Electronic Supplementary Information for

A novel strategy of polyelectrolyte materials based artificial light-harvesting system for photocatalysis of cross dehydrogenation coupling

Chao-Qun Ma,[a] Xing-Long Li,[a] Ning Han,*[b] Ying Wang,[a] Rong-Zhou Wang,[a] Shengsheng Yu,[a] Yue-Bo Wang,*[a] Ling-Bao Xing*[a]

[a]School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000, P. R. China

[b]Department of Materials Engineering, KU Leuven, Leuven 3001, Belgium.

*Corresponding author: Tel. /fax: +86 533 2781664. E-mail: ning.han@kuleuven.be; ybwang@sdut.edu.cn; lbxing@sdut.edu.cn.

Experimental

Synthesis 4PyTPE: Compound A1 was obtained by McMury coupling reaction. Under nitrogen protection, add 4,4-dibromobenzophenone (1.7 g, 5 mmol), 1.3 g zinc to a 50 mL three-necked flask powder (1.3 g, 20 mmol), tetrahydrofuran (30 mL), stirred for 0.5 h in an ice-water bath, then added titanium tetrachloride (1 mL) with a syringe, continued stirring for 0.5 h in an ice-water bath, and refluxed at 70 ℃ for reaction 12 hours. After the reaction was completed, it was cooled to room temperature, and water (100 mL) was added to quench titanium tetrachloride, then saturated potassium carbonate solution (30 mL) was added. Finally, an appropriate amount of dilute hydrochloric acid was added to adjust the pH to neutrality. Use di-chloromethane as an extractant and extract three times, combine the organic phases, dry and filter over anhydrous sodium sulfate, and remove the solvent by rotary evaporation to obtain a white solid crude product. Further purification was carried out by silica gel.

Energy-transfer efficiency calculation

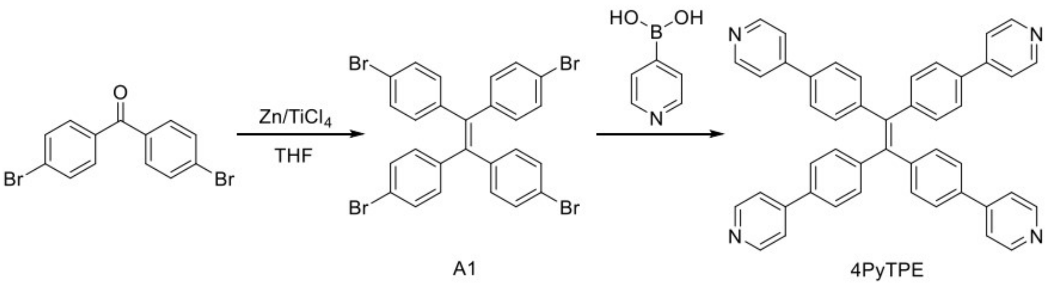
The energy-transfer efficiency (Φ_{ET}) was calculated from excitation fluorescence spectra through the equation S2: $\Phi_{ET} = 1 - I_{DA} / I_{D}$. Where I_{DA} and I_{D} are the fluorescence intensities of the emission of 4PyTPE-RSS+RhB assembly (donor and acceptor) and 4PyTPE-RSS assembly (donor) respectively when excited at 360 nm. The energy-transfer efficiency (Φ_{ET}) was calculated as 56.8% in aqueous environment, measured under the condition of [4PyTPE] = 2.0×10^{-5} M, [RSS] = 1.2×10^{-4} M, [Rh B] = 6.0×10^{-6} M.

Antenna effect calculation

The antenna effect was calculated based on the excitation spectra using equation S3: Antenna effect = $(I_{DA,\ 360} - I_{D,\ 360}) / I_{DA,\ 550}$. Where $I_{D,360}$, and $I_{DA,\ 360}$ are the fluorescence intensities at 550 nm with the excitation of the donor at 360 nm and the direct excitation of the acceptor at 550 nm, respectively. $I_{DA,\ 360}$ is the fluorescence intensities at 550 nm of the 4PyTPE-RSS assembly, which was normalized with the 4PyTPE-RSS+RhB assembly at 550 nm. The antenna effect value was calculated as 4.09 in water, measured under the condition of [4PyTPE] = 2.0×10^{-5} M, [RSS] = 1.2×10^{-4} M, [RhB] = 6.0×10^{-6} M.

General procedure for the photocatalytic cross dehydrogenation coupling reaction.

