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Supplementary Information

Ultrasound mediated synthesis of α-aminophosphonates and 3,4-dihydropyrimidin-2-ones using graphene oxide as a recyclable catalyst under solvent-free conditions

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General Information:

All reactions were carried out in air and monitored by TLC using Merck 60 F_{254} pre coated silica gel plates (0.25 mm thickness) and the products were visualized by UV detection. Flash chromatography was carried out with silica gel (200-300 mesh). FT-IR spectra were recorded on a Bruker Tensor-27 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance (III) 400 MHz spectrometer. Data for ^{1}H NMR are reported as a chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant J (Hz), integration, and assignment, data for ^{13}C are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS. UV-visible spectra were recorded in a Varian Cary 100 Bio spectrophotometer, TEM images were recorded on a Tecnai G^2 20 Ultra- Twin microscope. Powder XRD spectra were recorded on a Bruker D8 Advance diffractometer using Cu Kα as the X-ray Source. Thermal gravimetric analysis (TGA) was performed in a Mettler-Toledo TGA-DSC/1 star system. Zeta potential measurements were carried out using a micromeritics NanoPlus 3 system.

Materials: Graphite, all the amines, aldehydes, diethylphosphite, ethyl acetoacetate, and urea were purchased from Aldrich Chemicals. Potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) were purchased from Merck, India. All these chemicals were used without further purification. Milli Q water was used throughout the experiments.

Synthesis of graphene oxide by Modified Hummer's method[1,2]: In a typical procedure, graphite powder (2.0 gm), $NaNO_3$ (2.0 gm) and H_2SO_4 (100 ml) were mixed in reaction vessel. $KMnO_4$ (20 gm) was added gradually with stirring on an ice bath. After addition of $KMnO_4$, the reaction mixture was further stirred at room temperature for 24 hours. Subsequently, 200 ml water was added slowly and temperature of the reaction mixture was raised to 100 °C using an oil bath. After another 24 hours, 450 ml water was added, followed by addition of 30% H_2O_2 (40 ml). Finally, oxidation product was filtered and purified by

rinsing with 110 ml of 5% HCl solution. The filtrate cake was repeatedly washed with HPLC grade water until the pH was about 6. This dark brown oxidized material was dried in oven at 90 °C. The dried product was grounded with a mortar and pestle to fine powder.

Synthesis of α-aminophosphonates : A mixture of aldehyde (1.0 mmol), amine (1.0 mmol), dialkyl phosphite (2.0 mmol) and graphene oxide (10 mg) was added in a test tube. The reaction mixture was subjected to ultrasonic irradiation in an ultrasonic bath (PCI Analytics, India, Model 1.5L50, operating at 50 Hz) at room temperature for the time indicated in Table 2 (progress of the reaction was monitored using TLC). The Product formed was extracted with ethyl acetate and water washing. The solid product was obtained after concentrating the combined ethyl acetate extracts on rotary evaporator. After extraction the water fraction was centrifuged and the catalyst was recovered which was reused for further reactions.

Synthesis of 3, 4-dihydropyrimidin-2-ones (DHPMs) : To a test tube, aldehyde (5.0 mmol), ethyl acetoacetate (5.0 mmol), and urea (10.0 mmol) were added and the mixture was put in an ultrasonicator bath at room temperature in the presence of prepared catalyst (graphene oxide) (50 mg) for 2.0–4.0 hours. Completion of the reaction was monitored by TLC. The reaction mixture was extracted with DCM and water and the solid product was obtained after concentrating the combined DCM extracts on rotary evaporator. All the products were characterized by spectral (NMR) data.

Spectrophotometric assay for the ferrous oxidation in presence of Xylenol orange by H_2O_2 using FOX reagent:

The generation of H_2O_2 during the multicomponent coupling reaction was examined spectrophotometrically using the FOX method following a reported procedure[3]. The method is based on the oxidation of ferrous ions to ferric ions by hydrogen peroxide and simultaneous purple colored complex formation of the ferric ions with xylenol orange.

Briefly, the model coupling reaction between benzaldehyde (0.2 mmol), aniline (0.2 mmol) and diethylphosphite (0.4 mmol) in presence of GO (2 mg) was performed under solvent free and ultrasonic conditions. After 2 minutes of the reaction, 5ml of FOX reagent was added and the mixture was incubated at room temperature for 60 minutes before recording the UV-visible spectrum. The FOX reagent, which is yellowish in colour showed an absorption peak at 436 nm. On the other hand, the purple coloured complex from the reaction ferric ions with xylenol orange gives an absorption peak at around 580 nm. However, in the present case, we did not observe any peak position from 436 nm, even after incubated for 12 hours. The results confirmed that H_2O_2 was not generated during the multicomponent coupling reaction.

