

## Supporting information

### **Chemoenzymatic Synthesis of Amino-Esters as Precursors of Ammonium Salts Based Surfactants from 5-Hydroxymethylfurfural (HMF)**

Carlos Moriana Herraiz, Karen S. Arias, Maria J. Climent, Sara Iborra\* and Avelino Corma\*

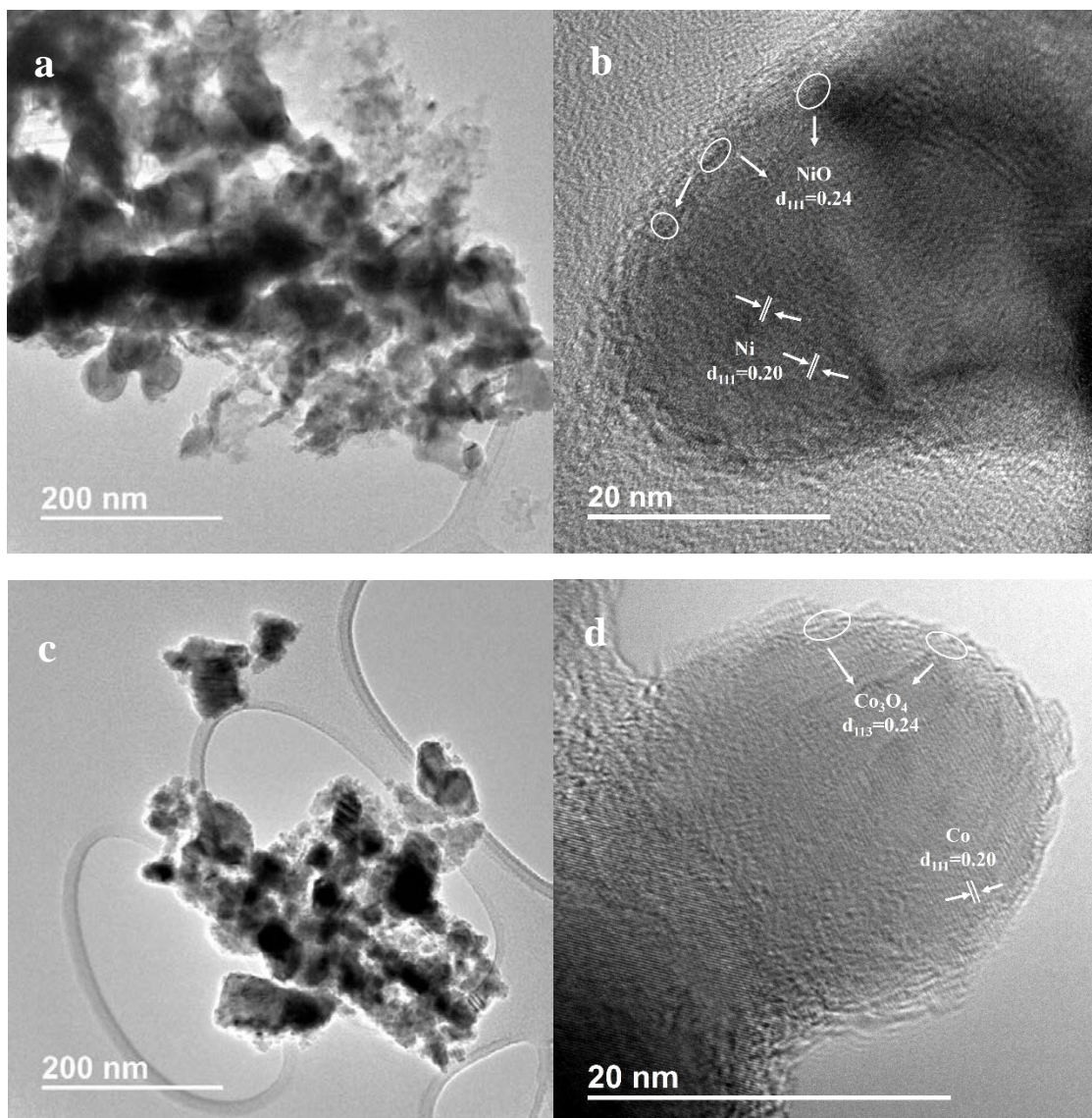
Instituto de Tecnología Química (Universitat Politècnica de València - Agencia Estatal Consejo Superior de Investigaciones Científicas)

*Avda dels Tarongers s/n, 46022, Valencia (Spain)*

*Fax: (+34) 963877809*

*E-mail: [siborra@itq.upv.es](mailto:siborra@itq.upv.es)*

*[acorma@itq.upv.es](mailto:acorma@itq.upv.es)*

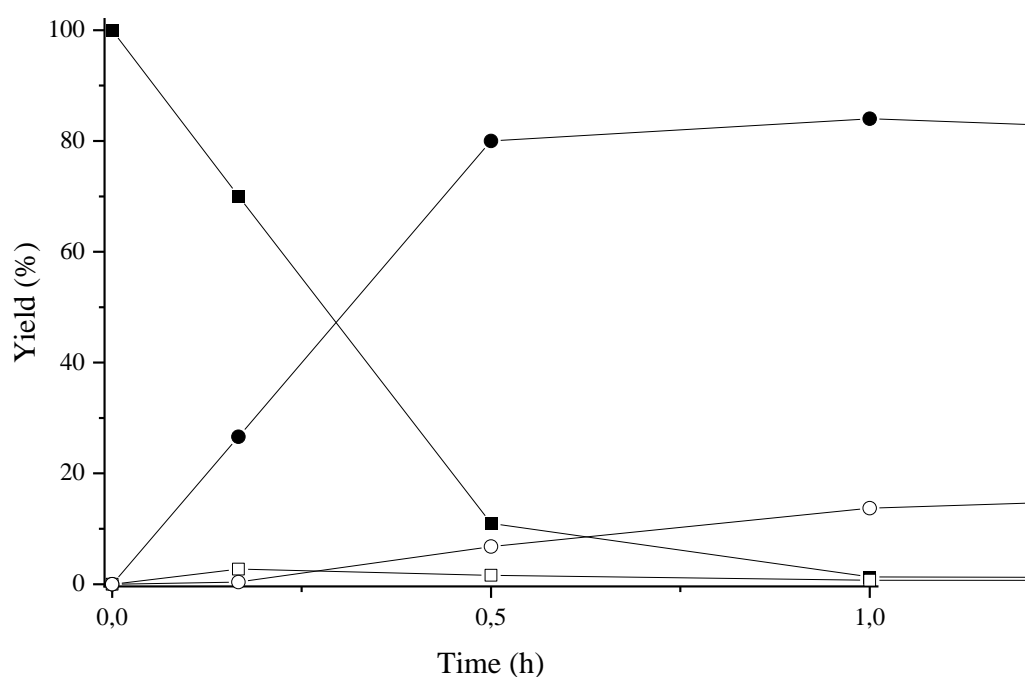


**Figure S1.** HRTEM images of catalysts (a, b) Ni@C NPs, (c, d) Co@C NPs.

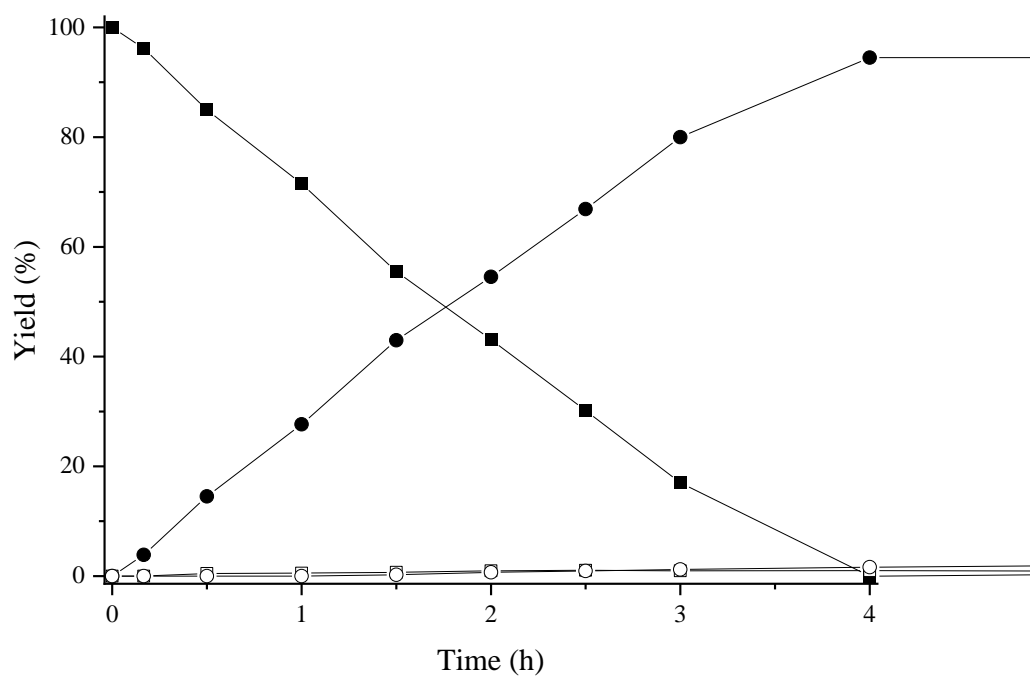
**Table S1.** Optimization of the reaction conditions of the reductive amination of HMF with aniline<sup>a</sup>

Entry	Temperature (°C)	Pressure H <sub>2</sub> (bar)	Time (h)	Conversion HMF (%)	Yield 2 (%)	Selectivity 2 (%)
1	100	6.5	1	99	90	91
2	80	6.5	4	100	95	95
3	60	6.5	5	100	97	97
4	60	4	6	99	98	99
5	60	3	22	100	96	96

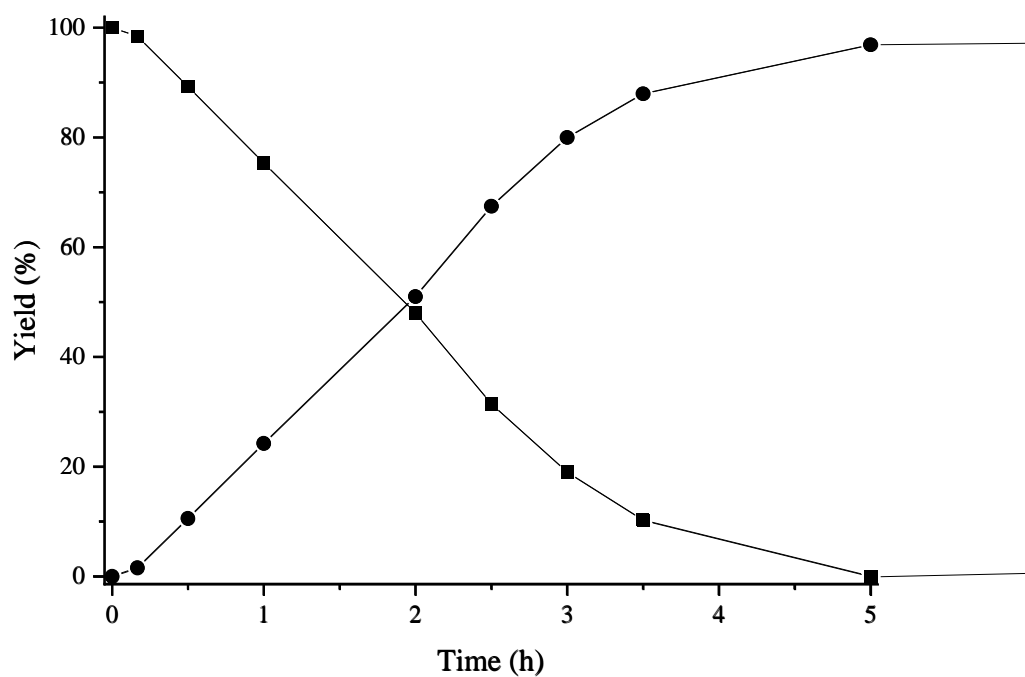
<sup>a</sup> Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), 20 mg of Co@C NPs (16.1 mol % of Co) in EtOH as a solvent (4 mL). Reactions performed after a previous pre-reduction of the catalyst.



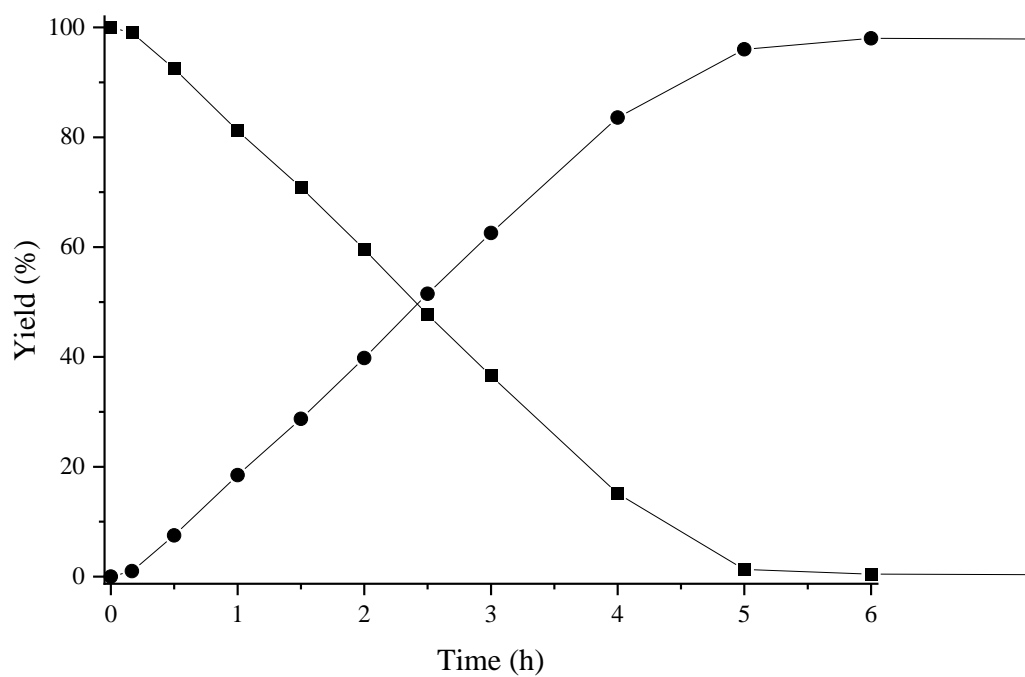
**Figure S2.** Kinetic study of the reductive amination of HMF with aniline using 6.5 bar of molecular H<sub>2</sub> at 100 °C (entry 1 Table S1). Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL) and 16.1 mol % of Co@C NPs (20 mg). Imine 1 (■), Amine 2 (●), Imine 3 (□), Amine 4 (○).



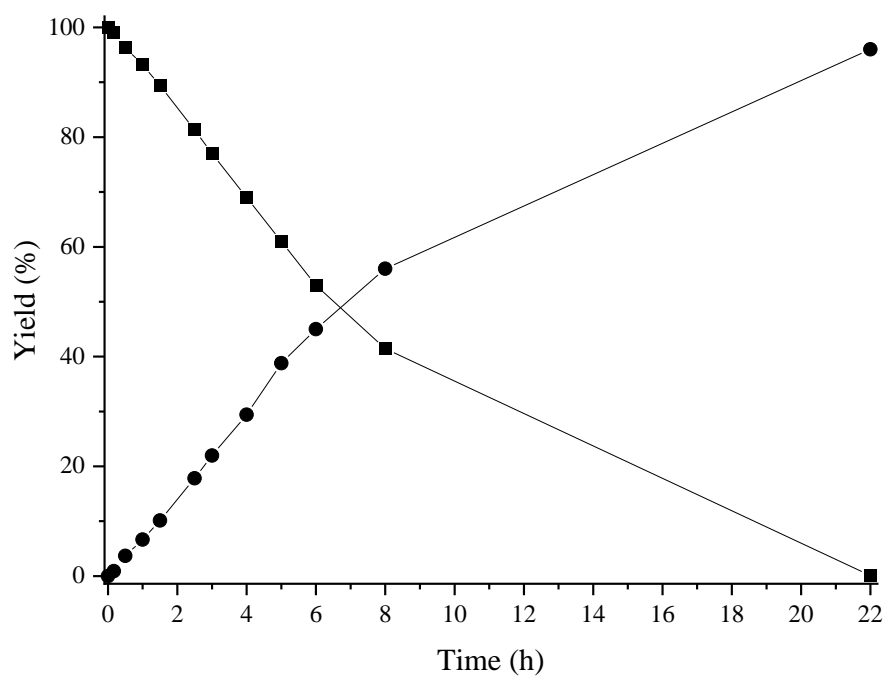
**Figure S3.** Kinetic study of the reductive amination of HMF with aniline using 6.5 bar of molecular  $H_2$  at 80 °C (entry 2 Table S1). Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL) and 16.1 mol % of Co@C NPs (20 mg). Imine 1 (■), Amine 2 (●), Imine 3 (□), Amine 4 (○).