The N-phenyl-1,2,3,4-tetrahydroisoquinoline (20 mg, 0.1 mmol) and indole (23.4 mg, 0.2 mmol) were dissolved into a freshly prepared 4PyTPE-RSS+RhB assembly solution (2 mL, [4PyTPE] = 5.0×10^{-5} M, [RSS] = 1.2×10^{-4} M, [RhB] = 6.0×10^{-6} M). The mixture was subsequently irradiated by white LEDs (10 W) at room temperature for 18 h. After that, the organic products were extracted by ethyl acetate, and the mixed organic layer was dried with anhydrous Na_2SO_4. Then the organic solution was concentrated in vacuo and purified by flash column chromatography with petroleum ether/ethyl acetate to afford the corresponding product, brown oil. The ^1H NMR analysis was conducted to analyse components of the obtained oil. CDC reaction product yield was calculated by the equation: yield (%) = number of moles of the product obtained/number of moles of the feeded reactant × 100%. Where ‘ number of moles of the product’ is calculated from the characteristic proton signal integration of the target product dividing by the corresponding proton number, and ‘number of moles of the feeded reactant’ is the sum number of the remaining substrate, target product and by-products calculated by the same way.



Scheme S1. Synthetic route of 4PyTPE

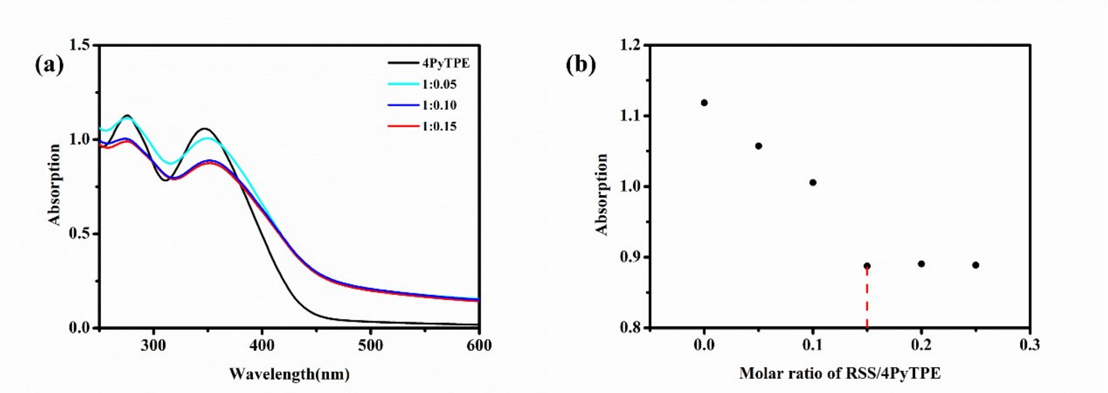


Figure S1. (a) UV-vis absorption spectra of 4PyTPE with different concentrations of RSS; (b) Absorption changes at different molar ratios of 4PyTPE and RSS. [4PyTPE] = 2 × 10^{-5} M, [RSS] = 1.2 × 10^{-4} M.

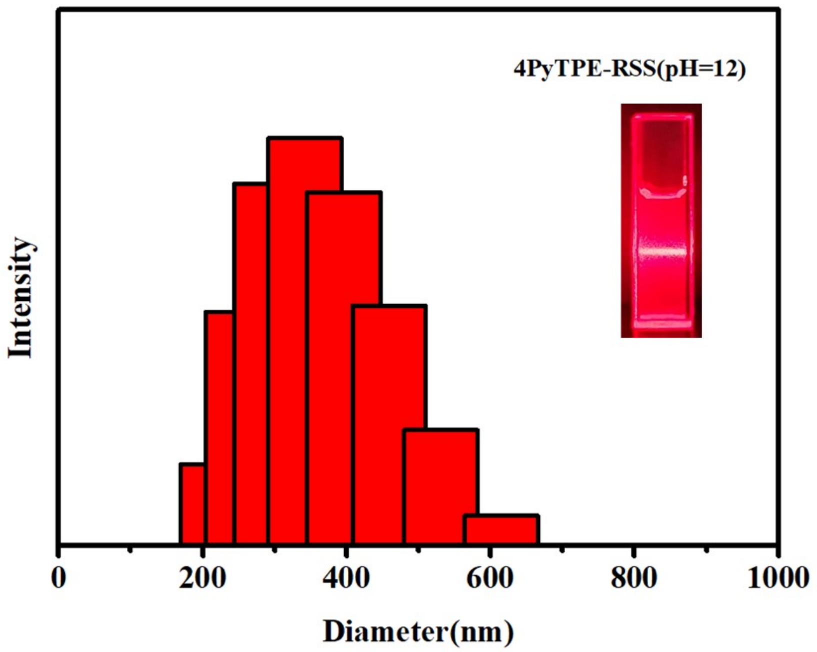


Figure S2. Particle size distribution and potential change of 4PyTPE aqueous solution after adding RSS (pH=2). Illustration: Tyndall effect of solution. [4PyTPE] = 2 × 10^{-5} M, [RSS] = 1.2 × 10^{-4} M.

