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Magnetic nanoparticle-supported eosin Y ammonium salt: An efficient heterogeneous catalyst for visible light oxidative C–C and C–P bond formation

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ABSTRACT

A highly efficient visible light mediated C–C and C–P coupling reactions of sp^3 C–H bonds adjacent to the nitrogen atom in tetrahydroisoquinoline derivatives with pronucleophiles such as nitroalkanes, malononitrile, dimethyl malonate and H-phosphonate diesters were achieved by using a magnetic nanoparticle-supported eosin Y bis-benzyltriethylammonium salt (MNPs-Eosin Y) as catalyst and air as the sole oxidant, affording the corresponding products in good to excellent yields under mild reaction conditions. Notably, the supported eosin Y catalyst can easily be separated from the reaction mixture by an external permanent magnet and can be recycled at least eight times without a significant loss of activity.

1. Introduction

Direct functionalization of the Csp^3-H bond has emerged as powerful synthetic approaches for the C–C and C-Heteroatom bond formation in organic chemistry [1]. Of particular note is the cross-dehydrogenative-coupling (CDC) reaction [2], which is the ideal process for building a C–C(X) linkage directly *via* the cleavage of dual Csp^3–H bonds or one Csp^3-H bond and one heteroatom–H bond using molecular oxygen as the terminal oxidant, has been successfully developed into the most atom-economic, clean, and efficient strategy in synthetic organic chemistry. Though functionalization of benzylic C(sp^3)–H bonds in *N*-aryl tetrahydroisoquinolines including Mannich [3], *aza*-Henry [4], cyanation [5] and phosphorylation [6] have been intensively investigated, most of these reactions have been reported with transition metals as catalysts and peroxo-compounds as terminal oxidants. Recently, the groups of Stephenson [7], König [8], Rueping [9], Wu [10] and others [11] shown that this type reaction can be photocatalyzed with iridium complex, $Ru(bpy)_3Cl_2$ or photosensitive dyes using various nucleophiles. However, the homogeneous photocatalysts are generally considered of low efficiency due to the high catalyst loading and the difficulty in separation from the products. Furthermore, their potential toxicity could lead to detrimental effects on the environment. Accordingly, the development of recyclable heterogeneous photocatalytic systems based on these homogeneous photocatalysts would be highly desirable.

In the past few years, conjugated microporous polymers (CMPs) have been serve as an ideal platform for incorporating photosensitive monomers into highly stable, recyclable, and reusable heterogeneous photocatalyst systems. For example, Lin and Liras reported the porous cross-linked polymers with phosphorescent $[Ru(bpy)_3]^{2+}$ and $[Ir(ppy)_2(bpy)]^+$ building blocks for efficient photocatalysis [12]. Cooper et al. reported a conjugated microporous polymers with Rose Bengal dye for the heterogeneous photocatalytic *aza*-Henry reactions [13]. Very recently, Chen and Han et al. reported the efficient heterogeneous photocatalytic *aza*-Henry reactions catalyzed by conjugated microporous polycarbazole containing tris(2-phenylpyridine) iridium(III) complexes and Eosin Y dye-based porous organic polymers, respectively [14]. In 2014, Kobayashi developed a polymer-immobilized iridium-

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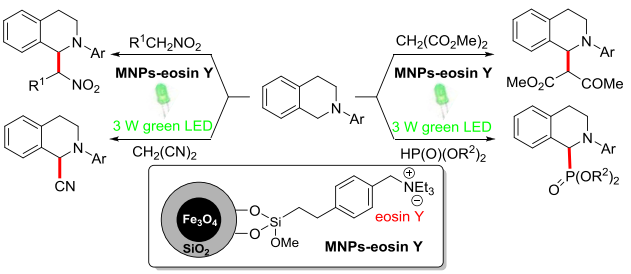
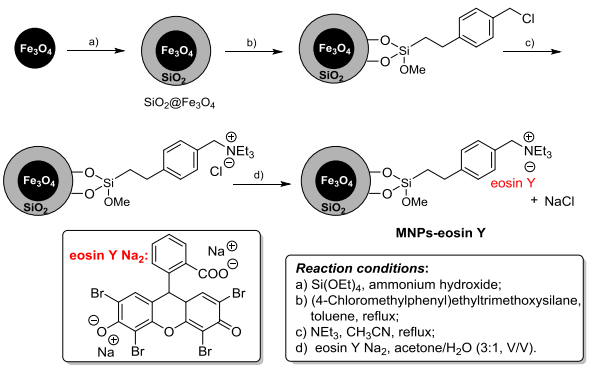
based photocatalyst and demonstrated its effectiveness as a visible light photocatalyst for the aerobic CDC reaction [15]. However, most of the photosensitive monomers used in the above-mentioned examples either require tedious experimental procedures to prepare or expensive, that limit the usability of preparation of the polymers on a large scale. Within the past few years, magnetic nanoparticles (MNPs) emerged as a new class of semi-heterogeneous supports for catalysts, and the intrinsic magnetic properties of the support allow for operationally convenient separation *via* magnetic decantation [16]. In continuation of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations from the viewpoint of green chemistry [17], herein we will report a very convenient method for immobilization of eosin Y on the quaternary ammonium salt functionalized magnetic nanoparticles by overall ion-exchange process. The results indicated that the MNPs supported eosin Y catalyst exhibits high photocatalytic activity for the C–C and C–P coupling reactions of sp^3 C–H bonds adjacent to the nitrogen atom in *N*-aryl tetrahydroisoquinoline derivatives with pronucleophiles such as nitroalkanes, malononitrile, dimethyl malonate and H-phosphonate diesters (Scheme 1). More importantly, the grafted catalyst could be recovered and reused well at least 8 times without significant loss of catalytic activity.

