1. Physicochemical properties of MSN supports.

Support	SA_{BET}[a] (m^2/g)	W_{BJH}[a] (nm)	Group Loading[b] (mmol/g)
MSN	1320	2.6	-
MP-MSN	1015	2.4	1.4
PyEt-MSN	702	2.1	0.94
PyEt-MSN-0.7	795	2.4	0.65
PyEt-MSN-1.4	771	2.1	1.4

[a] Measured by N_2 physisorption.

[b] Determined by CHNS elemental analysis.

Fig. S1 N_2 sorption isotherms of MSN supports.



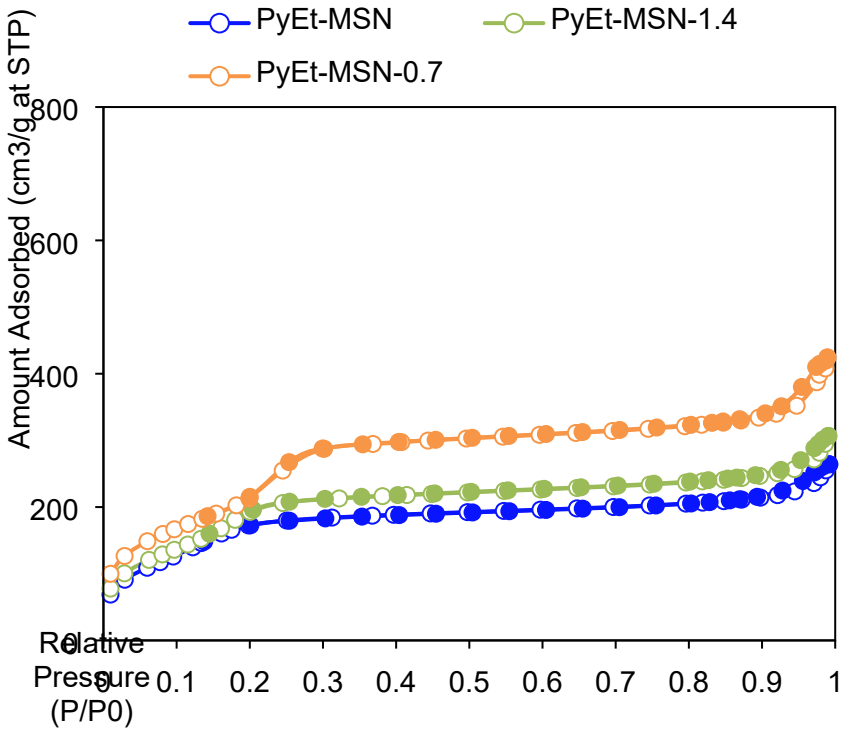


Fig. S2 Small angle XRD patterns of MSN supports.

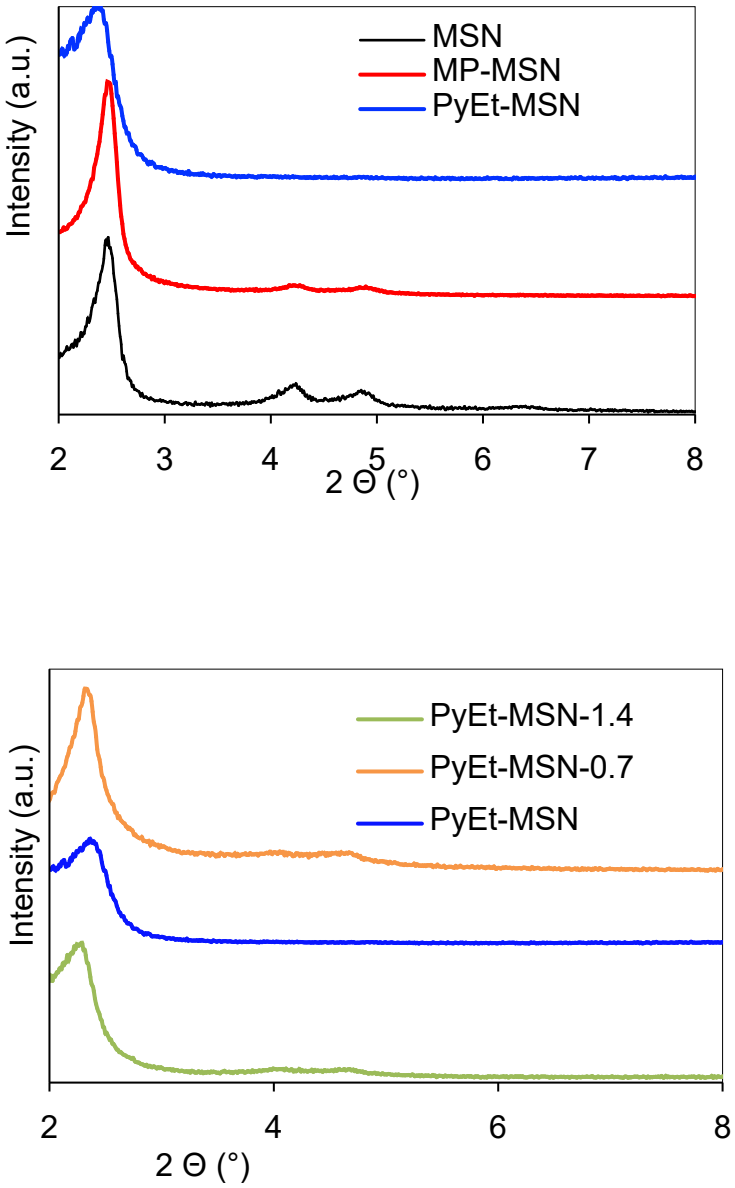


Fig. S3 DRIFT spectra of MP-MSN showing bands in the a) 2900-2950 cm^{-1} region assigned to C-H stretches and b) at 2582 cm^{-1} assigned to S-H stretch. The parent MSN did not show any absorption in these regions.

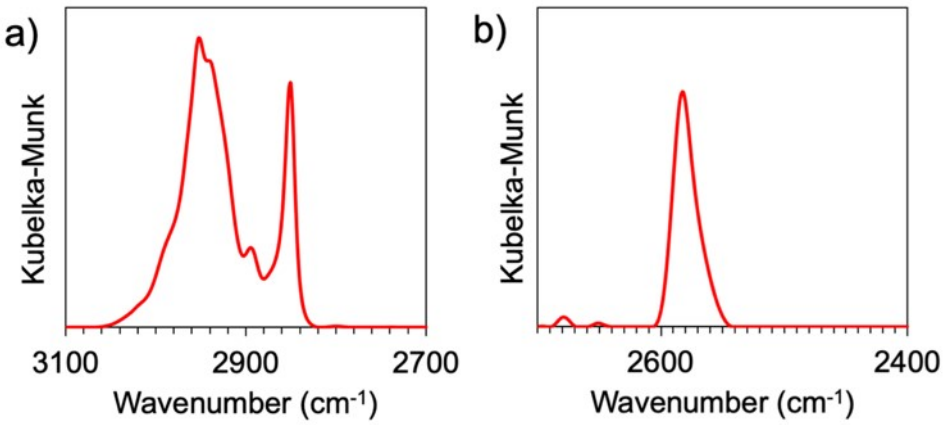


Fig. S4 DRIFT spectra of PyEt-MSN (blue traces) showing signals in the a) 3000-3100 cm^{-1} and 2800-3000 cm^{-1} regions indicating presence of aromatic and aliphatic C-H vibrations respectively. b) The additional intense band at ~1612 cm^{-1} is assigned to the C=N stretch of pyridine and the band at 1562 cm^{-1} peak is attributed to protonated pyridine. The parent MSN (black trace) presented an absorption at 1618 cm^{-1} assigned to physisorbed water.