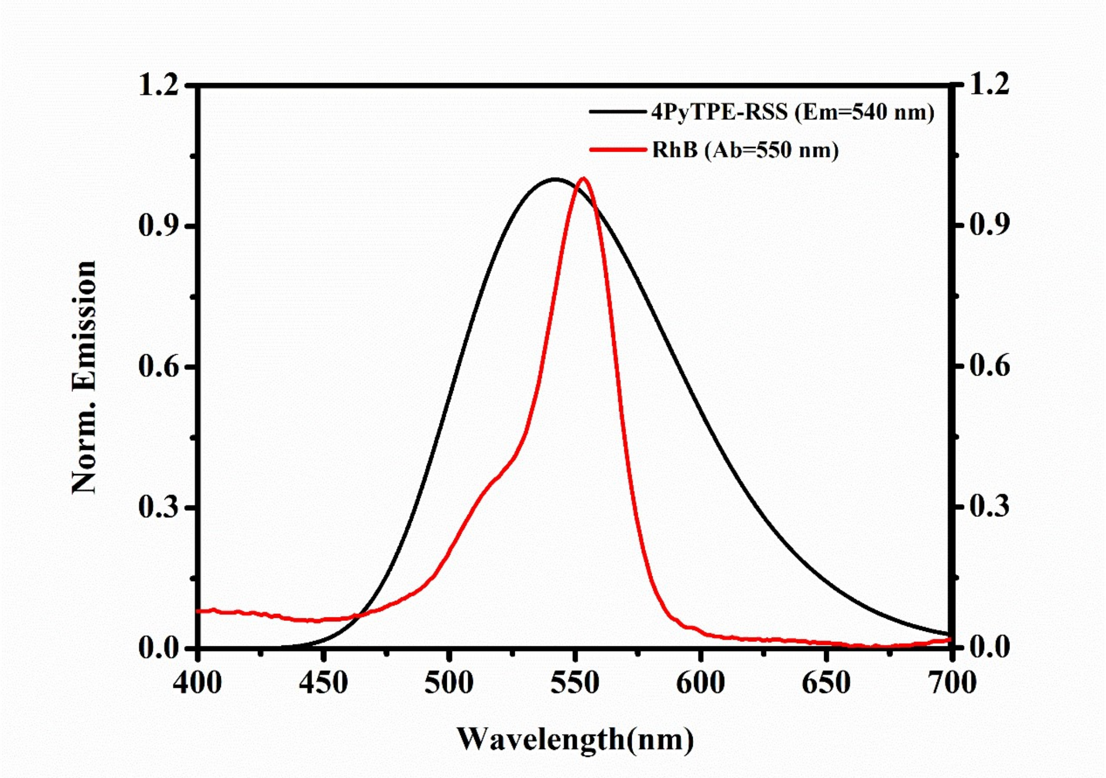


Figure S3. Normalized 4PyTPE-RSS fluorescence emission spectrum ($\lambda_{ex} = 360$ nm) and normalized UV absorption spectrum of RhB. [RSS] = 1.2×10^{-4} M, [4PyTPE] = 2×10^{-5} M, [RhB] = 6×10^{-6} M.

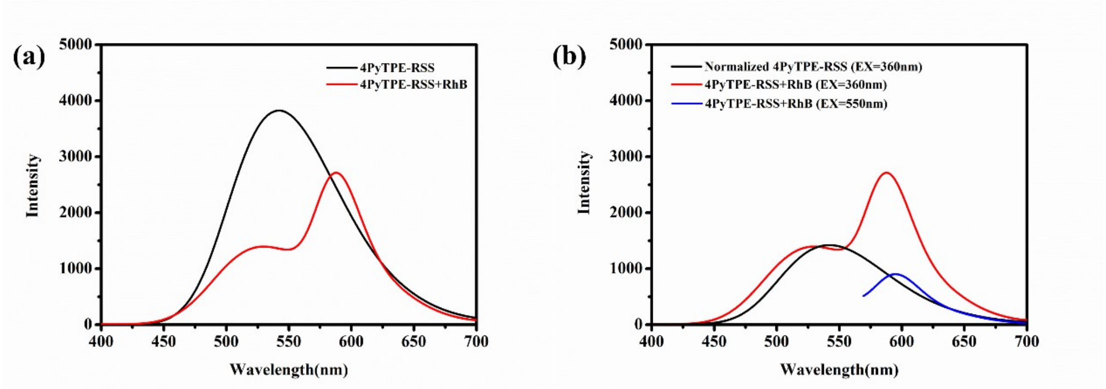


Figure S4. (a) Fluorescence spectra of 4PyTPE-RSS and 4PyTPE-RSS+RhB (λ_{ex} = 360 nm); (b) Fluorescence spectra of 4PyTPE-RSS+Rh B (red line, λ_{ex} = 360 nm), blue line (acceptor emission, λ_{ex} = 550 nm); the black line represents the fluorescence spectrum of 4PyTPE-RSS, normalized to the fluorescence intensity of the red line at 550 nm. [RSS] = 1.2×10^{-4} M, [4PyTPE] = 2×10^{-5} M, [RhB] = 6×10^{-6} M.