2. Results and discussion

The magnetic nanoparticles supported eosin Y catalyst was prepared according to the procedure in Scheme 2. Silica-coated Fe_3O_4 (SiO_2@Fe_3O_4) was prepared according to the literature [18]. Commercially available Fe_3O_4 nanoparticles, with an average diameter of 15 nm after sonication (Fig. 1a), were coated with a thin layer of silica using a sol–gel process to give silica-coated Fe_3O_4. TEM images of the SiO_2@Fe_3O_4 indicated the core–shell structure of the particles and the silica coating, which has a uniform thickness of 5 nm (Fig. 1b). The benzyl chloride was anchored easily onto the surface of SiO_2@Fe_3O_4 by using (4-chloromethylphenyl)ethyltrimethoxysilane at refluxing temperature in toluene, with a loading of 0.32 mmol of benzyl chloride per gram, which was quantified *via* CHN microanalysis based on carbon content determination. Immobilization of the benzyltriethylammonium chloride was carried out by the reaction of triethylamine with the benzyl chloride functionalized magnetic core–shell nanoparticles in anhydrous acetonitrile. The supported eosin Y catalyst was obtained by simply dissolving eosin Y in the mixture of acetone and water (3:1, V/V), and treating it with the above quaternary ammonium salt-functionalized SiO_2@Fe_3O_4, with a loading of 0.10 mmol of eosin Y per gram determined *via* spectrophotometric method. TEM image confirmed the nanometre dimensions of the supported catalyst as well as the existence of silica coating (Fig. 1c). XRD measurements of the supported eosin.



Scheme 1. Magnetic nanoparticles supported eosin Y catalyzed visible light oxidative C–C and C–P bond formation.



Scheme 2. Preparation of the magnetic nanoparticles supported eosin Y catalyst.

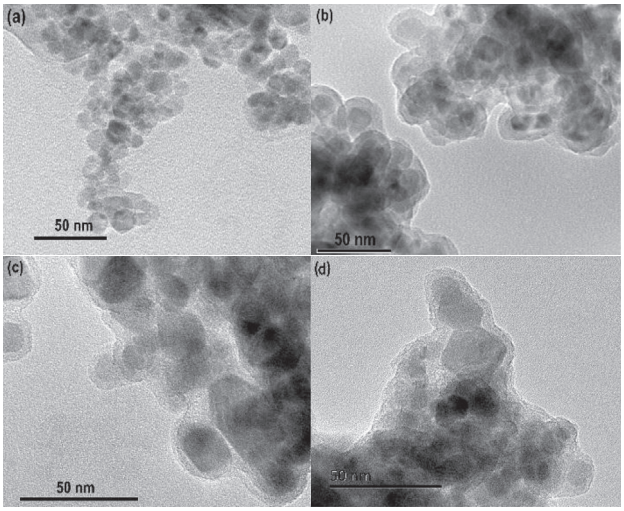


Fig. 1. TEM images of the catalysts: (a) Fe_3O_4 nanoparticles; (b) silica-coated Fe_3O_4 (SiO_2@Fe_3O_4); (c) MNPs-eosin Y catalyst; (d) recycled MNPs-eosin Y catalyst.

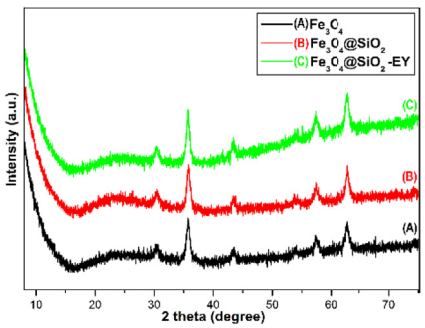


Fig. 2. XRD determination of the supported eosin Y catalyst.

Y catalyst shown in Fig. 2 exhibited diffraction peaks corresponding to the typical spinel maghemite structure and the diffraction peak of the layered amorphous silica was not obvious. Furthermore, TEM images showed that after eight reuses the supported eosin Y catalyst still maintained nanospheric dimensions as well as the silica coating but with slight aggregation (Fig. 1d).

In order to evaluate the catalytic activity of the magnetic nanoparticle-supported eosin Y, the cross-dehydrogenative coupling of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (1a) with nitromethane (2a) was chosen as model reaction to optimize the

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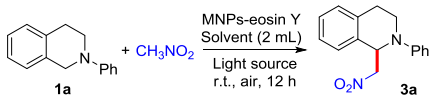
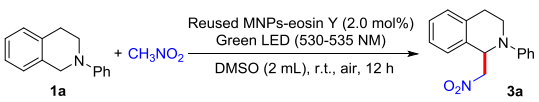
Table 1
Optimization of reaction conditions.[a]



Entry	Catalyst	Solvent	Light source	Yield (%)[b]
1	MNPs-Eosin Y	none	Green LED	72[c]
2	MNPs-Eosin Y	DMSO	Green LED	92
3	MNPs-Eosin Y	CH_3CN	Green LED	68
4	MNPs-Eosin Y	CH_3CH_2OH	Green LED	62
5	MNPs-Eosin Y	DMF	Green LED	47
6	MNPs-Eosin Y	1,4-dioxane	Green LED	32
7	MNPs-Eosin Y	toluene	Green LED	21
8	MNPs-Eosin Y	DMSO	Sunlight	87
9	none	DMSO	Green LED	n.r., n.r.[d]
10	MNPs-Eosin Y	DMSO	In dark	n.r., n.r.[d]
11	MNPs-Eosin Y	DMSO	Green LED	91[e]
12	MNPs-Eosin Y	DMSO	Green LED	n.r.[f]
13	MNPs-Eosin Y	DMSO	Green LED	66[g], 92[h]
14	MNPs-Eosin Y	DMSO	Green LED	76[i], 91[j]
15	MNPs-Eosin Y	DMSO	Green LED	80[k], 90[l]

[a] Reaction conditions: 1a (0.25 mmol), CH_3NO_2 (1.25 mmol), MNPs-Eosin Y catalyst (50 mg, 2.0 mol %), solvent (2 mL), under 3 W green LED (530–535 nm) irradiation for 12 h at room temperature in air.
[b] Isolated yield, n. r. = no reaction.
[c] CH_3NO_2 (2 mL) was added.
[d] At 60 °C.
[e] Oxygen balloon.
[f] nitrogen atmosphere.
[g] MNPs-Eosin Y catalyst (25 mg, 1.0 mol %).
[h] MNPs-Eosin Y catalyst (75 mg, 3.0 mol %).
[i] CH_3NO_2 (0.75 mmol) was added.
[j] CH_3NO_2 (2.0 mmol) was added.
[k] 8 h.
[l] 16 h.

Table 2
Recycling MNPs-eosin Y catalyst for the cross-dehydrogenative coupling reaction of *N*-phenyl tetrahydroisoquinoline with nitromethane.[a]



Run	Yield[b] (%)	Run	Yield[b] (%)
1	92	5	87
2	90	6	90
3	91	7	88
4	88	8	89

[a] Reaction conditions: 1a (0.25 mmol), CH_3NO_2 (1.25 mmol), reused MNPs-Eosin Y catalyst (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation for 12 h at room temperature in air.
[b] Isolated yield.

