

Electronic Supplementary Information

Aerobic Oxidative Coupling of Alcohols and Amines over Au-Pd/resin in Water: Au/Pd Molar Ratios Switch the Reaction Pathways to Amides or Imines

Leilei Zhang,^{a,b} Wentao Wang,^a Aiqin Wang,^a Yitao Cui,^c Xiaofeng Yang,^a Yanqiang Huang,^a Xiaoyan Liu,^a Wengang Liu,^b Jin-Young Son,^c Hiroshi Oji,^c and Tao Zhang^{*,a}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, 116023, China.

^b University of Chinese Academy of Sciences, Beijing, 100049, China.

^c Industrial Application Division, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan.

*Corresponding author. Email: taozhang@dicp.ac.cn

Contents:

1. General remarks	3
2. Preparation of Au-Pd/resin.....	4
3. General procedure for amidation over Au ₆ Pd/resin.	5
4. General procedure for imination over AuPd ₄ /resin.	5
5. Detailed optimization of reaction conditions and catalyst.	6
6. Gram-scale experiment.	8
7. Control experiments	8
8. Control experiments with 2-buten-1-ol and aniline as the substrates.....	9
9. Identification of the obtained products by NMR:	20
10. Copy of ¹ H NMR and ¹³ C NMR spectra for products.....	31

1. General remarks

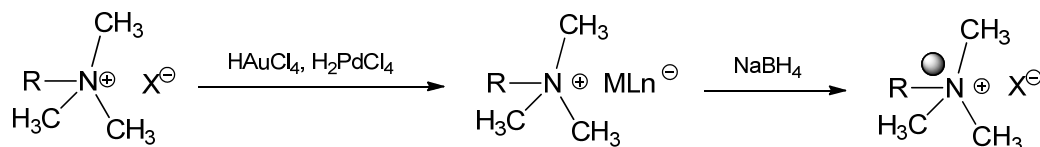
Reactions were carried out using commercially available reagents in over-dried apparatus. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F₂₅₄ plates and visualized under UV (254 nm) and/or by staining with KMnO₄. ¹H NMR spectra were recorded on commercial instruments (500 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ¹³C NMR spectra were collected on commercial instruments (125 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl₃, δ = 77.0). The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was tested on an IRIS Intrepid II XSP instrument (Thermo Electron Corp.). X-ray power diffraction (XRD) analysis was carried out on a PANalytical X'pert diffractometer using nickel-filtered Cu Kα radiation with a scanning angle (2θ) of 10°-80°, operated at 40kV and 40mA. HAADF-STEM was carried out with a Tecnai G2 Spirit (FEI) microscope operating at 200 kV. Prior to observations, powder sample of the catalyst was ultrasonicated in ethanol and dispersed on copper grids covered with a holey carbon film and dried at room temperature. Au and Pd core level spectra usually overlapped to each other in low binding energy region, which is difficult to distinguish them with lab XPS. To solve the problem, hard x-ray photoemission spectroscopy (HAXPES) was used to distinguish Au and Pd core level spectra in high binding energy region, since high excitation energy of several kilo-electronvolt can probe deeper core levels. The HAXPES characterization was performed using a SCIENTA R-4000 hemispherical electron energy analyzer at BL46XU of SPring-8 in Japan. The excitation energy used for HAXPES was monochromatized with Si (111) double crystal and Si (444) channel-cut monochromators. The photon energy and total energy resolution of the HAXPES measurements estimated from the Fermi edge of gold as a standard sample were 7938.95 eV and 235 meV, respectively. The composite samples were placed on a sample holder with a carbon conductive tape in an Ar-filled glove box. The sample holder was introduced into a load-lock chamber using a transfer vessel without air exposure. After reaching the pressure of the load-lock chamber to be < 10⁻⁶ Torr, the samples were transferred to a measurement chamber. The base pressure of the measurement chamber was mainly kept to ~5.0 × 10⁻⁸ Torr during the measurements. In order to remove the charging effects on the samples, both an electron flood gun and a beam attenuator were used. The binding energy of core levels were calibrated with careful measurement of C 1s spectra.

Aqueous solutions of HAuCl₄ with mass concentration of 9.56 mg_{Au}/mL and H₂PdCl₄ with concentration of 12.00 mg_{Pd}/mL were prepared. The water used in this study was deionized by milli-Q Plus system, having 18.2 MΩ electrical resistivity.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Au-Pd/resin catalyst



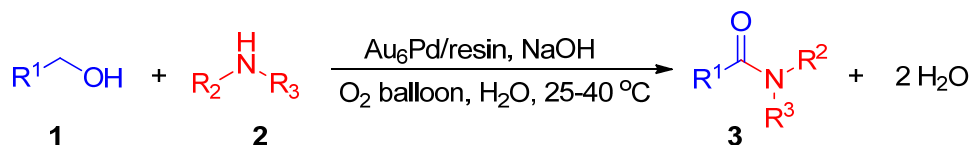
717# anion exchange resin was washed by water several times until the washed water became clean. After dried at 60 °C, the recovered resin was crushed with a ball mill at 250 rpm for 1 h and was sieved, particles between 100 mesh and 180 mesh were used as catalyst support. The support resin was soaked sequentially in 1.0 mol/L NaOH, 1.0 mol/L HNO₃, 1.0 mol/L NaOH for 8 h, and then soaked in 2.0 mol/L K₂CO₃ solution for 24 h. The resin was then filtered and washed with water until the filtrate was neutral and then dried under vacuum at 60 °C for 12 h.

Anion-exchange resin supported Au-Pd nanoparticles were prepared with anion exchange-NaBH₄ reduction method. Specifically, 1.92 mL 9.56 mg_{Au}/mL HAuCl₄ solution and 0.14 mL 12.00 mg_{Pd}/mL H₂PdCl₄ were added to 200 mL water, followed by addition of 1.0 g support and stirred for 2 h under dark. The mixture was filtered and washed with 300 mL water before re-dispersion in 30.0 mL water, and followed by addition of 15.0 mL NaBH₄ (10.0 equiv) solution. The mixture turned immediately from orange to dark brown. After being stirred under dark for another 0.5 h, the catalyst was filtered and washed with plentiful water until no Cl⁻ was detected and then dried at 60 °C for 8 h under vacuum. The prepared catalyst was denoted as Au₆Pd/resin. Catalysts with different Au/Pd molar ratios were synthesized with the same method except for different volume of precursor solutions. For all the catalysts with different Au/Pd molar ratios, the total metal loading determined by ICP-AES was 2.0 wt%. The ICP-AES results are shown in Table S1.

Table S1. Chemical compositions of the Au-Pd/resin catalysts

Sample	Nominal loading(%)		Actual loading(%)		Au/Pd (molar ratio)
	Au	Pd	Au	Pd	
Au	2.0	—	1.99	—	—
Au ₁₀ Pd	1.89	0.10	1.88	0.10	10.2
Au ₆ Pd	1.84	0.17	1.82	0.16	6.1
Au ₂ Pd	1.58	0.43	1.57	0.41	2.1
AuPd ₂	0.97	1.04	0.96	0.97	1.9
AuPd ₄	0.63	1.37	0.63	1.29	3.8

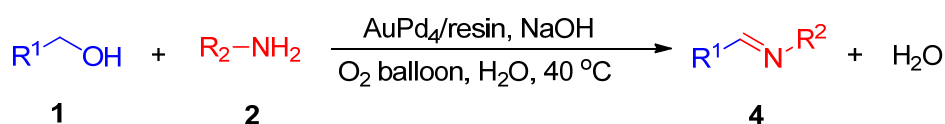
3. General procedure for amidation over Au₆Pd/resin.



Unless otherwise noted, reactions were carried out as following: a mixture of alcohol **1** (1.00 mmol, 2.0 equiv), amine **2** (0.50 mmol, 1.0 equiv), sodium hydroxide (0.55 mmol in 1.0 mL H₂O, 1.1 equiv) and Au₆Pd/resin (90 mg, 2 mol%) were vigorously stirred at 40 °C for 12 h under oxygen balloon. After cooling down to room temperature, the catalyst was separated by filtration and washed with ethyl acetate (15.0 mL). After adding 10.0 mL H₂O, the filtrate was extracted with ethyl acetate (3 x 15.0 mL). The combined organic layer was washed by saturated NaCl solution and dried over anhydrous magnesium sulfate and the solvent was removed under vacuum. The residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 10:1, 2:1, or 1:1) to afford the corresponding amide **3**.

The amount of Au-Pd/resin catalyst employed in the reaction was calculated based on the total moles of the two metals (Au+Pd). Take Au₆Pd/resin for example, for 1.0 g Au₆Pd/resin catalyst, the total moles of the two metals were calculated as follows: 1 g * 1.82 wt% / 197.0 g/mol + 1 g * 0.16 wt% / 106.4 g/mol = 0.107 mmol. For 0.5 mmol substrate, the weight of Au₆Pd/resin was 0.5 mmol * 2% / 0.107 mmol/g = 0.093 g.

4. General procedure for imination over AuPd₄/resin.



Unless otherwise noted, imination reactions were carried out as following: a mixture of alcohol **1** (0.75 mmol), amine **2** (0.50 mmol), sodium hydroxide (0.75 mmol in 1.0 mL H₂O) and AuPd₄/resin (93 mg, 3 mol%) were vigorously stirred at 40 °C for 12 h under oxygen balloon. After cooling down to room temperature, the catalyst was separated by filtration and washed with ethyl acetate (15.0 mL). After adding 10.0 mL H₂O, the filtrate was extracted with ethyl acetate (3 x 15.0 mL). The combined organic layer was washed by saturated NaCl solution and dried over anhydrous magnesium sulfate and the solvent was removed under vacuum. The residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate/triethylamine = 10:1:0.1) to afford the corresponding imine **4**.

5. Detailed optimization of reaction conditions and catalyst.

Table S2. Optimization of base for oxidative coupling of benzyl alcohol and aniline over Au/resin.

c1ccc(cc1)CO + Nc1ccccc1 $\xrightarrow{\text{Au/resin}}$ O=C(Nc1ccccc1)c2ccccc2

1a **2a** **3a**

Entry ^a	1a : 2a (equiv)	Base	T (°C)	t (h)	Yield of 3a (%) ^b
1	2:1	KOH	25	2	53
2	2:1	NaOH	25	2	53
3	2:1	K ₂ CO ₃	25	2	6
4	2:1	Na ₂ CO ₃	25	2	7
5	2:1	LiOH	25	2	50
6	2:1	(NH ₄) ₂ CO ₃	25	2	2

^a Reaction conditions: **2a** (1.1 mmol), **1a** (2.2 mmol), base (1.2 mmol), Au/resin (46 mg, 0.45 mol%), 2 mL H₂O, O₂ balloon, 25 °C, 2 h. ^b Determined by GC using 1,3,5-trimethylbenzene as an internal standard.