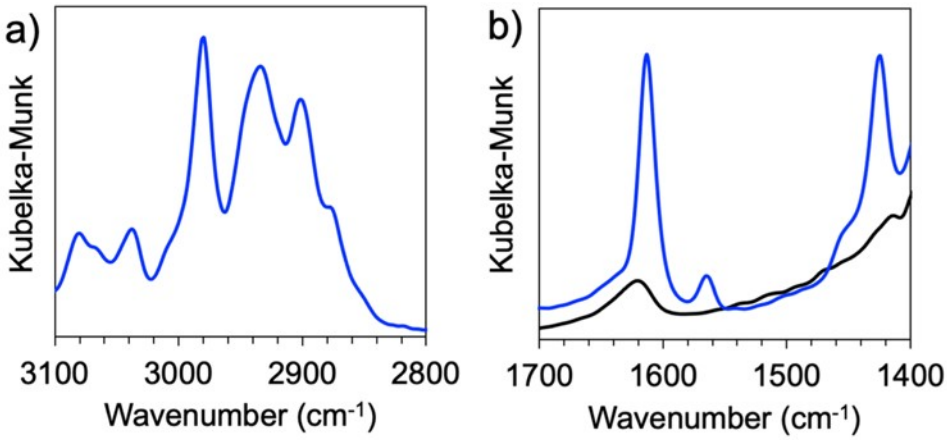
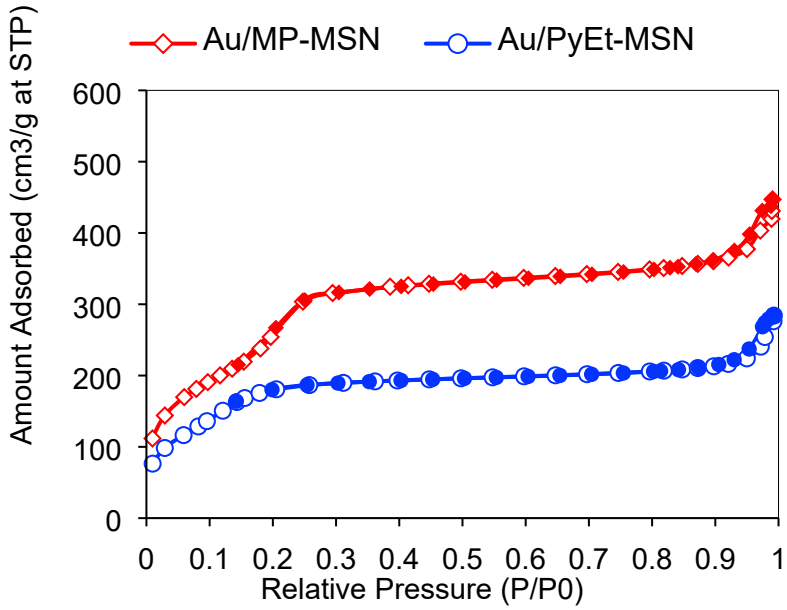


Fig. S5 N_2 sorption isotherms of the supported Au catalysts.



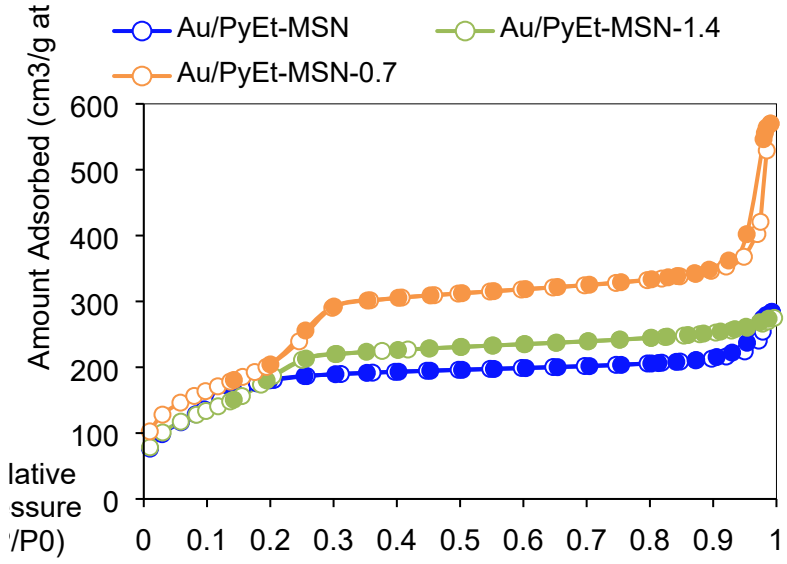


Fig. S6 Small angle XRD patterns of supported Au catalysts.