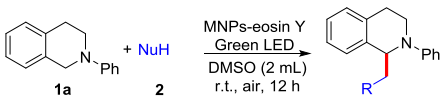
reaction conditions, and the results were shown in Table 1. To our delight, the model reaction proceeded well in the presence of magnetic nanoparticle-supported eosin Y, and the desired product was obtained in 72% isolated yield under irradiation with a 530–535 nm green LED light in neat reaction conditions for 12 h (Table 1, entry 1). Subsequently, various solvents were evaluated in this transformation. Among the solvents screened, DMSO exhibited the highest reactivity (Table 1, entry 2). Other solvents exhibited less reactivity towards the reaction in the following order: CH_3CN > CH_3CH_2OH > DMF > 1,4-dioxane > toluene (Table 1, entries 3–7). When the reaction was exposed to sunlight irradiation, the cross-dehydrogenative-coupling could also undergo smoothly to give 3a in 87% yield (Table 1, entry 8). In the absence of magnetic nanoparticle-supported eosin Y catalyst or visible-light irradiation, no desired product was observed, even the reaction was performed in a 60 °C oil bath (Table 1, entries 9 and 10). A comparable yield of 3a was achieved when an oxygen atmosphere was used instead of an air atmosphere (Table 1, entry 11). However, no product **3a** was obtained when the reaction was performed under a nitrogen atmosphere (Table 1, entry 12). The loading of the supported photocatalyst, the ratio of 1a to 2a, as well as the reaction time were optimized, which are also summarized in Table 1 (entries 13–15). In addition, under the optimized conditions, other pronucleophiles, such as malononitrile, dimethyl malonate and diethyl phosphate were also examined under the optimized conditions, and the desired products were obtained in good to excellent yields (71%, 86% and 96%, respectively) and found that for efficient conversion both light and catalyst are required, as shown in Scheme 3.

With the optimized reaction conditions in hand, the generality of the cross-dehydrogenative coupling reaction of *N*-aryl tetrahydroisoquinoline derivatives with nitromethane was investigated. As shown in Scheme 4, a series of *N*-aryl tetrahydroisoquinolines with both electron-donating (Me, OMe) and electron-withdrawing (Cl, Br) groups on the aromatic rings were able to undergo the CDC reaction with nitromethane efficiently, thus resulting in the corresponding products 3a–3g in good to excellent yields (81–92%). It is worth noting that the use of nitroethane as a nucleophile also gave the desired compounds 3h and 3i in good yields (the ratios of the two diastereoisomers are 2:1).

Subsequently, the present photocatalytic CDC method was further extended to the coupling of *N*-aryl tetrahydroisoquinolines and malononitrile, and the results were shown in Scheme 5. The *N*-phenyl tetrahydroisoquinoline derivatives 1 were treated smoothly with malononitrile in air under standard conditions, and α-amino nitriles (5a–5f) were obtained in good yields. It seems that the electronic effect of the substitute group was not obvious, both electron-withdrawing group and electron-donating group located at the phenyl ring of the substrates gave the comparable results.

Similarly, the photocatalytic aerobic CDC reaction was also applicable to the oxidative Mannich reaction between *N*-aryl tetrahydroisoquinolines 1 and dimethyl malonate, and the results were shown in Scheme 6. Under visible-light irradiation, the *N*-phenyl tetrahydroisoquinoline derivatives 1 reacted with dimethyl malonate under an air atmosphere to afford the desired products 7 in high yields.

The success of C–C bond formation by using the magnetic nanoparticle-supported eosin Y encouraged us to investigate C–P bond coupling reactions. In general, various *N*-aryl tetrahydroisoquinolines could react with diethyl phosphate and dibenzyl phosphate smoothly in the presence of the supported eosin Y catalyst to give the desired products in excellent yields under irradiation with 530–535 nm green LED for 12 h. Both electron-donating and electron-withdrawing groups on the aromatic rings were compatible in the oxidative C–P coupling reaction, and the



NuH = malononitrile, R = CN, **5a**, 71%;
NuH = dimethyl malonate, R = $CH(CO_2Me)$, **7a**, 86%;
NuH = diethyl phosphate, R = $PO(OEt)_2$, **9a**, 96%.

Scheme 3. Oxidative coupling reaction of *N*-aryl tetrahydroisoquinolines with other pronucleophiles under the optimized reaction conditions. 1 (0.25 mmol), 2 (0.5 mmol), MNPs-eosin Y (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation in air for 12 h; Isolated yields of the products are based on compound 1a.

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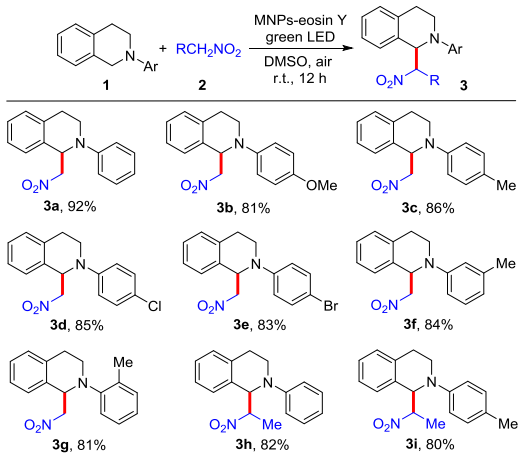
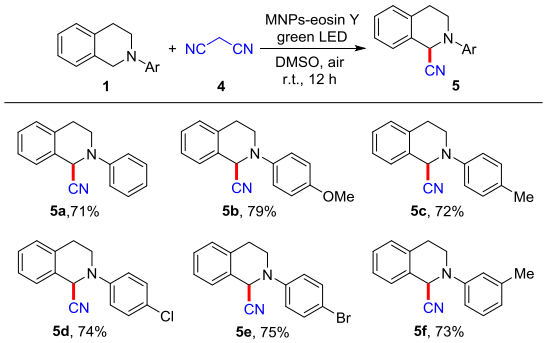
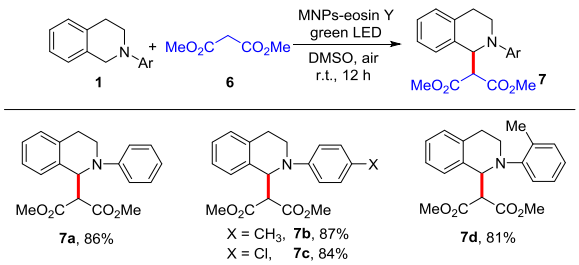


Scheme 4. Oxidative coupling reaction of *N*-aryl tetrahydroisoquinolines with nitroalkane using MNPs-eosin Y as photocatalyst. Reaction conditions: 1 (0.25 mmol), 2 (1.25 mmol), MNPs-eosin Y (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation in air for 12 h; isolated yields of the products are based on compound 1.