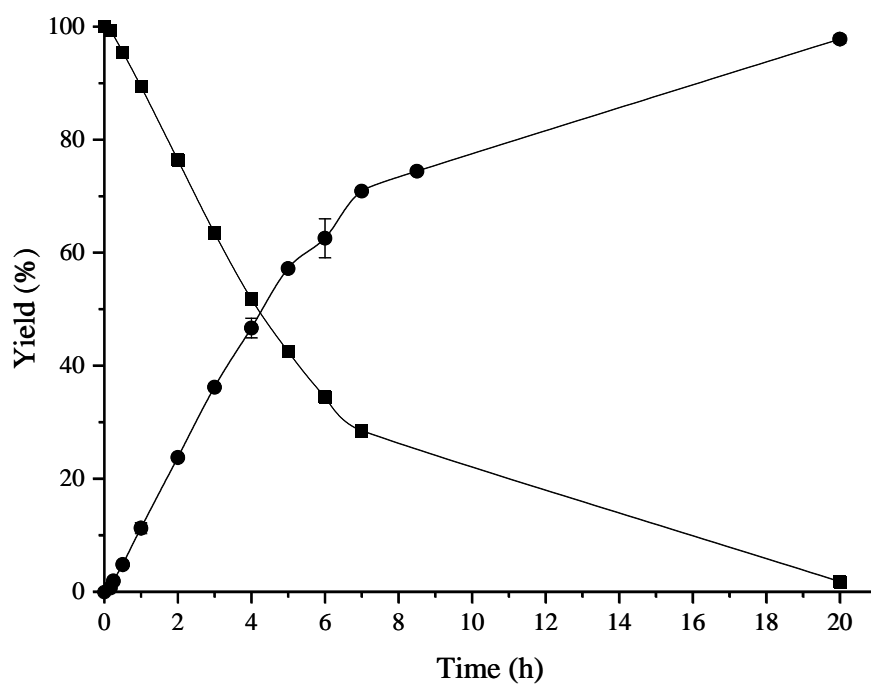
**Figure S4.** Kinetic study of the reductive amination of HMF with aniline using 6.5 bar of molecular  $H_2$  at 60 °C (entry 3 Table S1). Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL) and 16.1 mol % of Co@C NPs (20 mg). Imine 1 (■), Amine 2 (●).



**Figure S5.** Kinetic study of the reductive amination of HMF with aniline using 4 bar of molecular  $H_2$  at 60 °C (entry 4 Table S1). Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL) and 16.1 mol % of Co@C NPs (20 mg). Imine 1 (■), Amine 2 (●).

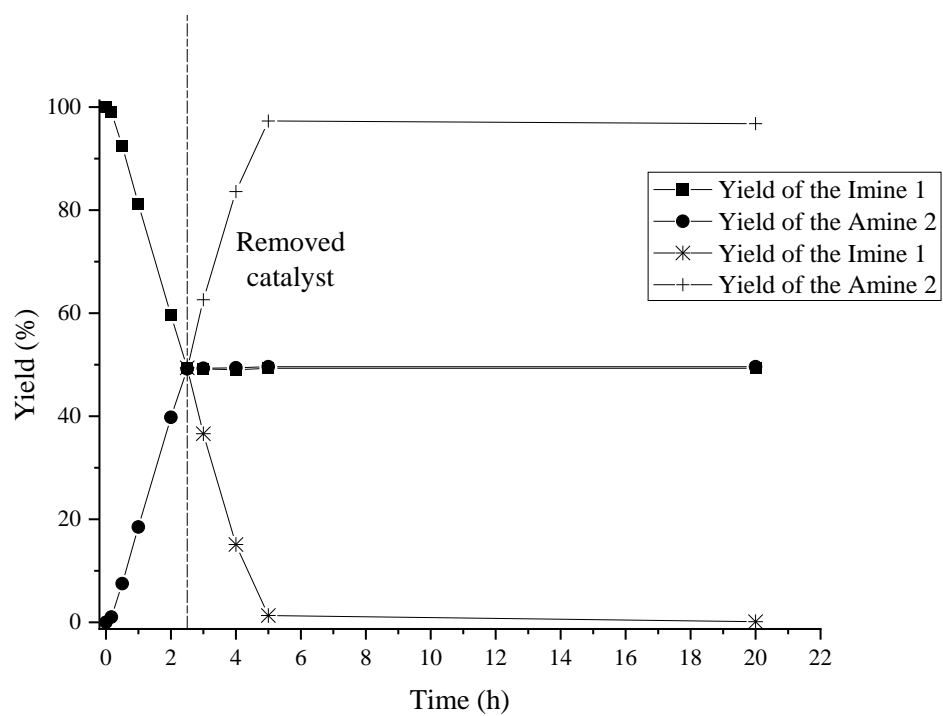


**Figure S6.** Kinetic study of the reductive amination of HMF with aniline using 3 bar of molecular  $H_2$  at 60 °C (entry 5 Table S1). Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL) and 16.1 mol % of Co@C NPs (20 mg). Imine 1 (■), Amine 2 (●).

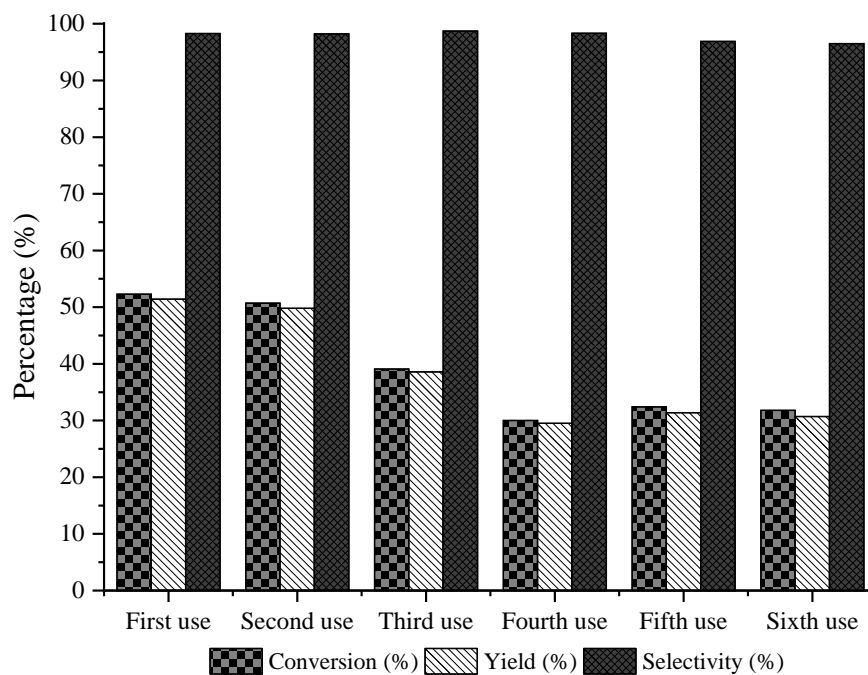


**Figure S7.** Kinetic study of the reductive amination of HMF with aniline using Ni@C NPs (16.1 mol %) as catalysts. Reaction conditions: HMF (2 mmol), aniline (2.4 mmol), EtOH (4 mL), 4 bar of H<sub>2</sub> and 60 °C. Imine 1 (■), Amine 2 (●).

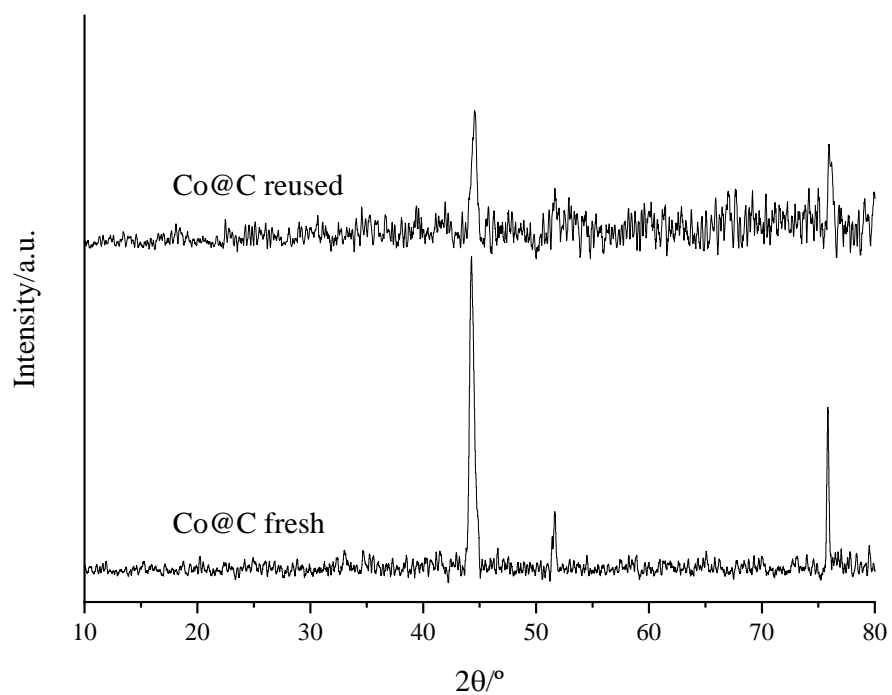




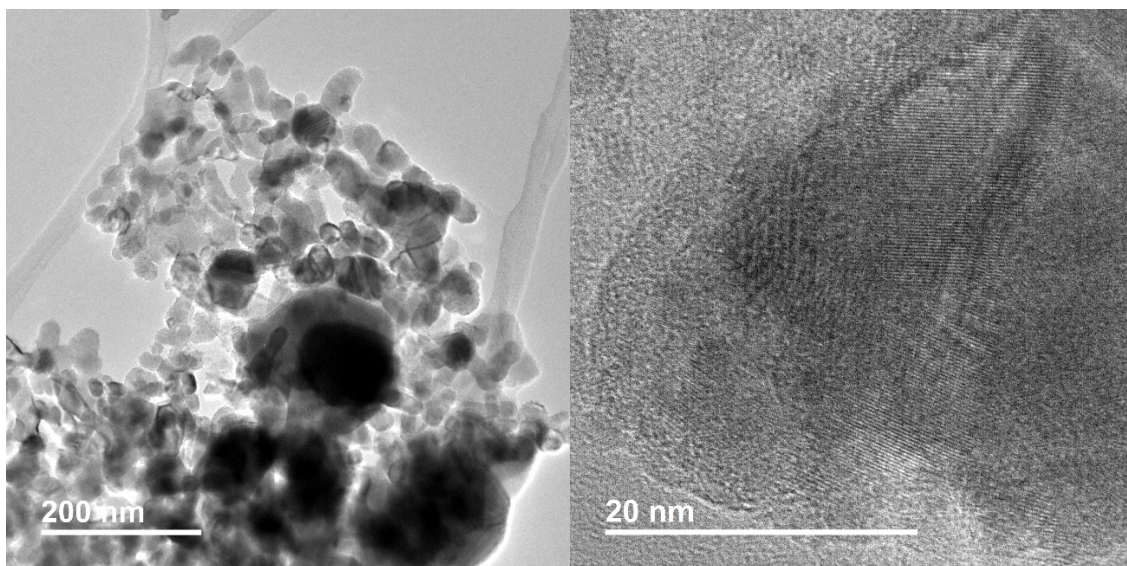
**Figure S8.** Leaching test of Co@C NPs in the reductive amination of HMF with aniline. Imine 1 (■), Amine 2 (●), and Imine 1 (\*), Amine 2 (+) if the reaction would continue normally.



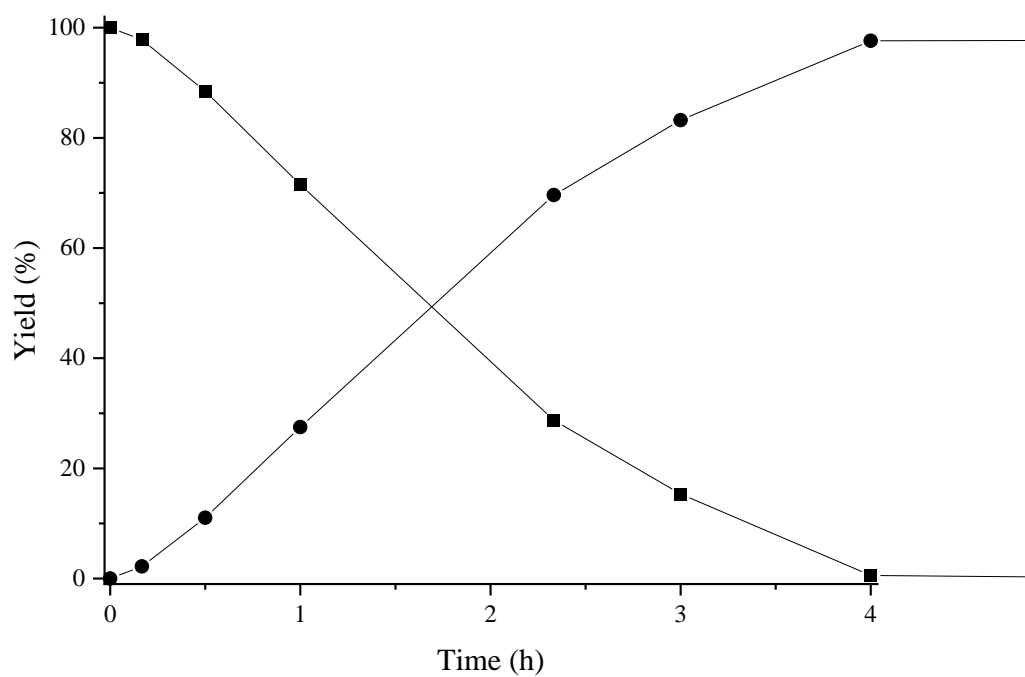
**Figure S9.** Recyclability of Co@C NPs catalyst for the reductive amination of HMF with aniline at 2.5 h of reaction.



