Supporting Information

A photoinduced cross-dehydrogenative-coupling (CDC) reaction between aldehydes and *N*-hydroxyimides by TiO_2-Co Ascorbic acid nanohybrid under visible light irradiation

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Experimental

General remarks

All chemicals were purchased from Merck and Fluka Chemical Companies. The FT-IR spectra were recorded on NICOLET system. TEM images were obtained by TEM instrumentation (Philips CM 10). The progress of the reactions was monitored by TLC using silica-gel SIL G/UV 254 plates. NMR spectra were recorded on a Brucker Avance DPX 250 and 400 MHz instruments. Powder X-ray diffraction (XRD) experiments were performed on a Bruker D8-advance X-ray diffractometer with Cu Ka (λ = 1.54178 A) radiation. Diffuse reflectance UV-vis spectra were recorded using an Avantes spectrometer (Avaspec-2048-TEC model).

Fabrication of TiO_2 nanoparticles

To a solution of $TiCl_3$ (0.05 mol, 7.71 g) in a mixture of double-distilled water and absolute ethanol (1:1) was added citric acid (0.15 mol, 31.52 g) and ethylene glycol (0.15 mol, 9.31 g) subsequently. The resulting mixture was dissolved at 45 ºC under ultrasound for 15 min to give a clear violet solution. The solution was refluxed at 120 ºC for 8 h which turned into a metal-citrate homogeneous complex with a little color change from clear violet to black-violet. After cooling down, in order to bring about the required chemical reactions for the development of polymerization and evaporation of the solvent, the sol was further slowly heated at 90ºC for 6 h in an open bath until a beige wet gel was obtained. During continuous heating at this temperature, the polymerization between citric acid, ethylene glycol and complexes is developed and ultimately sol became more viscous as a wet gel. In the final step of sol-gel process, the wet gel was fully dried by direct heating on the hot plate at 150 ºC for 6 h leading to a black powder.

Then the calcination was done at 600 ºC for 3 h with heating rate 5 ºC/min. Finally, TiO_2 nanoparticles with a white color were obtained.

The XRD pattern of TiO_2 nanoparticles exhibited two different phases of TiO_2 such as anatase (tetragonal, $a = b = 3.782$ A^0, $c = 9.502$ A^0) and rutile (tetragonal, $a = b = 4.584$ A^0, $c = 2.953$ A^0) (Fig. S1). The strong diffraction peaks observed at 2θ = 25, 38, 48, 54, 55, 63, 69, 70, 75 were assigned to the (101), (004), (200), (105), (211), (204), (116), (220), (215) reflection planes of tetragonal crystal of anatase TiO_2, respectively (JCPDs No. 21-1272). The other diffraction peaks observed at 2θ = 27, 35, 41, 56 were assigned to the (110), (101), (111), (220) reflection planes of tetragonal crystal of rutile TiO_2 respectively (JCPDS No. 21-1276). The size of particles were estimated to be 20 nm according to the Debye sherrer formula ($D=K\lambda/\beta Cos\theta$). It is well known that TiO_2 containing both the rutile and anatase phases exhibit higher photocatalytic activity in visible light than either pure phase alone.

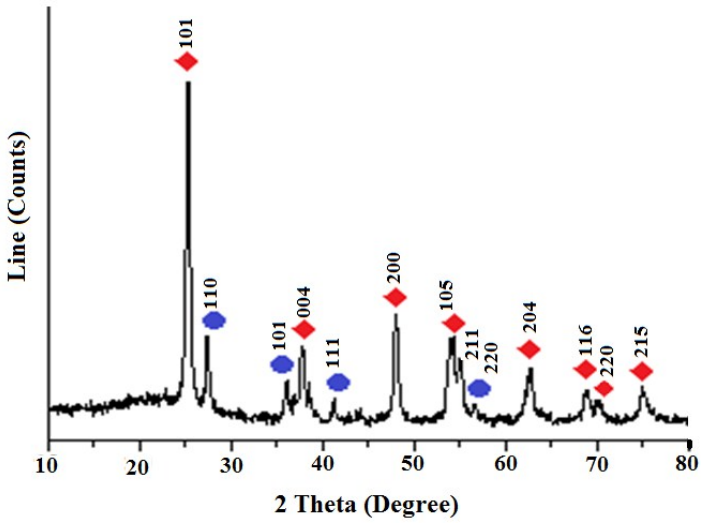


Figure S1. XRD pattern of nano TiO_2 ◆ (Anatase) ● (Rutile)