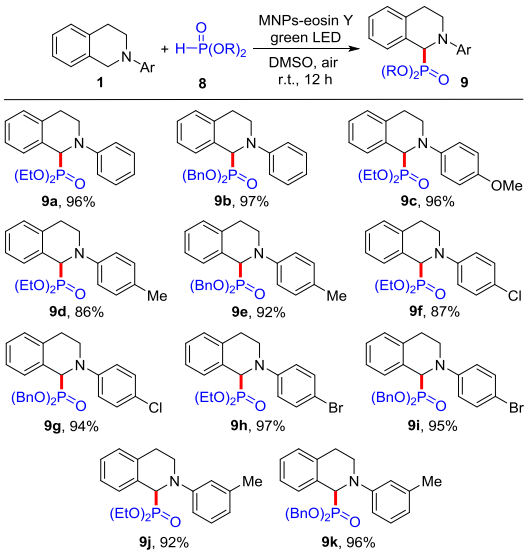
Scheme 5. Oxidative synthesis of α-amino nitriles using MNPs-eosin Y as photocatalyst. Reaction conditions: 1 (0.25 mmol), 4 (0.5 mmol), MNPs-eosin Y (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation in air for 12 h; Isolated yields of the products are based on compound 1.



Scheme 6. Oxidative coupling reaction of *N*-aryl tetrahydroisoquinolines with dimethyl malonate using MNPs-eosin Y as photocatalyst. Reaction conditions: 1 (0.25 mmol), 6 (0.5 mmol), MNPs-eosin Y (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation in air for 12 h; Isolated yields of the products are based on compound 1.

desired α-amino phosphonates (9a–9k) were obtained in excellent yields (86–97%), as shown in Scheme 7.

In order to determine the active species of oxygen for this transformation, 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-pyrroline-*N*-oxide (DMPO) were employed to capture $^1O_2$ and $O_2^{\bullet-}$, respectively. The resulting electron-spin resonance (ESR) spectra shown that there was a strong characteristic signal of



Scheme 7. Oxidative coupling reaction of *N*-aryl tetrahydroisoquinolines with dialkyl phosphate using MNPs-eosin Y as photocatalyst. Reaction conditions: 1 (0.25 mmol), 8 (0.5 mmol), MNPs-eosin Y (50 mg, 2.0 mol %), DMSO (2 mL), under 3 W green LED (530–535 nm) irradiation in air for 12 h; Isolated yields of the products are based on compound 1.

the $O_2^{\bullet-}$ adduct with DMPO was detected when DMPO was added into the reaction mixture under green LED irradiation. Meanwhile, no signal of the $^1O_2$ adduct with TEMP was observed when the reaction solution was irradiated with a green LED (See Supporting Information for detail). On the basis of the above investigation and literature [8], a plausible mechanism was proposed in Scheme 8. The reaction begins with the photoexcitation of eosin Y by visible light to generate its excited state (eosin Y *). Then a single electron transfer from 1a to the excited state of eosin Y gave an aminyl cation radical (I) along with the generation of eosin Y$^{\bullet-}$, which is subsequently oxidized by the molecular oxygen to regenerate eosin Y, along with the generation of superoxide radical anion ($O_2^{\bullet-}$). Subsequently, I lost a hydrogen atom by the superoxide radical anion ($O_2^{\bullet-}$) to generate iminium ion (II), which reacted with pronucleophiles resulted in the desired product. Apparent quantum efficiency (AQE) is an important factor to reflect the photon utilization in the photocatalytic process, and the AQE of the representative reaction at 530 nm was measured and calculated as 4.55%.

Finally, the viability of recovering and reusing the magnetic nanoparticle-supported eosin Y catalyst for the cross-dehydrogenative coupling reaction of *N*-phenyl tetrahydroisoquinoline (1a) with nitromethane was examined. It was found that the catalyst could be reused at least eight times without a noticeable loss of catalytic activity with minimal levels of eosin Y leaching, and the characteristic absorption of eosin Y could not be detected in the separated reaction crude by spectrometric method. The supported catalyst could be collected and reused by using an external permanent magnet and the separated catalyst was washed with ethyl acetate and diethyl ether, respectively. After being dried in air, it can be reused directly without any further treatment.

3. Conclusions

In summary, we have developed a simple and highly efficient magnetic nanoparticle-supported eosin Y catalyst and demonstrated its effectiveness as a recyclable visible light photocatalyst for the oxidative C–C and C–P bond formation. The cross-coupling

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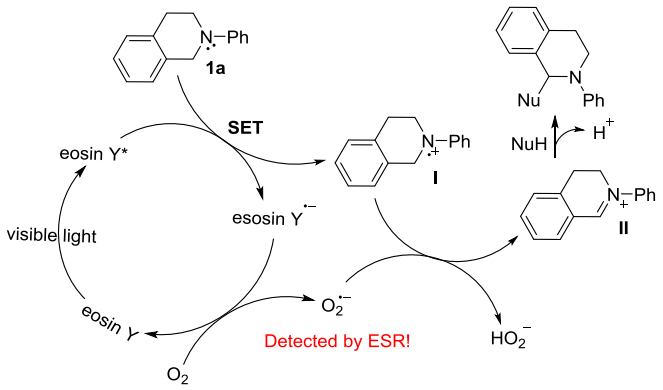

Scheme 8. The proposed mechanism.

reactions of *N*-aryl tetrahydroisoquinolines with pronucleophiles such as nitroalkanes, malononitrile, dimethyl malonate and H-phosphonate diesters generate the corresponding coupling products in good to excellent yields at the present reaction conditions. Furthermore, the catalyst is readily prepared, easily recoverable, and reusable for at least eight cycles without significant loss of its activity.

