A novel method for the enamination of 1,3-dicarbonyl compounds catalyzed by laccase in water

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Supporting Information

1 Materials

Rhus vernicifera laccase, *Trametes versicolor* laccase, *Trametes villosa* laccase and Bovine serum albumin used in this study were purchased from Sigma (Beijing, China). These enzymes were used for enzymatic reaction without further purification. All the chemical reagents were purchased from Shanghai Chemical Reagent Company (Shanghai, China). Commercially available reagents and solvents were used without further purification. The conversions were monitored by HPLC system (Agilent 1100) or GCsystem (Shimadzu 14B). ^{1}H-NMR spectra were recorded on an Inova 500 (1H, 500 MHz) spectrometer.

2 Determination of laccase activity according to reference (RSC Adv., 2013, 3, 19259–19263): A 0.1 M solution of ABTS (0.3 mL) in 0.01 M acetate buffer (pH = 4.5) was diluted with 0.01 M acetate buffer (2.6 mL, pH = 4.5) and treated with a solution of laccase in the same buffer (0.1mL). The change in absorption was followed via UV/Vis-spectroscopy (λ = 414 nm). One unit was defined as the amount of laccase (*Trametes versicolor*, Sigma) that converts 1 mmol of ABTS per minute at pH = 4.5 at r.t..

Laccase	Specific Activity
Rhus vernicifera laccase	55U/mg
Trametes versicolor laccase	18U/mg
Trametes villosa laccase	30U/mg

3 ^{1}H-NMR data of compounds 1-11

1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1H), 4.93 (s, 1H), 3.21 (dd, *J* = 13, 6.5 Hz, 2H), 1.97 (s, 3H), 1.90 (s, 3H), 1.55 (dd, *J* = 7.0, 14.5 Hz, 2H), 1.40 (dd, J = 7.5, 15Hz, 2H), 0.92 (t, *J* = 7.0 Hz, 3H).

2. ^{1}H NMR (500 MHz, CDCl3) δ 12.47 (s, 1H), 7.34 (m, 2H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.11 (*d*, *J* = 8.0 Hz, 2H), 5.19 (s, 1H), 2.10 (d, *J* = 2.5 Hz, 3H), 1.99 (d, *J* = 2.0 Hz, 3H).

3. ^{1}H NMR (500 MHz, $CDCl_3$) δ5.07 (s, 1H), 3.24 (t, *J* = 7.5 Hz, 4H), 2.53 (s, 3H), 2.08 (s, 3H), 1.57 (m, 4H), 1.35 (m, 4H), 0.97 (t, *J* = 7.0 Hz, 6H).

4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 4.89 (s, 1H), 3.35 (s, 1H), 1.96 (s, 3H), 1.92 (s, 3H), 1.83 (s, 2H), 1.74 (s, 2H), 1.56 (s, 1H), 1.30 (m, 5H).

5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.87（s, 2H), 4.95 (s, 2H), 3.23 (q, J = 6.5, 13 Hz, 4H), 1.99 (s, 6H), 1.91 (s, 6H), 1.60 (m, 4H), 1.42 (m, 4H).

6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.37 (s, 1H), 4.90 (s, 1H), 2.06 (s, 3H), 1.99 (s, 3H), 1.41 (s, 9H).

7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.14 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.09 (s, 1H), 2.02 (s, 3H), 1.93 (s, 3H).

8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (s, 1H), 6.87 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 4.65 (s, 1H), 4.15 (q, J = 7.0, 14 Hz, 2H), 1.86 (s, 3H), 1.28 (t, J = 7.5 Hz, 3H).

9. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 4.43 (s, 1H), 4.08 (q, J = 7.0, 14 Hz, 2H), 3.2 (dd, *J* = 7.0, 13 Hz, 2H), 1.91 (s, 3H), 1.55 (m, 2H), 1.40 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H).

10. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 4.43 (s, 1H), 3.61 (s, 3H), 3.19 (dd, *J* = 7.5, 14 Hz, 2H), 1.93 (s, 3H), 1.54 (m, 2H), 1.45 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

11. ^{1}H NMR (500 MHz, CDCl3) δ 11.50 (s, 1H), 7.86 (m, 2H), 7.38 (m, 3H), 5.65 (s, 1H), 3.31 (q, J = 7.0, 13 Hz, 2H), 2.05 (s, 3H), 1.63 (m, 2H), 1.45 (m, 2H), 0.96 (t, *J* = 7.0 Hz, 3H).