Preparation of TiO_2-AA nanohybrid

To 1.0 g TiO_2 particles was gradually added 10.0 ml of 0.01 M ascorbic acid in water over a period of 20 min at room temperature under ultrasonic agitation. Then, the reaction mixture was stirred at room temperature for 8 h. Afterwards, the product was centrifuged and washed by distilled water. Finally, TiO_2-AA nanohybrid was obtained after drying for 4 h at 100 °C.

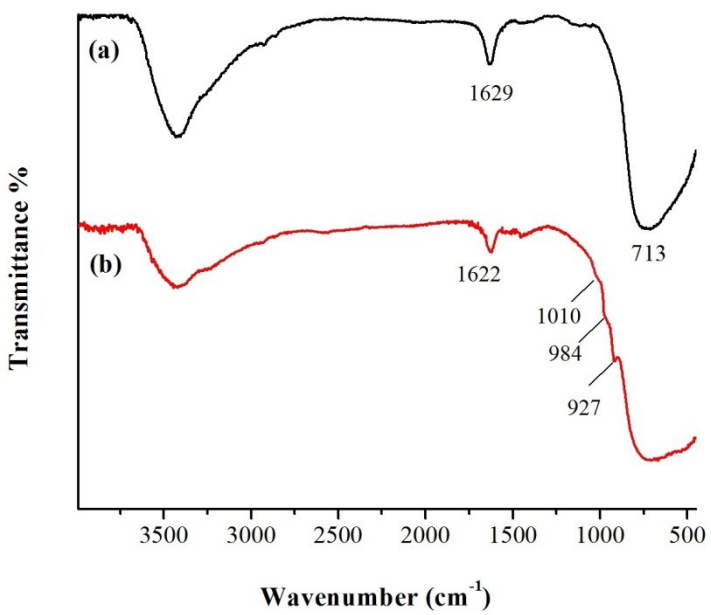
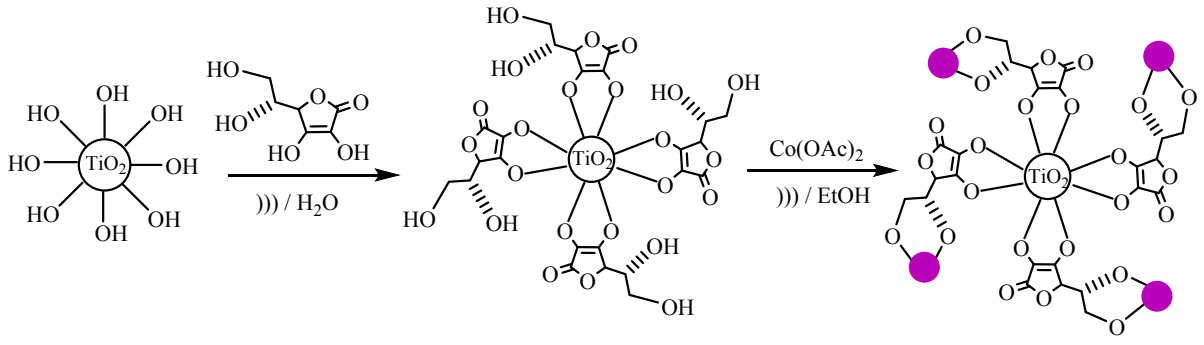


Figure S2. FTIR spectra of (a) TiO_2 nanoparticle and (b) TiO_2-AA

Preparation of TiO_2-AA-Co nanohybrid

To 0.2 g of TiO_2-AA nanohybrid was gradually added 1.0 mmol $Co(OAc)_2$ dissolved in ethanol over a period of 20 min at room temperature under ultrasonic agitation. Then, the as-obtained mixture was refluxed for 12 h. Afterwards, the product was centrifuged and washed by ethanol. Finally, TiO_2-AA-Co nanohybrid was obtained after drying for 12 h at 100 °C (Scheme S1) .