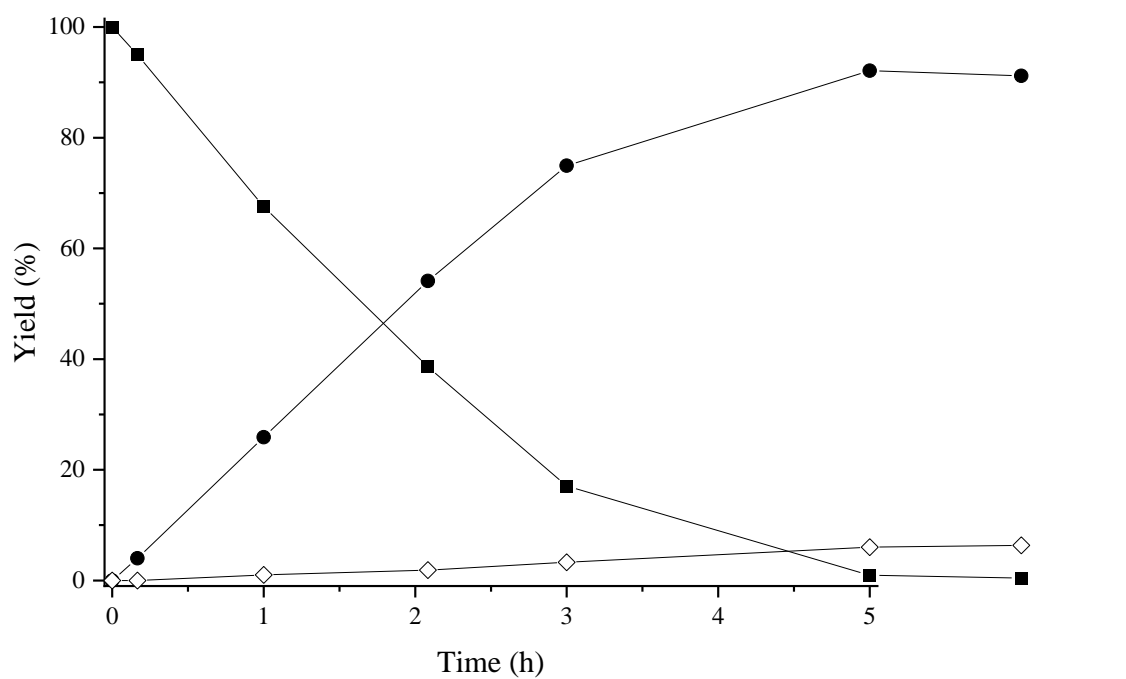
*Figure S10. XRD patterns of Co@C fresh and reused nanoparticles.*



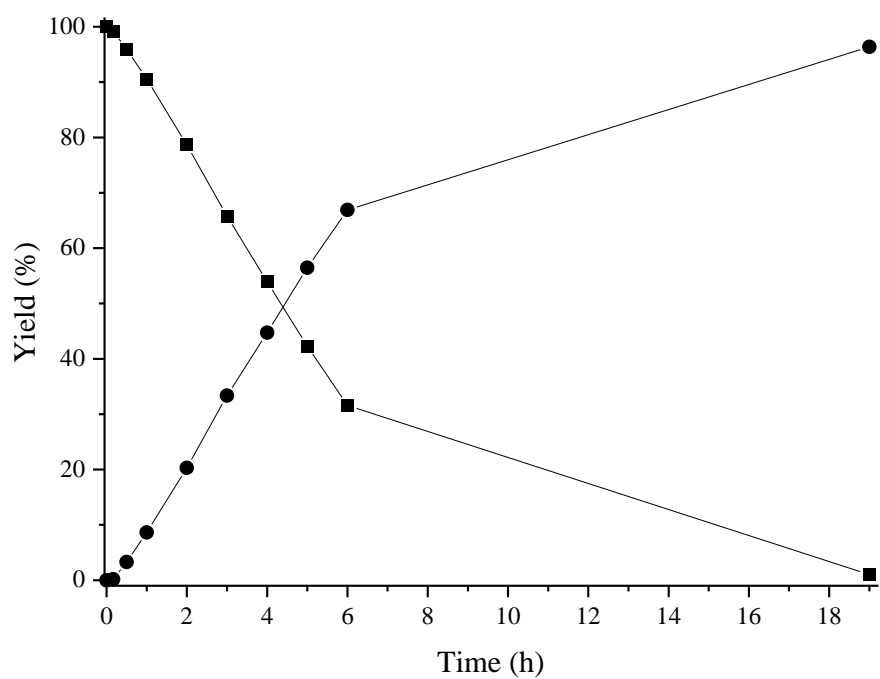
*Figure S11. HRTEM images of catalysts (a, b) Co@C NPs after the sixth cycle.*



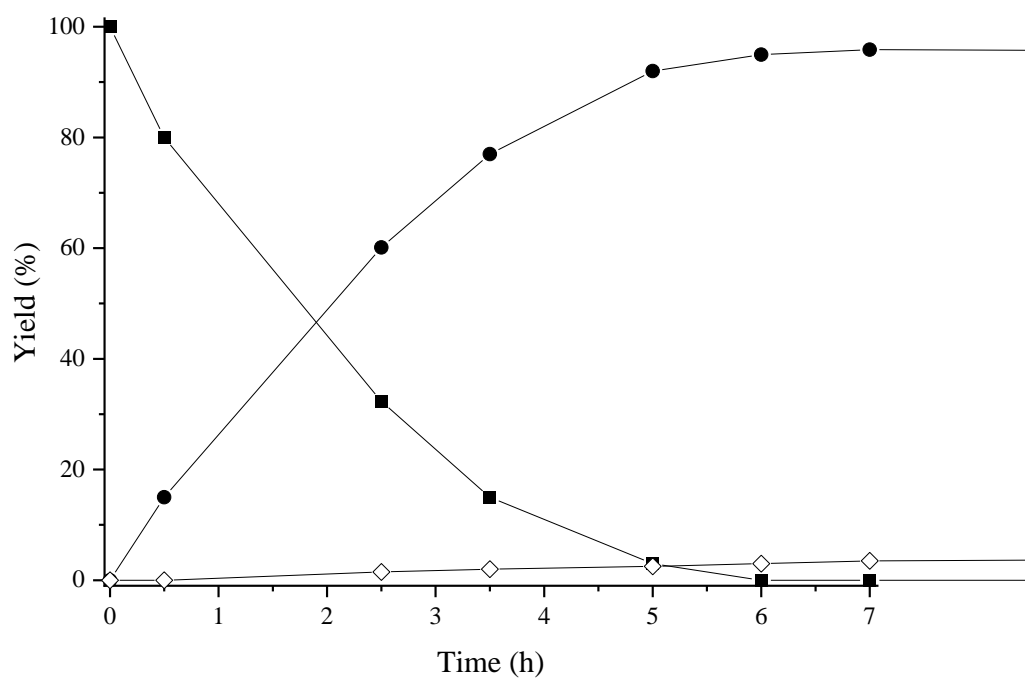
**Figure S12.** Kinetic study of the reductive amination of HMF with *p*-toluidine (Entry 2 Table 3). Reaction conditions: HMF (2 mmol), *p*-toluidine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



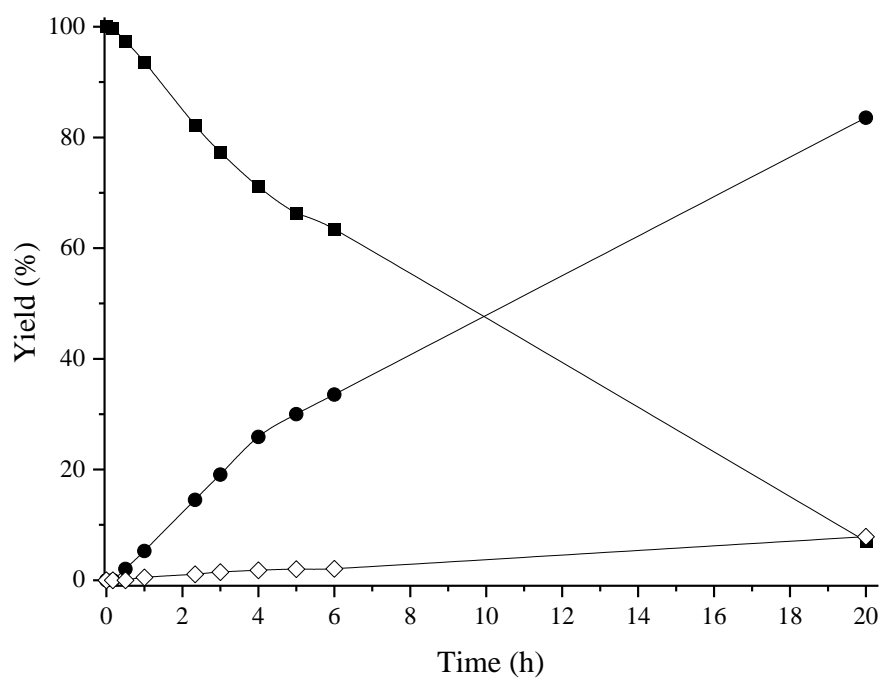
**Figure S13.** Kinetic study of the reductive amination of HMF with *o*-toluidine (Entry 3 Table 3). Reaction conditions: HMF (2 mmol), *o*-toluidine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●), BHMf (◇).



**Figure S14.** Kinetic study of the reductive amination of HMF with *p*-anisidine (Entry 4 Table 3). Reaction conditions: HMF (2 mmol), *p*-anisidine (2 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).

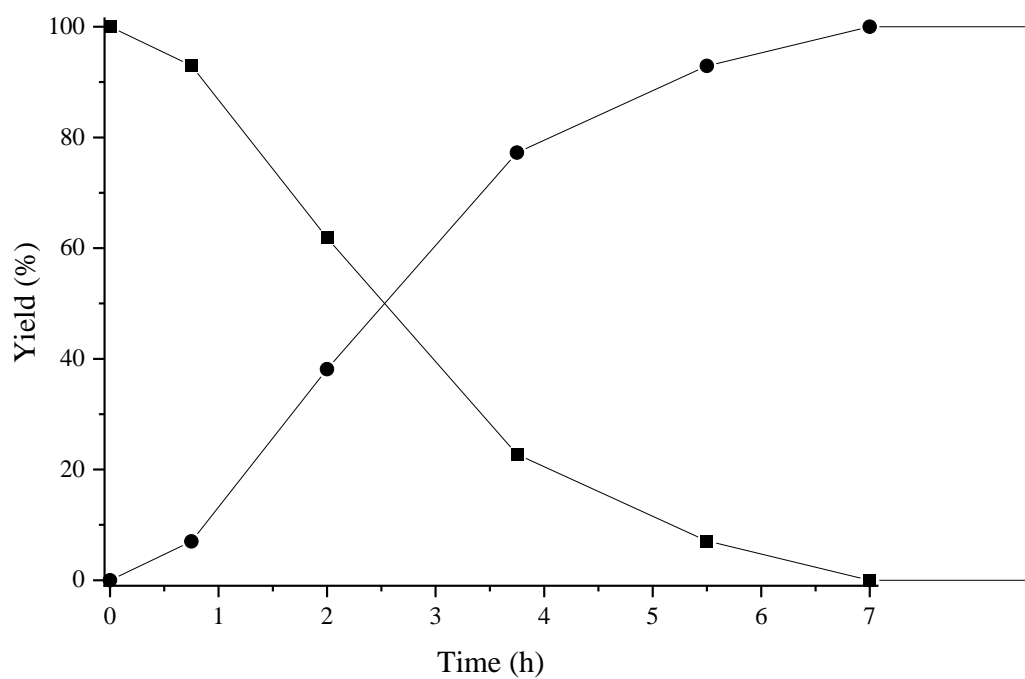


**Figure S15.** Kinetic study of the reductive amination of HMF with *p*-bromoaniline (Entry 5 Table 3). Reaction conditions: HMF (2 mmol), *p*-bromoaniline (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●), BHMf (◇).

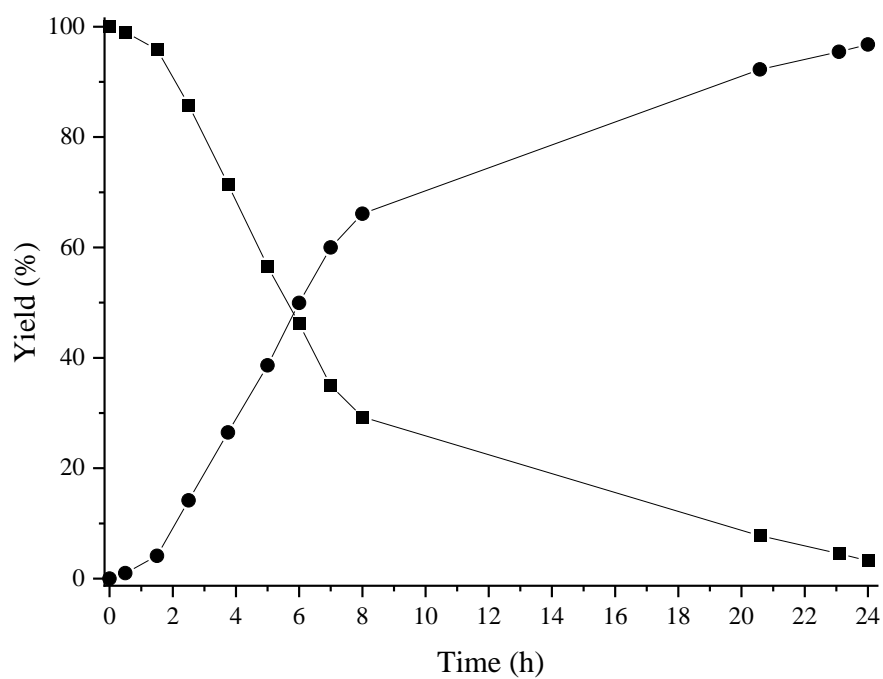


**Figure S16.** Kinetic study of the reductive amination of HMF with 4-aminocetophenone (Entry 6 Table 3). Reaction conditions: HMF (2 mmol), 4-aminocetophenone (2 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●), BHMF (◇).

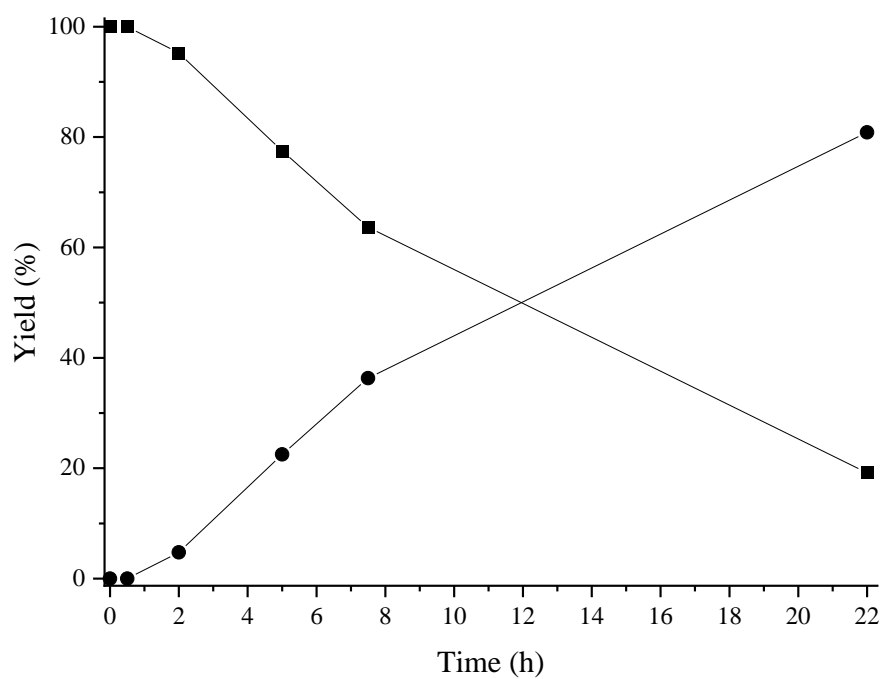




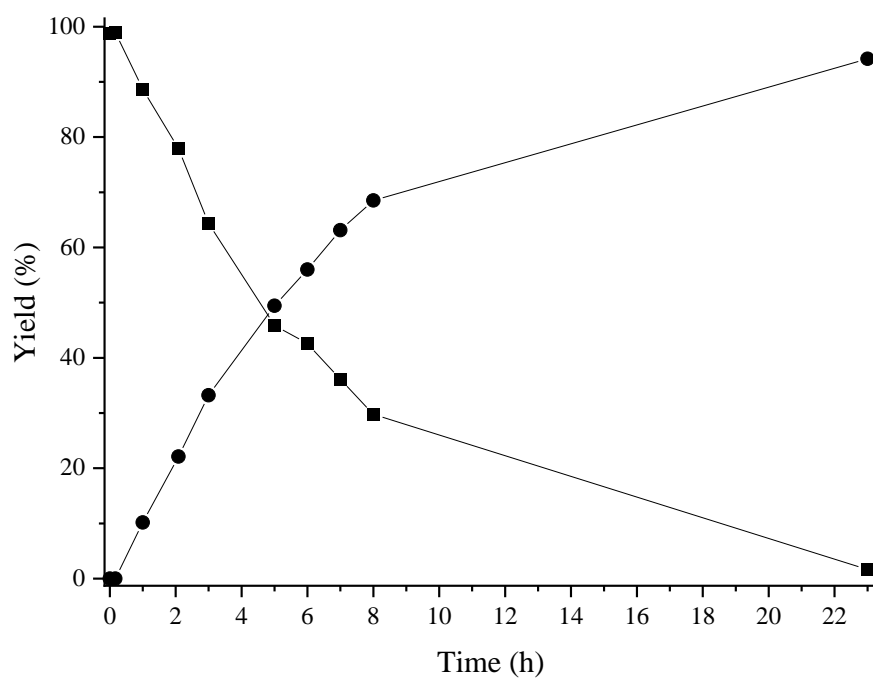
**Figure S17.** Kinetic study of the reductive amination of HMF with methylamine (Entry 7 Table 3). Reaction conditions: HMF (2 mmol), methylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