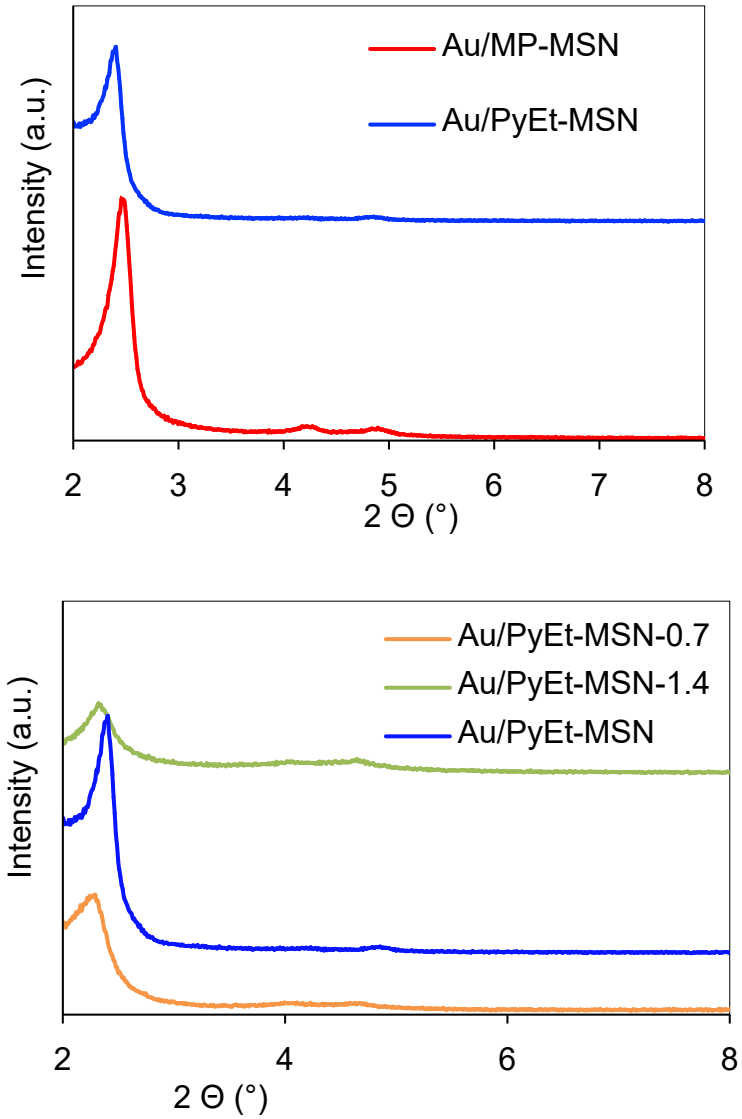
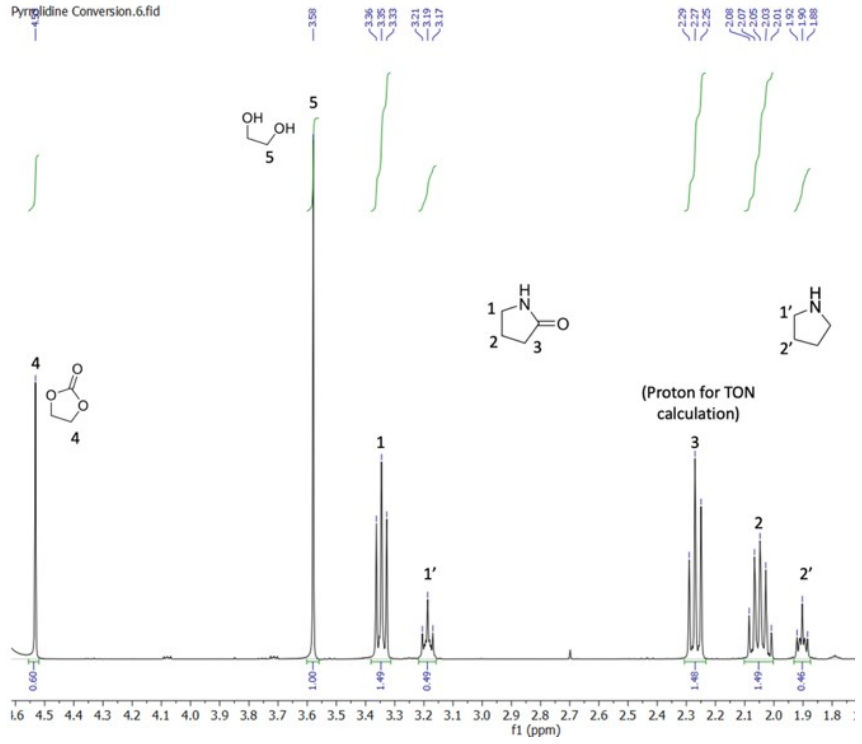


Fig. S7 Sample ^{1}H NMR spectra of reaction mixtures obtained from the Au/PyEt-MSN catalyzed oxidation of pyrrolidine (top) and N-methyl pyrrolidine (bottom).



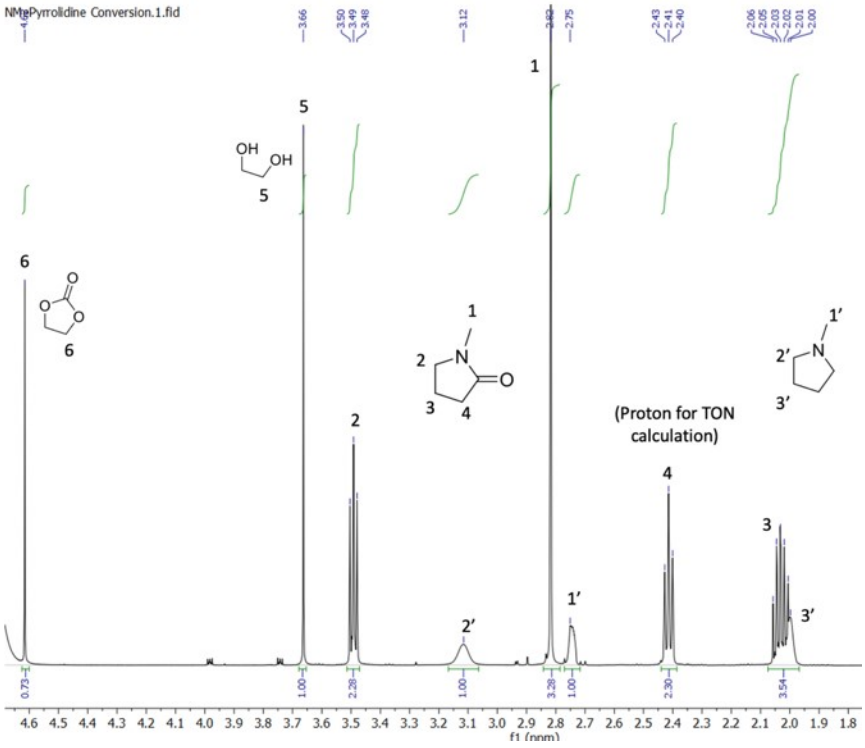


Table S2. Physicochemical properties of the catalysts.

Catalyst	SA_{BET} (m^2/g)[a]	W_{BJH} (nm)[a]	Au Loading (wt.%)[b]	% Dispersion[c]
Au/MP-MSN (0.5 wt %)	964	2.3	0.46 ± 0.02	52
Au/MP-MSN (4.8 wt %)	899	2.4	4.8 ± 0.1	47
Au/PyEt-MSN (0.5 wt %)	716	2.0	0.50 ± 0.07	44
Au/PyEt-MSN-0.7 (0.5 wt %)	746	2.3	0.50 ± 0.02	43
Au/PyEt-MSN-1.4 (0.5 wt %)	716	2.4	0.49 ± 0.04	30
Au/PyEt-MSN (3.9 wt %)	849	2.3	3.9 ± 0.2	15

[a] Measured by N_2 physisorption.
[b] Determined by ICP-OES analysis.
[c] Estimated by CO pulsed chemisorption.

Fig. S8 Comparison of DRIFT spectra in the 1450 – 1700 cm^{-1} region of PyEt-MSN (blue), Au/PyEt-MSN (0.5 wt % Au) (yellow) and Au/PyEt-MSN (3.9 wt % Au) (brown). New bands are indicative of pyridyl-Au interaction.