Scheme S1. Schematic representation of the procedure for the fabrication of TiO_2-AA-Co nanohybrid

TiO_2-AA-Co nanohybrid containing 1.3 wt% Co according to ICP-AES analysis. Therefore, each gram of heterogeneous catalyst contains 0.22 mmol Co or Co ascorbic acid complex.

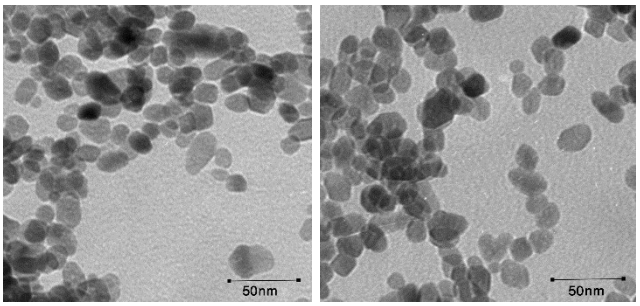


Figure S3. TEM images of TiO_2-AA-Co nanohybrid

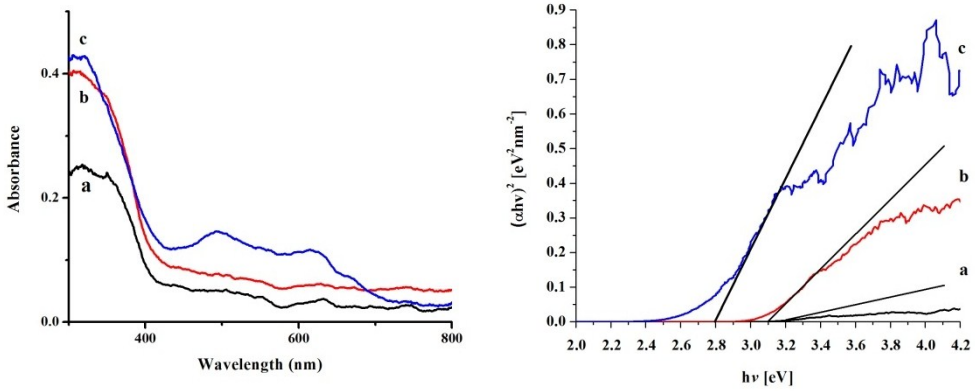


Figure S4. Diffuse reflectance UV-vis spectra of (a) bare TiO_2 NPs, (b) TiO_2-AA and (c) TiO_2-AA-Co.

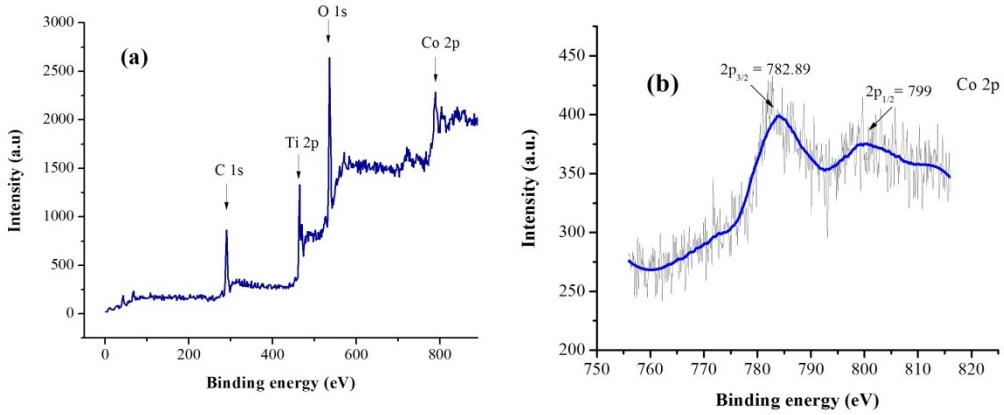


Figure S5. XPS spectra of TiO_2-AA-Co nanohybrid (a) wide scan, (b) Co 2p

General procedure for photo-cross dehydrogenative coupling reaction using TiO_2-AA-Co