Substrate expansion ^{1}HNMR

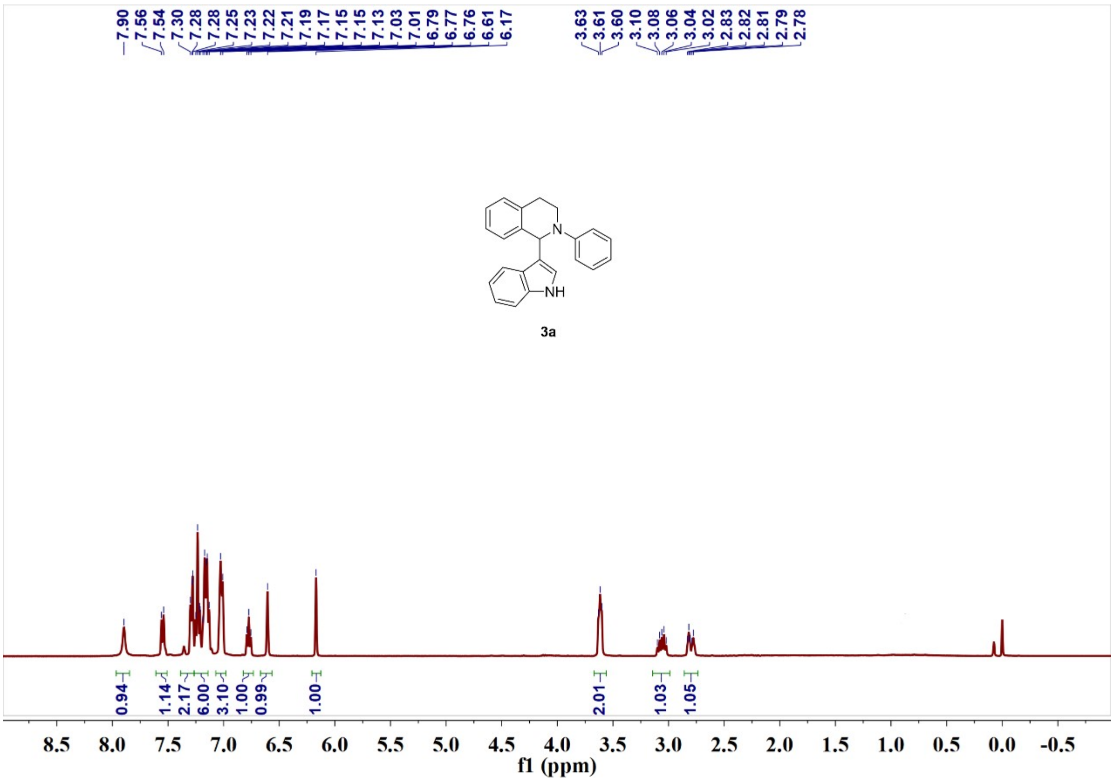


Figure S5. ^{1}H NMR spectra of 3a in $CDCl_3$.

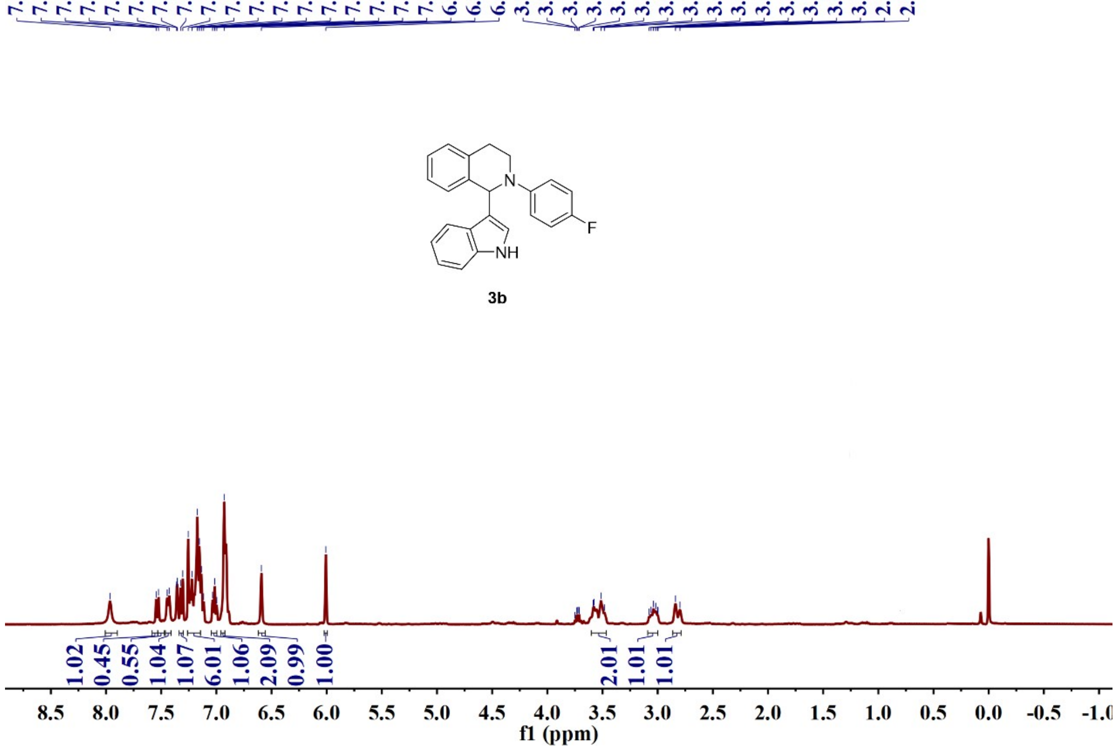


Figure S6. ^{1}H NMR spectra of 3b in $CDCl_3$.