Table S3. Optimization of substrate ratios for oxidative coupling of benzyl alcohol and aniline over Au/resin.

c1ccc(cc1)CO + Nc1ccccc1 $\xrightarrow{\text{Au/resin}}$ O=C(Nc1ccccc1)c2ccccc2

1a **2a** **3a**

Entry ^a	1a : 2a (equiv)	T (°C)	t (h)	Yield of 3a (%) ^b
1	2:1	25	2	53
2	1.5:1	25	2	51
3	1:1	25	2	48
4	1:1.5	25	2	45
5	1:2	25	2	44

^a Reaction conditions: **2a**, **1a**, NaOH (2.2 mmol), Au/resin (46 mg, 0.45 mol%), 2 mL H₂O, O₂ balloon, 25 °C, 2 h, 1 equiv = 1.1 mmol. ^b Determined by GC using 1,3,5-trimethylbenzene as an internal standard.

Table S4. Optimization of the amount of NaOH and H₂O for oxidative coupling of benzyl alcohol and aniline over Au/resin.

c1ccc(cc1)CO + Nc1ccccc1 $\xrightarrow{\text{Au/resin}}$ O=C(Nc1ccccc1)c2ccccc2

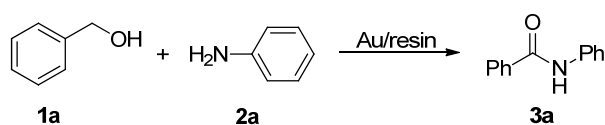
1a **2a** **3a**

Entry ^a	Base (equiv)	H ₂ O (mL)	Yield of 3a (%) ^b
1	NaOH (2.2)	2	46
2	NaOH (0.8)	2	50

3	NaOH (0.55)	2	28
4	NaOH (0)	2	0
5	NaOH (1.1)	1	41
6	NaOH (1.1)	2	53
7	NaOH (1.1)	3	40
8	NaOH (1.1)	5	44

^a Reaction conditions: **2a** (1.1 mmol), **1a** (2.2 mmol), NaOH, Au/resin (45 mg, 0.45 mol%), H₂O, O₂ balloon, 25 °C, 2 h, 1 equiv=1.1 mmol. ^b Determined by GC using 1,3,5-trimethylbenzene as an internal standard.

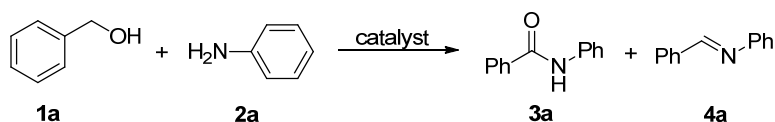
Table S5. Optimization of reaction temperature, and reaction atmosphere for oxidative coupling of benzyl alcohol and aniline over Au/resin.



Entry ^a	T(°C)	Cat. (mol%)	t (h)	Atmosphere	Solvent	Yield of 3a (%) ^b
1	25	0.45	6	air	H ₂ O	59
2	25	0.45	2	Ar	H ₂ O	No reaction
3	40	0.45	2	O₂	H₂O	61
4	50	0.45	2	O ₂	H ₂ O	58

^a Reaction conditions: **2a** (1.1mmol), **1a** (2.2 mmol), NaOH (1.2 mmol), Au/resin (45 mg, 0.45 mol%), 2 mL H₂O, O₂ balloon. ^b Determined by GC using 1,3,5-trimethylbenzene as an internal standard.

Table S6. Optimization of the catalysts for oxidative coupling of benzyl alcohol and aniline.



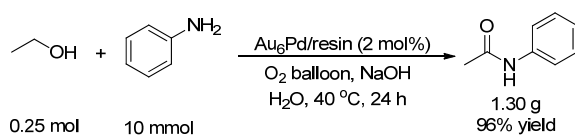
Entry ^a	Catalysts	Conversion (%) ^c	Selectivity (%) ^c	
			3a	4a
1	Au/resin	47	93	6
2	Au ₁₀ Pd/resin	63	91	8
3	Au₆Pd/resin	77	97	2
4	Au ₂ Pd/resin	51	71	28
5 ^b	AuPd/resin	75	77	22
6 ^b	AuPd ₂ /resin	60	32	67
7 ^b	AuPd ₄ /resin	42	5	94
8 ^b	Pd/resin	16	0	99

^a Reaction conditions: **2a** (1.1mmol), **1a** (2.2 mmol), NaOH (1.2 mmol), catalyst (0.45 mol%), 2 mL H₂O, O₂ balloon, 25 °C, 2 h. ^b **1a** (1.0 mmol), **2a** (0.5 mmol), catalyst (2 mol%), 1 mL H₂O, 5 h. ^c Determined by GC using 1,3,5-trimethylbenzene as an internal standard.

Table S7. Optimized reaction conditions for amidation and imination.

Entry	1a : 2a (mmol)	Catalyst	NaOH (mmol)	T (°C)	t (h)	Atmosphere	H ₂ O (mL)	Isolated yield (%)	
								3a	4a
1	1.0:0.5	Au ₆ Pd/resin (2 mol%)	0.55	40	12	O ₂ balloon	1	91	—
2	0.75:0.5	AuPd ₄ /resin (3 mol%)	0.55	40	12	O ₂ balloon	1	—	80

6. Gram-scale experiment.



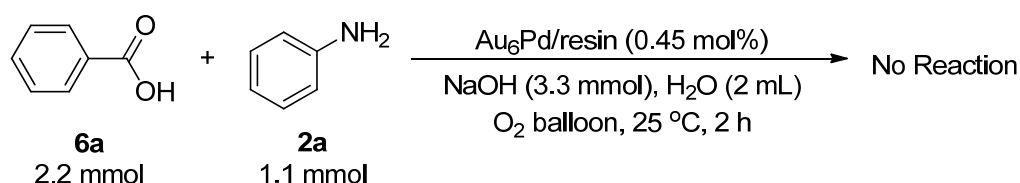
Scheme S1. Gram-scale experiment of amidation with aniline and ethanol over Au₆Pd/resin.

7. Control experiments

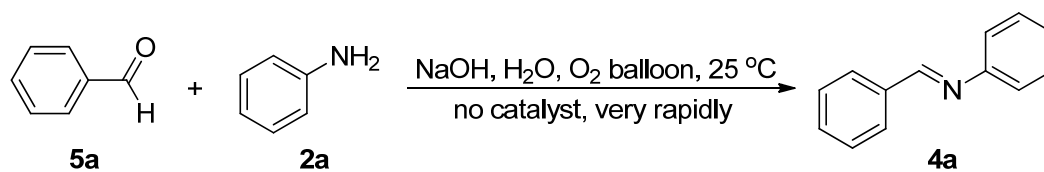
Table S8. Oxidation of benzyl alcohol over different catalysts.

Catalysts	Conversion(%) ^b	Selectivity(%) ^b		
		5a	6a	7a
Au/resin	95	3	65	32
Au ₆ Pd/resin	>99	0	60	40
AuPd ₂ /resin	>99	13	68	19
Pd/resin	40	24	74	2

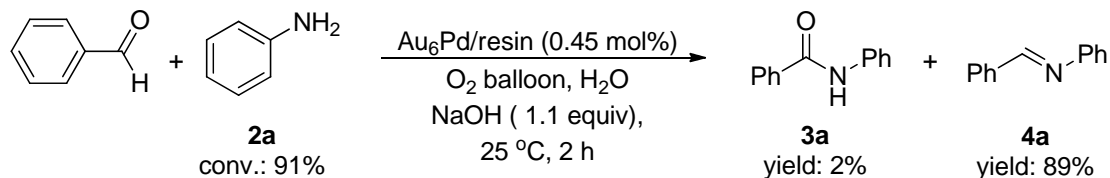
^a Reaction conditions: **1a** (1.0 mmol), NaOH (1.1 mmol), H₂O (2 mL), O₂ balloon, 25 °C, 2 h. ^b Determined by GC using 1,3,5-trimethylbenzene as an internal standard.



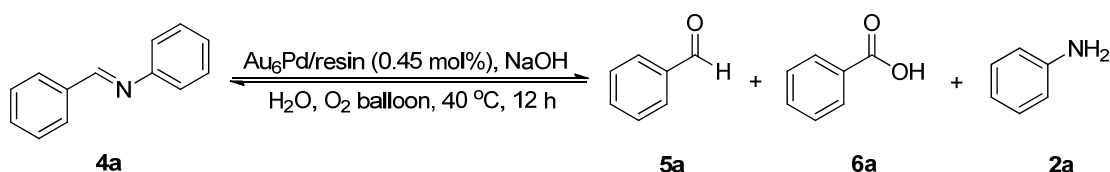
Scheme S2. The reaction from benzoic acid and aniline over Au₆Pd/resin.



Scheme S3. The reaction from benzaldehyde and aniline without Au-Pd/resin.



Scheme S4. The reaction from benzaldehyde and aniline over Au₆Pd/resin.



Scheme S5. The reaction of N-benzylideneaniline over Au₆Pd/resin.

The coupling reaction of benzoic acid and aniline did not proceed over Au₆Pd/resin at all. Benzaldehyde condensed rapidly with aniline to yield N-benzylideneaniline without Au₆Pd/resin while accompanied by little of N-phenylbenzamide when Au₆Pd/resin was added. The condensation reaction of benzaldehyde and aniline is reverse. Using Au₆Pd/resin as a catalyst, the N-benzylideneaniline **4a** decomposed into benzaldehyde **5a**, benzoic acid **6a**, aniline **2a**, and the amide **3a** was not detected.