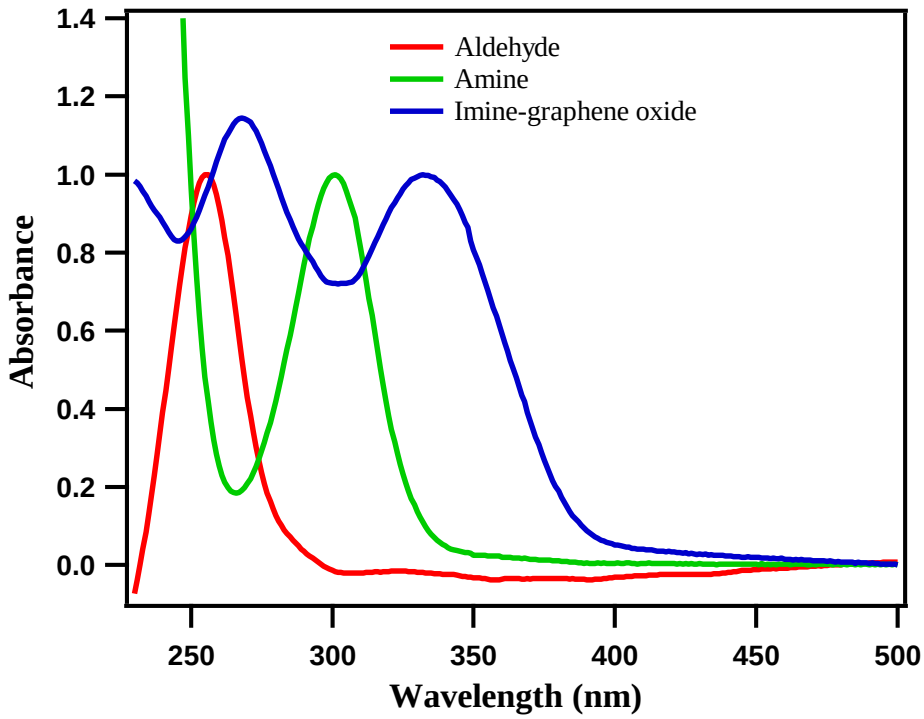


Figure S1. Normalized UV-Visible spectrum of benzaldehyde, aniline and imine intermediate formed catalyzed by graphene oxide. The starting materials benzaldehyde and aniline exhibited peaks at 270 nm and 320 nm respectively, whereas the imine intermediate formed after catalysis by graphene oxide showed peak at 334 nm. The peak at 260 nm in the spectra of imine-graphene oxide conjugate is assigned to graphene oxide.

Table S1: Elemental analysis of graphene oxide and graphene oxide recovered after 5th catalytic cycle of multicomponent reaction for the formation of α-amino phosphonates

Element	C	H	O	N	S	Adsorbed water	C/O ratio
Wt% of Pristine graphene oxide	31.4	2.2	43.2	0	1.3	21.9	0.97
Atom ratio	2.62	1.1	2.7	------	0.04	1.22	
Wt % of recovered GO after 5th catalytic cycle	33.7	2.1	41.2	1.8	0.9	20.3	1.09
Atom ratio	2.81	1.05	2.575	0.13	0.03	1.13	

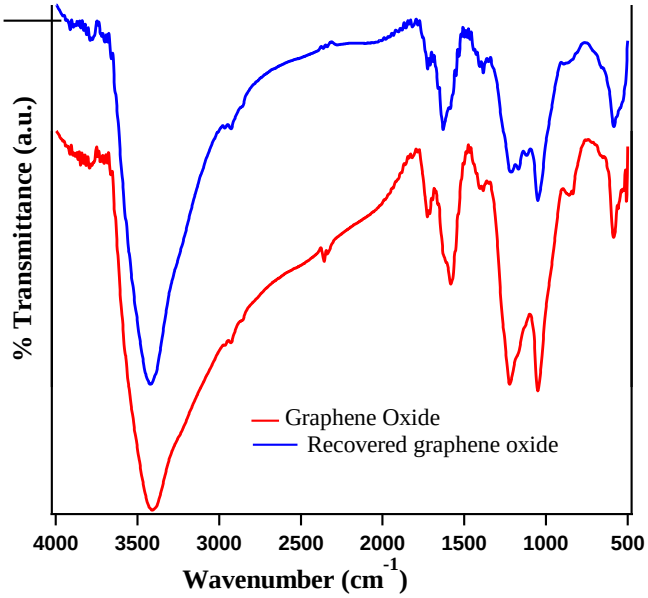


Figure S2. FTIR spectrum of graphene oxide (red line) and the graphene oxide recovered after 5th cycle of catalysis (blue line).

The FTIR spectra of both the pristine graphene oxide and the recovered graphene oxide exhibited broad and intense peaks centered at 3407 cm^{-1} attributed to the O-H stretching mode. Further peaks at 1703 cm^{-1} (C=O), 1557 cm^{-1} (C=C) and 1234 cm^{-1} (C-O) were observed in the FTIR spectrum indicating little changes in the bonding pattern of the graphene oxide before and after its participation as catalyst in the reaction.