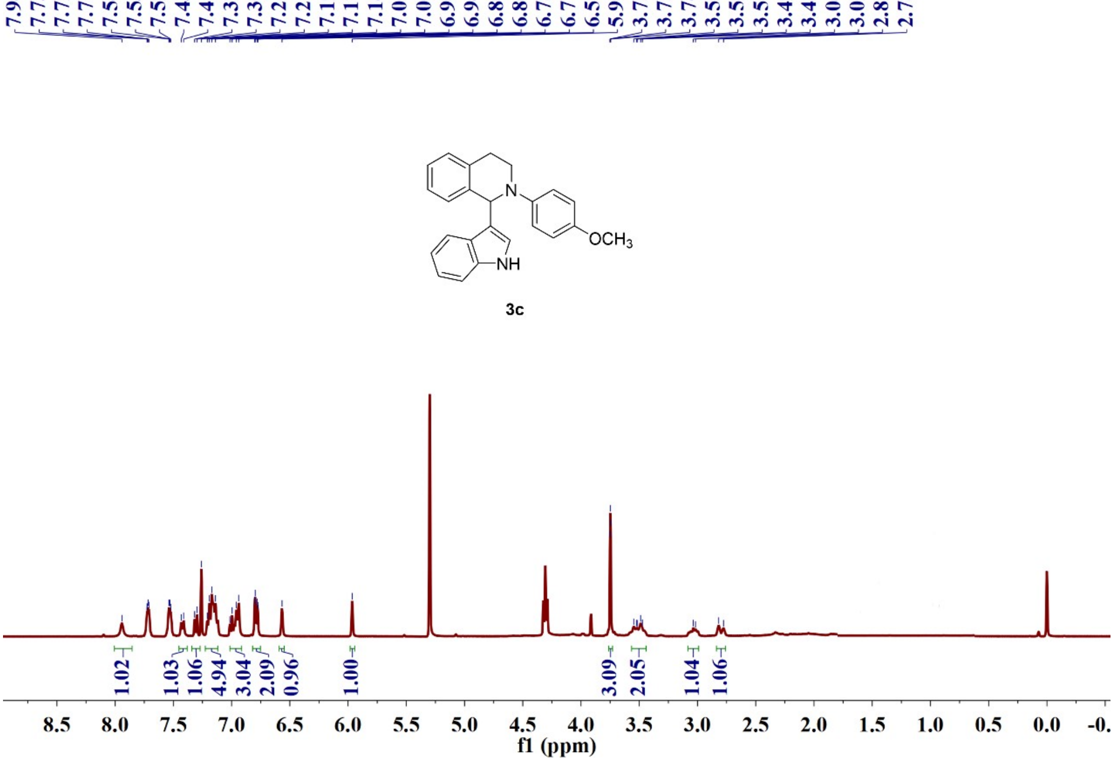


Figure S7. ^{1}H NMR spectra of 3c in $CDCl_3$.