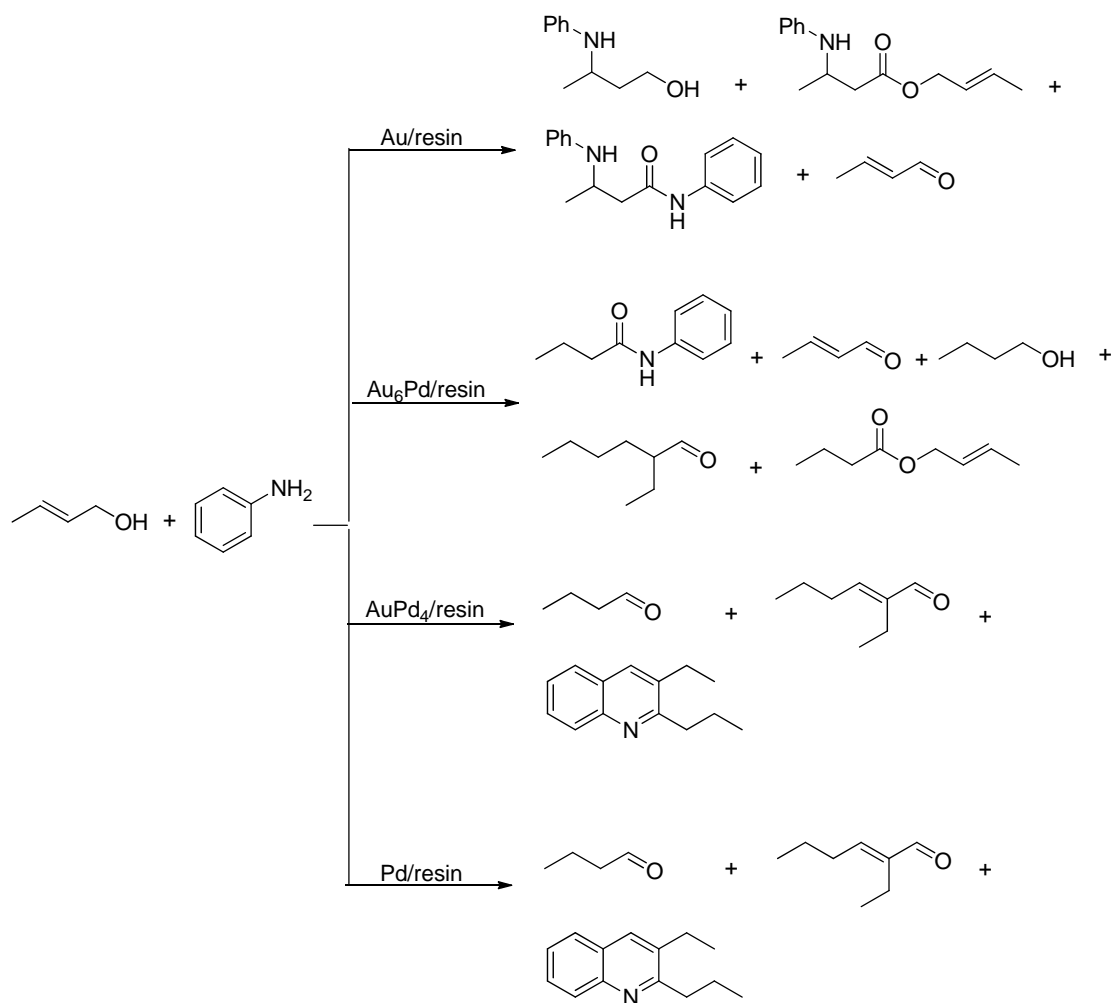
8. Control experiments with 2-buten-1-ol and aniline as the substrates.

Table S9. Oxidation coupling of 2-buten-1-ol and aniline over different catalysts.

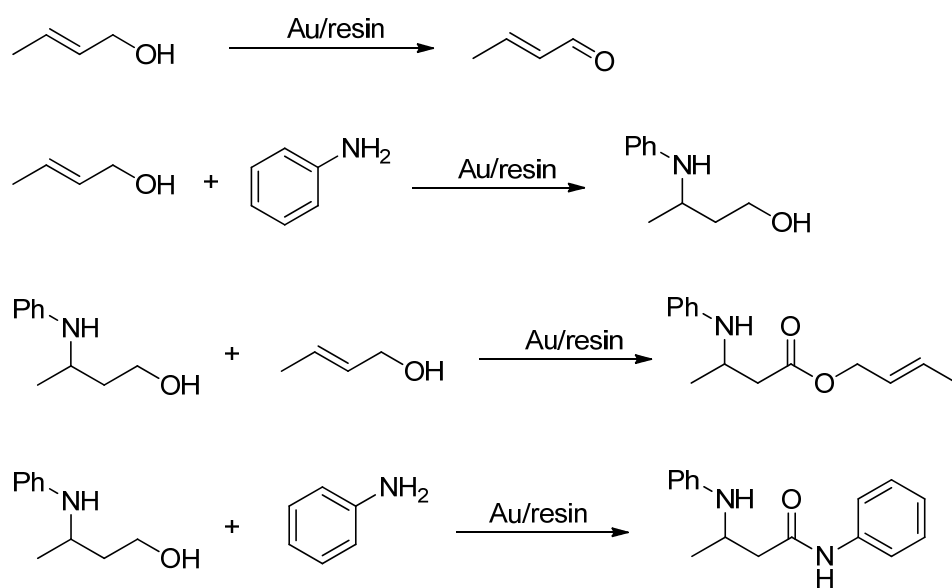
Catalysts	Products			
	Au/resin	Au ₆ Pd/resin	AuPd ₄ /resin	Pd/resin
Conversion(%) ^a	>99	>99	89	88

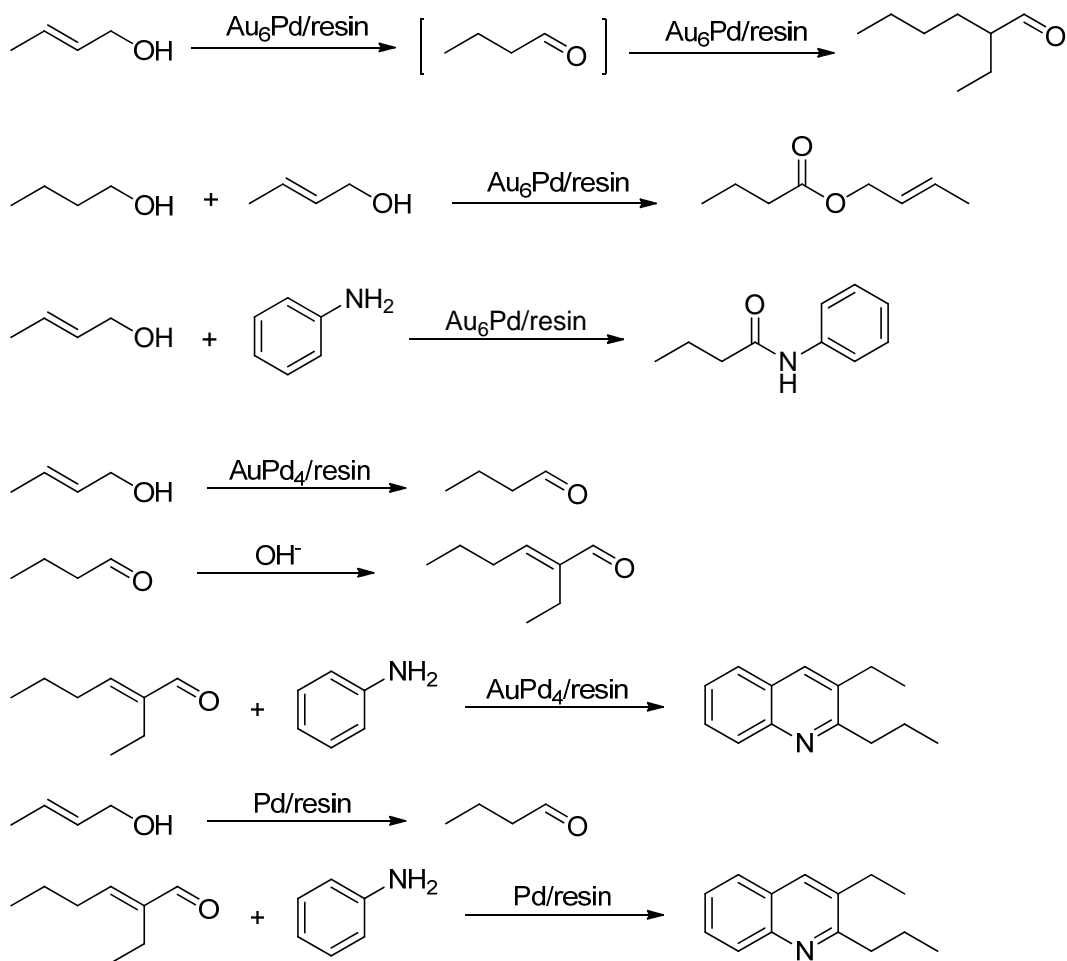
^a Determined by GC using 1,3,5-trimethylbenzene as an internal standard and calculated based on aniline.

Products of oxidation coupling of 2-buten-1-ol and aniline over different catalyst:



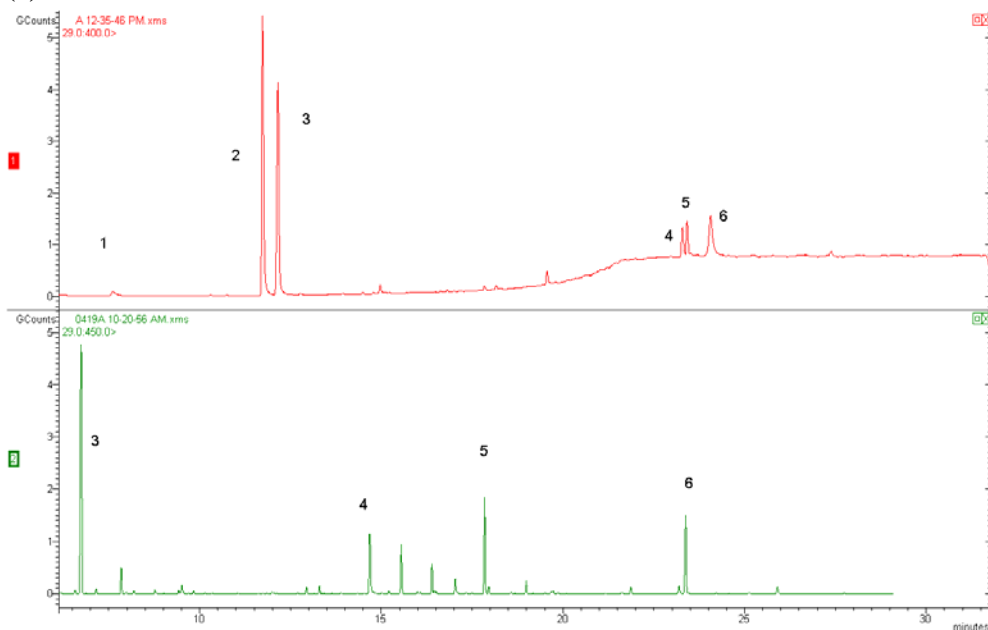
Possible reaction pathways:



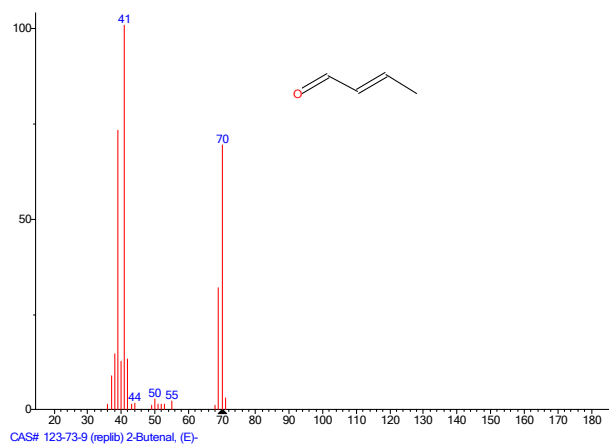


GC-MS spectra of the crude reaction mixtures:

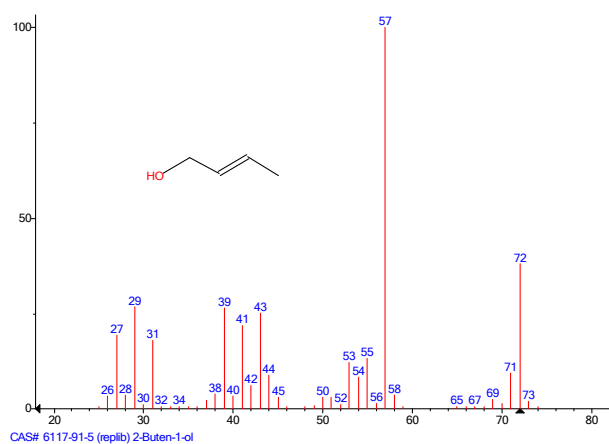
(a) Au/resin



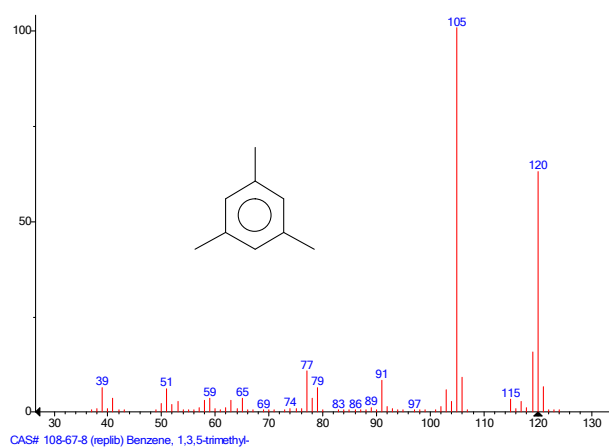
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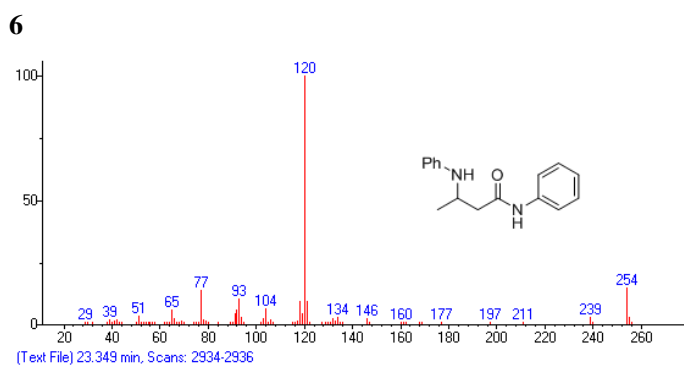
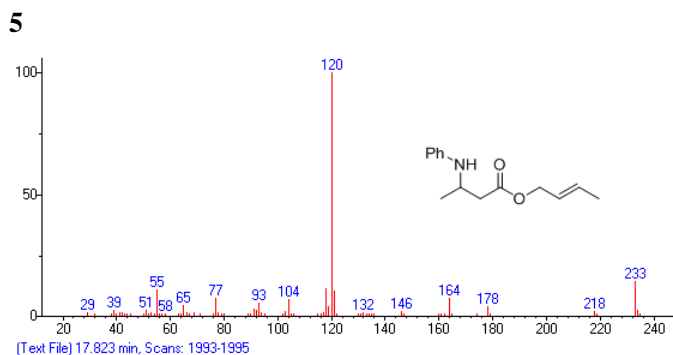
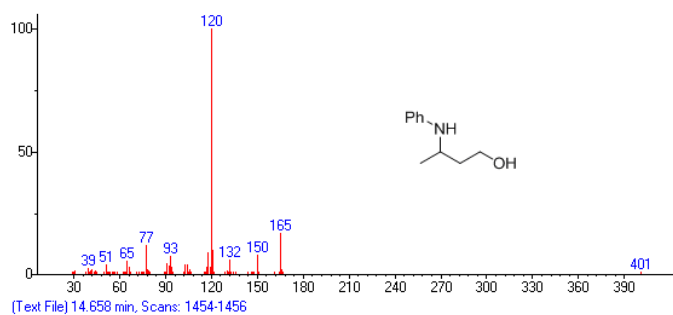
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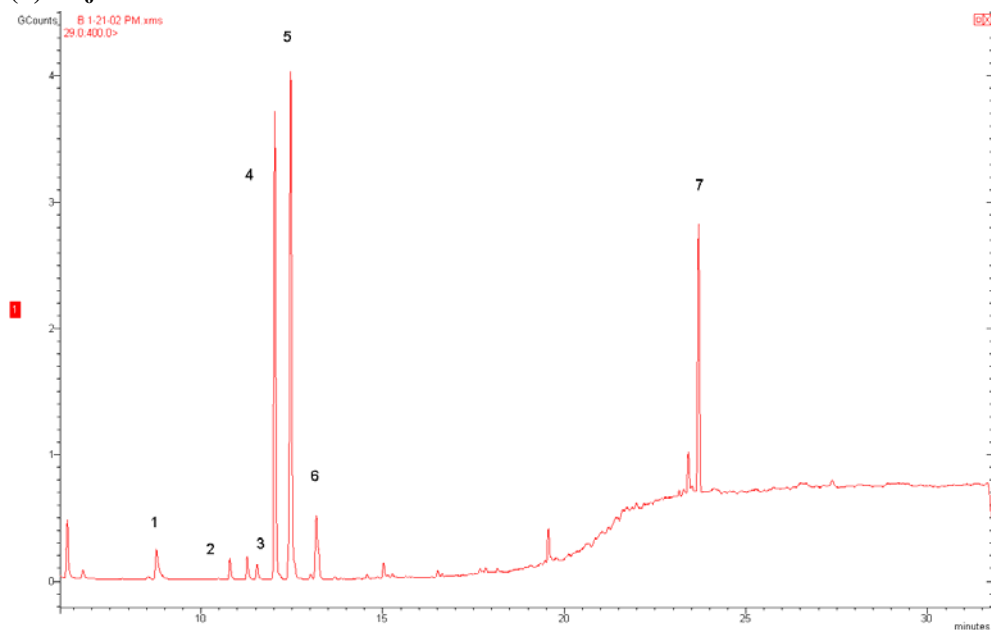
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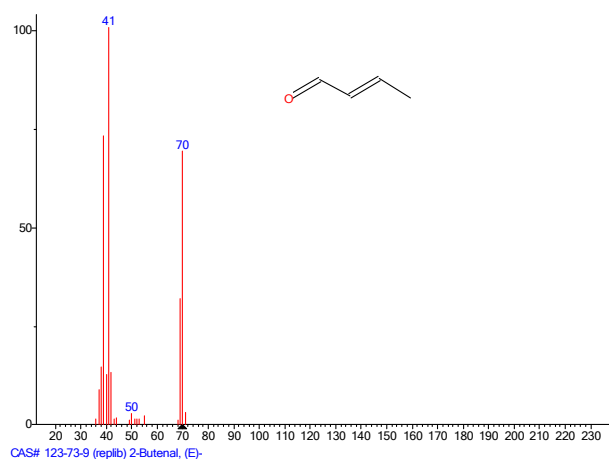
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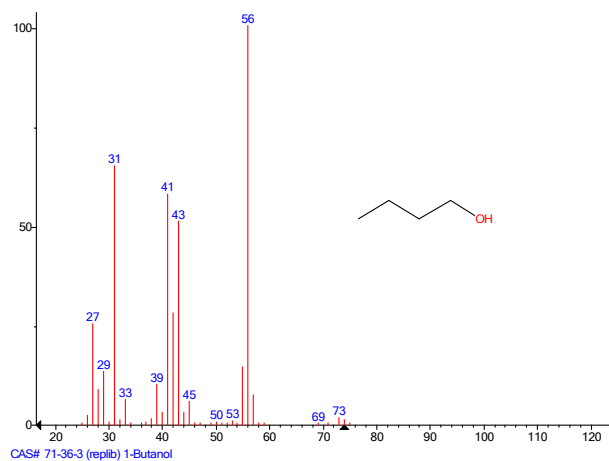
(b) Au₆Pd/resin