4. Experimental section

4.1. General considerations

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400 MHz and 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). CHN analysis was performed using a Vario EL III elementar. Transmission electron micrographs (TEM) were obtained using a JEOL-2010 transmission electron microscope. X-ray diffraction (XRD) measurements were carried out at room temperature using a Bruker D8 Advance X-ray powder diffractometer. All the solvents and commercially available reagents were purchased from commercial suppliers. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

4.2. Typical procedure for oxidative coupling reaction of N-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane using the supported eosin Y

N-phenyl-1,2,3,4-tetrahydroisoquinoline (1a, 0.25 mmol), nitromethane (1.25 mmol, 5.0 equiv), the prepared MNPs-eosin Y (50 mg, 2.0 mol %) and DMSO (2 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W green LED (530–535 nm) for 12 h under air atmosphere at room temperature. After the reaction was completed (monitored by TLC), the mixture was transferred to the separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give the desired product 2a in 92% yield as a pale oil.

5. Characterization data for all products

5.1. Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**3a**) [8a]

Pale yellow oil (61.7 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33–7.15 (m, 6H), 7.02–7.00 (m, 2H), 6.88 (t, J = 7.2 Hz, 1H), 5.58 (t, J = 7.2 Hz, 1H), 4.92–4.87 (m, 1H), 4.61–4.56 (m, 1H), 3.73–3.61 (m, 2H), 3.15–3.08 (m, 1H), 2.85–2.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 135.2, 132.9, 129.5, 129.2, 128.1, 127.0, 126.7, 119.4, 115.1, 78.8, 58.1, 42.1, 26.4.

5.2. 2-(4-Methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**3b**) [8a]

Yellow oil (60.4 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.12 (m, 4H), 6.91 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.38 (t, J = 7.2 Hz, 1H), 4.84–4.79 (m, 1H), 4.57–4.53 (m, 1H), 3.74 (s, 3H), 3.57–3.54 (m, 2H), 3.05–2.96 (m, 1H), 2.70–2.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.9, 143.0, 135.4, 132.8, 129.4, 127.8, 126.9, 126.6, 118.8, 114.6, 78.9, 58.9, 55.5, 43.1, 25.7.

5.3. 2-(4-Methyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (**3c**)

Pale yellow oil (60.9 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.05 (m, 6H), 6.87 (d, J = 8.4 Hz, 2H), 5.48 (t, J = 7.2 Hz, 1H), 4.86–4.81 (m, 1H), 4.56–4.52 (m, 1H), 3.66–3.53 (m, 2H), 3.09–3.01 (m, 1H), 2.77–2.70 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 135.3, 133.0, 129.9, 129.2, 129.1, 128.0, 126.9, 126.6, 115.9, 78.8, 58.4, 42.3, 26.2, 20.3.

5.4. 2-(4-Chlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**3d**) [10a]

Yellow oil (64.1 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.12 (m, 6H), 6.89 (d, J = 8.8 Hz, 2H), 5.48 (t, J = 7.2 Hz, 1H), 4.87–4.82 (m, 1H), 4.59–4.54 (m, 1H), 3.66–3.56 (m, 2H), 3.10–3.02 (m, 1H), 2.81–2.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1, 135.0, 132.5, 129.3 (double), 128.2, 126.9, 126.8, 124.4, 116.5, 78.6, 58.2, 42.2, 26.1.

5.5. 2-(4-Bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**3e**) [8a]

Yellow oil (72.1 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J = 8.4 Hz, 2H), 7.27–7.23 (m, 3H), 7.17–7.11 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 5.48 (t, J = 7.2 Hz, 1H), 4.85–4.80 (m, 1H), 4.58–4.53 (m, 1H), 3.64–3.58 (m, 2H), 3.09–3.02 (m, 1H), 2.80–2.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.5, 135.0, 132.4, 132.2, 129.2, 128.2, 126.9, 126.8, 116.7, 111.5, 78.6, 58.1, 42.0, 26.1.

5.6. 1-(Nitromethyl)-2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (**3f**) [13]

Pale yellow oil (59.1 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22–7.11 (m, 5H), 6.78 (d, J = 5.2 Hz, 2H), 6.66 (s, 1H), 5.53–5.52 (m, 1H), 4.87–4.81 (m, 1H), 4.56–4.52 (m, 1H), 3.62–3.61 (m, 2H), 3.07–3.06 (m, 1H), 2.79–2.74 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 139.2, 135.3, 133.0, 129.3, 129.1, 128.0, 127.0, 126.6, 120.3, 115.9, 112.2, 78.7, 58.1, 42.1, 26.5, 21.8.

5.7. 1-(Nitromethyl)-2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline (**3g**) [9c]

Pale yellow oil (57.2 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ:

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7.27–7.24 (m, 2H), 7.20–7.16 (m, 3H), 7.00–6.98 (m, 2H), 6.73–6.71 (m, 1H), 5.15–5.11 (m, 1H), 4.83–4.78 (m, 1H), 4.61–4.57 (m, 1H), 3.53–3.46 (m, 1H), 3.23–3.18 (m, 1H), 2.88–2.79 (m, 1H), 2.56–2.52 (m, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 136.3, 134.2, 133.2, 131.2, 129.8, 127.6, 126.6, 126.5, 126.3, 124.4, 122.8, 79.4, 59.6, 43.3, 24.5, 17.7.

5.8. 1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**3h**) [8a]

Pale yellow oil (57.9 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.19 (m, 3H), 7.18–7.07 (m, 3H), 7.00–6.96 (m, 2H), 6.81–6.78 (m, 1H), 5.25–5.21 (m, 1H), 5.06–4.99 and 4.90–4.83 (m, 1H), 3.84–3.77 and 3.59–3.52 (m, 2H), 3.06–2.99 (m, 1H), 2.92–2.83 (m, 1H), 1.67 and 1.51 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.1, 148.8, 135.5, 134.7, 133.7, 131.9, 129.4, 129.2, 129.0, 128.6, 128.3, 128.1, 127.2, 126.5, 126.0, 119.2, 118.7, 115.3, 114.4, 88.9, 85.4, 62.7, 61.1, 43.4, 42.6, 26.7, 26.3, 17.3, 16.3.