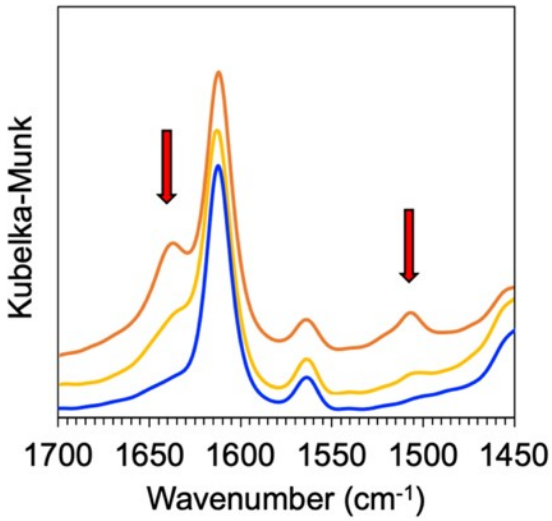
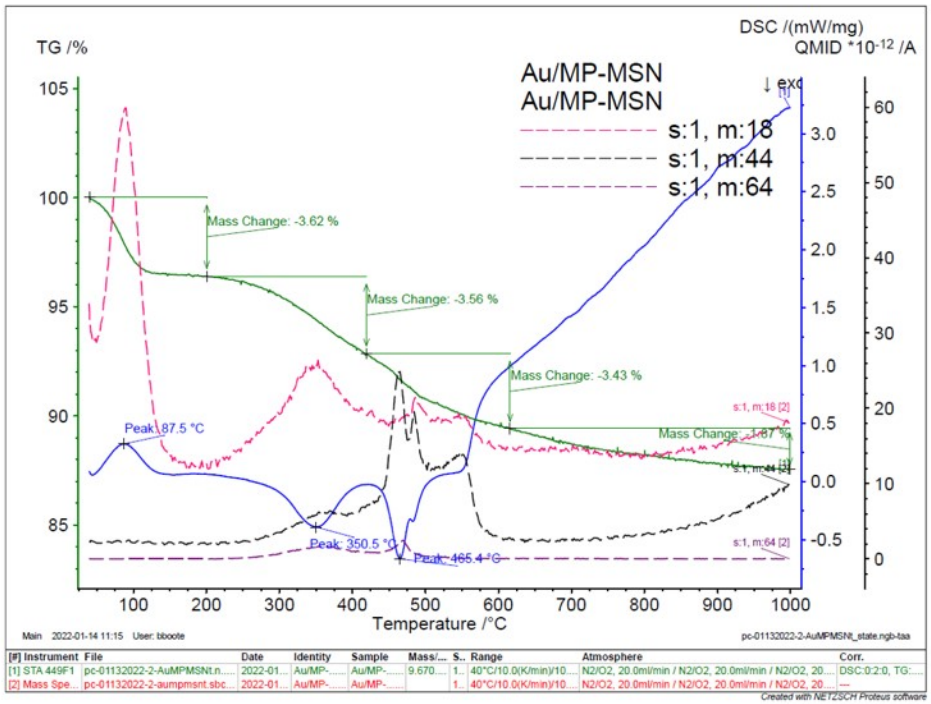


Fig. S9 Thermogravimetric analyses of a) Au/MP-MSN and b) Au/PyEt MSN. Losses below 200 °C correspond to water. Evolution of CO_2 and SO_2 indicative of organic group decomposition were observed in the 200 to 700 °C range.

a)



b)

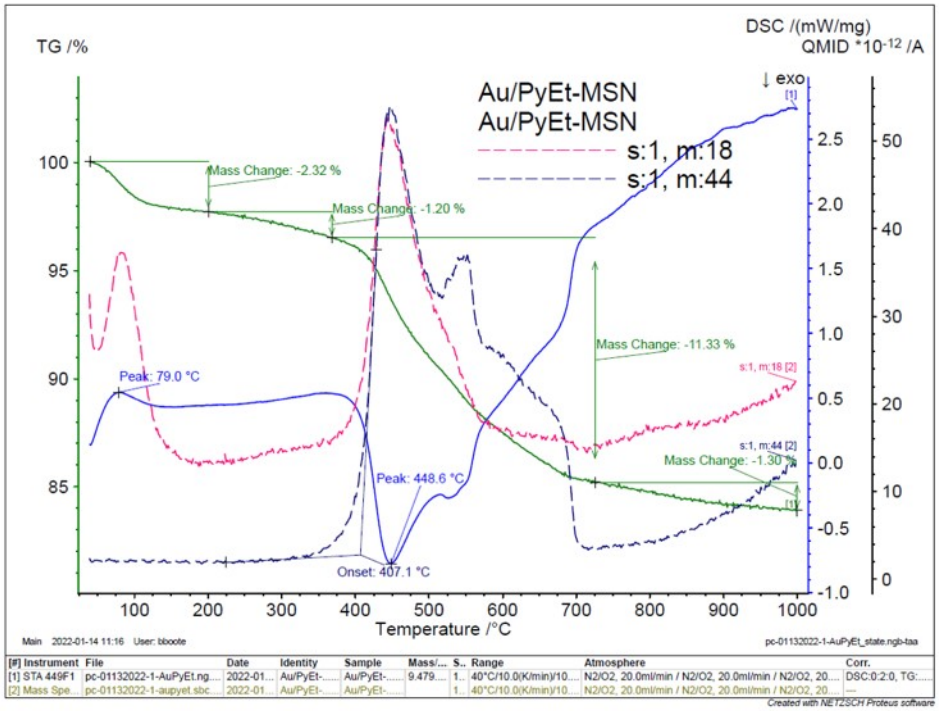


Fig. S10 Particle aggregation upon exposure of Au/MSN to the electron beam in the TEM. Scale bar is 10 nm in all images except for the bottom left (50 nm).

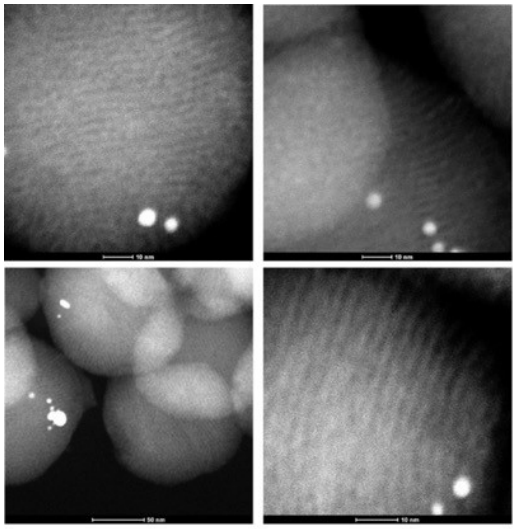


Fig. S11 Representative STEM images of fresh (left) and spent (right) Au/MP-MSN (top) and Au/PyEt-MSN (bottom). Scale bar 20 nm in all images. Due to the small particle size of Au/MP-MSN it was not possible to reliably determine size distribution, however no large Au aggregates were observed upon inspection of the full field. Particle size distribution histograms of Au/PyEt-MSN are below their images. Average particle sizes were 2.1 ± 0.6 nm for the fresh and 2.3 ± 0.6 nm for the spent catalyst, based on 100 counts.