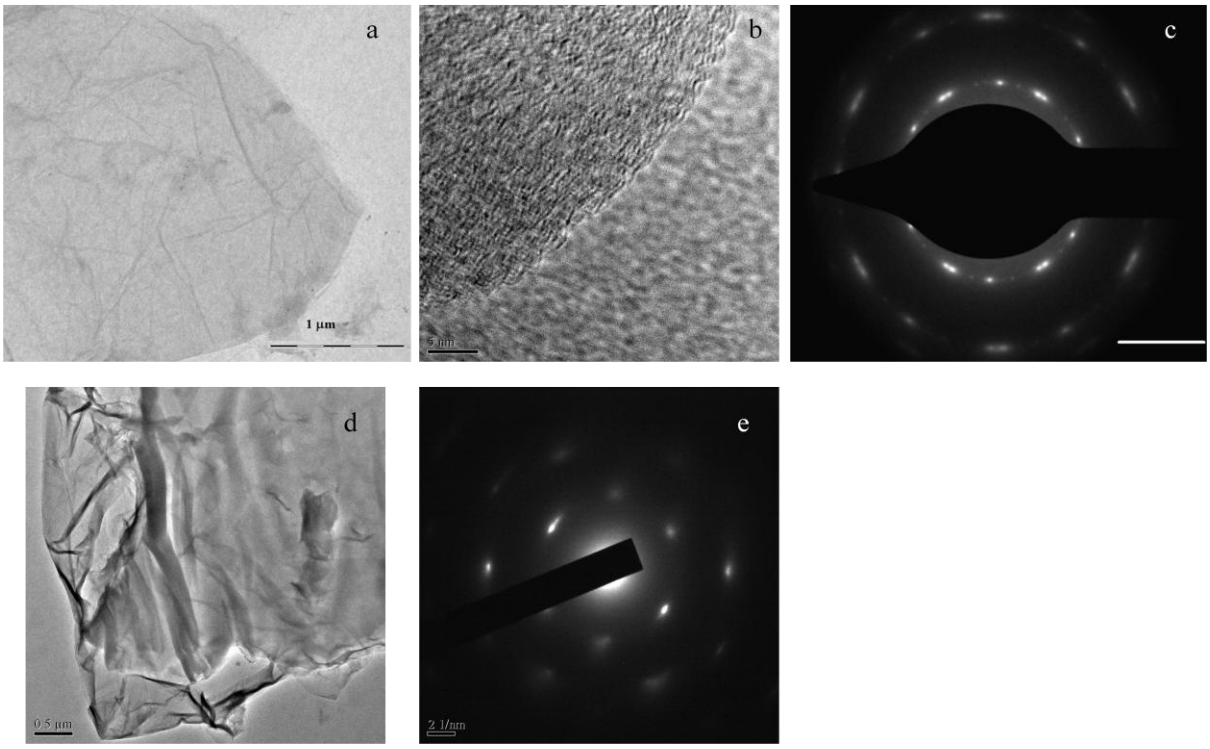


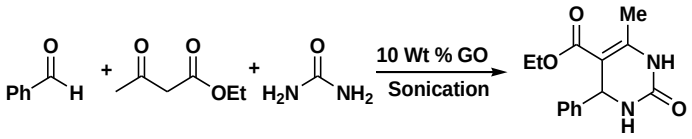
Figure S3: (a) Transmission electron micrograph (scale bar 1 µm); (b) HRTEM image (scale bar 5 nm) and (c) SAED pattern of graphene oxide. (d) Transmission electron micrograph (scale bar 0.5 µm) and (e) SAED pattern of recovered GO after their participation in catalytic reactions.

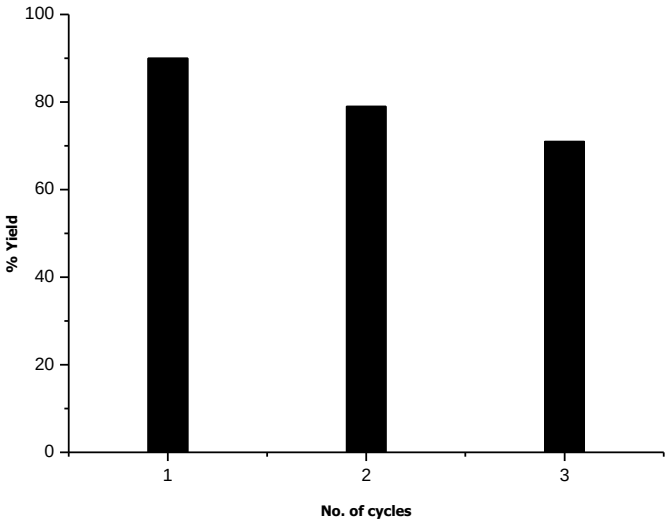
Transmission electron microscopy studies were carried out on a JEOL JEM-2100F microscope in order to observe if there was any morphological changes after graphene oxide participated as catalysts during the multicomponent reactions. For this purpose, GO and recovered GO after catalysis were transferred to a copper TEM grid. The TEM image in figure S1 showed the sheet like structure of graphene oxide having a wrinkled paper like morphology with the direct deposition on standard grids having the advantage of producing larger areas of GO. The HRTEM image of the GO sheet showed a monolayer structure (Fig. 1a). Fig. 1b depicts a selected area electron diffraction (SAED) pattern of GO that was taken using a selected area from the GO sheet suspended above a micrometer-sized hole on a 200 mesh copper transmission electron microscopy (TEM) grid and clearly demonstrates that the GO had a crystalline structure.