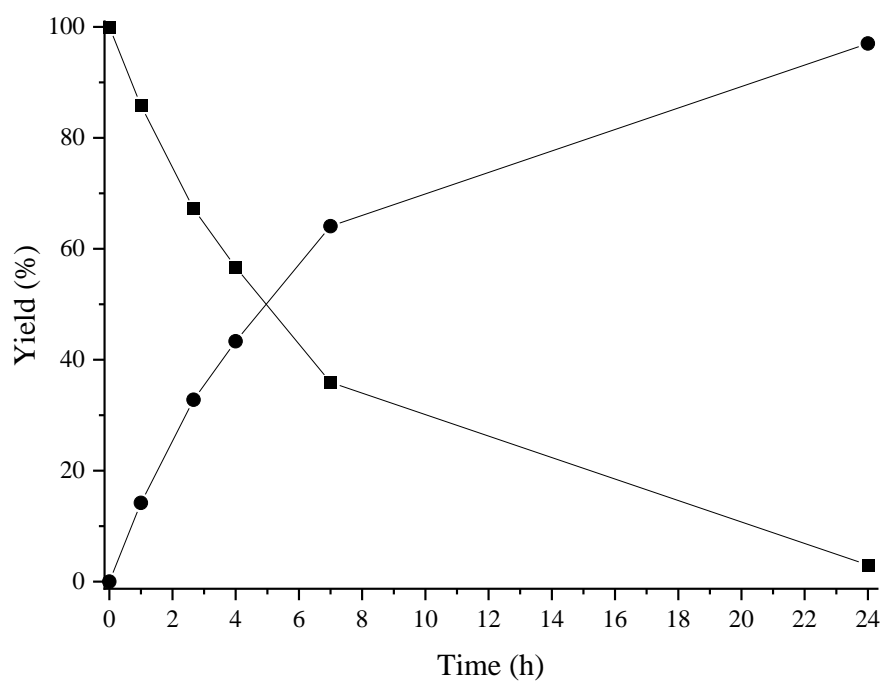
**Figure S18.** Kinetic study of the reductive amination of HMF with ethylamine (Entry 8 Table 3). Reaction conditions: HMF (2 mmol), ethylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●), BHMf (◇).



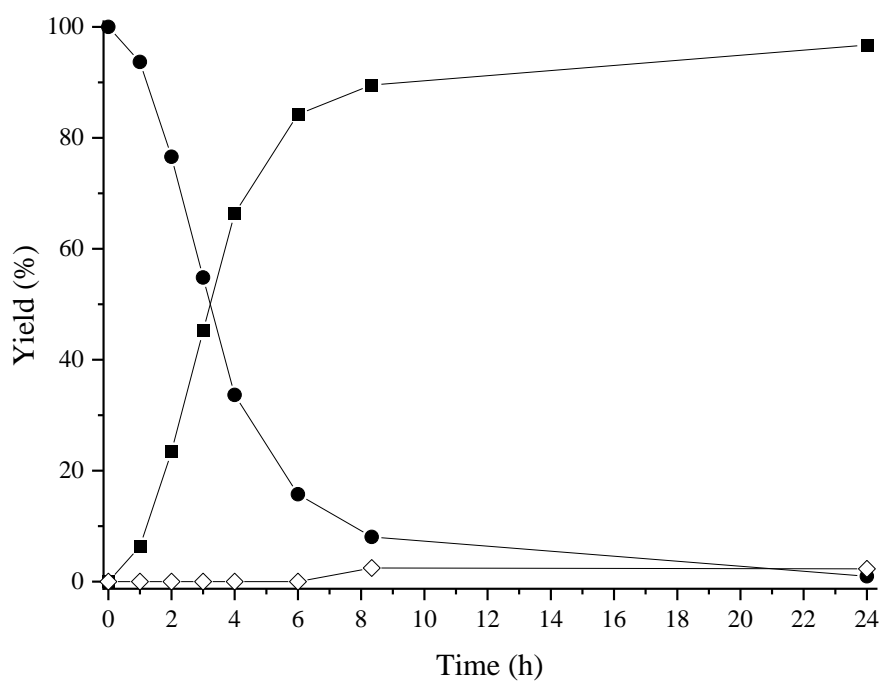
**Figure S19.** Kinetic study of the reductive amination of HMF with propylamine (Entry 9 Table 3). Reaction conditions: HMF (2 mmol), propylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



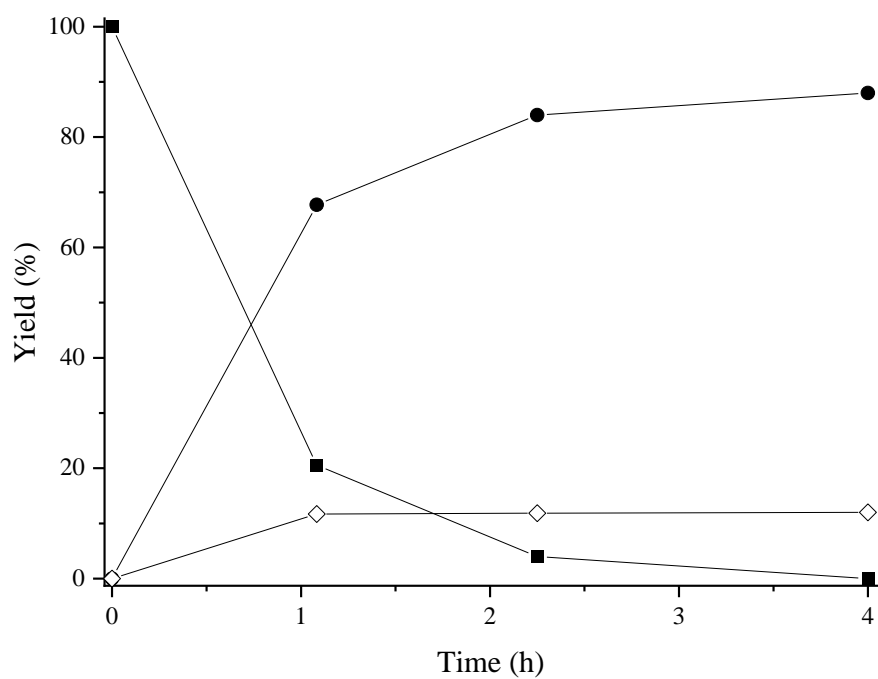
**Figure S20.** Kinetic study of the reductive amination of HMF with octylamine (Entry 10 Table 3). Reaction conditions: HMF (2 mmol), octylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



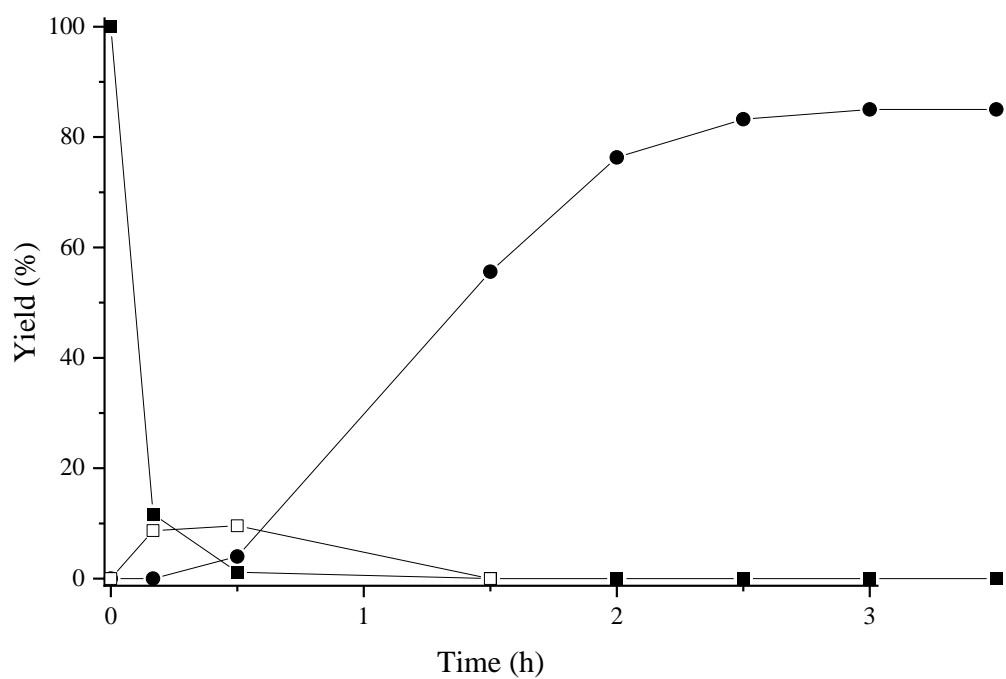
**Figure S21.** Kinetic study of the reductive amination of HMF with ethanolamine (Entry 11 Table 3). Reaction conditions: HMF (2 mmol), ethanolamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Silylated Imine (■), Silylated Amine.



**Figure S22.** Kinetic study of the reductive amination of HMF with amino-2-propanol (Entry 12 Table 3). Reaction conditions: HMF (2 mmol), amino-2-propanol (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Silylated Imine (■), Silylated Amine (●), BHMF (◇).

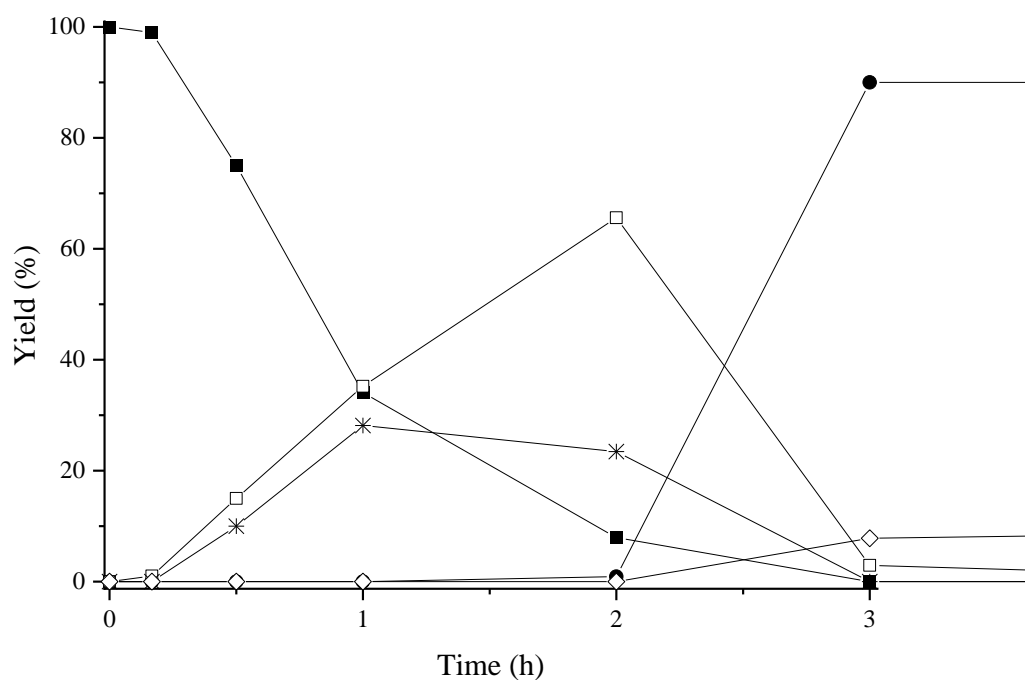


**Figure S23.** Kinetic study of the reductive amination of HMF with diethylamine (Entry 13 Table 3). Reaction conditions: HMF (2 mmol), diethylamine (4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. HMF (■), Amine (●), BHMF (◇).

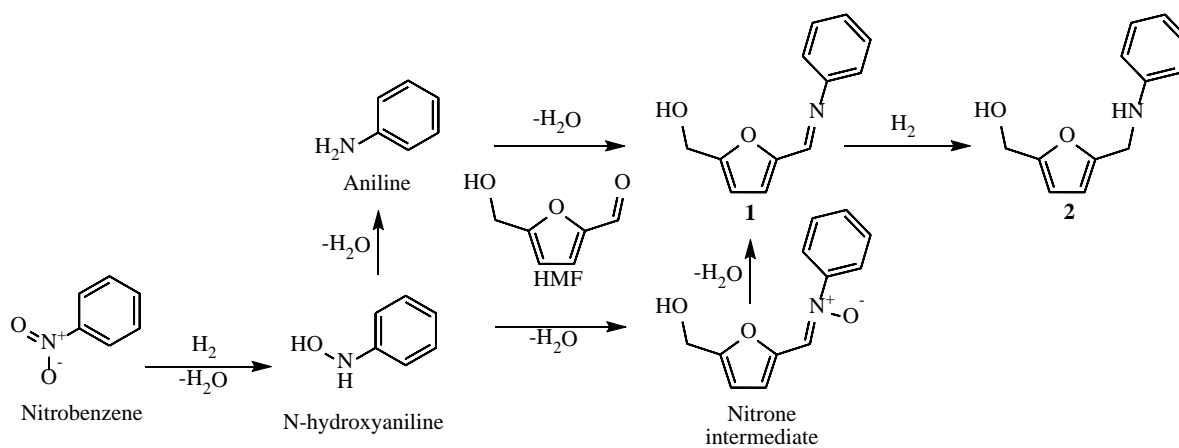


**Figure S24.** Kinetic study of the reductive amination of HMF with  $\text{NH}_3$  2 M in MeOH (Entry 14 Table 3). Reaction conditions: HMF (2 mmol),  $\text{NH}_3$  2 M in MeOH (4 mL, 8 mmol of  $\text{NH}_3$ ), Co@C NPs (20 mg), 10 bar of  $\text{H}_2$  and 60 °C. HMF (■), Imine (□), Amine (●).



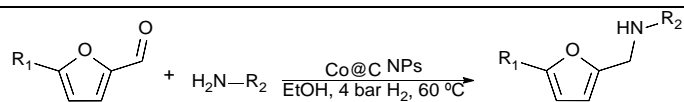


**Figure S25.** Kinetic study of the one-pot reductive amination of HMF with nitrobenzene (Entry 15 Table 3). Reaction conditions: HMF (2 mmol), nitrobenzene (2.8 mmol), EtOH (4 mL), Co@C NPs (20 mg), 20 bar of H<sub>2</sub> and 120 °C. HMF (■), Imine (□), Amine (●), Nitron intermediate (\*), BHMF (◇).



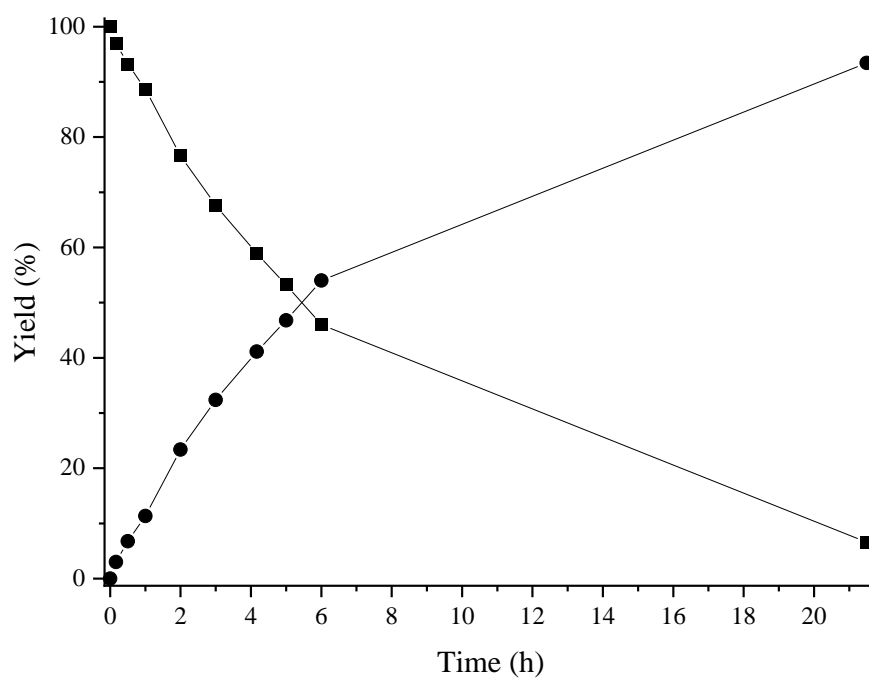
**Scheme S1.** Proposed reaction pathway for the direct reductive amination of HMF with nitrobenzene.