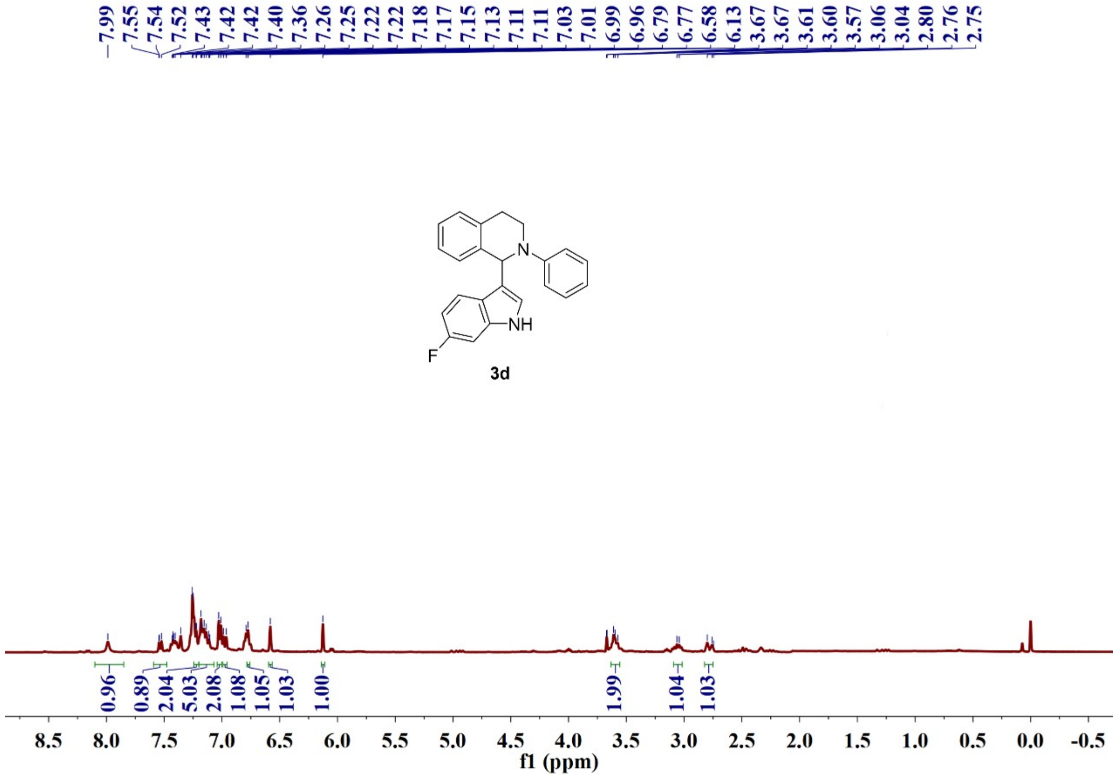


Figure S8. ^{1}H NMR spectra of 3d in $CDCl_3$.

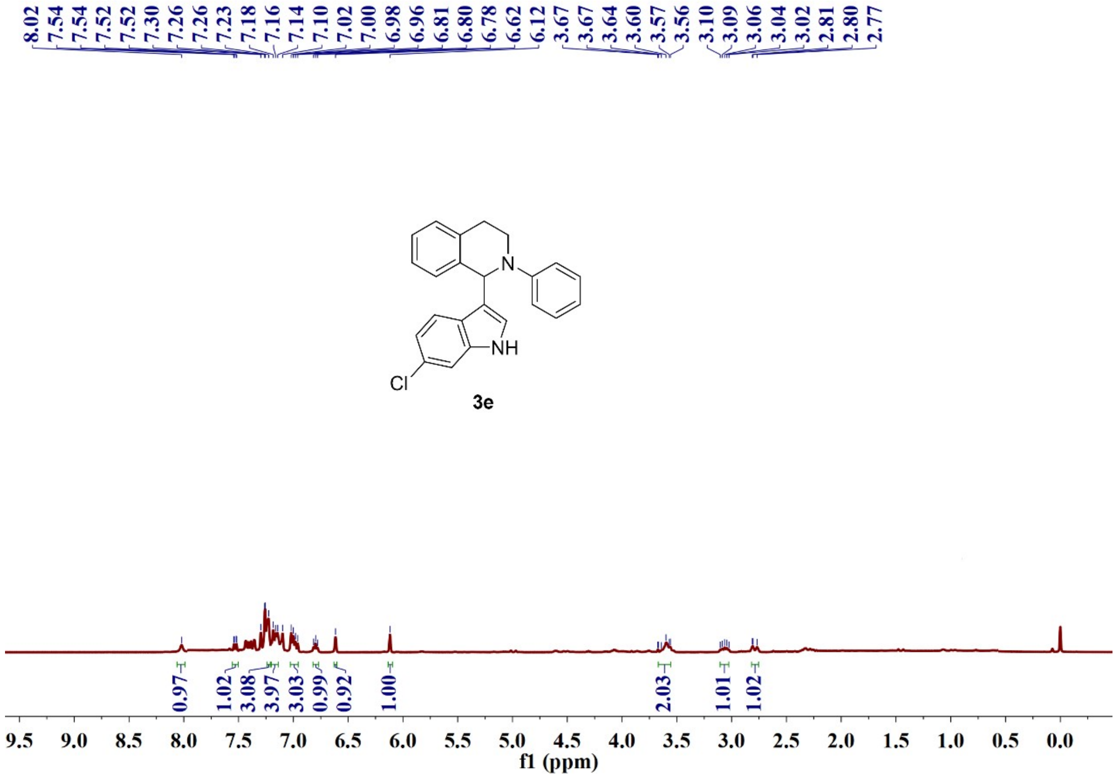


Figure S9. ^{1}H NMR spectra of 3e in $CDCl_3$.