5.9. 1-(1-Nitroethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (**3i**) [13]

Pale yellow oil (59.3 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24–7.21 (m, 1H), 7.18–7.13 (m, 2H), 7.09–6.99 (m, 3H), 6.88 (d, J = 8.4 Hz, 2H), 5.18–5.14 (m, 1H), 5.05–4.98 and 4.90–4.83 (m, 1H), 3.83–3.76 and 3.56–3.51 (m, 2H), 3.05–2.98 (m, 1H), 2.89–2.79 (m, 1H), 2.25 and 2.23 (s, 3H), 1.68 and 1.52 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 146.8, 135.8, 134.9, 133.8, 132.1, 129.9, 129.8, 129.2, 128.9, 128.8, 128.4, 128.1, 127.3, 126.5, 126.1, 116.1, 115.2, 89.0, 85.5, 62.9, 61.5, 43.9, 43.1, 26.6, 26.3, 20.4, 20.3, 17.4, 16.4.

5.10. 2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5a**) [8a]

Pale yellow solid (41.5 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.26 (m, 6H), 7.12 (d, J = 8.0 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 5.55 (s, 1H), 3.83–3.78 (m, 1H), 3.56–3.49 (m, 1H), 3.23–3.15 (m, 1H), 3.03–2.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.3, 134.6, 129.6, 129.5, 129.3, 128.7, 127.0, 126.8, 121.8, 117.7, 117.6, 53.2, 44.2, 28.5.

5.11. 2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5b**) [8a]

Pale yellow solid (52.2 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.22 (m, 4H), 7.09 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.37 (s, 1H), 3.80 (s, 3H), 3.60–3.56 (m, 1H), 3.47–3.40 (m, 1H), 3.21–3.12 (m, 1H), 2.95–2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.7, 142.6, 134.3, 129.7, 129.4, 128.6, 127.1, 126.7, 121.0, 117.6, 114.8, 55.6, 55.5, 44.9, 28.7.

5.12. 2-(p-Tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5c**) [11b]

Pale yellow solid (44.7 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: H: 7.32–7.21 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 3.72–3.68 (m, 1H), 3.47–3.41 (m, 1H), 3.19–3.11 (m, 1H), 2.96–2.92 (m, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.3, 134.5, 131.8, 130.1, 129.7, 129.4, 128.7, 127.1, 126.7, 118.3, 117.7, 54.1, 44.4, 28.6, 20.5.

5.13. 2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5d**) [11c]

Pale yellow solid (49.72 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.23 (m, 6H), 7.01 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 3.71–3.70 (m, 1H), 3.49–3.42 (m, 1H), 3.19–3.10 (m, 1H), 2.99–2.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 134.3, 129.5, 129.3, 129.2, 128.9, 127.0, 126.9 (double), 118.8, 117.4, 53.1, 44.3, 28.4.

5.14. 2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5e**) [8a]

Pale yellow solid (58.7 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J = 8.4 Hz, 2H), 7.32–7.23 (m, 4H), 6.94 (d, J = 8.8 Hz, 2H), 5.45 (s, 1H), 3.72–3.70 (m, 1H), 3.49–3.42 (m, 1H), 3.18–3.10 (m, 1H), 3.00–2.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 134.4, 132.4, 129.3, 129.2, 128.9, 127.0, 126.9, 119.0, 117.4, 114.3, 52.8, 44.2, 28.4.

5.15. 2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**5f**) [11j]

Pale yellow solid (45.3 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.22 (m, 5H), 6.90–6.82 (m, 3H), 5.50 (s, 1H), 3.77–3.74 (m, 1H), 3.49–3.42 (m, 1H), 3.18–3.10 (m, 1H), 2.97–2.93 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 139.3, 134.6, 129.6, 129.3 (double), 128.7, 127.0, 126.8, 122.7, 118.3, 117.7, 114.7, 53.3, 44.1, 28.5, 21.7.

5.16. Dimethyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) malonate (**7a**) [8a]

Colourless oil (72.9 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22–7.18 (m, 3H), 7.16–7.14 (m, 1H), 7.11–7.09 (m, 2H), 6.99–6.97 (m, 2H), 6.76–6.73 (m, 1H), 5.71 (d, J = 9.2 Hz, 1H), 3.95 (d, J = 9.2 Hz, 1H), 3.72–3.66 (m, 1H), 3.63 (s, 3H), 3.61–3.58 (m, 1H), 3.53 (s, 3H), 3.09–3.01 (m, 1H), 2.88–2.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 167.2, 148.6, 135.5, 134.6, 129.0, 128.8, 127.5, 126.9, 125.9, 118.5, 115.1, 59.0, 58.0, 52.4, 42.0, 25.9.

5.17. Dimethyl-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) malonate (**7b**) [11e]

Colourless oil (76.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–7.19 (m, 1H), 7.17–7.14 (m, 1H), 7.11–7.07 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.61 (d, J = 9.6 Hz, 1H), 3.96 (d, J = 8.4 Hz, 1H), 3.70–3.61 (m, 2H), 3.64 (s, 3H), 3.58 (s, 3H), 3.11–3.02 (m, 1H), 2.83–2.76 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 167.4, 146.7, 135.5, 134.8, 129.6, 129.0, 128.1, 127.5, 127.0, 125.9, 115.8, 59.1, 58.5, 52.5, 42.3, 25.7, 20.3.

5.18. Dimethyl-2-(2-(4-chlorophenyl)-1,2,3,4 tetrahydroisoquinolin-1-yl)malonate (**7c**) [10a]

Colourless oil (78.5 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21–7.18 (m, 2H), 7.17–7.10 (m, 4H), 6.90 (d, J = 9.2 Hz, 2H), 5.64 (d, J = 9.6 Hz, 1H), 3.91 (d, J = 9.6 Hz, 1H), 3.70–3.63 (m, 1H), 3.66 (s, 3H), 3.59–3.52 (m, 1H), 3.55 (s, 3H), 3.09–3.01 (m, 1H), 2.93–2.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 167.2, 147.3, 135.4, 134.5, 128.9, 128.8, 127.8, 127.0, 126.2, 123.2, 116.1, 59.0, 58.1, 52.6, 42.4, 26.0.