*Table S2. Results of the reductive amination of biomass derived aldehydes with different amines<sup>a</sup>*

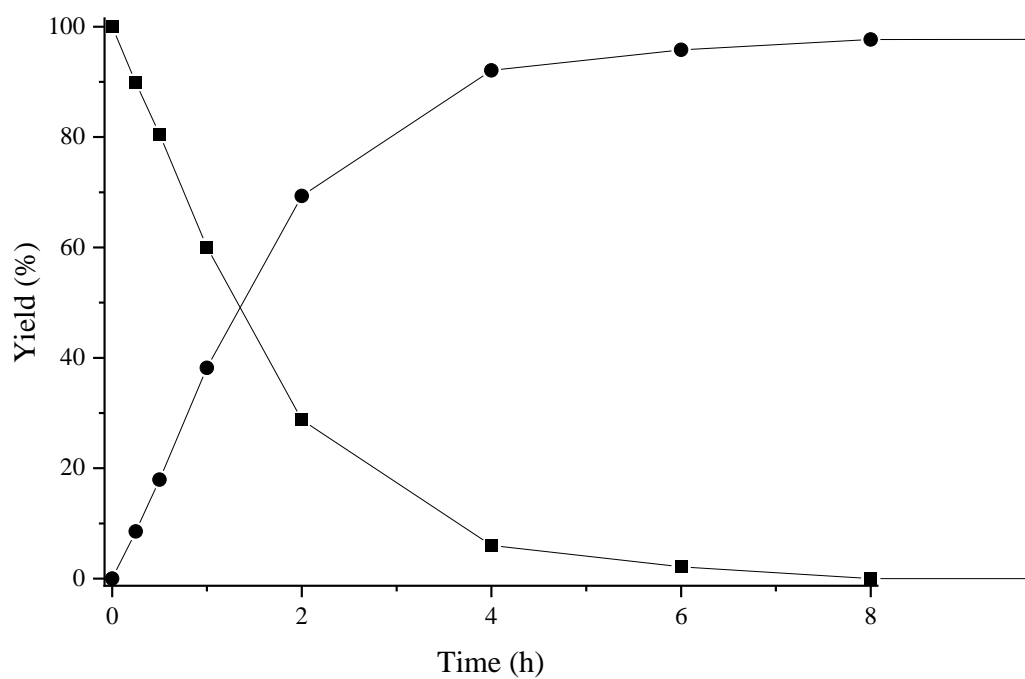


Entry	Product	Time (h)	Conversion Imine (%)	Yield Amine (%)	Selectivity Amine (%)
1		1	11	11	100
		21.5	97	95	98
2		1	39	38	97
		8	100	98	98
3		1	61	61	100
		6	100	100	100
4		1	18	17	97
		24	80	78	98
5		1	22	22	100
		21	99	99	100
6		1	17	16	94
		27	45	43	96
7		1	25	25	100
		27	99	99	100
8		1	8	8	100
		25	67	33	100
9 <sup>b</sup>		1	40 <sup>c</sup>	17	42
		8	100 <sup>c</sup>	41	41

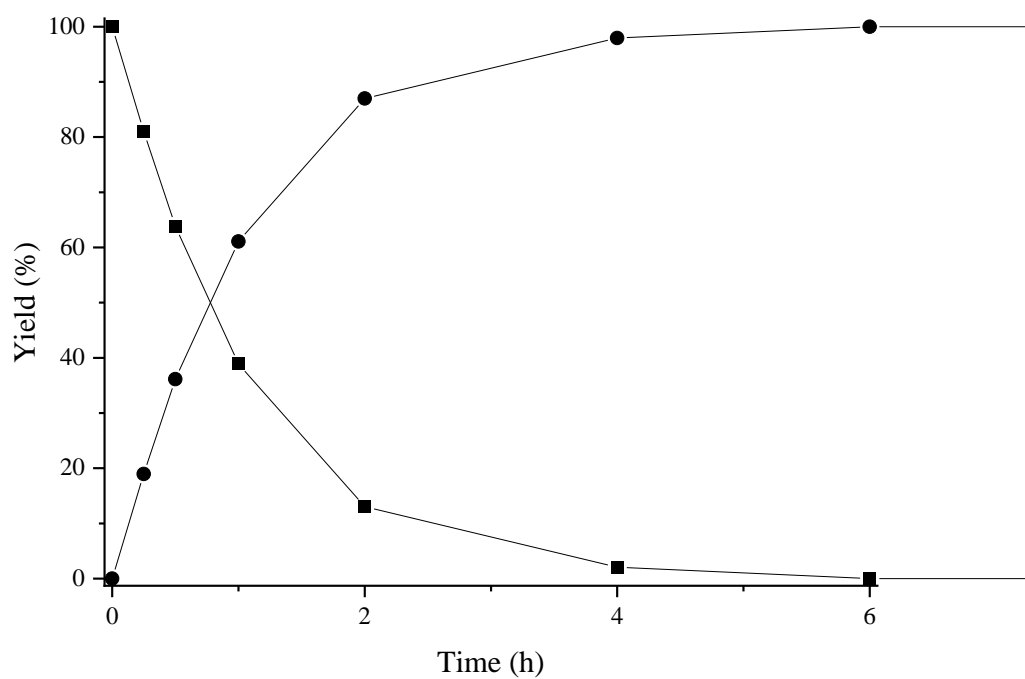
<sup>a</sup> Reaction conditions: Furanic aldehyde (2 mmol), amine (2.4 mmol), Co@C NPs (20 mg), EtOH (4 mL), 60 °C, and 4 bar of H<sub>2</sub>. <sup>b</sup> Using 4 mmol of the secondary amine. <sup>c</sup> HMF conversion.



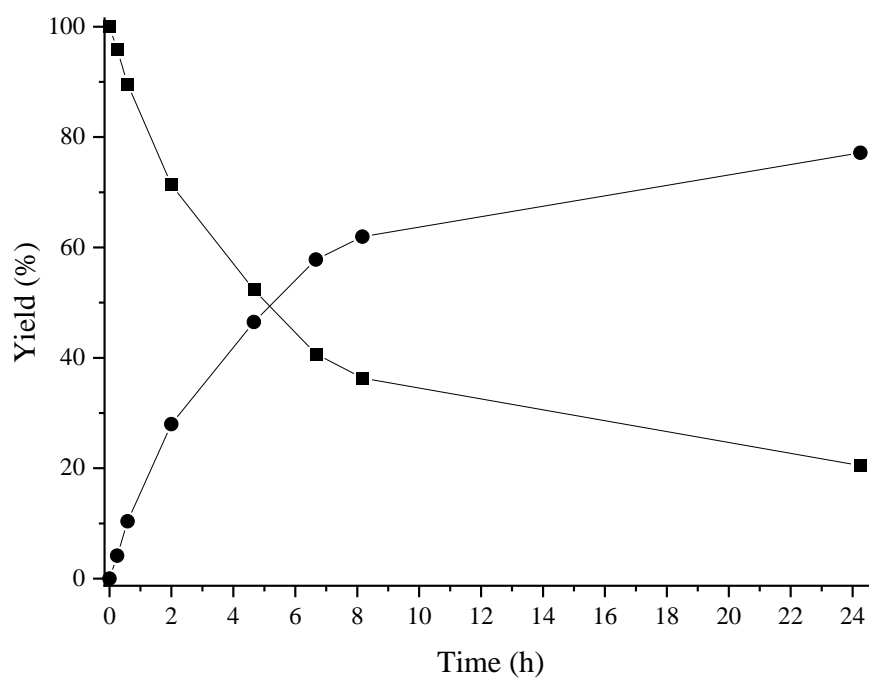
**Figure S26.** Kinetic study of the reductive amination of furfural with aniline (Entry 1 Table S2). Reaction conditions: Furfural (2 mmol), aniline (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of  $H_2$  and 60 °C. Imine (■), Amine (●).



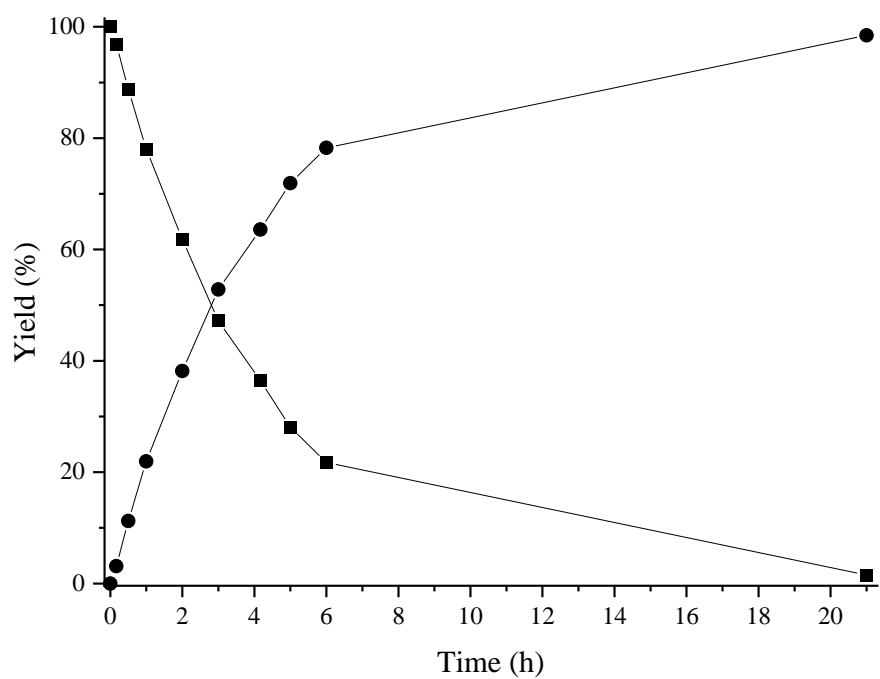
**Figure S27.** Kinetic study of the reductive amination of furfural with *p*-toluidine (Entry 2 Table S2). Reaction conditions: Furfural (2 mmol), *p*-toluidine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



**Figure S28.** Kinetic study of the reductive amination of furfural with methylamine (Entry 3 Table S2). Reaction conditions: Furfural (2 mmol), methylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).

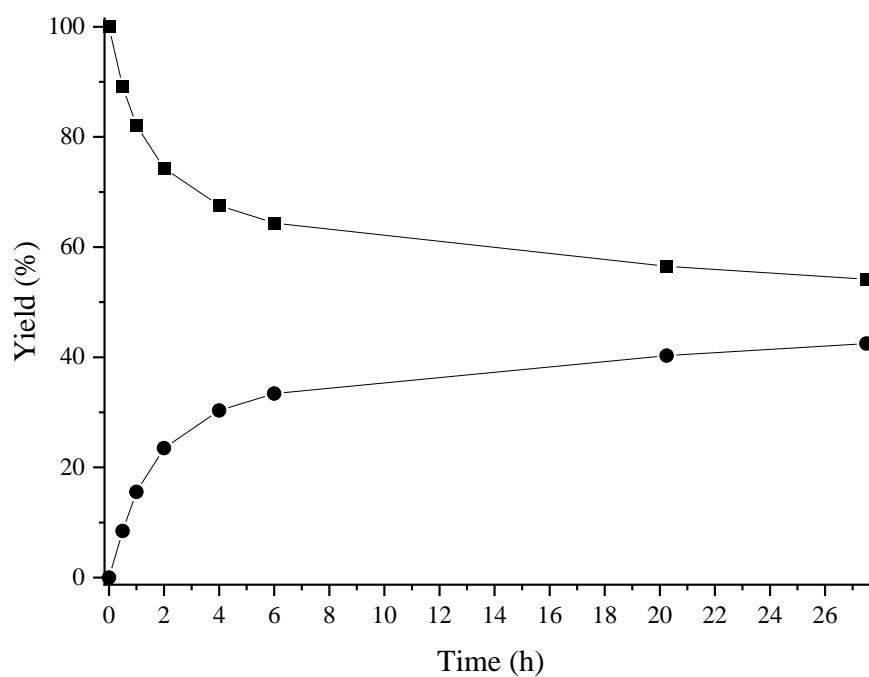


**Figure S29.** Kinetic study of the reductive amination of furfural with octylamine (Entry 4 Table S2). Reaction conditions: Furfural (2 mmol), octylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of  $H_2$  and 60 °C. Imine (■), Amine (●).

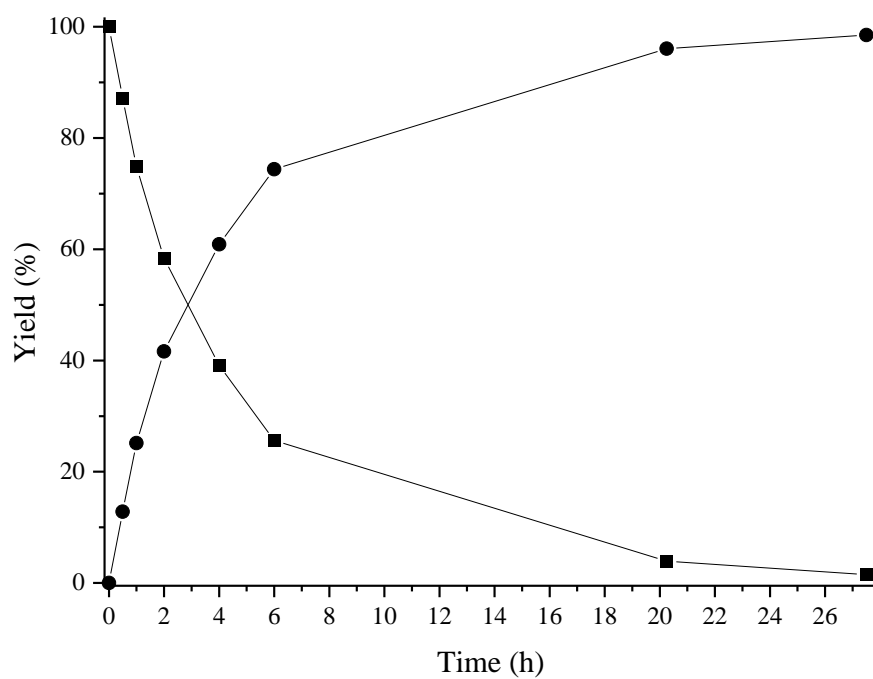


**Figure S30.** Kinetic study of the reductive amination of 5-methylfurfural with aniline (Entry 5 Table S2). Reaction conditions: 5-methylfurfural (2 mmol), aniline (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).