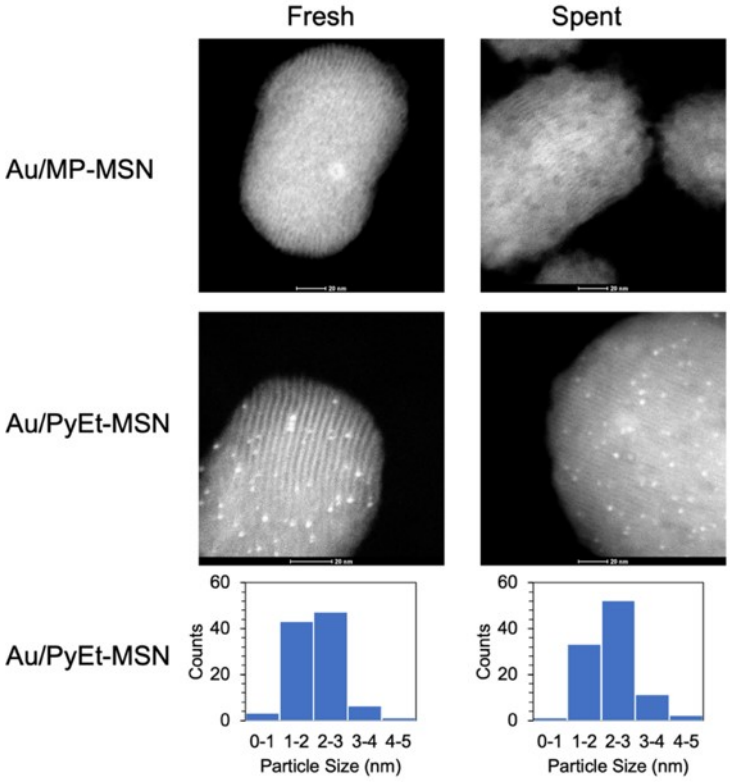


Fig. S12 Representative STEM images and Au particle size histogram (based on 100 particle counts) of Au/MP-MSN with a 4.8 wt % metal loading.

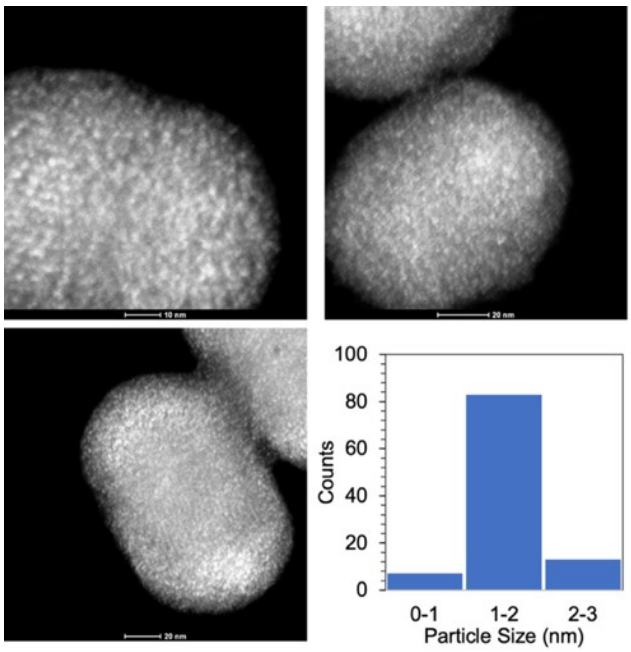


Fig. S13 Comparison between the activities of Au/MP-MSN with different particle sizes. The different particle sizes were obtained using different Au wt %. 0.5 wt % of Au gave particles smaller than 1 nm, and 4.8 wt % of Au gave particles averaging 1.6 nm.

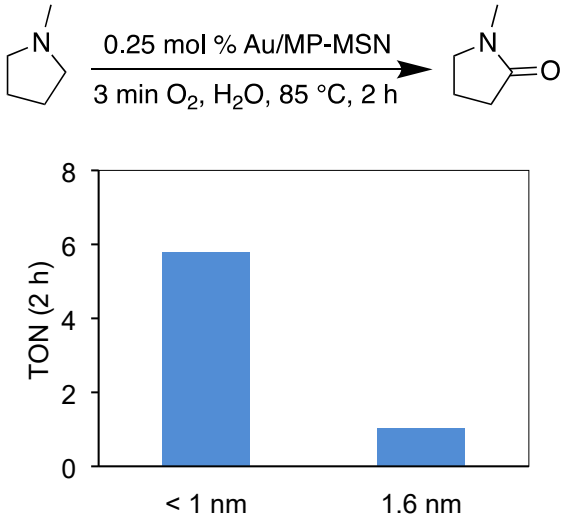


Fig. S14 Representative STEM images and Au particle size histogram (based on 100 particle counts) of Au/PyEt-MSN with a 3.9 wt. % metal loading.

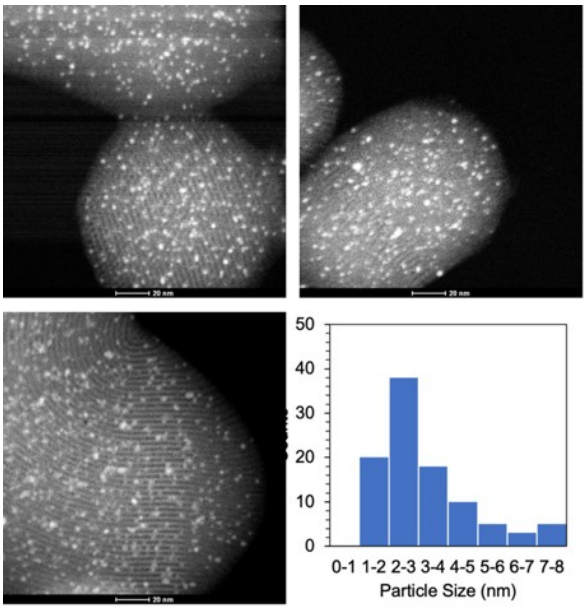


Fig. S15 Comparison between the catalytic activities of Au/PyEt-MSN with different particle sizes. The different particle sizes were obtained using different Au wt %. 0.5 wt % of Au gave particles of ca. 2.1 nm, and 3.9 wt % of Au gave particles averaging 3.2 nm.