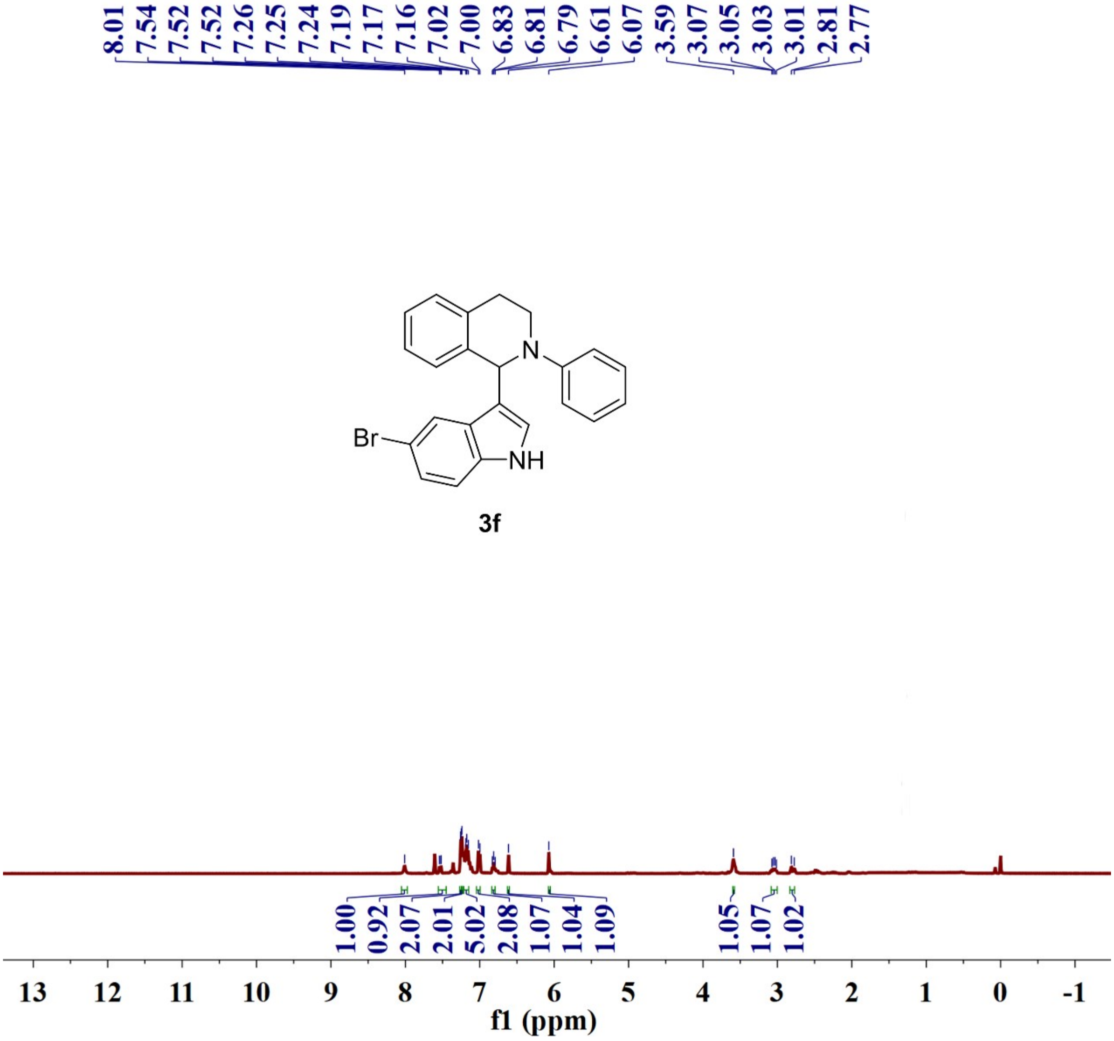


Figure S10. ^{1}H NMR spectra of 3f in $CDCl_3$.