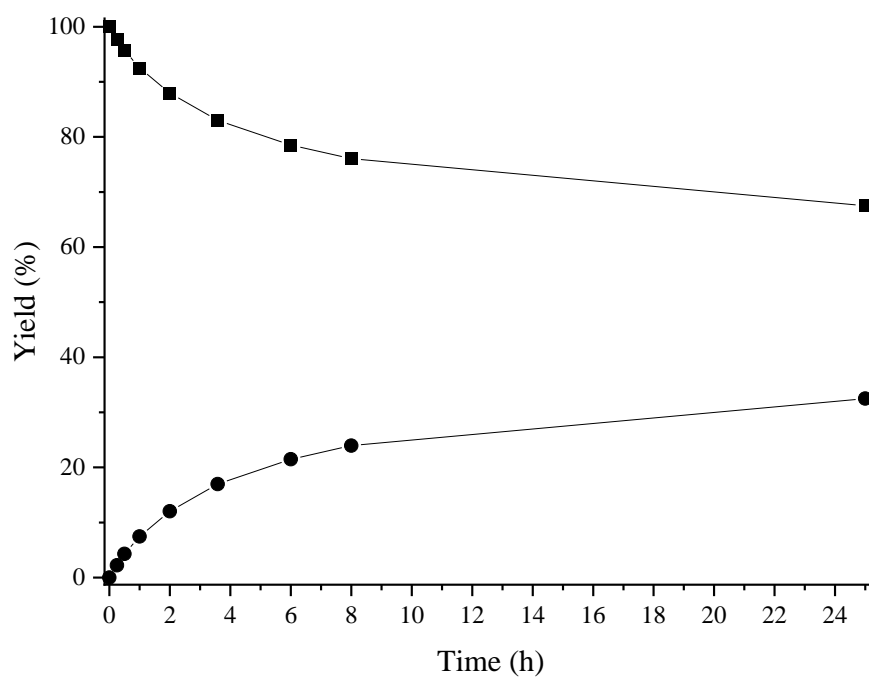




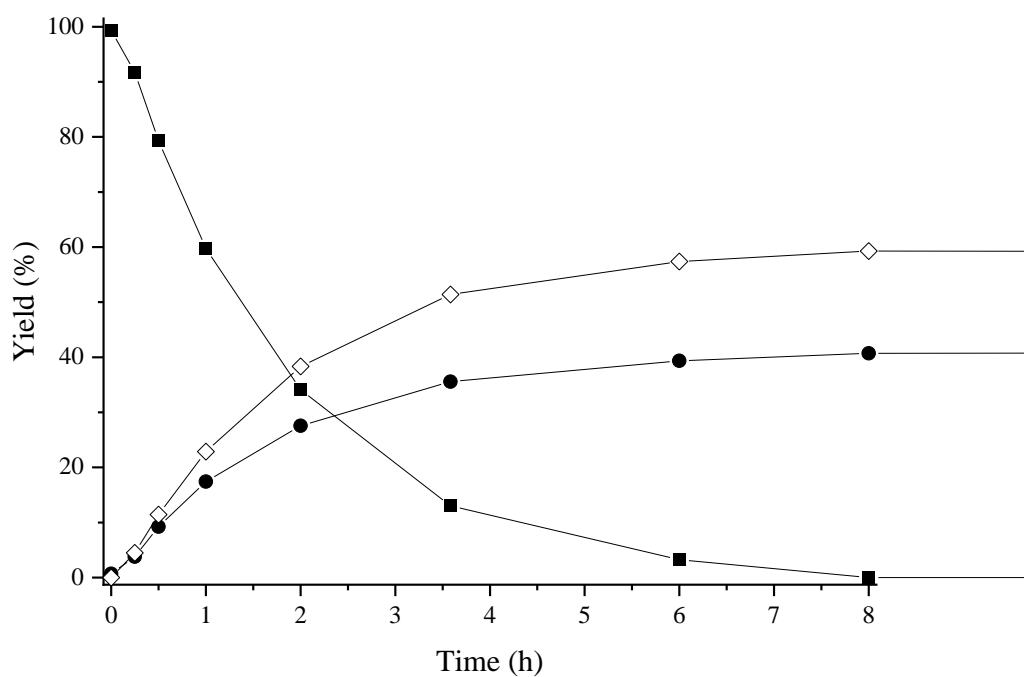
**Figure S31.** Kinetic study of the reductive amination of 5-methylfurfural with *p*-toluidine (Entry 6 Table S2). Reaction conditions: 5-methylfurfural (2 mmol), *p*-toluidine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



**Figure S32.** Kinetic study of the reductive amination of 5-methylfurfural with methylamine (Entry 7 Table S2). Reaction conditions: 5-methylfurfural (2 mmol), methylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).



**Figure S33.** Kinetic study of the reductive amination of 5-methylfurfural with octylamine (Entry 8 Table S2). Reaction conditions: 5-methylfurfural (2 mmol), octylamine (2.4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●).

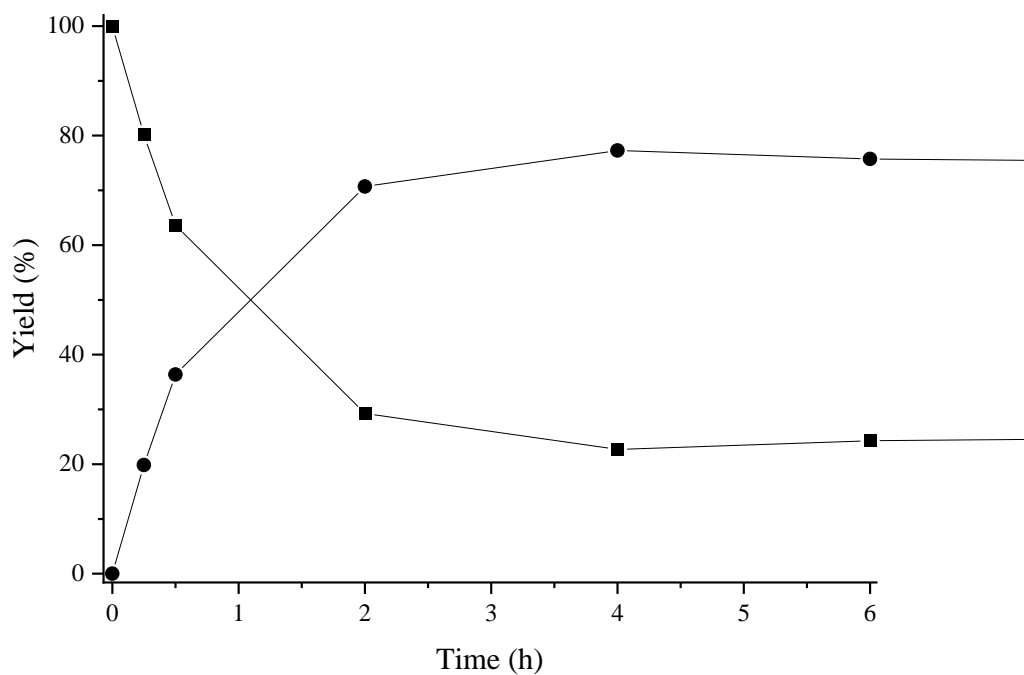


**Figure S34.** Kinetic study of the reductive amination of 5-methylfurfural with diethylamine (Entry 9 Table S2). Reaction conditions: 5-methylfurfural (2 mmol), diethylamine (4 mmol), EtOH (4 mL), Co@C NPs (20 mg), 4 bar of H<sub>2</sub> and 60 °C. Imine (■), Amine (●), 5-methylfurfural hydrogenated (◇).

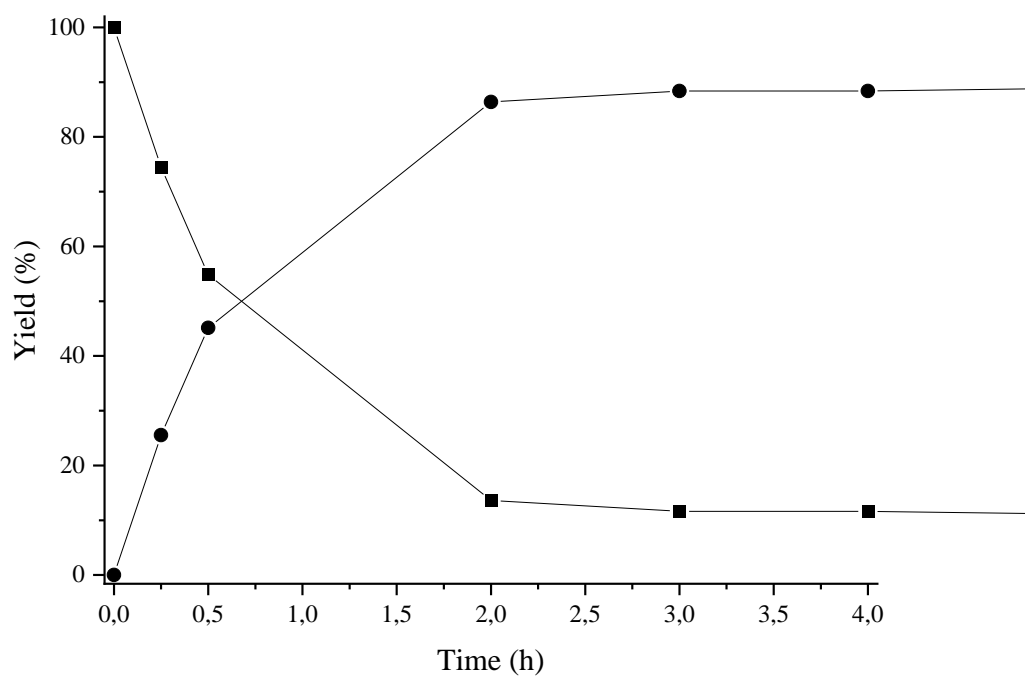
**Table S3.** Optimization of the substrate ratio and Novozym 435 loading for the esterification reaction of **5** with hexanoic acid<sup>a</sup>

Entry	Ratio 5 : Hexanoic Acid	Lipase (mg)	$r^0$	Time (h)	Yield (%)	Selectivity (%)
1	1 : 1	62.4	0.081	4	77	100
2	1 : 2	62.4	0.104	3	88	100
3	1 : 3	62.5	0.123	2.5	99	100
4	2 : 1	62.1	0.131	6	85	100
5	1 : 3	30.9	0.044	6	96	100

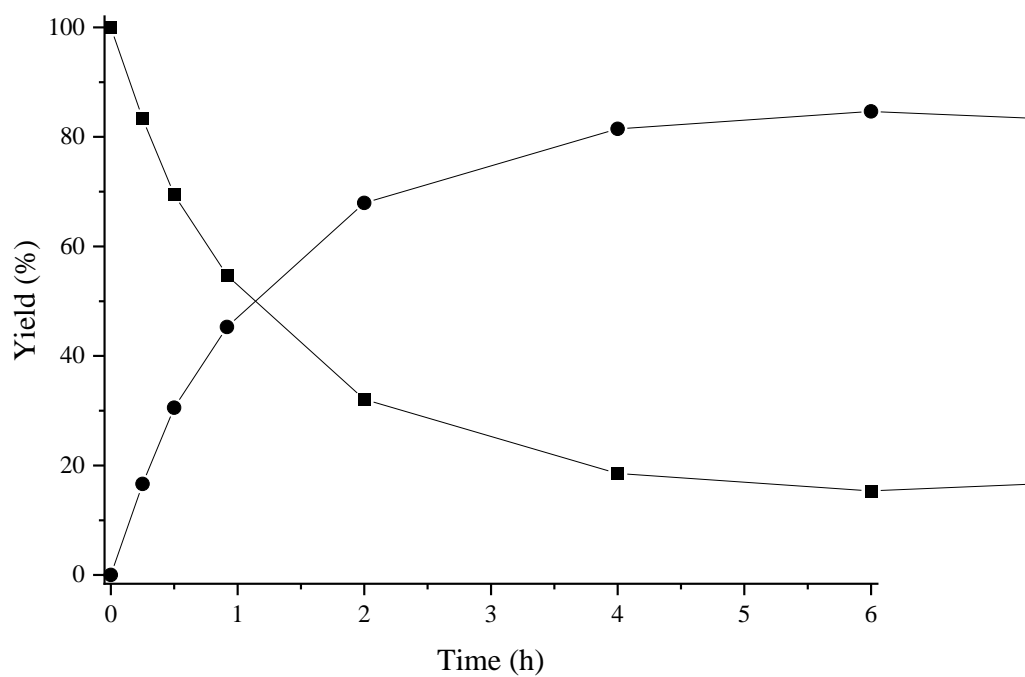
<sup>a</sup> Reaction conditions: **5** (0.1-0.2 mmol), Hexanoic Acid (0,1-0,3 mmol), Novozym 435, 2-MTHF (2.5 mL), molecular sieves (500 mg), 35 °C and 800 rpm.  $r^0$ : initial reaction rate of appearance of amino-ester **6** (mmol·h<sup>-1</sup>).



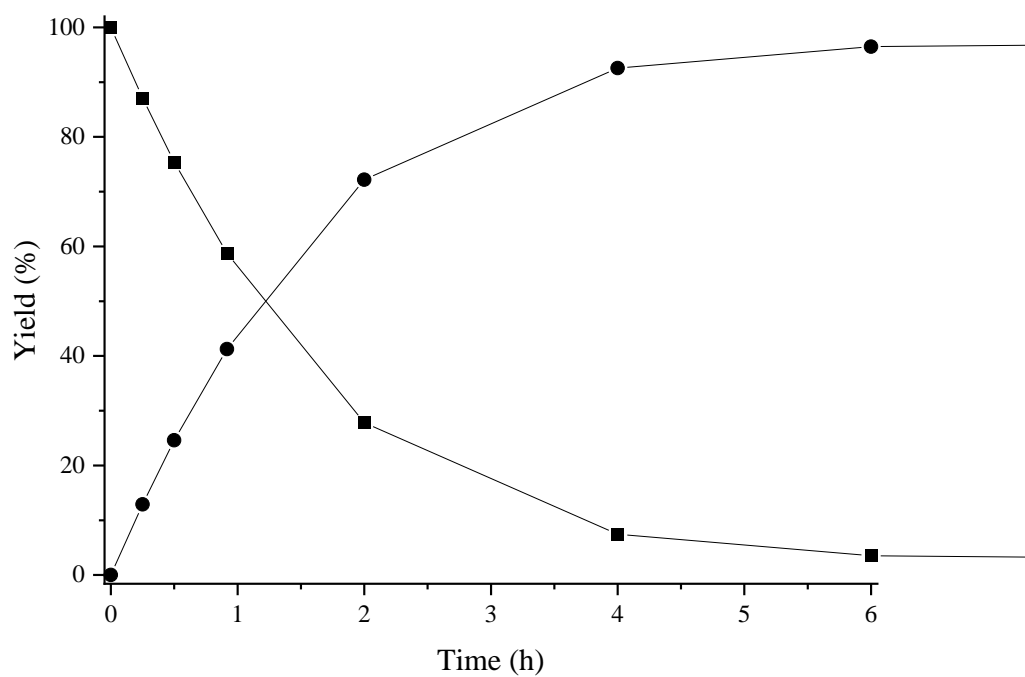
**Figure S35.** Kinetic study of the esterification of Amino-alcohol **5** (0.1 mmol) with hexanoic acid (0.1 mmol) (entry 1 Table S3), using Novozym 435 (62.4 mg) in 2-MTHF (2.5 mL), and molecular sieves (500 mg) at 35 °C. Amino-alcohol **5** (■); amino-ester **6** (●).



**Figure S36.** Kinetic study of the esterification of Amino-alcohol **5** (0.1 mmol) with hexanoic acid (0.2 mmol) (entry 2 Table S3), using Novozym 435 (62.4 mg) in 2-MTHF (2.5 mL), and molecular sieves (500 mg) at 35 °C. Amino-alcohol **5** (■); amino-ester **6** (●).

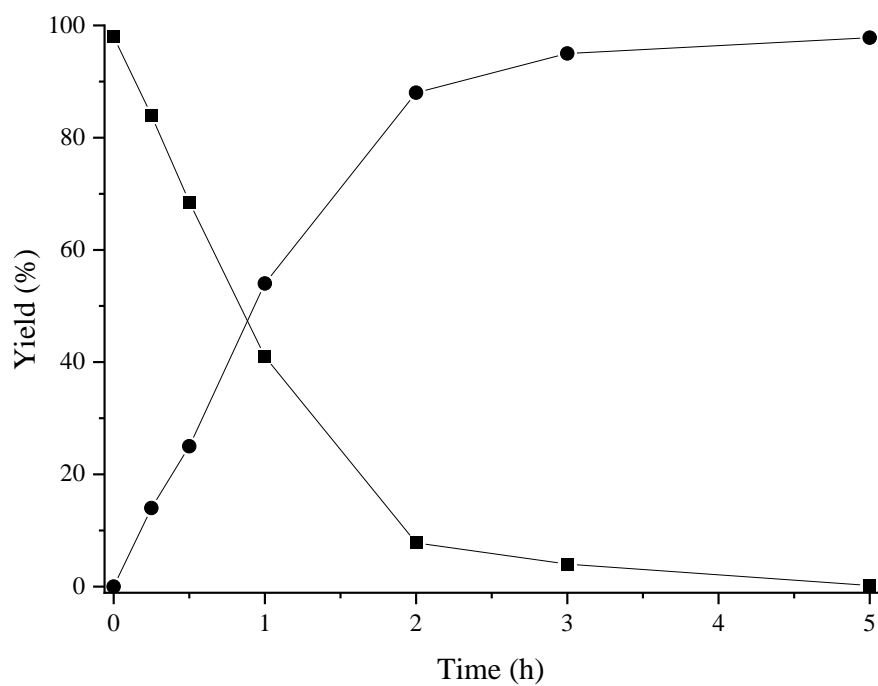


**Figure S37.** Kinetic study of the esterification of Amino-alcohol 5 (0.2 mmol) with hexanoic acid (0.1 mmol) (entry 4 Table S3), using Novozym 435 (62.1 mg) in 2-MTHF (2.5 mL), and molecular sieves (500 mg) at 35 °C. Amino-alcohol 5 (■); amino-ester 6 (●).