To a mixture of benzaldehyde (1 mmol), TiO_2-AA-Co nanocatalyst (0.06 mol%) in EtOAc (1 mL) in a glass test tube (10 cm tall× 1 cm diameter), was added NHPI or NHSI (0.5 mmol) and the reaction mixture was heated at 60 °C under air and visible light conditions for the required time. The reaction progress was monitored by TLC. After completion of the reaction, EtOAc (3 mL) was added to the reaction mixture. TiO_2-AA-Co nanocatalyst (solid phase) was separated by centrifuging followed by decantation (3×5 mL EtOAc). Desired product (liquid phase) was purified by plate chromatography eluted with n-hexane/EtOAc (10/5). Assignments of products were made by ^{1}H NMR spectral data.

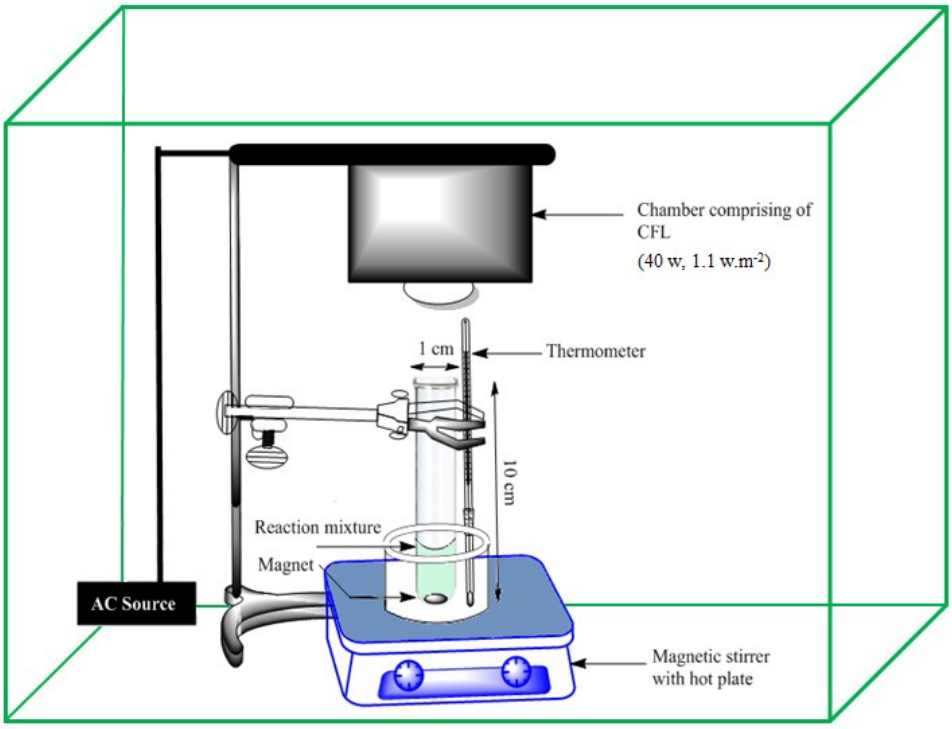


Figure S6. diagram of the apparatus

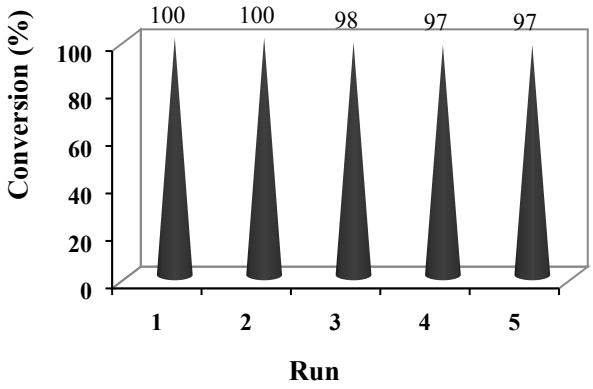


Fig. S7. Recycling of the catalytic system for synthesis of *N*-hydroxyesters under Air, in EtOAc (1 ml) at 60 °C using NHPI (0.5 mmol), 4-chlorobenzaldehyde (1 mmol) and TiO_2-AA-Co (0.06 mol%) in visible light