5.19. Dimethyl-2-(2-(o-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) malonate (**7d**) [11e]

Colourless oil (71.6 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.20 (m, 2H), 7.17–7.11 (m, 3H), 6.96–6.93 (m, 2H), 6.74–6.71 (m, 1H), 5.15 (d, J = 9.6 Hz, 1H), 4.04 (d, J = 9.6 Hz, 1H), 3.66 (s, 3H), 3.62 (s, 3H), 3.61–3.56 (m, 1H), 3.18 (dd, J = 5.2 Hz and 14.0 Hz, 1H),

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2.81–2.72 (m, 1H), 2.58 (dd, J = 2.0 Hz and 14.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.2, 167.4, 149.5, 135.7, 135.4, 132.7, 131.0, 129.4, 127.3, 126.6, 126.3, 126.1, 123.6, 122.3, 60.2, 59.8, 52.3, 43.7, 24.9, 17.8.

5.20. Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) phosphonate (**9a**) [8a]

Pale yellow oil (82.9 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37–7.36 (m, 1H), 7.26–7.22 (m, 2H), 7.19–7.12 (m, 3H), 6.97 (d, J = 8.0 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 5.18 (d, J = 20 Hz, 1H), 4.11–3.86 (m, 5H), 3.65–3.59 (m, 1H), 3.09–2.97 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.3 (d, J = 5.7 Hz), 136.3 (d, J = 5.5 Hz), 130.5 (d, J = 0.9 Hz), 129.0, 128.6 (d, J = 2.6 Hz), 128.0 (d, J = 4.7 Hz), 127.3 (d, J = 3.5 Hz), 125.7 (d, J = 2.8 Hz), 118.4, 114.7 (d, J = 1.0 Hz), 63.2 (d, J = 7.2 Hz), 62.2 (d, J = 7.7 Hz), 59.5, 57.9, 43.4, 26.6, 16.3 (d, J = 5.5 Hz), 16.2 (d, J = 5.7 Hz).

5.21. Dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9b**) [8a]

Pale yellow oil (113.9 mg, 97% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.10 (m, 16H), 6.96 (d, J = 8.0 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 5.28 (d, J = 19.6 Hz, 1H), 5.03–4.74 (m, 4H), 4.04–3.98 (m, 1H), 3.62–3.59 (m, 1H), 3.08–2.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.1 (d, J = 5.6 Hz), 136.4 (d, J = 5.6 Hz), 136.3 (d, J = 5.9 Hz), 136.1 (d, J = 5.9 Hz), 130.3, 129.1, 128.7 (d, J = 2.7 Hz), 128.3 (d, J = 8.4 Hz), 128.2, 128.1, 128.1, 127.9 (d, J = 4.9 Hz), 127.5 (d, J = 3.6 Hz), 125.9 (d, J = 2.9 Hz), 123.1, 118.8, 118.5, 114.7, 68.5 (d, J = 7.3 Hz), 67.6 (d, J = 7.7 Hz), 59.7, 58.1, 43.5, 26.7.

5.22. Diethyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9c**) [8a]

Pale yellow oil (90.1 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40–7.38 (m, 1H), 7.19–7.12 (m, 3H), 6.92 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.02 (d, J = 21.6 Hz, 1H), 4.13–3.91 (m, 5H), 3.74 (s, 3H), 3.56–3.51 (m, 1H), 2.93 (br, 2H), 1.25 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.0, 144.1 (d, J = 8.2 Hz), 136.3 (d, J = 5.8 Hz), 130.4 (d, J = 1.1 Hz), 128.8 (d, J = 2.6 Hz), 128.1 (d, J = 4.4 Hz), 127.2 (d, J = 3.5 Hz), 125.7 (d, J = 2.9 Hz), 117.5, 114.4, 63.3 (d, J = 7.2 Hz), 62.2 (d, J = 7.6 Hz), 59.4 (d, J = 157.7 Hz), 55.6, 44.6, 26.0, 16.4 (d, J = 5.5 Hz), 16.3 (d, J = 5.9 Hz).

5.23. Diethyl (2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9d**) [9c]

Pale yellow oil (77.1 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.37 (m, 1H), 7.17–7.11 (m, 3H), 7.04 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.12 (d, J = 20.8 Hz, 1H), 4.13–3.88 (m, 5H), 3.62–3.56 (m, 1H), 2.98 (br, 2H), 2.24 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3 (d, J = 7.0 Hz), 136.3 (d, J = 5.7 Hz), 130.5 (d, J = 1.1 Hz), 129.5, 128.7 (d, J = 2.6 Hz), 128.0 (d, J = 4.6 Hz), 127.8, 127.2 (d, J = 3.5 Hz), 125.7 (d, J = 2.9 Hz), 115.2, 63.2 (d, J = 7.1 Hz), 62.1 (d, J = 7.6 Hz), 58.9 (d, J = 158.4 Hz), 43.7, 26.3, 20.3, 16.4 (d, J = 5.4 Hz), 16.3 (d, J = 5.8 Hz).

5.24. Dibenzyl (2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) phos-phonate (**9e**) [9c]

Pale yellow oil (111.2 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32–7.12 (m, 14H), 7.02 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz,2H), 5.23 (d, J = 19.6 Hz, 1H), 5.04–4.75 (m, 4H), 4.05–3.99 (m, 1H), 3.60–3.57 (m, 1H), 2.97 (br, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1 (d, J = 6.5 Hz), 136.4 (d, J = 3.8 Hz), 136.3 (d, J = 4.2 Hz), 136.2 (d, J = 6.0 Hz), 130.2, 129.6, 128.8 (d, J = 2.6 Hz), 128.3 (d, J = 8.0 Hz), 128.1, 128.1, 128.0, 127.9 (d, J = 8.8 Hz), 127.3 (d, J = 3.5 Hz), 125.8 (d, J = 2.9 Hz), 115.3, 68.5 (d, J = 7.2 Hz), 67.5 (d, J = 7.8 Hz), 59.1 (d, J = 156.7 Hz), 43.8, 26.5, 20.3.

5.25. Diethyl (2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-phosphonate (**9f**) [9c]

Pale yellow oil (82.7 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.34 (m, 1H), 7.19–7.17 (m, 5H), 6.88 (d, J = 8.8 Hz, 2H), 5.10 (d, J = 19.2 Hz, 1H), 4.11–3.84 (m, 5H), 3.54–3.51 (m, 1H), 3.15–3.11 (m, 1H), 2.97–2.93 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.13 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8 (d, J = 5.0 Hz), 136.1 (d, J = 5.4 Hz), 130.3, 128.7, 128.5 (d, J = 2.7 Hz), 127.9 (d, J = 4.8 Hz), 127.4 (d, J = 3.5 Hz), 125.8 (d, J = 2.8 Hz), 123.0, 115.5 (d, J = 0.8 Hz), 63.1 (d, J = 7.3 Hz), 62.3 (d, J = 7.7 Hz), 58.7 (d, J = 159.5 Hz), 43.6, 26.8, 16.3 (d, J = 5.4 Hz), 16.2 (d, J = 5.8 Hz).