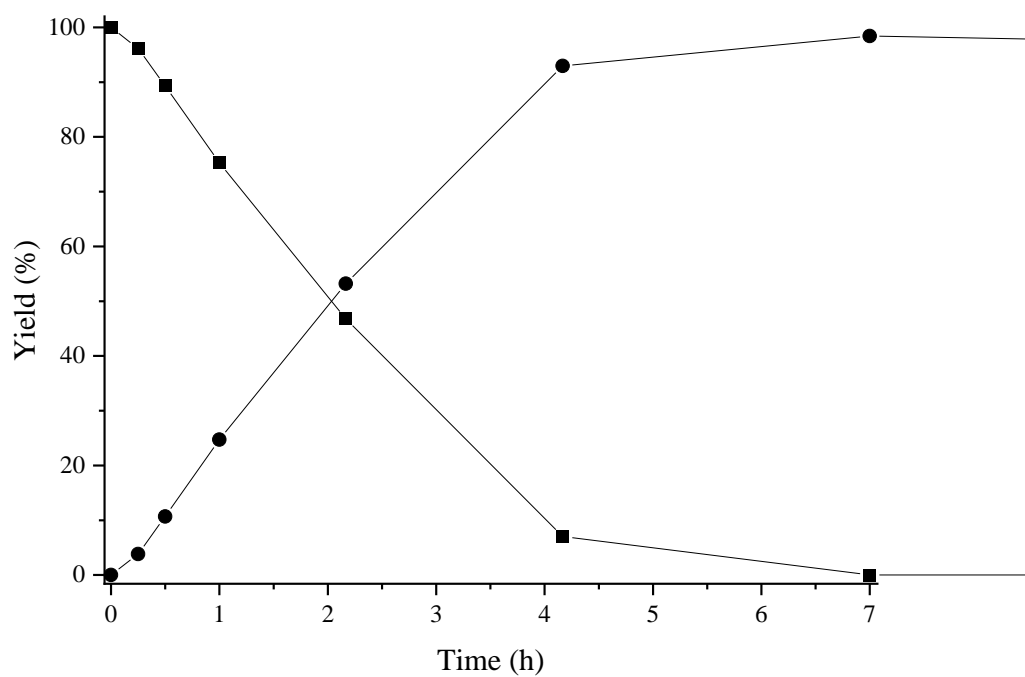


**Figure S38.** Kinetic study of the esterification of Amino-alcohol 5 (0.1 mmol) with hexanoic acid (0.3 mmol) (entry 5 Table S3), using Novozym 435 (30.9 mg) in 2-MTHF (2.5 mL), and molecular sieves (500 mg) at 35 °C. Amino-alcohol 5 (■); amino-ester 6 (●).

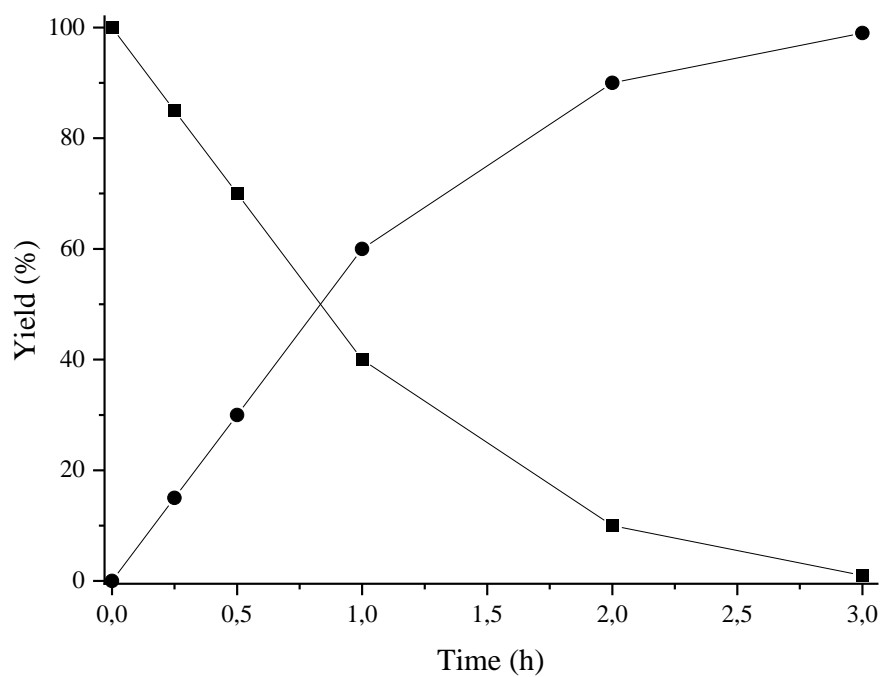




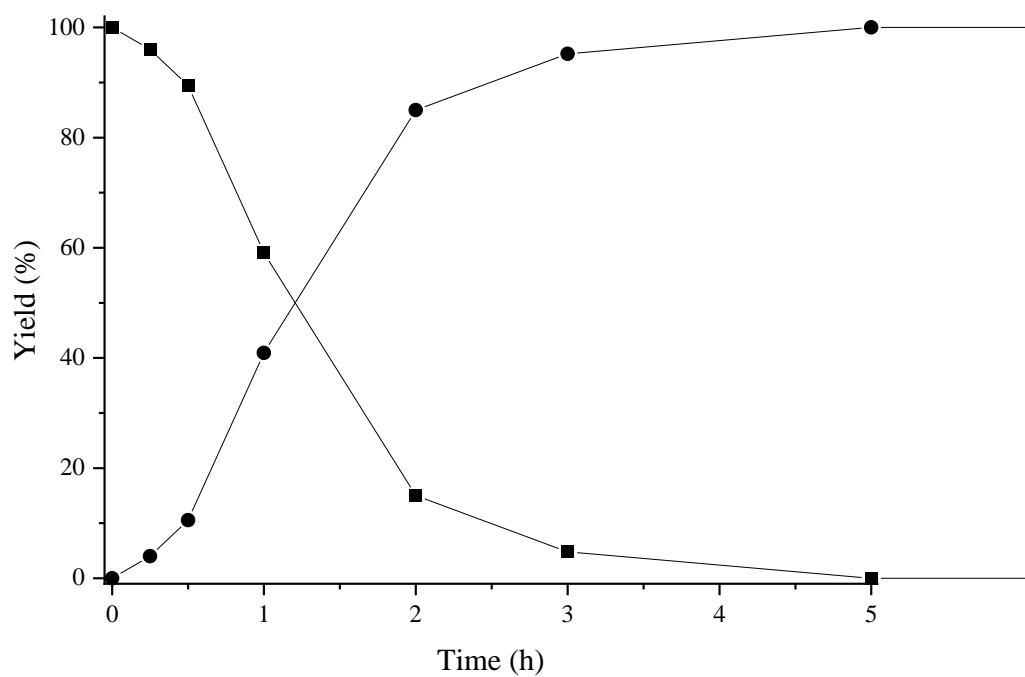
**Figure S39.** Kinetic study of the reductive amination of HMF with methylamine using 2-MTHF as solvent. Reaction conditions: HMF (2 mmol), methylamine 2 M in THF (2.4 mmol), 2-MTHF (4 mL), 20 mg of Co@C NPs, 4 bar of H<sub>2</sub> and 60 °C.



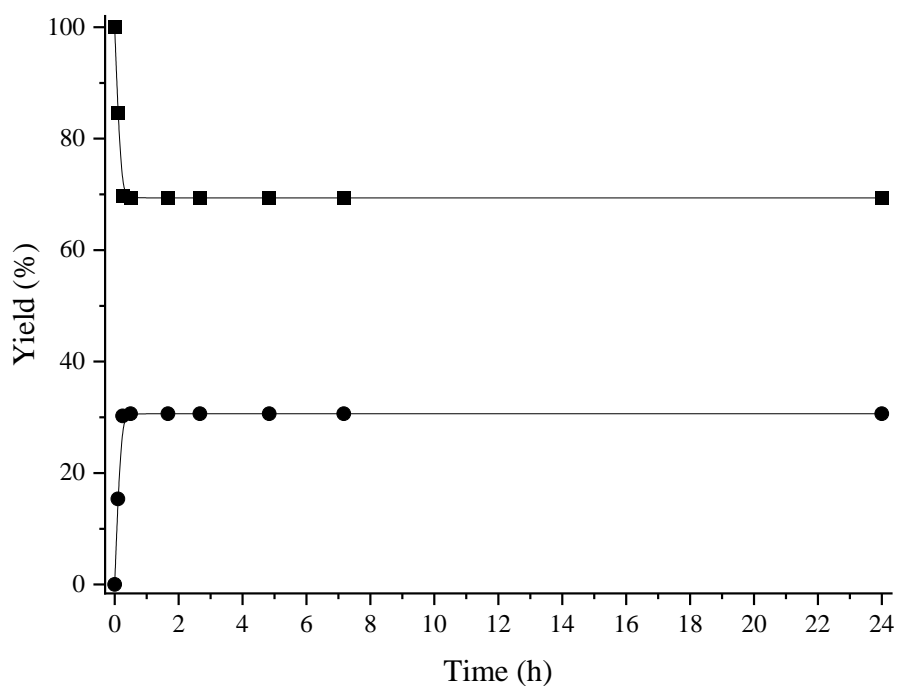
**Figure S40.** Kinetic study of the esterification of amino-alcohol **5** with butyric acid (Entry 1 Table 5). Reaction conditions: Amino-alcohol **5** (0.1 mmol), butanoic acid (0.3 mmol), Novozym 435 (62.5 mg), molecular sieves (500 mg) in 2-MTHF (2.5 mL) at 35 °C. Amino-alcohol **5** (■), amino-ester **8** (●).



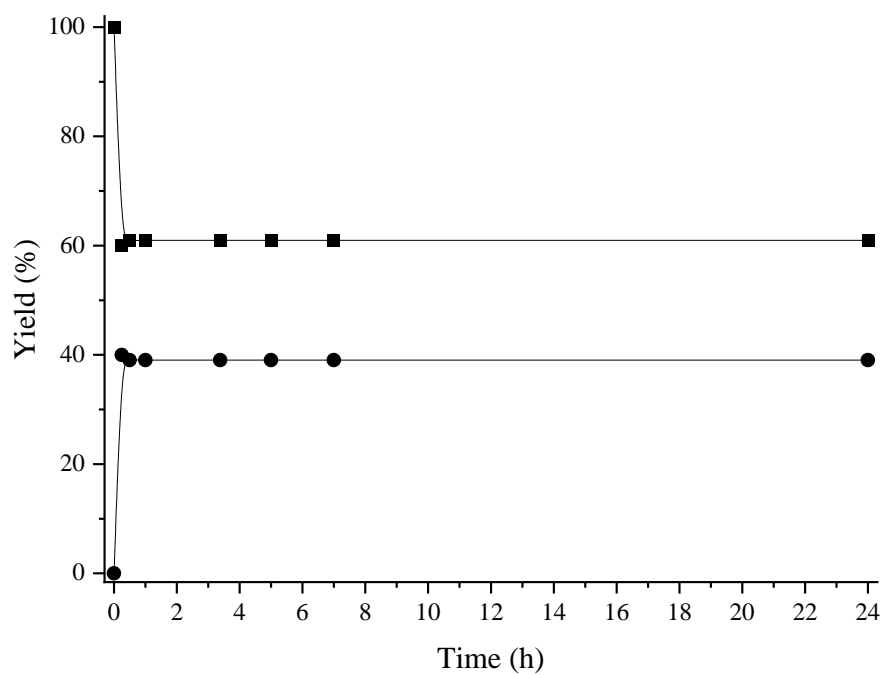
**Figure S41.** Kinetic study of the esterification of amino-alcohol **5** with octanoic acid (Entry 3 Table 5). Reaction conditions: Amino-alcohol **5** (0.1 mmol), octanoic acid (0.3 mmol), Novozym 435 (62.5 mg), molecular sieves (500 mg) in 2-MTHF (2.5 mL) at 35 °C. Amino-alcohol **5** (■), amino-ester **9** (●).



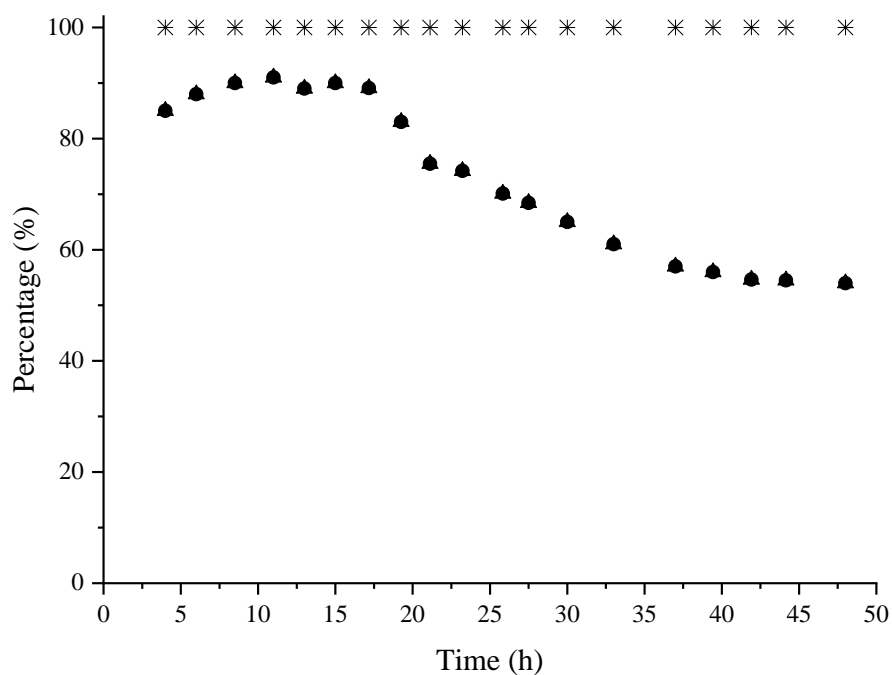
**Figure S42.** Kinetic study of the esterification of amino-alcohol **5** with palmitic acid (Entry 4 Table 5). Reaction conditions: Amino-alcohol **5** (0.1 mmol), palmitic acid (0.3 mmol), Novozym 435 (62.5 mg), molecular sieves (500 mg) in 2-MTHF (2.5 mL) at 35 °C. Amino-alcohol **5** (■), amino-ester **10** (●).



**Figure S43.** Kinetic study of the esterification of amino-alcohol **5** with ethyl hexanoate (Entry 5 Table 5). Reaction conditions: Amino-alcohol **5** (0.1 mmol), ethyl hexanoate (0.3 mmol), Novozym 435 (62.5 mg) in 2-MTHF (2.5 mL) at 35 °C. Amino-alcohol **5** (■), amino-ester **6** (●).



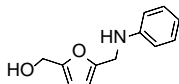
**Figure S44.** Kinetic study of the esterification of amino-alcohol **5** with ethyl octanoate (Entry 6 Table 5). Reaction conditions: Amino-alcohol **5** (0.1 mmol), ethyl octanoate (0.3 mmol), Novozym 435 (62.5 mg) in 2-MTHF (2.5 mL) at 35 °C. Amino-alcohol **5** (■), amino-ester **9** (●).