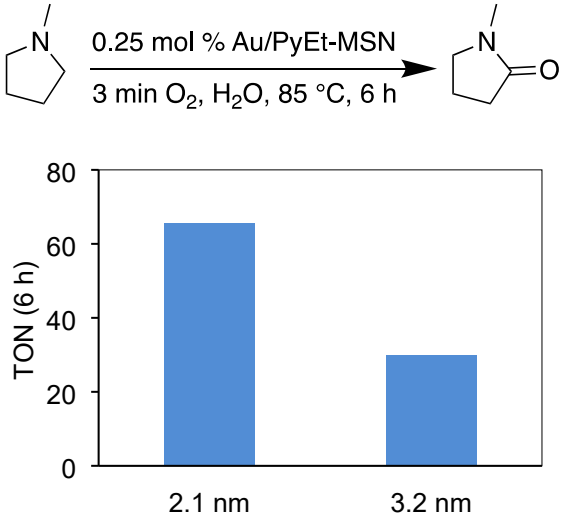


Fig. S16 Variation in catalyst properties as a function of PyEt group loading. a) Catalytic activity for the oxidation of N-methylpyrrolidine to N-methylpyrrolidone using Au/PyEt-MSN with 0.65, 0.94 and 1.4 mmol PyEt groups per g of material (conditions: 0.25 mol % Au, 2 mL H_2O, 100 °C, 6 h, 3 min O_2 overhead flow). b) STEM images of Au/PyEt-MSN with 0.65 mmol PyEt/g and the corresponding particle size histogram. c) STEM images of Au/PyEt-MSN with 1.4 mmol PyEt/g and the corresponding particle size histogram.

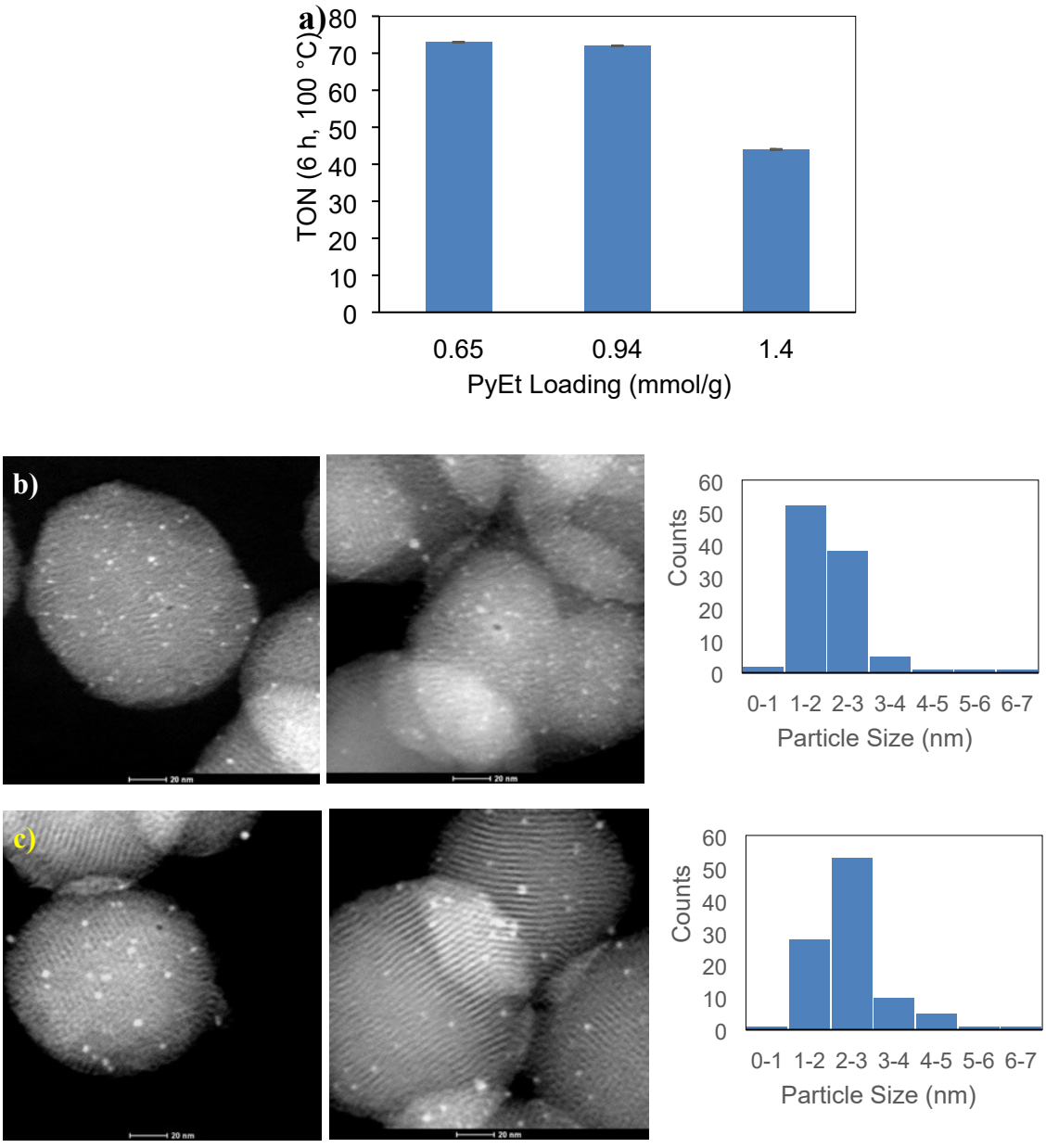


Fig. S17 Deconvolution of N 1s XPS of Au/PyEt-MSN shows ca. 41% N coordinated with Au (400 eV, red line), 42% pyridinic N (398.9 eV, green line), 11% protonated N (401.9 eV, light blue line) and 6 % pyridine N-oxide (402.9 eV, orange line).