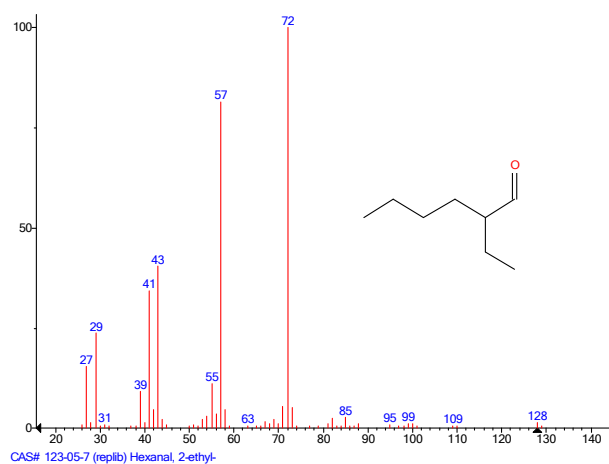
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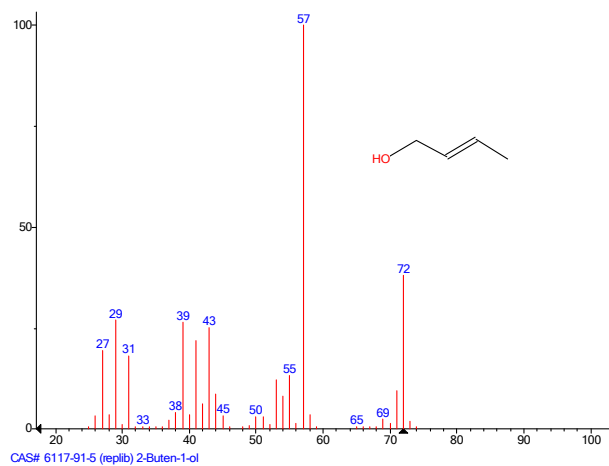
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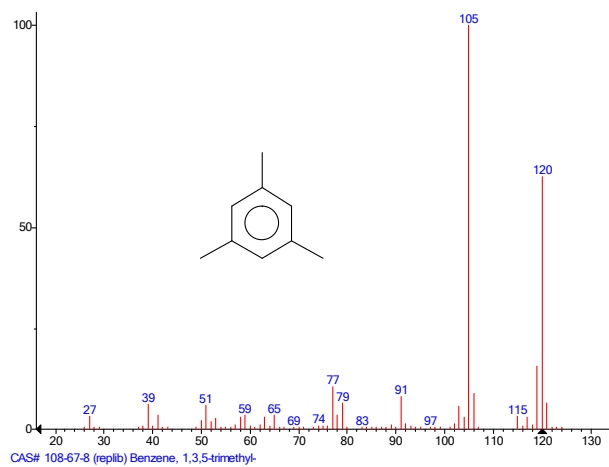
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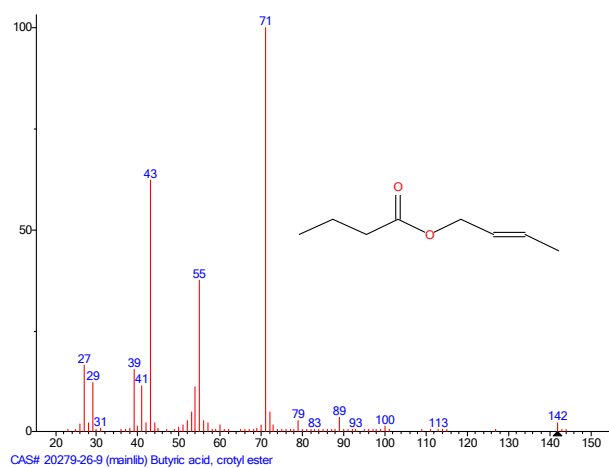
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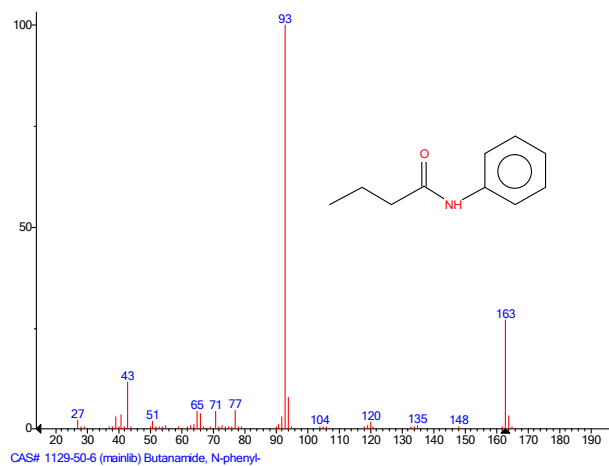
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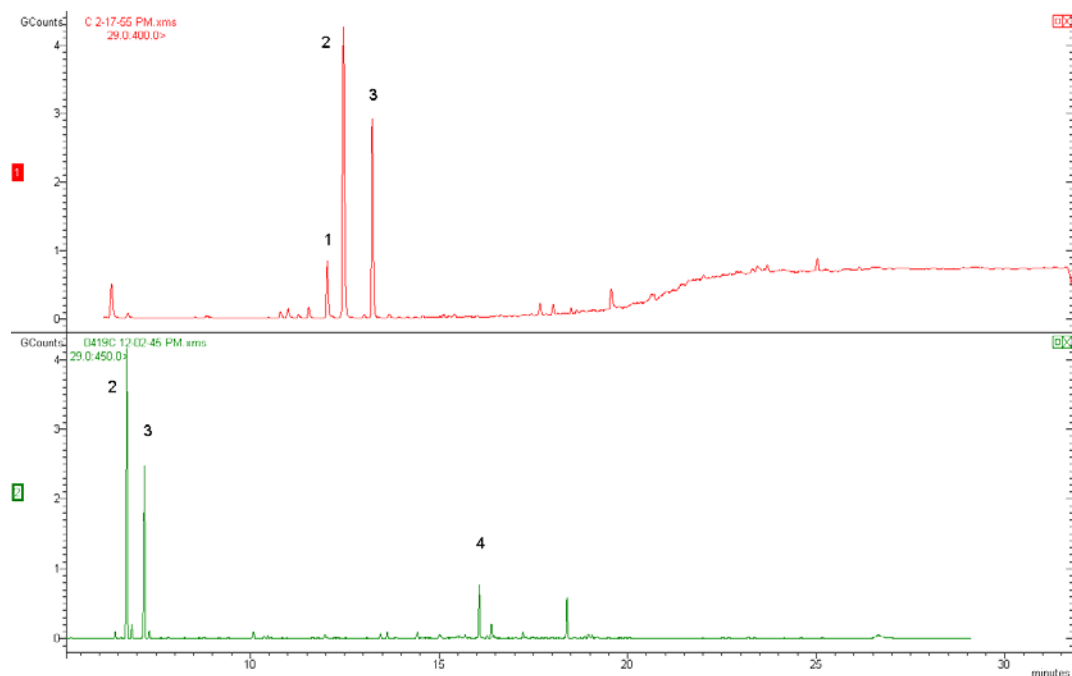
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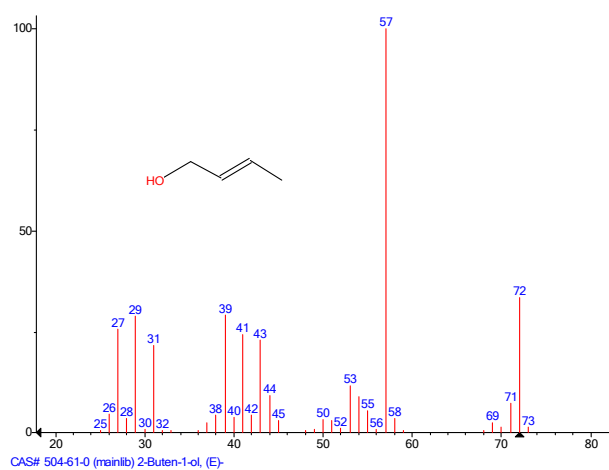
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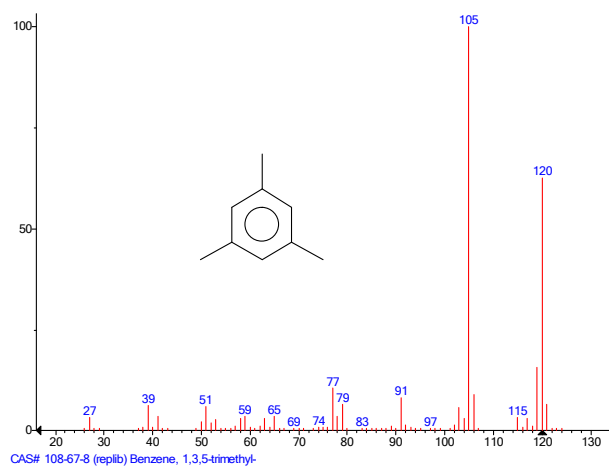
(c) AuPd₄/resin



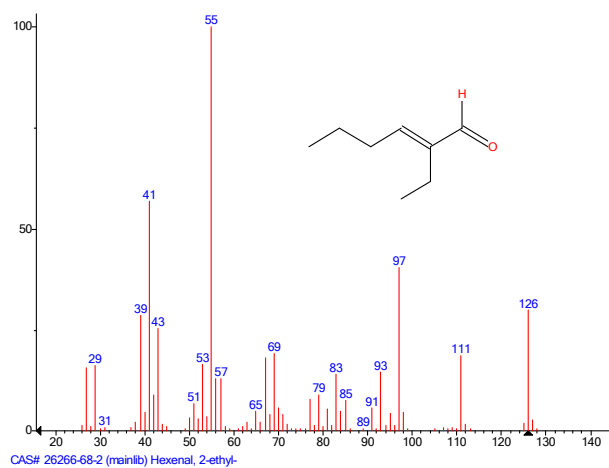
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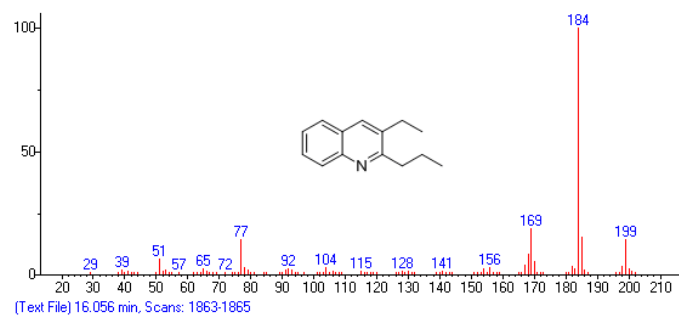
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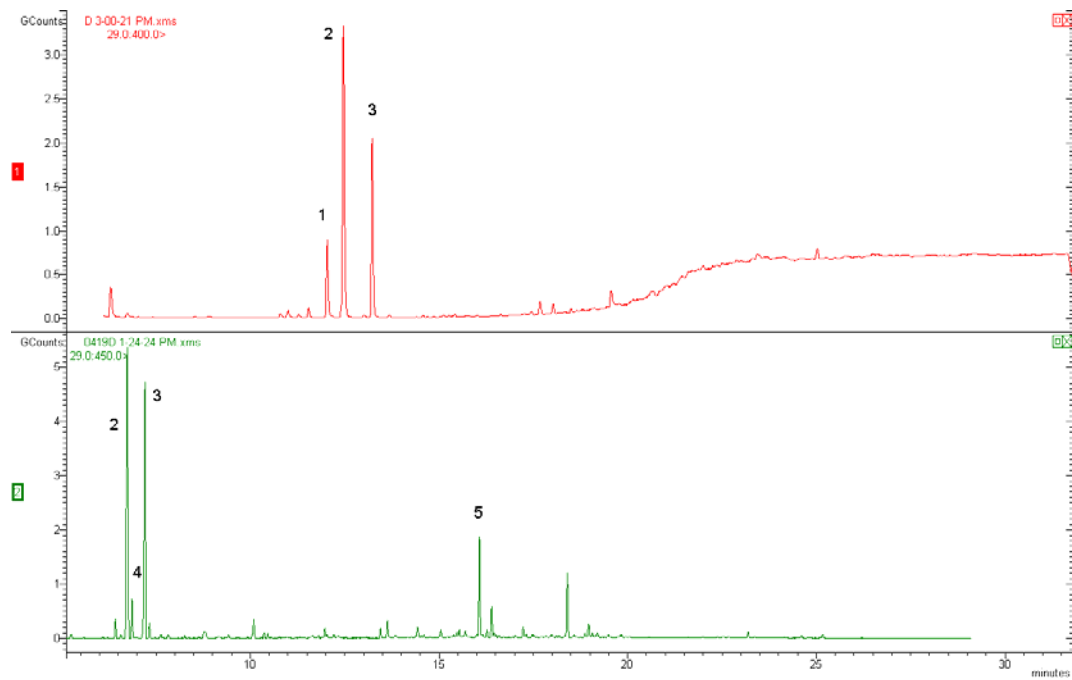
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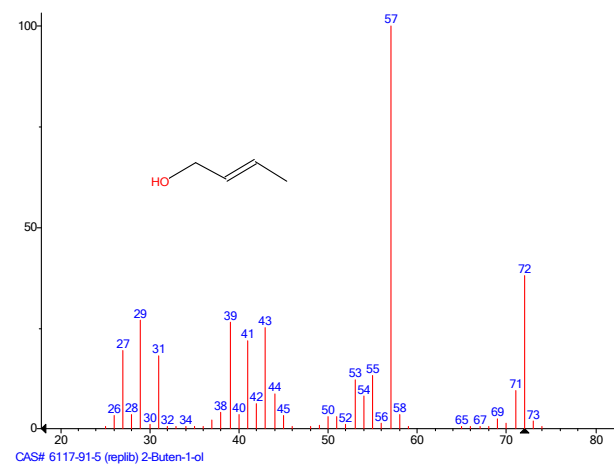
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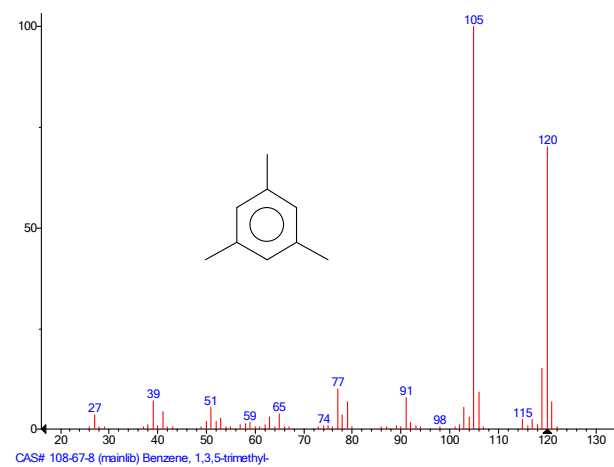
(d) Pd/resin