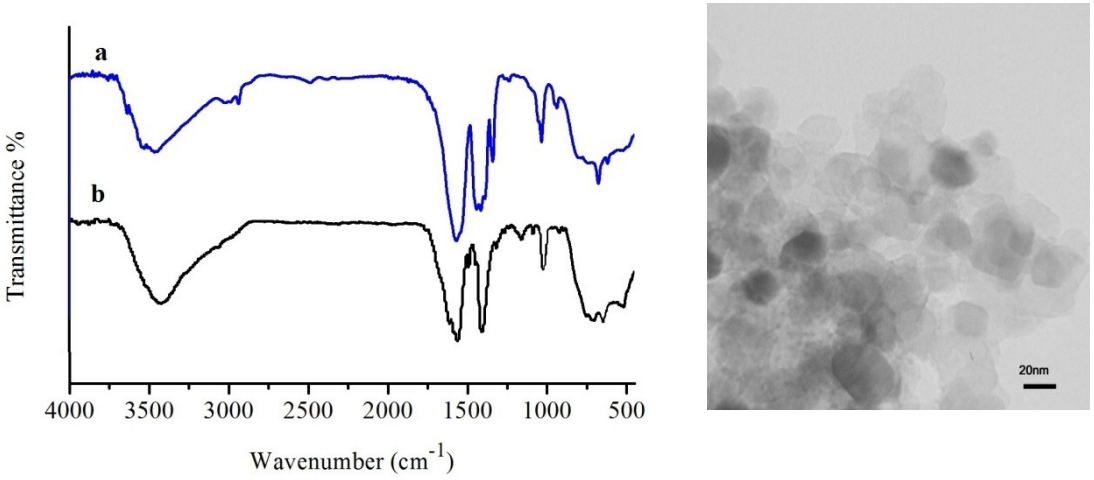


Fig. S8. (Left) FT-IR spectra of TiO_2-AA-Co itself (a) and after 5 times reuses (b) (Right) TEM image of TiO_2-AA-Co after reuses

Spectra data:

1,3-dioxoisoindolin-2-yl benzoate (Table 1, 3a)

White solid, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.2 (d, *J* = 8.0 Hz, 2 H), 7.9 (m, 2 H), 7.8 (m, 2 H), 7.6 (t, *J* = 7.6 Hz, 1 H), 7.5 (td, *J* = 15.2, 8.0 Hz, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2, 162.2, 133.8, 131.8, 129.5, 129.3, 128.9, 125.7, 123.4. ppm.

1,3-dioxoisoindolin-2-yl 4-methylbenzoate (Table 1, 3b)

White solid, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.1 (d, *J* = 8.1 Hz, 2 H), 7.9 (dd, *J* = 5.6, 3.2 Hz, 2 H), 7.8 (dd, *J* = 5.6, 3.2 Hz, 2 H), 7.7 (d, *J* = 8.1 Hz, 2 H), 2.4 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 162.4, 140.2, 134.9, 131.9, 129.8, 129.3, 124.2, 122.6, 22.2 ppm.

1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (Table 1, 3c)

White solid, 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.1 (d, *J* = 8.8 Hz, 2 H), 7.9-7.8 (ddd, *J* = 22, 5.2, 3.2 Hz, 2 H), 7.8-7.7 (ddd, *J* = 20, 5.2, 3.2 Hz, 2 H), 7.0 (d, *J* = 8.8 Hz, 2 H), 3.9 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 162.7, 162.4, 134.9, 133.0, 129.2, 124.1, 117.4, 114.5, 55.6.ppm.

1,3-dioxoisoindolin-2-yl 4-chlorobenzoate (Table 1, 3d)

White solid, 97%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.1 (d, *J* = 8.2 Hz, 2H), 7.9 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.8 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.5 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 161.9, 141.6, 133.8, 131.9, 129.3, 128.9, 124.1, 123.7 ppm.

1,3-dioxoisoindolin-2-yl 2-chlorobenzoate (Table 1, 3g)

White solid, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.1 (d, *J* = 8.4 Hz, 1 H), 8.0 (d, *J* = 8.4 Hz, 1 H), 7.9 (m, 2 H), 7.8 (m, 2 H), 7.5 (d, *J* = 8.4 Hz, 1 H), 7.4 (d, *J* = 8.4 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 161.9, 141.7, 134.9, 132.0, 131.6, 129.3, 128.98, 128.94, 124.1, 123.7 ppm.