5.26. Dibenzyl (2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9g**) [9c]

Pale yellow oil (118.4 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31–7.11 (m, 16H), 6.83 (d, J = 8.4 Hz, 2H), 5.19 (d, J = 18.4 Hz, 1H), 4.98–4.72 (m, 4H), 3.96-3.90 (m, 1H), 3.51–3.46 (m, 1H), 3.12–3.08 (m, 1H), 2.95–2.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6 (d, J = 4.7 Hz), 136.2 (d, J = 5.5 Hz), 136.0 (d, J = 5.7 Hz), 135.9 (d, J = 5.3 Hz), 130.0, 128.8, 128.6 (d, J = 2.7 Hz), 128.3, 128.3, 128.2, 128.2, 128.0 (d, J = 4.8 Hz), 127.9 (d, J = 2.2 Hz), 127.6 (d, J = 3.5 Hz), 126.0 (d, J = 2.9 Hz), 123.2, 115.7 (d, J = 0.9 Hz), 68.5 (d, J = 7.4 Hz), 67.8 (d, J = 7.7 Hz), 59.0 (d, J = 156.8 Hz), 43.6, 26.9.

5.27. Diethyl (2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9h**) [8a]

Pale yellow oil (102.8 mg, 97% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.30 (m, 3H), 7.21–7.15 (m, 3H), 6.84 (d, J = 8.8 Hz, 2H), 5.10 (d, J = 19.2 Hz, 1H), 4.10–3.84 (m, 5H), 3.56–3.50 (m, 1H), 3.17–3.13 (m, 1H), 2.98–2.94 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.2 (d, J = 4.9 Hz), 136.2 (d, J = 5.4 Hz), 131.7, 130.3, 128.5 (d, J = 2.8 Hz), 128.0 (d, J = 4.8 Hz), 127.5 (d, J = 3.5 Hz), 125.9 (d, J = 2.8 Hz), 116.0 (d, J = 1.0 Hz), 110.2 (d, J = 0.9 Hz), 63.2 (d, J = 7.3 Hz), 62.4 (d, J = 7.6 Hz), 58.7 (d, J = 158.6 Hz), 43.5, 26.9, 16.4 (d, J = 5.4 Hz), 16.3 (d, J = 5.8 Hz).

5.28. Diethyl (2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**9h**) [8a]

Pale yellow oil (130.3 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.12 (m, 14H), 7.10–7.09 (m, 2H), 6.79 (d, J = 8.4 Hz, 2H), 5.18 (d, J = 18.8 Hz, 1H), 4.98–4.82 (m, 3H), 4.77–4.72 (m, 1H), 3.96–3.89 (m, 1H), 3.53–3.47 (m, 1H), 3.14–3.10 (m, 1H), 2.96–2.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.0 (d, J = 4.5 Hz), 136.2 (d, J = 5.5 Hz), 136.1 (d, J = 4.0 Hz), 136.0 (d, J = 4.1 Hz), 131.7, 130.0, 128.6 (d, J = 2.8 Hz), 128.4, 128.4, 128.3, 128.2, 128.1 (d, J = 4.9 Hz), 127.9 (d, J = 1.3 Hz), 127.7 (d, J = 2.2 Hz), 127.6, 126.0 (d, J = 2.7 Hz), 116.2, 110.4, 68.5 (d, J = 7.4 Hz), 67.8 (d, J = 7.8 Hz), 58.8 (d, J = 156.9 Hz), 43.6, 26.9.

5.29. Dibenzyl (2-(m-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) phos-phonate (**9j**) [8a]

Pale yellow oil (82.7 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38–7.37 (m, 1H), 7.17–7.11 (m, 4H), 6.80–6.77 (m, 2H), 6.61 (d,

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J = 7.2 Hz, 1H), 5.18 (d, J = 20 Hz, 1H), 4.12–3.87 (m, 5H), 3.66–3.60 (m, 1H), 3.07–2.96 (m, 2H), 2.31 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.4 (d, J = 6.0 Hz), 138.7, 136.3 (d, J = 5.6 Hz), 130.6 (d, J = 1.1 Hz), 128.9, 128.6 (d, J = 2.6 Hz), 128.0 (d, J = 4.5 Hz), 127.2 (d, J = 3.4 Hz), 125.7 (d, J = 2.8 Hz), 119.3, 115.4 (d, J = 0.9 Hz), 111.8 (d, J = 0.9), 63.2 (d, J = 7.2 Hz), 62.2 (d, J = 7.7 Hz), 58.8 (d, J = 158.0 Hz), 43.3, 26.6, 21.8, 16.3 (d, J = 5.5 Hz), 16.2 (d, J = 5.8 Hz).

5.30. Dibenzyl (2-(m-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) phos-phonate (**9k**) [19]

Pale yellow oil (116.0 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.11 (m, 15H), 6.78 (br, 2H), 6.61 (d, J = 7.2 Hz, 1H), 5.28 (d, J = 19.6 Hz, 1H), 5.03–4.75 (m, 4H), 4.05–3.98 (m, 1H), 3.65–3.60 (m, 1H), 3.07–2.96 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2 (d, J = 5.7 Hz), 138.8, 136.5 (d, J = 5.6 Hz), 136.3 (d, J = 6.1 Hz), 136.2 (d, J = 6.1 Hz), 130.3, 128.9, 128.7 (d, J = 2.6 Hz), 128.3 (d, J = 9.0 Hz), 128.2 (d, J = 11.6 Hz), 128.1 (d, J = 4.7 Hz), 127.9 (d, J = 7.6 Hz), 127.4 (d, J = 3.5 Hz), 125.8 (d, J = 2.8 Hz), 119.5, 115.7, 112.0, 68.6 (d, J = 7.2 Hz), 67.6 (d, J = 7.7 Hz), 59.0 (d, J = 157.0 Hz), 43.5, 26.8, 21.8.

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Appendix A. Supplementary data

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