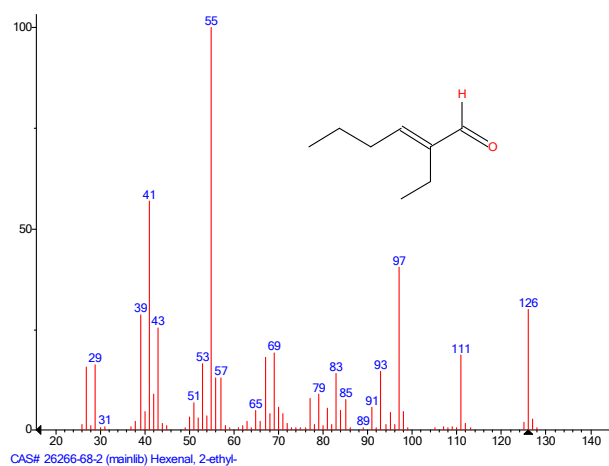
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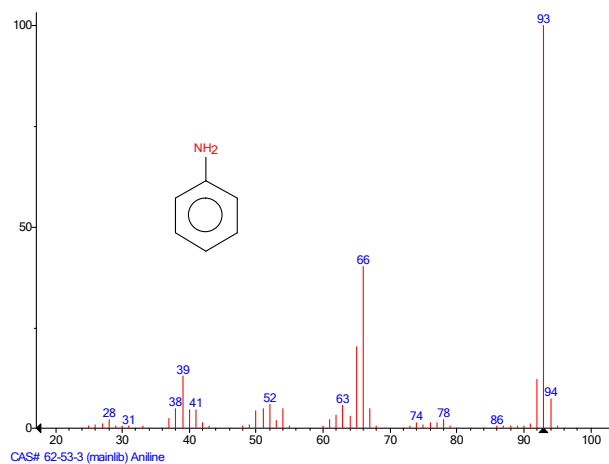
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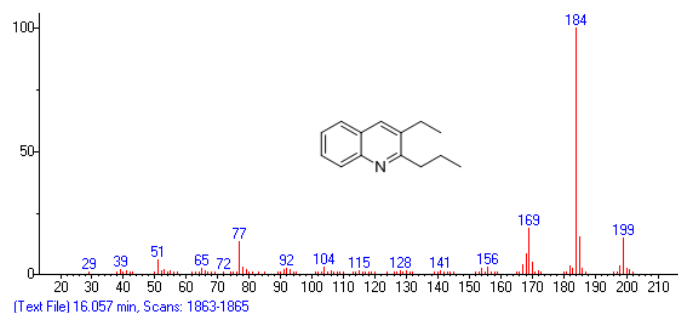
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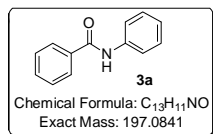
4



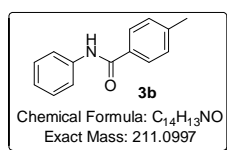
5



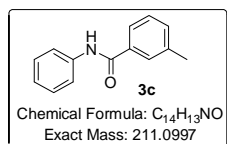
9. Identification of the obtained products by NMR:



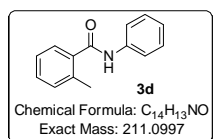
N-phenylbenzamide 3a: The reaction was carried out according to the general procedure with phenylmethanol (108.0 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a white solid (89.5 mg, 91% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 (d, $J = 7.3$ Hz, 2H), 7.64 (d, $J = 7.9$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.90, 138.07, 135.16, 131.97, 129.23, 128.92, 127.16, 124.71, 120.36 ppm.



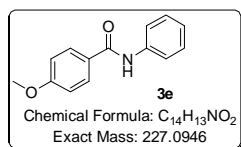
4-methyl-N-phenylbenzamide 3b: The reaction was carried out according to the general procedure with *p*-tolylmethanol (122.1 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a white solid (100.8 mg, 96% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.25 (d, $J = 7.8$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.85, 142.47, 138.19, 132.24, 129.54, 129.18, 127.17, 124.54, 120.33, 21.61 ppm.



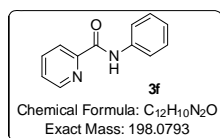
3-methyl-N-phenylbenzamide 3c: The reaction was carried out according to the general procedure with *m*-tolylmethanol (268.4 mg, 2.2 mmol, 2.0 equiv) and aniline (102.3 mg, 1.1 mmol, 1.0 equiv) by 1 mol% Au_6Pd /resin catalyst for 8 h. The product was obtained as a white solid (191.7 mg, 83% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.71 – 7.59 (m, 4H), 7.34 (m, 4H), 7.13 (t, $J = 7.4$ Hz, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.14, 138.78, 138.14, 135.11, 132.67, 129.17, 128.73, 127.93, 124.60, 124.10, 120.35, 21.49 ppm.



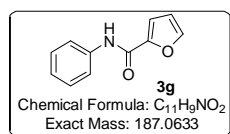
2-methyl-N-phenylbenzamide 3d: The reaction was carried out according to the general procedure with *o*-tolylmethanol (122.1 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au_6Pd /resin catalyst for 24 h. The product was obtained as a white solid (75.3 mg, 71% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.52 (s, 1H), 7.47 (d, $J = 7.4$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 3H), 7.25 (dd, $J = 11.6, 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.19, 138.10, 136.58, 131.41, 130.43, 129.25, 126.72, 126.04, 124.69, 119.98, 19.95 ppm.



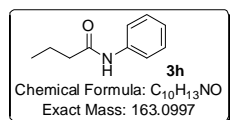
4-methoxy-N-phenylbenzamide 3e: The reaction was carried out according to the general procedure with (4-methoxyphenyl)methanol (138.1 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a white solid (107.8 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.76 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 165.35, 162.64, 138.25, 129.22, 129.03, 127.32, 124.49, 120.28, 114.14, 55.62 ppm.



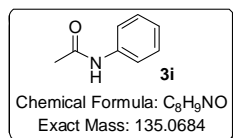
N-phenylpicolinamide 3f: The reaction was carried out according to the general procedure with pyridin-2-ylmethanol (239.8 mg, 2.2 mmol, 2.0 equiv) and aniline (102.3 mg, 1.10 mmol, 1.0 equiv) by 1 mol% Au₆Pd/resin catalyst for 12 h. The product was obtained as a yellow solid (206.4 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 10.03 (s, 1H), 8.61 (d, *J* = 4.7 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.79 (t, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 7.2, 5.1 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 162.11, 149.96, 148.09, 137.88, 137.80, 129.21, 126.56, 124.43, 122.53, 119.81 ppm.



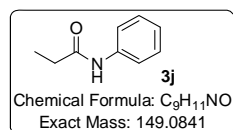
N-phenylfuran-2-carboxamide 3g: The reaction was carried out according to the general procedure with furan-2-ylmethanol (98.0 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 18 h. The product was obtained as a brown solid (62.5 mg, 67% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 3.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.57 – 6.52 (m, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 156.20, 147.96, 144.29, 137.51, 129.23, 124.65, 120.05, 115.38, 112.75 ppm.



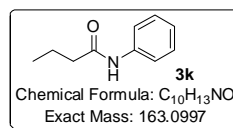
N-phenylbutyramide 3h: The reaction was carried out according to the general procedure with (*E*)-but-2-en-1-ol (540.8 mg, 7.5 mmol, 15.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (43.5 mg, 53% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.74 (dt, *J* = 16.5, 8.2 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.47, 138.11, 131.07, 129.09, 124.28, 119.93, 39.80, 19.20, 13.88 ppm.



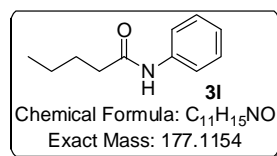
N-phenylacetamide 3i: The reaction was carried out according to the general procedure with ethanol (1.15 g, 25.0 mmol, 50.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 18 h. The product was obtained as a white solid (67.3 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 8.0 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 2.16 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 168.61, 138.05, 129.09, 124.42, 120.07, 24.68 ppm.



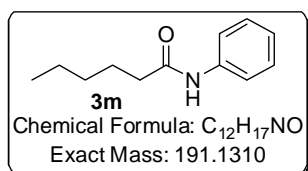
N-phenylpropionamide 3j: The reaction was carried out according to the general procedure with propan-1-ol (751.3 mg, 12.5 mmol, 25.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (70.2 mg, 94% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.45 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 172.30, 138.14, 129.07, 124.26, 119.97, 30.83, 9.81 ppm.



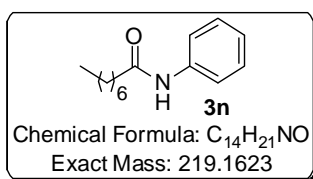
N-phenylbutyramide 3k: The reaction was carried out according to the general procedure with butan-1-ol (926.3 mg, 12.5 mmol, 25.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (81.0 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.53 (t, *J* = 10.6 Hz, 2H), 7.37 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.55, 138.10, 129.09, 124.31, 119.99, 39.80, 19.21, 13.87 ppm.