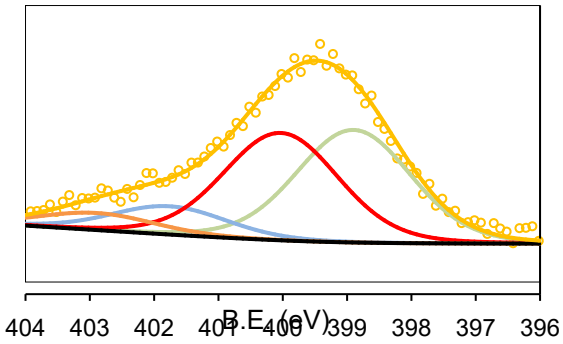
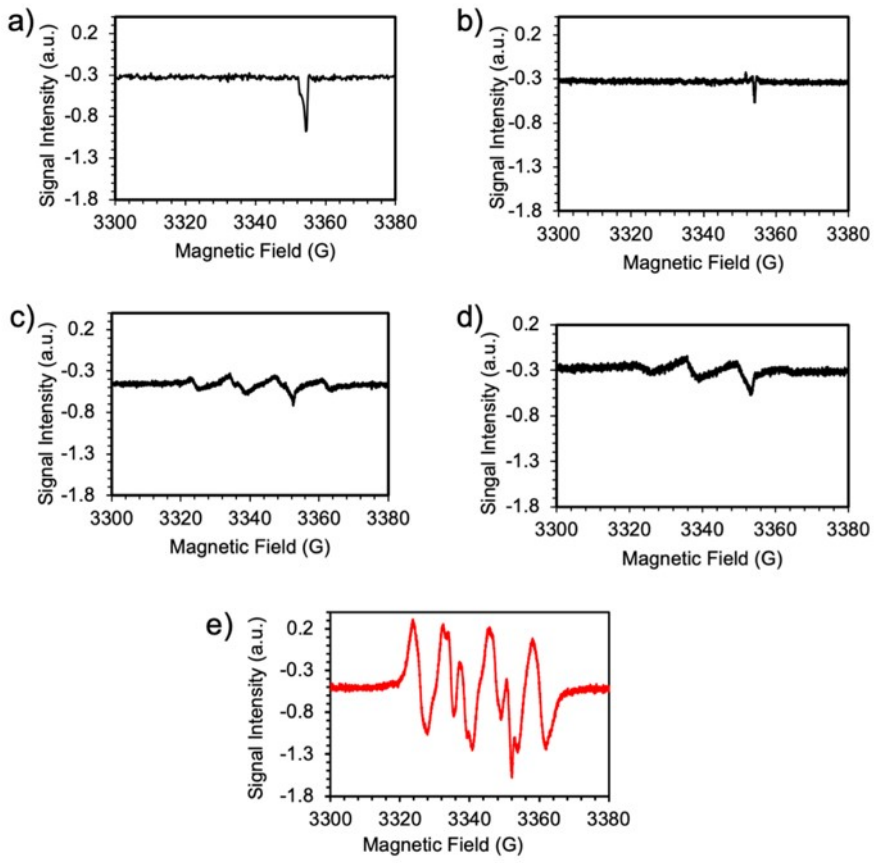


Fig. S18 EPR spectra of a) Au/PyEt-MSN in air, b) DMPO-Toluene mixture in air, and c) Au/PyEt-MSN with DMPO-Toluene under N_2, d) Au/MP-MSN with DMPO in air, and e) Au/PyEt-MSN with DMPO in air. All



samples contain the same amount of DMPO (0.62 mmol), and the same amount of catalyst (ca. 20 mg, except sample b that has no catalyst).

Fig. S19 Recycling of Au/PyEt-MSN.

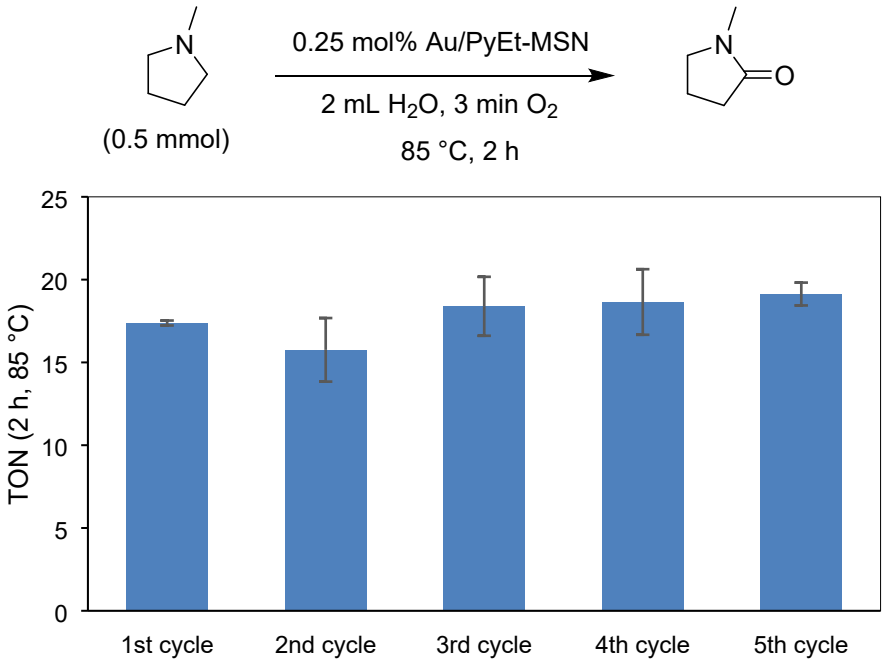


Fig. S20 XP spectrum of the spent Au/PyEt-MSN catalyst (bottom) compared to that of the fresh catalyst. A small shift of the Au 4f $_{7/2}$ peak to higher binding energy is observed. However, the spent catalyst still has a lower binding energy than bulk Au (discontinuous line at 83.9 eV) indicating that the it remains electron rich.

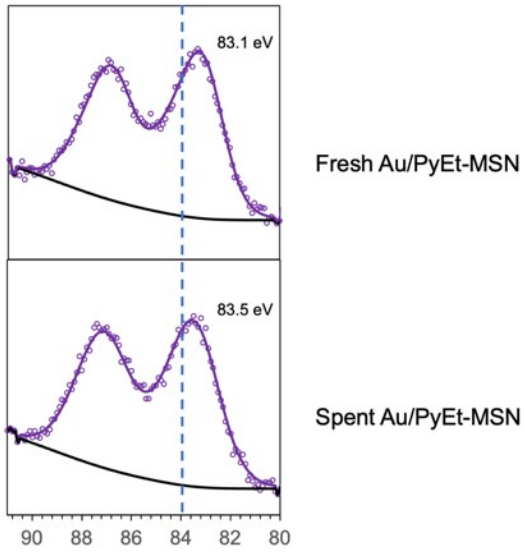
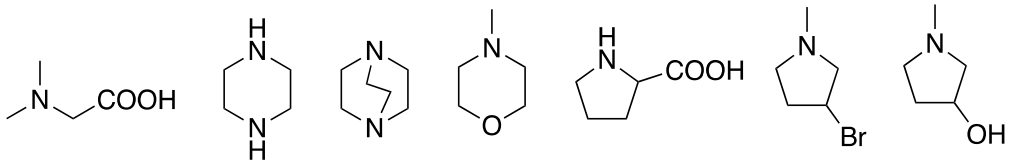
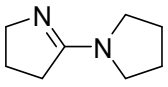
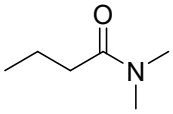


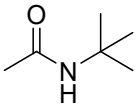
Fig. S21 Amines with different functional groups investigated as substrates for the Au/PyEt-MSN catalyzed aerobic oxidation. None of these substrates was converted to the corresponding amides under the standard reaction conditions (0.25 mol % catalyst, 2 mL H_2O, 100 °C, 6 h, 3 min O_2 overhead flow).

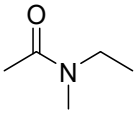


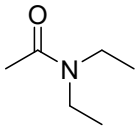
Characterization of Products.