On the other hand, the recovered GO exhibited a typical rippled and crumpled morphology and paper-like structure with single or very thin multi layers. The recovered GO also showed highly crystalline structure. The inner six member ring came from the (1100) plane, while the six brilliant points were related to the [0001] diffractions and retained the hexagonal

symmetry of the [0001] diffraction pattern[2]. The diffraction pattern images show that the resulting recovered GO has been somewhat restored into the hexagonal graphene framework.

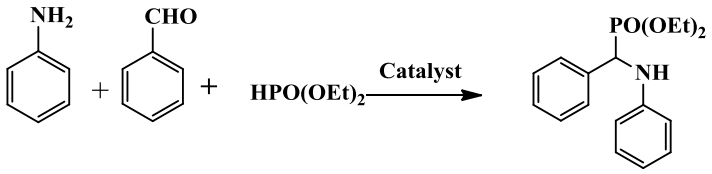
Recyclability of GO as a catalyst for the multicomponent reaction towards the formation of 3,4-dihydropyrimidinones





Reaction conditions: benzaldehyde (5.0 mmol), urea (10.0 mmol), ethylacetoacetate (5.0 mmol), graphene oxide catalyst (50 mg), under solvent free conditions using ultrasound at room temperature.

Table S2: multicomponent reaction for the formation of α-amino phosphonates

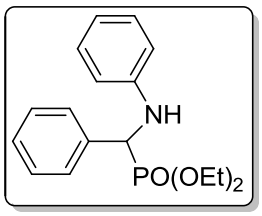


Entry	Catalyst (mg or mol%)	Reaction condition	Yield[b] (%)
1	GO (10)	[c,e] No solvent, 25°C, 1 h.	73
2	GO (10)	[d,e] No solvent, 25°C, 5 min.	93

[a]Unless otherwise specified, all the reactions were carried out with benzaldehyde (1.0 mmol), aniline (1.0 mmol) and diethylphosphite (2.0 mmol), [b]isolated yields, [c]under magnetic stirring, [d]under ultrasonic irradiation (50 Hz), [e]under argon atmosphere.

NMR Data of α-amino phosphonates (Table 2 in the manuscript):

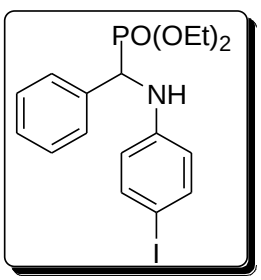
1.



3aa (Entry 1, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.49 (m, 2H, C_6H_5), 7.31-7.35 (t, 2H, C_6H_5), 7.08-7.12 (t, 2H, C_6H_5), 6.69 (t, 2H, C_6H_5), 6.59 (d, 2H, C_6H_5), 4.70-4.80 (d, 1H, CH), 4.09-4.15 (m, 2H,-OCH_2CH_3), 3.91-3.97 (m, 1H, OCH_2CH_3), 3.64-3.71 (m, 1H, OCH_2CH_3), 1.27-1.30 (t, 3H, -OCH_2CH_3), 1.10-1.13(t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.62, 146.47, 135.87, 129.13, 128.57, 127.80, 118.35, 113.82, 63.81, 55.28 (d, *J*=150 Hz), 16.43 (d, *J*=6 Hz, -OCH_2CH_3), 16.13 (d, *J*=6 Hz, -OCH_2CH_3).

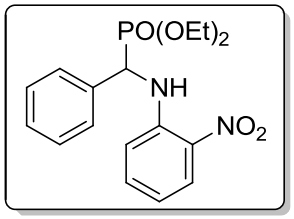
2.



3ab (**Entry 2, Table 2)**

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.46 (m, 2H, C_6H_5), 7.35-7.31 (t, 2H, C_6H_5), 7.12-7.08 (m, 2H, C_6H_5), 6.67-6.71 (t, 1H, C_6H_5), 6.61-6.59 (m, 2H, C_6H_5), 4.71(d, 1H) 4.15-4.08 (d, 2H, $-OCH_2CH_3$), 3.97-3.91 (m, 1H, $-OCH_2CH_3$), 3.71-3.64 (m, 1H, $-OCH_2CH_3$), 1.30-1.27 (t, 3H, $-OCH_2CH_3$), 1.13-1.09 (t, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.54, 146.39, 136.06, 129.19, 128.60, 127.93, 118.37, 113.90, 63.34-63.28 (d, *J*=6 Hz), 56.85-55.36 (d, *J*=150 Hz), 16.47.