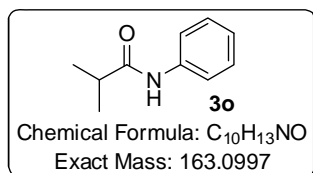
N-phenylpentanamide 3l: The reaction was carried out according to the general procedure with pentan-1-ol (660.8 mg, 7.5 mmol, 15.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (88.5 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.41 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.70 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.43 – 1.36 (m, 2H), 0.93 (t, *J* = 9.4, 5.3 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.71, 138.14, 129.07, 124.27, 119.97, 37.65, 27.84, 22.51, 13.93 ppm.



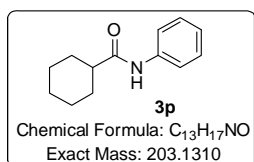
N-phenylhexanamide 3m: The reaction was carried out according to the general procedure with hexan-1-ol (510.5 mg, 5.0 mmol, 10.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (75.4 mg, 79% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.53 (s, 1H), 7.51 (s, 1H), 7.34 – 7.25 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.39 – 1.32 (m, *J* = 9.6, 6.2 Hz, 4H), 0.91 (t, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.63, 138.09, 129.11, 124.30, 119.90, 37.94, 31.55, 25.46, 22.57, 14.07 ppm.



N-phenyloctanamide 3n: The reaction was carried out according to the general procedure with octan-1-ol (650.5 mg, 5.0 mmol, 10.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (76.2 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.37 (s, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.77 – 1.67 (m, 2H), 1.35 – 1.26 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.71, 138.11, 129.08, 124.28, 119.93, 37.96, 31.80, 29.36, 29.17, 25.79, 22.73, 14.20 ppm.

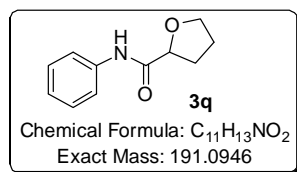


N-phenylisobutyramide 3o: The reaction was carried out according to the general procedure with 2-methylpropan-1-ol (555.8 mg, 7.5 mmol, 15.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (80.5 mg, 99% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.53 (s, 1H), 7.52 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.51 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.25 (s, 3H), 1.23 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 175.45, 138.19, 129.08, 124.25, 119.93, 36.81, 19.74 ppm.

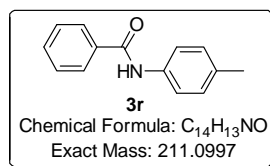


N-phenylcyclohexanecarboxamide 3p: The reaction was carried out according to the general procedure with cyclohexylmethanol (570.5 mg, 5.0 mmol, 10.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (80.2 mg, 79% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* =

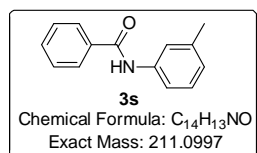
7.8 Hz, 3H), 7.08 (t, $J = 7.3$ Hz, 1H), 2.28 – 2.19 (m, 2H), 1.95 (d, $J = 12.6$ Hz, 1H), 1.83 (d, $J = 12.0$ Hz, 2H), 1.70 (d, $J = 7.0$ Hz, 1H), 1.61 – 1.48 (m, 2H), 1.35 – 1.19 (m, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 174.56, 138.25, 129.07, 124.19, 119.91, 46.67, 29.79, 25.79 ppm.



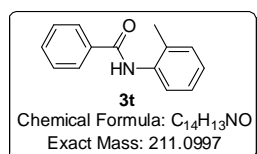
***N*-phenyltetrahydrofuran-2-carboxamide 3q:** The reaction was carried out according to the general procedure with (tetrahydrofuran-2-yl)methanol (765.8 mg, 7.5 mmol, 15.0 equiv) and aniline (46.5 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au_6Pd /resin catalyst for 24 h. The product was obtained as a white solid (65.5 mg, 69% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.46 (s, 1H), 7.57 (d, $J = 7.7$ Hz, 2H), 7.32 (t, $J = 7.9$ Hz, 2H), 7.14 – 7.07 (m, 1H), 4.46 (dd, $J = 8.4, 5.9$ Hz, 1H), 4.08 – 4.01 (m, 1H), 3.95 (dd, $J = 15.1, 6.9$ Hz, 1H), 2.36 (ddd, $J = 15.3, 12.6, 7.7$ Hz, 1H), 2.23 – 2.14 (m, 1H), 1.99 – 1.90 (m, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.46, 137.38, 129.15, 124.53, 119.74, 78.75, 69.81, 30.32, 25.72 ppm.



***N*-(*p*-tolyl)benzamide 3r:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv) and *p*-toluidine (53.6 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a white solid (96.0 mg, 91% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.90 (s, 1H), 7.85 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 7.3$ Hz, 3H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 165.85, 135.48, 135.17, 134.34, 131.83, 129.68, 128.84, 127.13, 120.45, 21.03 ppm.

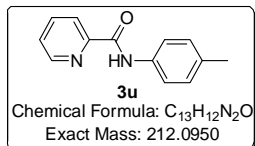


***N*-(*m*-tolyl)benzamide 3s:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv) and *m*-toluidine (53.6 mg, 0.50 mmol, 1.0 equiv) for 24 h. The product was obtained as a white solid (85.8 mg, 81% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.85 (d, $J = 7.3$ Hz, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.39 (m, 3H), 7.23 (dd, $J = 14.6, 6.8$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 165.98, 139.12, 138.01, 135.17, 131.89, 129.00, 128.86, 127.19, 125.50, 121.08, 117.51, 21.64 ppm.

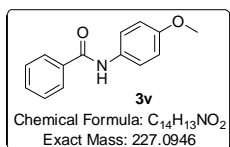


***N*-(*o*-tolyl)benzamide 3t:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv) and *o*-toluidine (53.6 mg, 0.50 mmol, 1.0 equiv)

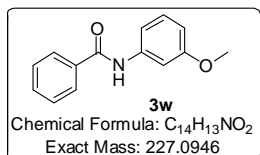
by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (65.1 mg, 62% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (t, *J* = 11.7 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.67 (s, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.21 (m, 2H), 7.12 (dd, *J* = 10.8, 4.1 Hz, 1H), 2.34 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 165.85, 135.91, 135.12, 131.97, 130.70, 129.64, 128.95, 127.22, 127.00, 125.56, 123.44, 115.16, 17.98 ppm.



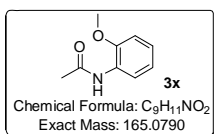
***N*-(*p*-tolyl)picolinamide 3u:** The reaction was carried out according to the general procedure with pyridin-2-ylmethanol (109.1 mg, 1.0 mmol, 2.0 equiv) and *p*-toluidine (53.6 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a yellow solid (101.8 mg, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 9.97 (s, 1H), 8.61 (d, *J* = 4.7 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 161.97, 150.04, 148.05, 137.78, 135.33, 134.04, 129.70, 126.48, 122.48, 119.78, 21.06 ppm.



***N*-(4-methoxyphenyl)benzamide 3v:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv), 4-methoxyaniline (61.6 mg, 0.50 mmol, 1.0 equiv) and *t*-BuOH (370.5 mg, 5.0 mmol) for 24 h. The product was obtained as a white solid (84.8 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.81 (s, 1H), 7.53 (t, *J* = 6.5 Hz, 3H), 7.46 (t, *J* = 7.0 Hz, 2H), 6.89 (d, *J* = 7.5 Hz, 2H), 3.80 (s, 3H) pm; ¹³C NMR (126 MHz, CDCl₃) δ 165.77, 156.76, 135.16, 131.82, 131.12, 128.86, 127.11, 122.24, 114.36, 55.63 ppm.

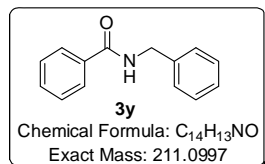


***N*-(3-methoxyphenyl)benzamide 3w:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv) and 3-methoxyaniline (61.6 mg, 0.50 mmol, 1.0 equiv) for 24 h. The product was obtained as a white solid (110.1 mg, 97% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.02 (s, 1H), 7.83 (t, *J* = 10.1 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.23 (dd, *J* = 16.7, 8.6 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.70 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.80 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 166.04, 160.32, 139.33, 135.06, 131.99, 130.25, 129.87, 128.89, 127.18, 112.49, 110.68, 105.97, 55.45 ppm.

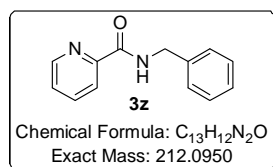


***N*-(2-methoxyphenyl)acetamide 3x:** The reaction was carried out according to the general procedure with ethanol (575.0 mg, 12.5 mmol, 25.0 equiv) and 2-methoxyaniline (61.6 mg, 0.50

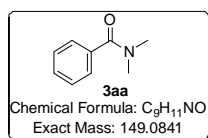
mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 24 h. The product was obtained as a white solid (80.8 mg, 98% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.34 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.77 (s, 1H), 7.01 (td, *J* = 7.9, 1.3 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.18 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 168.30, 147.80, 127.83, 123.71, 121.17, 119.90, 109.99, 55.75, 25.03 ppm.



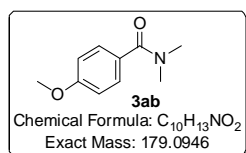
***N*-benzylbenzamide 3y:** The reaction was carried out according to the general procedure with phenylmethanol (108.1 mg, 1.0 mmol, 2.0 equiv) and phenylmethanamine (53.6 mg, 0.50 mmol, 1.0 equiv) by 3 mol% Au₆Pd/resin catalyst for 18 h. The product was obtained as a white solid (87.6 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 4.2 Hz, 4H), 7.32 – 7.27 (m, 1H), 6.48 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 167.49, 138.32, 134.52, 131.68, 128.92, 128.73, 128.05, 127.76, 127.09, 44.27 ppm.



***N*-benzylpicolinamide 3z:** The reaction was carried out according to the general procedure with pyridin-2-ylmethanol (109.1 mg, 1.0 mmol, 2.0 equiv) and phenylmethanamine (53.6 mg, 0.50 mmol, 1.0 equiv). The product was obtained as a yellow solid (96.4 mg, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.53 (d, *J* = 4.2 Hz, 1H), 8.40 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.86 (td, *J* = 7.7, 1.6 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.36 (dt, *J* = 15.1, 7.3 Hz, 4H), 7.31 – 7.27 (m, 1H), 4.68 (d, *J* = 6.1 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 164.39, 149.93, 148.21, 138.31, 137.53, 130.31, 129.29, 128.84, 128.00, 127.61, 126.36, 122.53, 43.64 ppm.