1,3-dioxoisoindolin-2-yl 3-methoxybenzoate (Table 1, 3i)

White solid, 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.9 (dd, *J* = 5.2, 2.8 Hz, 2 H), 7.8 (m, 3 H), 7.6 (dd, *J* = 2.4, 1.6 Hz, 1 H), 7.4 (t, *J* = 8.0 Hz, 1 H), 7.2 (m, 1 H), 3.9 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 162.1, 159.7, 134.8, 129.9, 129.0, 128.6, 124.0, 123.6, 121.7, 114.6, 55.6 ppm

1,3-dioxoisoindolin-2-yl 2,4,6-trimethylbenzoate (Table 1, 3j)

White solid, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.9 (dd, *J* = 5.6, 3.2 Hz, 2 H), 7.8 (dd, *J* = 5.6, 3.2 Hz, 2 H), 6.9 (s, 2 H), 2.5 (s, 6 H), 2.3 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 162.5, 137.3, 135.2, 133.8, 129.5, 128.7, 128.2, 124.4, 22.0, 20.4. ppm.

1,3-dioxoisoindolin-2-yl 1-naphthoate (Table 1, 3k)

Pale yellow solid, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.8 (d, *J* = 8.8 Hz, 1 H), 8.5 (dd, *J* = 7.4, 1.2 Hz, 1 H), 8.1 (d, *J* = 8.4 Hz, 1 H), 7.9 (m, 3 H), 7.8 (dd, J = 5.6, 3.2 Hz, 2 H), 7.7-7.6 (m, 1 H), 7.6 (m, 2 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 162.5, 136.0, 135.2, 134.1, 132.3, 131.9, 129.3, 129.2, 129.1, 127.2, 125.7, 124.8, 124.4, 122.1 ppm.

1,3-dioxoisoindolin-2-yl-cinnamate (Table 1, 3l)

White solid, 62%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.2 (d, *J* = 7.8 Hz, 1 H), 7.5-7.4 (m, 1 H), 7.4 (m, 3 H), 7.3 (m, 5 H), 6.6 (d, *J* = 7.8 Hz, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6, 159.9, 144.4, 134.9, 132.9, 131.3, 130.8, 128.8, 127.6, 124.1, 119.4 ppm.

2,5-dioxopyrrolidin-1-yl 4-methoxybenzoate (Table 2, 4b)

White solid, 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0 (dd, *J* = 11.1 ,8.7 Hz, 2 H), 7.4 (dd, *J* = 11.1, 8.7 Hz, 2 H), 3.8 (s, 3 H), 2.8 (s, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.3, 161.8, 146.1, 130.6, 129.5, 122.2, 55.4, 25.6 ppm.

2,5-dioxopyrrolidin-1-yl 4-chlorobenzoate (Table 2, 4c)

White solid, 93%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0 (d, *J* = 8.7 Hz, 2 H), 7.4 (d, *J* = 8.4 Hz, 2 H), 2.8 (s, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1, 161.1, 140.6, 131.8, 130.3, 125.5, 25.6 ppm.

2,5-dioxopyrrolidin-1-yl 2,4,6-trimethylbenzoate (Table 2, 4f)

White solid, 76%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.9 (s, *J* = 10.8 Hz, 2 H), 2.9 (s, 4 H), 2.4 (s, 6 H), 2.3 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.7, 161.5, 145.2, 137.8, 135.6, 129.2, 25.6, 22.3, 21.3 ppm.

2,5-dioxopyrrolidin-1-yl -cinnamate (Table 2, 4h)

White solid, 41%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7 (d, *J* = 15.9 Hz, 1 H), 7.5-7.4 (m, 2 H), 7.3 (dd, *J* = 6.0, 3.6 Hz, 3 H), 6.3 (d, *J* = 15.9 Hz, 1 H), 2.8 (s, 4 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 161.0, 145.4, 132.8, 131.4, 130.8, 128.6, 106.3, 25.6 ppm.