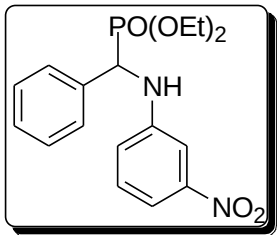
3.



3ac (Entry 3, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.99-8.97 (d, 1H, C_6H_5), 8.22-8.20 (d, 1H, C_6H_5), 7.50-7.49 (d, 2H, C_6H_5), 7.39-7.29 (m, 2H, C_6H_5), 6.72-6.67 (m, 3H, C_6H_5), 4.98-4.91 (d, 1H), 4.14-3.91 (m, 4H, $-OCH_2CH_3$), 1.29-1.25 (m, 6H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.06, 143.93, 136.11, 134.59, 128.91, 128.42, 127.59, 126.88, 116.68, 114.68, 63.75-63.52, 56.28-54.78 (d, *J*=150 Hz), 16.38.

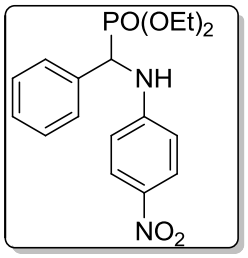
4.



3ad (Entry 4, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.43 (m, 2H, C_6H_5), 7.40-7.38 (dd, 2H, C_6H_5), 7.27-7.20 (m, 1H, C_6H_5), 7.12-7.20 (m, 2H, C_6H_5), 7.12-7.08 (t, 1H, C_6H_5), 6.83-6.80 (dd, 1H, C_6H_5), 4.78-4.70 (dd, 1H), 4.13-4.08 (m, 2H, $-OCH_2CH_3$), 3.91-3.85 (m, 2H), 1.25-1.21(t, 3H, $-OCH_2CH_3$), 1.05-1.01 (t, 3H, $-OCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 148.79, 147.17, 134.63, 129.26, 128.39, 127.89, 127.64, 118.81, 112.21, 107.83, 63.40-62.92 (dd, *J*=46 Hz), 56.11-54.60 (d, *J*=151 Hz), 16.10-15.76 (dd, *J*=34 Hz).

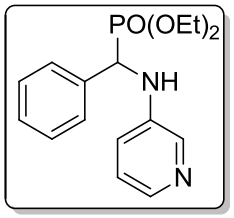
5.



3ae (**Entry 5, Table 2)**

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.00 (m, 2H, C_6H_5), 7.52-7.47 (d, 2H, C_6H_5), 7.41-7.32 (m, 3H, C_6H_5), 6.69-6.62 (m, 2H, C_6H_5), 4.87 (d, 1H), 4.21-4.12 (m, 2H, -OCH_2CH_3), 3.96-3.90 (m, 1H, -OCH_2CH_3), 3.67-3.63 (m, 1H, -OCH_2CH_3), 1.36-1.32 (t, 3H, -OCH_2CH_3), 1.16-1.12 (t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.15, 151.83, 138.51, 134.20, 128.54, 127.42, 125.72, 112.08, 63.54 63.06, 55.91 54.40-54.33 (d, *J*=150 Hz), 16.44-16.04(dd, *J*=20 Hz).

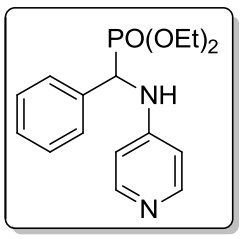
6.



3af (Entry 6, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04-8.01 (dd, 1H), 7.90-7.86 (dd, 1H), 7.29-7.22 (m, 3H), 6.99-6.91 (m, 2H), 6.82-6.80 (m, 1H), 5.36 (s, 1H), 4.75-4.67 (dd, 1H), 4.10-4.05 (m, 2H), 3.91-3.85 (m, 1H), 3.65-3.59 (m, 1H), 1.25-1.21 (t, 3H, -OCH_2CH_3), 1.07-1.03 (t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.56, 148.84, 147.23, 142.02, 136.01, 126.91, 124.81, 123.20, 121.42, 70.65-69.05 (d, *J*=160 Hz), 62.37-62.16 (d, *J*=21 Hz), 15.47.

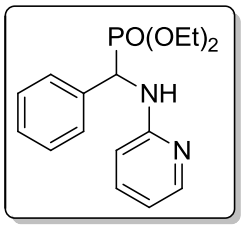
7.



3ag (Entry 7, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.8 (d, 2H), 7.44-7.28 (m, 5H), 6.38 (d, 2H), 5.12-4.98 (dd, 1H), 3.96-3.90 (m, 4H), 1.18-1.14 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.03, 137.62, 128.17,127.89, 127.40, 127.34, 109.55, 71.41-69.80 (d, *J*=161 Hz), 63.24-63.06, 16.47.

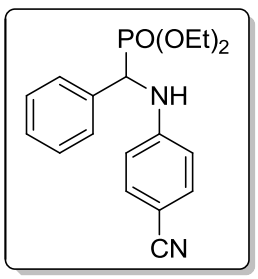
8.