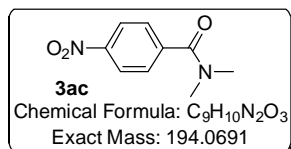


***N,N*-dimethylbenzamide 3aa:** The reaction was carried out according to the general procedure with phenylmethanol (54.1 mg, 0.50 mmol, 1.0 equiv) and dimethylamine (40 wt% in H₂O) (1.125 g, 10 mmol, 20.0 equiv) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a colourless oil (67.7 mg, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.36 (m, 5H), 3.09 (s, 3H), 2.96 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.76, 136.46, 129.61, 128.45, 127.15, 39.69, 35.45 ppm.

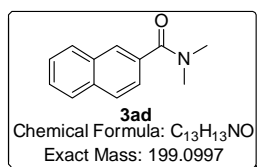


4-methoxy-*N,N*-dimethylbenzamide 3ab: The reaction was carried out according to the general

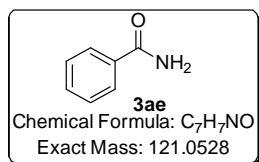
procedure with (4-methoxyphenyl)methanol (69.1 mg, 0.50 mmol, 1.0 equiv) and dimethylamine (40 wt% in H₂O) (1.125 g, 10 mmol, 20.0 equiv) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a colourless oil (84.6 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.35 (m, 2H), 6.91 – 6.85 (m, 2H), 3.80 (s, 3H), 3.03 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.60, 160.71, 129.21, 128.58, 113.66, 55.41, 39.92, 35.62 ppm.



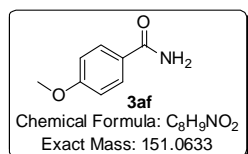
***N,N*-dimethyl-4-nitrobenzamide 3ac:** The reaction was carried out according to the general procedure with (4-nitrophenyl)methanol (76.5 mg, 0.50 mmol, 1.0 equiv), dimethylamine (40 wt% in H₂O) (1.125 g, 10 mmol, 20.0 equiv) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a yellow solid (52.4 mg, 57% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 3.11 (s, 3H), 2.94 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 169.37, 148.38, 142.61, 128.18, 123.89, 39.42, 35.46 ppm.



***N,N*-dimethyl-2-naphthamide 3ad:** The reaction was carried out according to the general procedure with naphthalen-2-ylmethanol (79.1 mg, 0.50 mmol, 1.0 equiv), dimethylamine (40 wt% in H₂O) (1.125 g, 10 mmol, 20.0 equiv) and *t*-BuOH (185.3 mg, 2.5 mmol) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a white solid (94.1 mg, 95% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.90 (s, 1H), 7.87 – 7.82 (m, 3H), 7.53 – 7.49 (m, 3H), 3.13 (s, 3H), 3.02 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 171.76, 133.76, 133.72, 132.79, 128.52, 128.31, 127.91, 127.11, 126.97, 126.75, 124.56, 39.79, 35.54 ppm.

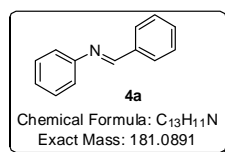


Benzamide 3ae: The reaction was carried out according to the general procedure with phenylmethanol (54.1 mg, 0.50 mmol, 1.0 equiv), ammonia (30 wt% in H₂O) (1.167 g, 10 mmol, 20.0 equiv) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a white solid (29.4 mg, 49% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.78 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.13 (s, 1H), 6.06 (s, 1H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 169.66, 133.45, 132.15, 128.76, 127.46 ppm.

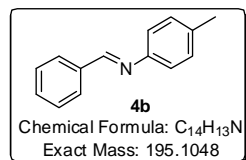


4-methoxybenzamide 3af: The reaction was carried out according to the general procedure with (4-methoxyphenyl)methanol (69.1 mg, 0.50 mmol, 1.0 equiv), ammonia (30 wt% in H₂O) (1.167 g,

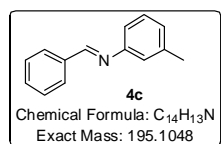
10 mmol, 20.0 equiv) by 3 mol% Au₆Pd/resin catalyst at 25 °C for 24 h. The product was obtained as a white solid (40.4 mg, 54% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.04 (s, 1H), 5.81 (s, 1H), 3.85 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 169.11, 162.76, 129.44, 125.53, 113.94, 55.57 ppm.



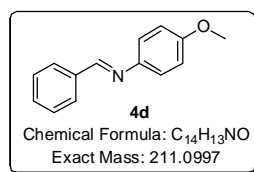
(E)-N-benzylideneaniline 4a: The reaction was carried out according to the general procedure with benzyl alcohol (108.2 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 24 h and the product was obtained as a yellow solid (72.4 mg, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.46 (s, 1H), 7.94 – 7.87 (m, 2H), 7.51 – 7.45 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.58, 152.22, 136.34, 131.53, 129.29, 128.95, 128.92, 126.08, 121.00 ppm.



(E)-N-benzylidene-4-methylaniline 4b: The reaction was carried out according to the general procedure with benzyl alcohol (81.2 mg, 0.75 mmol, 1.5 equiv) and 4-methylaniline (53.6 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 24 h and the product was obtained as a yellow solid (61.3 mg, 63% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.48 (s, 1H), 7.91 (dd, *J* = 6.1, 2.4 Hz, 2H), 7.50 – 7.45 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.38 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.75, 149.59, 136.48, 135.94, 131.34, 129.90, 128.88, 128.85, 120.95, 21.16 ppm.

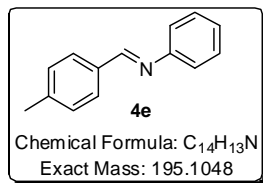


(E)-N-benzylidene-3-methylaniline 4c: The reaction was carried out according to the general procedure with benzyl alcohol (81.2 mg, 0.75 mmol, 1.5 equiv) and 3-methylaniline (53.6 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (48.4 mg, 50% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.46 (s, 1H), 7.91 (dd, *J* = 6.2, 2.6 Hz, 2H), 7.51 – 7.45 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.00 (m, 3H), 2.41 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.30, 152.23, 139.11, 136.43, 131.44, 129.11, 128.91, 128.89, 126.85, 121.77, 117.98, 21.55 ppm.

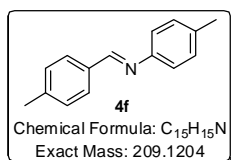


(E)-N-benzylidene-4-methoxyaniline 4d: The reaction was carried out according to the general procedure with benzyl alcohol (81.2 mg, 0.75 mmol, 1.5 equiv) and 4-methoxyaniline (61.6 mg,

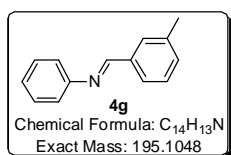
0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (68.5 mg, 65% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.48 (s, 1H), 7.92 – 7.86 (m, 2H), 7.48 – 7.43 (m, 3H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 158.54, 158.42, 145.05, 136.59, 131.16, 128.87, 128.72, 122.33, 114.51, 55.62 ppm.



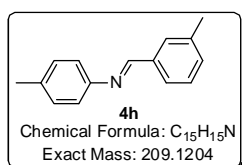
(E)-N-(4-methylbenzylidene)aniline 4e: The reaction was carried out according to the general procedure with 4-methylbenzyl alcohol (91.7 mg, 0.75 mmol, 1.5 equiv) and aniline (46.5 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (59.4 mg, 61% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.20 (m, 3H), 2.43 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.49, 152.41, 142.00, 133.83, 129.66, 129.26, 128.96, 125.88, 121.02, 21.77 ppm.



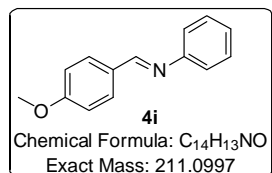
(E)-4-methyl-N-(4-methylbenzylidene)aniline 4f: The reaction was carried out according to the general procedure with 4-methylbenzyl alcohol (91.7 mg, 0.75 mmol, 1.5 equiv) and 4-methylaniline (53.6 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (43.0 mg, 41% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 6.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.71, 149.78, 141.78, 135.69, 133.93, 129.86, 129.61, 128.84, 120.93, 21.74, 21.13 ppm.



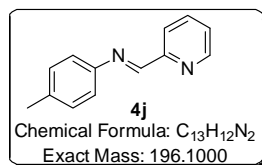
(E)-N-(3-methylbenzylidene)aniline 4g: The reaction was carried out according to the general procedure with 3-methylbenzyl alcohol (122.2 mg, 1.0 mmol, 2.0 equiv) and aniline (46.5 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 24 h and the product was obtained as a yellow solid (80.9 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 3H), 2.43 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.84, 152.30, 138.69, 136.29, 132.39, 129.27, 129.09, 128.79, 126.57, 126.00, 121.00, 21.44 ppm.



(E)-4-methyl-N-(3-methylbenzylidene)aniline 4h: The reaction was carried out according to the general procedure with 3-methylbenzyl alcohol (91.7 mg, 0.75 mmol, 1.5 equiv) and 4-methylaniline (53.6 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (62.6 mg, 60% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.45 (s, 1H), 7.77 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.02, 149.68, 138.64, 136.44, 135.85, 132.21, 129.89, 128.99, 128.76, 126.48, 120.94, 21.44, 21.14 ppm.



(E)-N-(4-methoxybenzylidene)aniline 4i: The reaction was carried out according to the general procedure with 4-methoxybenzyl alcohol (103.6 mg, 0.75 mmol, 1.5 equiv) and aniline (46.5 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 12 h and the product was obtained as a yellow solid (55.4 mg, 53% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.39 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.00 (t, *J* = 8.3 Hz, 2H), 3.87 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 162.39, 159.83, 152.52, 130.65, 129.25, 125.70, 121.02, 114.33, 55.56 ppm.



(E)-4-methyl-N-(pyridin-2-ylmethylene)aniline 4j: The reaction was carried out according to the general procedure with pyridin-2-ylmethanol (81.8 mg, 0.75 mmol, 1.5 equiv) and 4-methylaniline (53.6 mg, 0.5 mmol, 1.0 equiv) by AuPd₄/resin (93 mg, 3 mol%) at 40 °C for 24 h and the product was obtained as a yellow solid (52.1 mg, 53% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, *J* = 4.4 Hz, 1H), 8.62 (s, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.35 (dd, *J* = 6.7, 5.3 Hz, 1H), 7.22 (s, 4H), 2.38 (s, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.78, 154.83, 149.77, 148.45, 137.78, 136.93, 136.82, 130.00, 129.87, 125.14, 121.94, 121.25, 21.21 ppm.

10. Copy of ^1H NMR and ^{13}C NMR spectra for products.