**Figure S45.** Results of the bioesterification of the amino-alcohol **5** with hexanoic acid in a continuous-flow reactor using Novozym 435 as catalyst and molecular sieves. Reaction conditions: Amino-alcohol **5** in 2-MTHF feed (0.5 wt %), hexanoic acid (1.8 wt %), Novozym 435 (50 mg), molecular sieves 4 A 0.4-0.6 mm (2.4 g), flow rate 1 mL h<sup>-1</sup> (WHSV: 0.089 h<sup>-1</sup>) at 60 °C. Amino-alcohol **5** conversion (▲); amino-ester **6** yield (●); selectivity to **6** (\*).

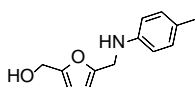
## Spectral data of the reductive amination of HMF with different primary and secondary amines (Table 3)

**Amino-alcohol 2 (entry 1 Table 3):** (5-((phenylamino)methyl)furan-2-yl)methanol



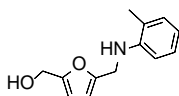
GC/MS (relative intensity) m/z: 203 (M<sup>+</sup>, 54), 172 (21), 111 (100), 106 (37), 94 (13), 93 (15), 83 (37), 77 (28), 65 (20), 55 (25), 51 (15), 39 (11).

**Entry 2 Table 3:** (5-((p-tolylamino)methyl)furan-2-yl)methanol



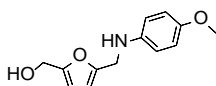
GC/MS (relative intensity) m/z: 217 (M<sup>+</sup>, 54), 186 (19), 120 (11), 111 (100), 110 (31), 108 (21), 107 (41), 106 (25), 91 (20), 83 (27), 77 (16), 65 (25), 55 (24), 53 (10).

**Entry 3 Table 3:** (5-((o-tolylamino)methyl)furan-2-yl)methanol



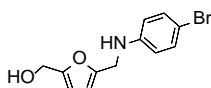
GC/MS (relative intensity) m/z: 217 (M<sup>+</sup>, 67), 186 (14), 111 (100), 108 (13), 107 (18), 106 (12), 91 (15), 83 (34), 77 (11), 65 (19), 55 (19).

**Entry 4 Table 3:** (5-(((4-methoxyphenyl)amino)methyl)furan-2-yl)methanol



GC/MS (relative intensity) m/z: 233 (M<sup>+</sup>, 60), 215 (13), 124 (15), 123 (94), 122 (68), 111 (100), 108 (34), 95 (26), 94 (11), 92 (11), 83 (39), 80 (10), 77 (14), 65 (21), 64 (11), 63 (10), 55 (30), 53 (14), 52 (14), 51 (10), 41 (10), 39 (11).

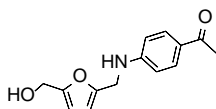
**Entry 5 Table 3:** (5-(((4-bromophenyl)amino)methyl)furan-2-yl)methanol



GC/MS (relative intensity) m/z: 282 (M<sup>+</sup>, 1), 281 (18), 265 (94), 264 (48), 263 (100), 262 (37), 253 (14), 248 (10), 221 (18), 220 (24), 207 (34), 195 (16), 184 (16), 182 (12), 173 (16), 171 (17), 169 (29), 157 (13), 156 (16), 155 (12), 143 (15), 141 (10), 115 (21), 95 (100), 81 (17), 79 (12), 77 (14), 75 (20), 73 (14), 64 (11), 50 (28), 43 (14), 39 (14), 28 (18).

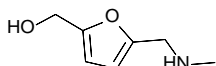


**Entry 6 Table 3:** 1-(4-(((5-(hydroxymethyl)furan-2-yl)methyl)amino)phenyl)ethan-1-one



GC/MS (relative intensity) m/z: 245 ( $M^+$ , 24), 111 (100), 83 (25), 55 (15).

**Entry 7 Table 3:** Amino-alcohol **5** (N-methyl-(5-hydroxymethyl)furfurylamine)

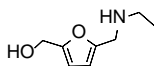


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.17 (d,  $J = 3.1$  Hz, 1H), 6.12 (d,  $J = 3.1$  Hz, 1H), 4.52 (s, 2H), 3.70 (s, 2H), 3.43 (s, 1H), 2.39 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  154.15, 152.83, 108.41, 108.23, 57.29, 47.88, 35.38.

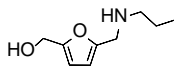
GC/MS (relative intensity) m/z: 141 ( $M^+$ , 22), 140 (21), 111 (28), 110 (100), 83 (19), 82 (11), 81 (12), 65 (10), 55 (21), 44 (14), 42 (14).

**Entry 8 Table 3:** (5-((ethylamino)methyl)furan-2-yl)methanol



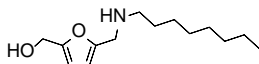
GC/MS (relative intensity) m/z: 155 ( $M^+$ , 29), 154 (11), 153 (26), 138 (71), 124 (51), 122 (10), 121 (19), 117 (10), 111 (100), 96 (61), 94 (16), 83 (20), 81 (28), 79 (28), 74 (14), 73 (22), 65 (30), 64 (13), 57 (14), 56 (11), 55 (16), 41 (10), 39 (18), 38 (15), 27 (16), 14 (10).

**Entry 9 Table 3:** (5-((propylamino)methyl)furan-2-yl)methanol



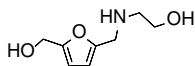
GC/MS (relative intensity) m/z: 169 ( $M^+$ , 15), 140 (30), 137 (11), 112 (21), 111 (100), 109 (12), 97 (10), 95 (13), 83 (28), 81 (10), 72 (10), 69 (10), 65 (13), 55 (26), 53 (10), 51 (17), 43 (11), 41 (26), 40 (10), 39 (17), 32 (13), 30 (10), 29 (11), 38 (35), 27 (10).

**Entry 10 Table 3:** (5-((octylamino)methyl)furan-2-yl)methanol



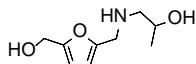
GC/MS (relative intensity) m/z: 239 ( $M^+$ , 3), 140 (11), 111 (100).

**Entry 11 Table 3:** 2-(((5-(hydroxymethyl)furan-2-yl)methyl)amino)ethan-1-ol



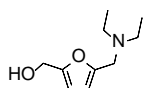
GC/MS (relative intensity) m/z: 171 ( $M^+$ , 4), 141 (13), 140 (46), 122 (16), 112 (10), 111 (100), 83 (26), 56 (10), 55 (18).

**Entry 12 Table 3:** 1-(((5-(hydroxymethyl)furan-2-yl)methyl)amino)propan-2-ol



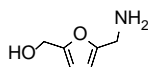
GC/MS (relative intensity) m/z: 185 ( $M^+$ , 82), 181 (33), 177 (35), 155 (55), 141 (28), 140 (13), 139 (15), 138 (61), 137 (56), 136 (46), 123 (57), 122 (31), 120 (18), 111 (100), 109 (99), 108 (17), 97 (29), 83 (15), 81 (40), 80 (16), 79 (65), 73 (39), 68 (14), 67 (17), 55 (25), 51 (49=), 48 (40), 46 (10 (44 (29), 38 (12), 35 (21), 29 (29), 28 (48), 17 (15), 15 (24).

**Entry 13 Table 3:** (5-((diethylamino)methyl)furan-2-yl)methanol



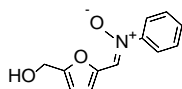
GC/MS (relative intensity) m/z: 183 ( $M^+$ , 26), 168 (31), 128 (17), 111 (100), 109 (16), 97 (35), 83 (29), 81 (15), 70 (16), 65 (13), 55 (14), 50 (11), 41 (17), 39 (11), 29 (12), 28 (15).

**Entry 14 Table 3:** (5-(aminomethyl)furan-2-yl)methanol



GC/MS (relative intensity) m/z: 127 ( $M^+$ , 39), 124 (14), 109 (21), 96 (100), 83 (18), 82 (11), 79 (16), 78 (21), 71 (23), 69 (13), 68 (26), 55 (15), 53 (17), 51 (10), 46 (15), 45 (40), 43 (18), 42 (14), 41 (31), 39 (35), 31 (46), 30 (20), 29 (14).

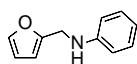
**Nitron intermediate Scheme S1:** 1-(5-(hydroxymethyl)furan-2-yl)-N-phenylmethanimine oxide



GC/MS (relative intensity) m/z: 217 ( $M^+$ , 36), 202 (11), 201 (86), 199 (21), 188 (11), 171 (10), 170 (31), 155 (13), 154 (15), 143 (11), 142 (36), 125 (13), 104 (36), 91 (97), 81 (10), 79 (13), 78 (12), 77 (100), 64 (11), 52 (14), 51 (44), 50 (15), 41 (17), 39 (18).

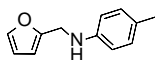
**Spectral data of the the reductive amination of biomass derived aldehydes with different amines (Table S2)**

**Entry 1 Table S2:** N-(furan-2-ylmethyl)aniline



GC/MS (relative intensity) m/z: 173 ( $M^+$ , 67), 172 (51), 81 (100), 77 (16), 53 (22), 51 (10).

**Entry 2 Table S2:** N-(furan-2-ylmethyl)-4-methylaniline



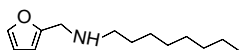
GC/MS (relative intensity) m/z: 187 ( $M^+$ , 61), 186 (58), 91 (10), 81 (100), 77 (14), 53 (23).

**Entry 3 Table S2:** 1-(furan-2-yl)-N-methylmethanamine



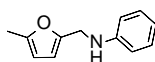
GC/MS (relative intensity) m/z: 111 ( $M^+$ , 46), 110 (17), 82 (48), 81 (100), 78 (11), 67 (10), 57 (22), 55 (17), 54 (12), 53 (40), 52 (12), 51 (16), 45 (44), 44 (27), 43 (19), 42 (64), 41 (25), 40 (15), 39 (27), 29 (16), 28 (42), 27 (29).

**Entry 4 Table S2:** N-(furan-2-ylmethyl)octan-1-amine



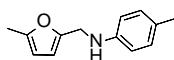
GC/MS (relative intensity) m/z: 209 ( $M^+$ , 5), 110 (46), 81 (100), 53 (10).

**Entry 5 Table S2:** N-((5-methylfuran-2-yl)methyl)aniline



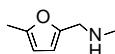
GC/MS (relative intensity) m/z: 187 ( $M^+$ , 32), 95 (100), 93 (15), 77 (10).

**Entry 6 Table S2:** 4-methyl-N-((5-methylfuran-2-yl)methyl)aniline



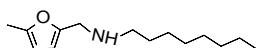
GC/MS (relative intensity) m/z: 201 ( $M^+$ , 27), 107 (23), 95 (100).

**Entry 7 Table S2:** N-methyl-1-(5-methylfuran-2-yl)methanamine



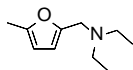
GC/MS (relative intensity) m/z: 125 ( $M^+$ , 35), 124 (32), 110 (38), 108 (11), 95 (100), 53 (11), 51 (12), 45 (17), 44 (25), 43 (35), 42 (31), 41 (15), 28 (17), 27 (11).

**Entry 8 Table S2:** N-((5-methylfuran-2-yl)methyl)octan-1-amine



GC/MS (relative intensity) m/z: 223 ( $M^+$ , 5), 95 (100).

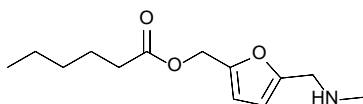
**Entry 9 Table S2:** N-ethyl-N-((5-methylfuran-2-yl)methyl)ethanamine



GC/MS (relative intensity) m/z: 167 ( $M^+$ , 21), 95 (100).

**Spectral data of the N-methyl substituted amino-esters**

**Amino-ester 6:** (5-((methylamino)methyl)furan-2-yl)methyl hexanoate

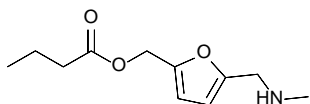


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  6.32 (d,  $J = 3.1$  Hz, 1H), 6.16 (d,  $J = 3.1$  Hz, 1H), 5.01 (s, H), 3.74 (s, 2H), 2.43 (s, 3H), 2.36 – 2.18 (m, 2H), 1.62 (p,  $J = 7.4$  Hz, 3H), 1.39 – 1.12 (m, 4H), 0.90 – 0.84 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.64, 154.38, 149.13, 111.36, 108.33, 58.16, 48.02, 35.60, 34.29, 31.39, 24.70, 22.42, 14.02.

GC/MS (relative intensity) m/z: 239 ( $M^+$ , 6), 124 (17), 122 (12), 110 (100), 99 (19), 96 (12), 95 (11), 94 (26), 81 (10), 71 (13), 44 (13), 43 (22), 42 (14), 41 (10).

**Amino-ester 6a:** (5-((methylamino)methyl)furan-2-yl)methyl butyrate

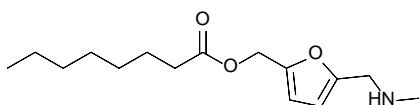


$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  6.31 (d,  $J = 3.2$  Hz, 1H), 6.15 (d,  $J = 3.2$  Hz, 1H), 5.01 (s, 2H), 3.73 (s, 2H), 2.43 (s, 3H), 2.32 – 2.26 (m, 3H), 1.76 – 1.58 (m, 2H), 0.94 (t,  $J = 7.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.41 (d,  $J = 4.9$  Hz), 154.47, 149.09, 111.35, 108.26, 58.11, 48.13, 36.15, 35.72, 18.50, 13.72.

GC/MS (relative intensity) m/z: 211 ( $M^+$ , 9), 181 (13), 180 (14), 124 (17), 123 (10), 122 (18), 110 (100), 96 (10), 94 (25), 81 (13), 71 (28), 44 (15), 43 (19), 42 (14).

**Amino-ester 6b:** (5-((methylamino)methyl)furan-2-yl)methyl octanoate

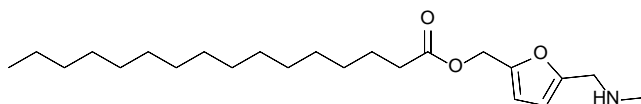


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.34 (d,  $J = 3.1$  Hz, 1H), 6.28 (d,  $J = 3.2$  Hz, 1H), 5.01 (s, 2H), 3.84 (s, 2H), 2.48 (s, 3H), 2.35 – 2.28 (m, 2H), 1.67 – 1.56 (m, 3H), 1.36 – 1.17 (m, 8H), 0.93 – 0.82 (m, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  173.59, 152.23, 149.78, 111.51, 109.72, 58.06, 47.14, 34.70, 34.32, 31.79, 29.19, 29.03, 25.02, 22.72, 14.19.

GC/MS (relative intensity)  $m/z$ : 267 ( $\text{M}^+$ ), 207 (19), 172 (14), 139 (13), 124 (32), 112 (16), 111 (13), 110 (100), 96 (18), 95 (30), 94 (37), 81 (14), 44 (16), 43 (17), 42 (23), 41 (23), 32 (18), 29 (11), 28 (15).

**Amino-ester 6c:** (5-((methylamino)methyl)furan-2-yl)methyl palmitate



$^1\text{H}$  NMR (401 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55 (d,  $J = 3.2$  Hz, 1H), 6.38 (d,  $J = 3.2$  Hz, 1H), 5.01 (s, 2H), 4.04 (s, 2H), 2.58 (s, 3H), 2.30 (t,  $J = 6.0$  Hz, 2H), 1.61 (td,  $J = 14.8, 6.0$  Hz, 2H), 1.35 – 1.14 (m, 24H), 0.86 (t,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.48, 151.14, 147.07, 112.99, 111.86, 57.88, 44.97, 34.23, 32.49, 32.04, 29.80, 29.77, 29.76, 29.71, 29.57, 29.47, 29.37, 29.36, 29.27, 29.22, 24.95, 22.80, 14.23.

GC/MS (relative intensity)  $m/z$ : 379 ( $\text{M}^+$ , 4), 124 (27), 123 (14), 122 (10), 110 (89), 96 (17), 95 (55), 94 (100), 57 (10), 43 (17), 42 (11), 41 (11).