3ai (Entry 9, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52-8.50 (d, 1H), 8.01-7.89 (t, 1H), 7.51-7.29 (m, 5H), 6.62-6.59 (d, 1H), 6.53-6.51 (m, 1H), 5.06-5.03 (d, 1H), 4.08-3.98 (m, 4H), 1.29-1.17 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.48, 134.74, 138.72, 137.38, 130.02, 129.27, 128.41, 127.44, 122.12, 71.68-70.09(d, *J*=159Hz), 63.61-63.21(dd, *J*=20 Hz), 16.60-16.14 (dd, *J*=23Hz).

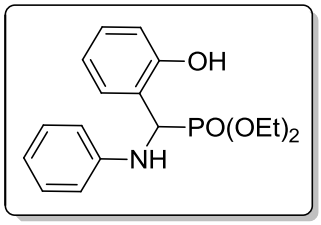
9.



3aj (Entry 10, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.46 (d, 2H, C_6H_5), 7.36-7.28 (m, 5H, C_6H_5), 6.65-6.63 (d, 2H, C_6H_5), 4.82-4.76 (d, 1H, C_6H_5), 4.18-4.12 (m, 2H), 3.95-3.89 (m, 1H), 3.67-3.62 (m, 1H), 1.32-1.28 (t, 3H, -OCH_2CH_3), 1.12-1.09 (t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.69, 133.42, 129.94, 128.71, 128.27, 127.74, 120.00, 113.35, 111.65, 63.74-63.28 (d, *J*=46 Hz), 55.97-54.46 (d, *J*=151 Hz), 16.34-16.02

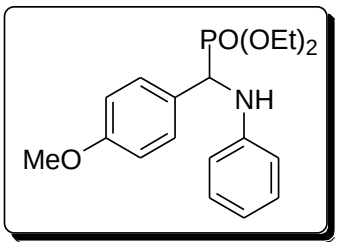
10.



3ba (Entry 11, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.28 (d, 1H, C_6H_5), 7.15-7.11 (m, 3H, C_6H_5), 6.95-6.93 (d, 1H, C_6H_5), 6.88-6.84 (t, 1H, C_6H_5), 6.76-6.73 (t, 1H, C_6H_5), 6.71-6.69 (d, 2H, C_6H_5), 5.15-5.09 (d, 1H, CH), 4.83 (bs, 1H, OH), 4.21-4.06 (m, 3H), 3.96-3.92 (m, 1H, -OCH_2CH_3), 1.31-1.27 (t, 3H, -OCH_2CH_3), 1.22-1.19 t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.58, 146.27, 129.12, 121.12, 121.42, 120.30, 119.02, 114.25, 63.94 (d, *J*=7 Hz), 63.55 (d, *J*=6 Hz), 53.71 (d, *J*=153 Hz), 16.33 (d, *J*=5 Hz), 16.16 (d, *J*=5 Hz).

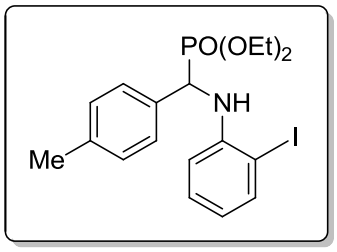
11.



3da (Entry 13, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.36 (dd, 2H, C_6H_5), 7.12-7.06 (t, 2H, C_6H_5), 6.87-6.85 (d, 2H, C_6H_5), 6.70-6.67 (d, 1H, C_6H_5), 6.60-6.58 (d, 2H, C_6H_5), 4.74-4.68 (d, 1H, CH), 4.17-4.07 (m, 2H), 3.97-3.91 (m, 1H), 3.77 (s, 3H, -OCH_3), 3.73-3.67 (m, 1H, -OCH_2CH_3), 1.30-1.26 (t, 3H, -OCH_2CH_3), 1.15-1.12 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.34 ,150.35, 131.64, 128.01, 128.49, 128.09, 126.04, 113.01, 63.88 (d, *J*=7 Hz), 63.61 (*J*=7Hz), 55.55 (s, 1H), 16.73 (d, *J*=5 Hz), 16.48 (d, *J*=5 Hz)

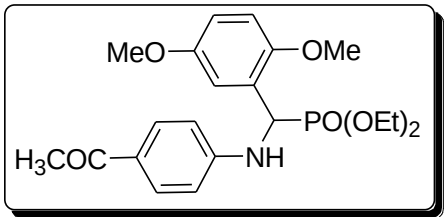
12.



3ek (Entry14, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.87 (d, 1H, C_6H_5), 7.56-7.54 (dd, 1H, C_6H_5), 7.25-7.22 (m, 2H, C_6H_5), 7.05-7.03 (d, 2H, C_6H_5), 6.96-6.92 (t, 1H, C_6H_5), 6.35-6.29 (m, 1H, C_6H_5), 4.94-4.66 (d, 1H), 4.06-3.92 (m, 3H, , -OCH_2CH_3), 3.80-3.73 (m, 1H, -OCH_2CH_3), 2.21(s, 3H,-CH_3), 1.21-1.17 (t, 3H, -OCH_2CH_3), 1.13-1.09 (t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.93, 139.26, 130.33, 129.62, 129.49, 127.77, 120.03, 112.30, 64.11 (d, *J*=7 Hz), 63.87 (d, *J*=7 Hz), 57.13 (d, *J*=150 Hz), 21.36, 16.71(d, *J*=6 Hz), 16.55 (d, *J*=6 Hz).