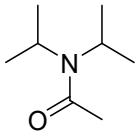
Product 1.  ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.61 (t, J = 7.0 Hz, 2H), 3.34 (t, 4H), 2.46 (t, J = 8.1 Hz, 2H), 1.92 (dt, J = 16.0, 7.6 Hz, 2H), 1.84 (t, 6.7 Hz, 4H). MS (EI): m/z = 138 [M^+].

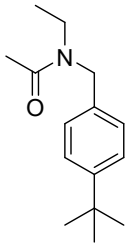
Product of reaction of 2.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.16 (s, 6H), 2.15 (t, J = 7.4 Hz, 2H), 1.76 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). MS (ESI): m/z = 118.1 [MH^+].

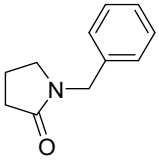
Product of reaction 5.  ^{1}H-NMR (600 MHz, D_2O): δ = 1.91 (s, 3H), 1.31 (s, 9H). MS (ESI): m/z = 118 [MH^+].

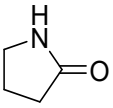
Product of reaction 6.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.05 (s, 3H), 2.85 (q, J = 7.2 Hz, 2H), 1.91 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H). MS (EI): m/z = 101 [M^+].

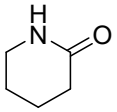
Product of reaction 7.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.31 (q, J = 7.3 Hz, 4H), 1.95 (s, 3H), 1.29 (t, J = 7.2 Hz, 6 H). MS (ESI): m/z = 118.1 [MH^+].

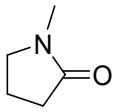
Product of reaction 8.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.46 (p, J = 6.5 Hz, 1H), 2.95 (q, J = 7.4 Hz, 1H), 2.22 (s, 3H), 1.22 (d, J = 6.5 Hz, 8H), 1.13 (t, J = 5.8 Hz, 4H). MS (ESI): m/z = 145.9 [MH^+].

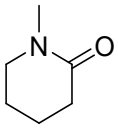
Product of reaction 11.  ^{1}H-NMR (600 MHz, D_2O): δ = 7.44-7.50 (m, 4H), 4.51 (s, 2H), 3.11 (q, J = 7.4 Hz, 2H), 2.22 (m, 2H), 1.28-1.33 (m, 12H). MS (ESI): m/z = 235.2 [MH^+].

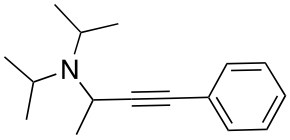
Product of reaction 12.  ^{1}H-NMR (600 MHz, D_2O): δ = 7.31-7.58 (m, 5H), 4.51 (s, 2H), 4.00 (s, 2H), 3.42 (t, 2H), 2.51 (t, 2H), 2.04 (q, 2H). MS (ESI): m/z = 176.1 [MH^+].

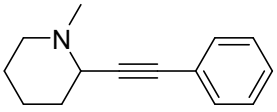
Product of reaction 13.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.42 (t, J = 7.1 Hz, 2H), 2.35 (t, J = 8.1 Hz, 2H), 2.13 (qd, 8.1, 6.8 Hz, 2H). MS (EI): m/z = 85 [M^+].

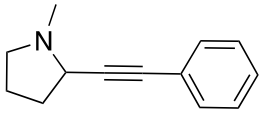
Product of reaction 14.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.20 (t, J = 5.7 Hz, 2H), 2.24 (t, J = 6.3 Hz, 2H), 1.51-1.63 (m, 4H). MS (EI): m/z = 99 [M^+].

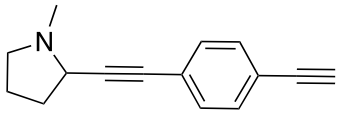
Product of reaction 15.  ^{1}H-NMR (600 MHz, D_2O): δ = 3.49 (t, 2H), 2.81 (s, 3H), 2.41 (t, J = 8.1 Hz, 2H), 2.03 (qd, J = 8.1, 6.9 Hz, 2H). MS (ESI): m/z = 100.1 [MH^+].

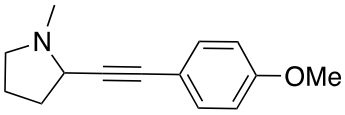
Product of reaction 16.  ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.30 (t, 2H), 2.96 (s, 3H), 2.39 (t, J = 6.1 Hz, 2H), 1.82 (m, 4H). MS (EI): m/z = 113 [M^+].

Product 17.  ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.26-7.36 (m, 2H), 7.18-7.22 (m, 3H), 4.08 (q, 1H), 3.25-3.33 (m, 2H), 1.05-1.33 (m, 15H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ = 20.45, 24.17, 26.66, 125.1, 127.68, 128.31, 131.57. MS (ESI): m/z = 230.2 [MH^+].

Product 18.  ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.25-7.43 (m, 5H), 3.52 (t, 1H), 2.60 (t, 1H), 2.36 (s, 3H), 2.34 (t, 1H), 1.86 (t, 1H), 1.79 (t, 1H), 1.64 (t, 1H), 1.57 (m, 2H), 1.43 (t, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 20.84, 25.72, 31.80, 44.43, 52.02, 54.81, 77.15, 86.35, 87.33, 123.4, 127.7, 128.2, 131.8. MS (EI): m/z = 199 [M^+].

Product 19.  ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.26-7.50 (m, 5H), 3.36 (t, J = 7.1 Hz, 1H), 2.94 (dt, J = 8.8 Hz and 3.9 Hz, 1H), 2.50 (s, 3H), 2.45 (q, J= 8.8 Hz, 1H), 2.18-2.23 (m, 1 H), 1.96-2.06 (m, 1 H), 1.79-1.83 (m, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 22.42, 32.26, 39.69, 54.70, 57.11, 83.67, 88.8, 123.1, 128.1, 128.3, 131.7. MS (EI): m/z = 185 [M^+].

Product 20.  ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.46 (s, 4H), 3.38 (t, 1H), 3.18 (s, 1H), 2.31-2.26 (m, 2H), 2.18 (s, 3H), 2.09-1.94 (m, 4H).^{13}C-NMR (400 MHz, $CDCl_3$): δ = 22.56, 30.94, 40.88, 54.88, 57.18, 77.97, 79.91, 82.40, 89.36, 122.7, 131.8. MS (ESI): m/z = 210 [MH^+].

Product 21.  ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.44 (d, 2H), 6.84 (d, 2H), 3.92 (s, 3H), 3.47 (t, 1H), 2.72 (t, 1H), 2.56 (t, 1H), 2.35 (m, 1H), 2.22 (m, 1H), 2.12 (m, 1H), 1.96 (m, 1H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 22.46, 33.66, 39.91, 54.56, 54.87, 57.18, 84.67, 87.17, 114.2, 115.4, 133.3, 160.3. MS (EI): m/z = 214 [M^+].