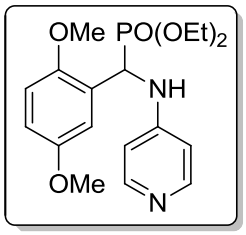
13.



3fh (Entry 15, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.72 (d, 2H), 7.02-7.01 (d, 1H), 6.84-6.77 (m, 2H), 6.61-6.59 (d, 2H), 5.43-5.36 (d, 1H), 4.18-4.14 (d, 2H), 3.90-3.78 (m, 1H), 3.65-3.62 (m, 1H), 3.89 (s, 3H), 3.67 (s, 3H), 2.42 (s, 3H), 1.31-1.27 (t, 3H), 1.07-1.03 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.41, 154.27, 154.18, 130.84, 127.86, 125.16, 125.07, 114.31, 112.67, 111.98, 63.78, 63.45, 56.59-55.90, 26.26, 16.66-16.36.

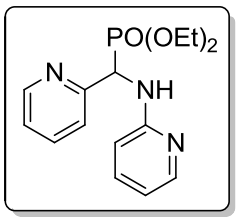
14.



3fg (Entry 16, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.87 (d, 2H), 6.77 (s, 1H), 6.48-6.47 (d, 1H), 6.05-6.03 (d, 1H), 5.55-552 (d, 2H), 4.14-4.07 (d, 1H), 4.05-3.97 (m, 3H), 3.96-3.91 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 1.27-1.23 (t, 3H), 1.19-1.16 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.26, 153.59, 150.63, 147.18, 127.05, 114.10, 111.5, 109.17, 64.58, 62.77, 55.94-55.43(d, *J*= 51Hz), 16.18.

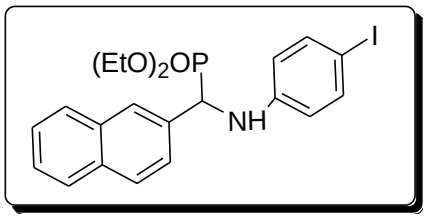
15.



3ii (Entry 20, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.35-8.34 (d, 1H), 7.67 (d, 1H), 7.53-7.51 (d, 1H), 7.44-7.42 (d, 1H), 7.22 (s, 1H),7.05-7.04 (d, 1H),6.49-6.47 (d, 1H), 6.35-6.34 (d, 1H), 5.03-5.00 (d, 1H), 4.02-3.78 (d, 2H), 3.97-3.94 (m, 1H), 3.68-3.64 (m,1H), 1.11-1.07 (t, 3H), 1.03-1.00 (t, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.50, 155.19, 147.93, 143.00, 139.08, 136.08, 136.56, 122.82, 122.10, 112.13, 110.54, 71.21-69.62 (d, 150 Hz), 16.30-16.12.

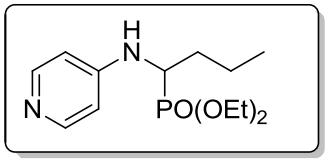
16.



3jb (Entry 21, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (s, 1H, C_6H_5), 7.72-7.67 (m, 3H, C_6H_5), 7.49-7.47 (dd, 1H, C_6H_5), 7.35-7.33 (dd, 2H, C_6H_5), 7.22-7.20 (d, 2H, C_6H_5),6.34-6.32 (d, 2H, C_6H_5), 4.82-4.76 (dd, 1H), 4.06-4.01 (m, 2H, -OCH_2CH_3), 3.85-3.78 (m, 1H), 3.58-3.51 (m, 1H), 1.20-1.17 (t, 3H, -OCH_2CH_3), 0.98-0.95 (t, 3H, -OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.06, 133.15, 132.99, 132.88, 127.84, 127.58, 126.86-126.79 (d, *J*=7 Hz), 126.20-126.09 (d, *J*=7 Hz), 116.03, 79.33, 63.37-63.21 (dd, *J*=16 Hz), 56.81-55.31 (d, *J*=150 Hz), 16.39-16.08 (dd, *J*=31 Hz).

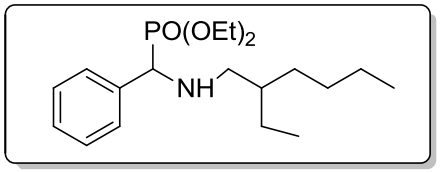
17.



3kg (Entry 22, Table 2)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, 2H), 6.46-6.45 (d, 2H), 4.60 (t, 1H), 4.13-4.05 (m, 2H), 3.83-3.78 (m, 2H), 1.68-1.55 (m, 3H), 1.39-1.33 (m, 1H), 1.28-1.24 (t, 6H), 0.88-0.85 (t, 3H,); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.99, 148.31, 109.56, 68.36-66.77 (d, *J*=159 Hz), 62.60-62.48 (dd, *J*=12 Hz), 33.40, 19.01-18.87(d, *J*=14 Hz), 16.56-16.50 (d, *J*=6 Hz), 13.71.

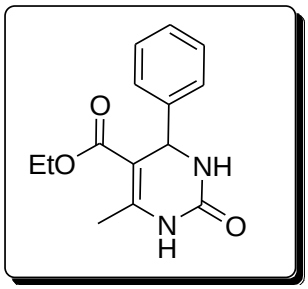
18.



3al (Entry 23, Table 2)

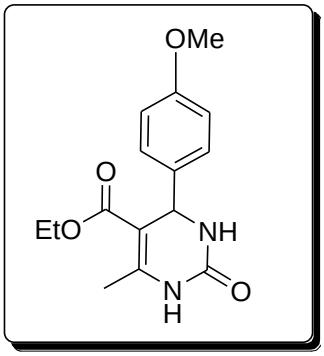
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.32 (d, 2H), 7.24-7.21 (t, 1H), 7.18-7.15 (d, 2H), 4.04-3.97 (m, 2H), 3.92-3.87 (d, 1H), 3.91- 3.70 (m, 3H), 2.34-2.25 (m, 2H), 1.35-1.20(m, 8H), 1.19-1.16 (t, 3H), 1.04-1.01 (t, 3H), 0.79-.067 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.38, 132.31, 129.76, 128.46, 128.21, 127.64, 62.95-62.88 (d, *J*=7 Hz), 62.64-62.57 (d, *J*=7 Hz), 62.27-60.74 (dd, *J*=153 Hz), 51.16-50.99 (d, *J*=17 Hz), 39.48-39.35 (d, *J*=13 Hz), 28.96-28.76 (d, *J*=20 Hz), 24.45-24.29 (d, *J*=16 Hz), 23.01-22.96 (d, *J*=5 Hz), 16.37-16.31 (d, *J*=5 Hz), 16.37-16.31 (d, *J*=6 Hz), 16.17-16.11 (d, *J*=6 Hz), 13.99-13.96 (d, *J*=3 Hz), 10.95-10.88 (d, *J*=7 Hz).

NMR data of 3,4-dihydropyrimidin-2-ones (DHPMs) (Table 3 in the manuscript):

1. 

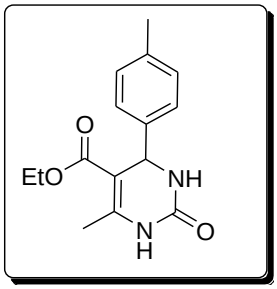
5a (Entry 1, Table 3)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (s, 1H), 7.32-7.31 (m, 4H), 5.41-5.40 (d, 1H), 4.10-4.04 (q, 2H), 2.35 (s, 3H), 1.18-1.14 (t, 3H).

2. 

5b (Entry 2, Table 3)

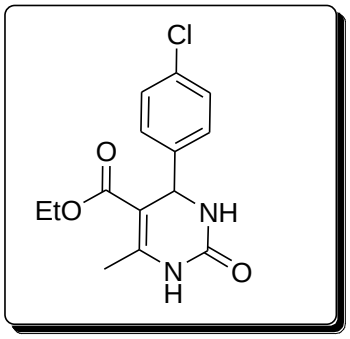
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H), 7.23-6.83 (d, 4H), 6.08 (s, 1H), 5.34 (d, 1H), 4.10-4.06 (q, 2H), 3.78 (s, 3H), 2.32 (s, 3H), 1.18-1.14 (t, 3H).

3. 

5c (Entry 3, Table 3)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H), 7.31-7.19 (m, 4H), 5.39 (d, 1H), 4.07-3.95 (q, 2H), 2.31 (s, 3H), 2.19 (s, 3H), 1.17-1.11 (t, 3H).

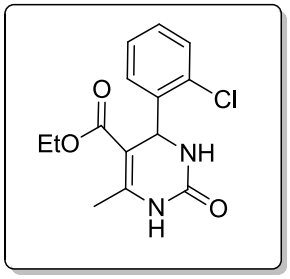
4.



5d (Entry 4, Table 3)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (s, 1H), 7.45-7.43 (d, 2H), 7.21-7.18 (d, 2H), 5.83 (s, 1H), 5.37 (s, 1H), 4.11-4.05 (q, 2H), 2.34 (t, 3H), 1.19-1.16 (t, 3H).

5.



5e (Entry 5, Table 3)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.86 (s, 1H), 7.40-7.38 (d, 2H), 7.26-7.23 (m, 3H), 5.90 (s, 1H), 4.06-4.01 (q, 2H), 2.45 (s, 1H), 1.09-1.06 (t, 3H).

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3. S. G. Rhee, T. S. Chang, W. Jeong and D. Kang, *Mol. Cells*, 2010, **29**, 539-549.