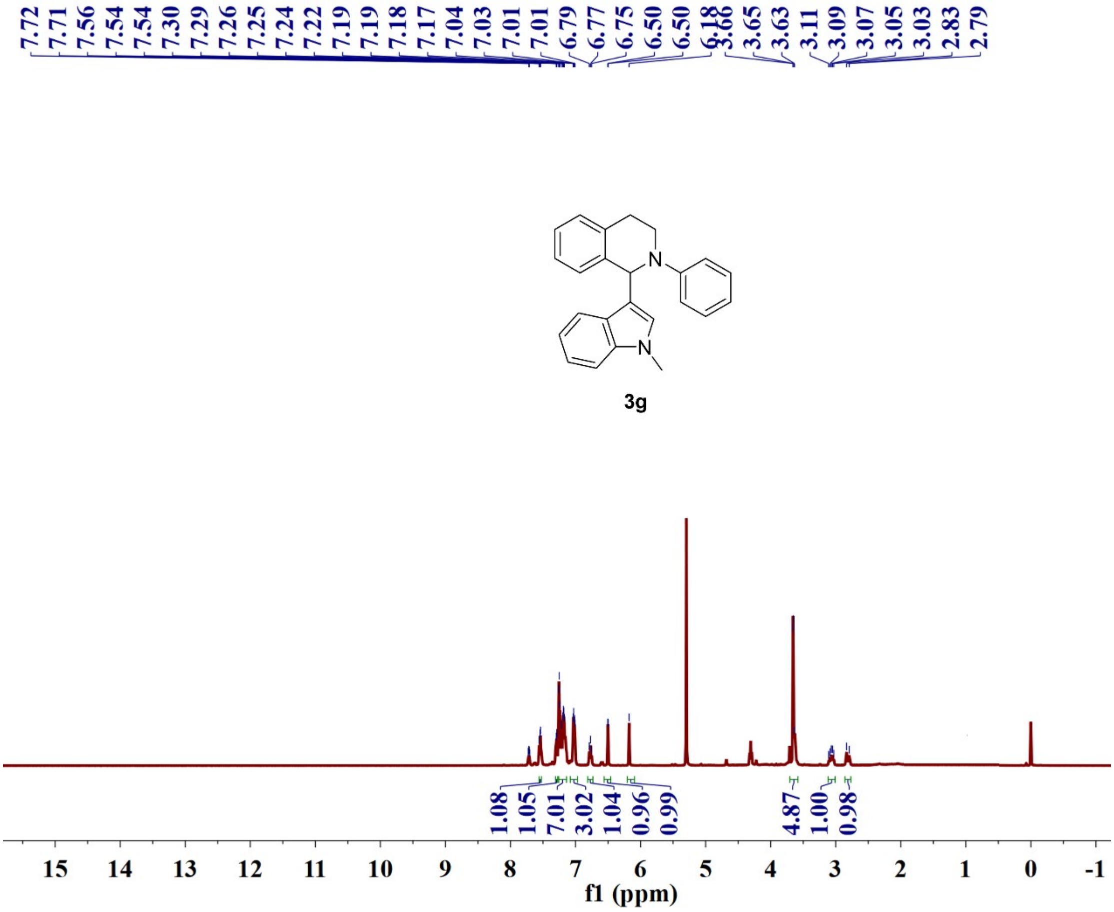


Figure S11. ^{1}H NMR spectra of 3g in $CDCl_3$.

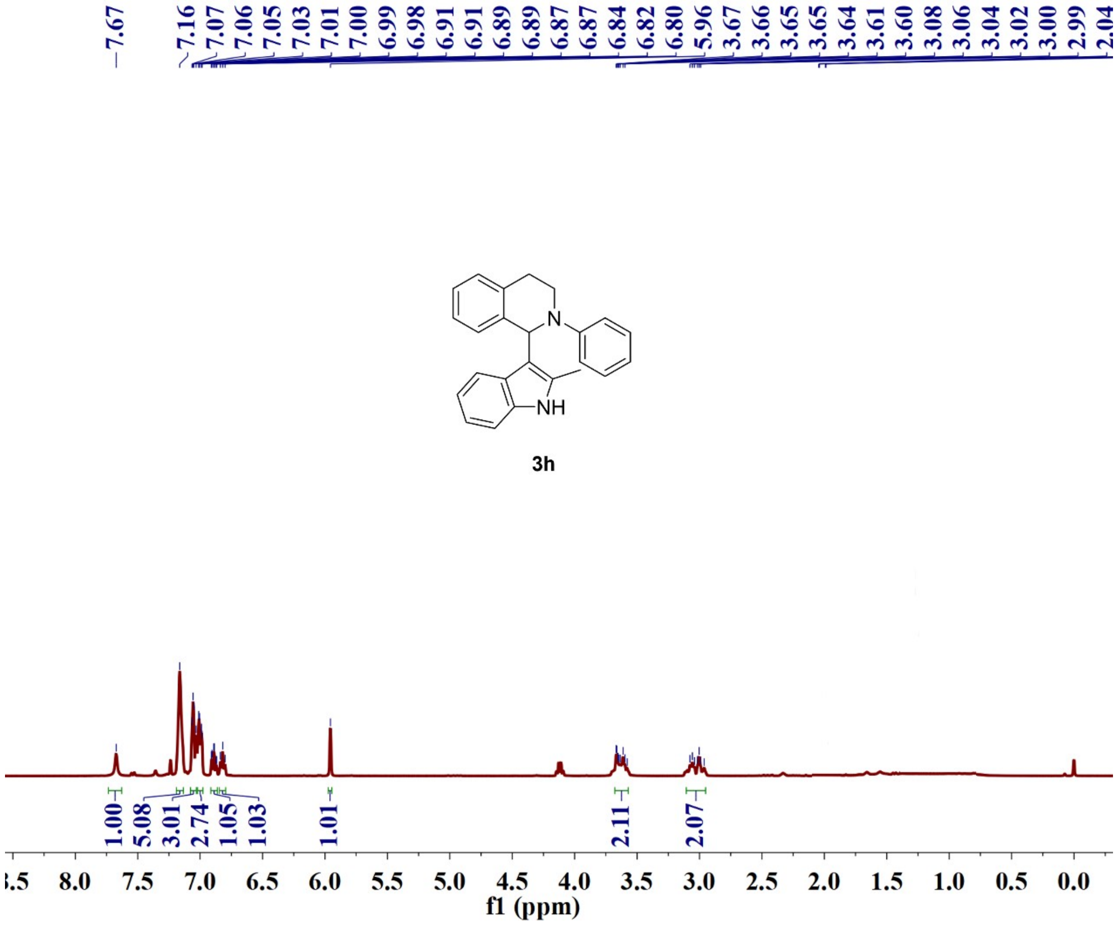


Figure S12. ^{1}H NMR spectra of 3h in $CDCl_3$.

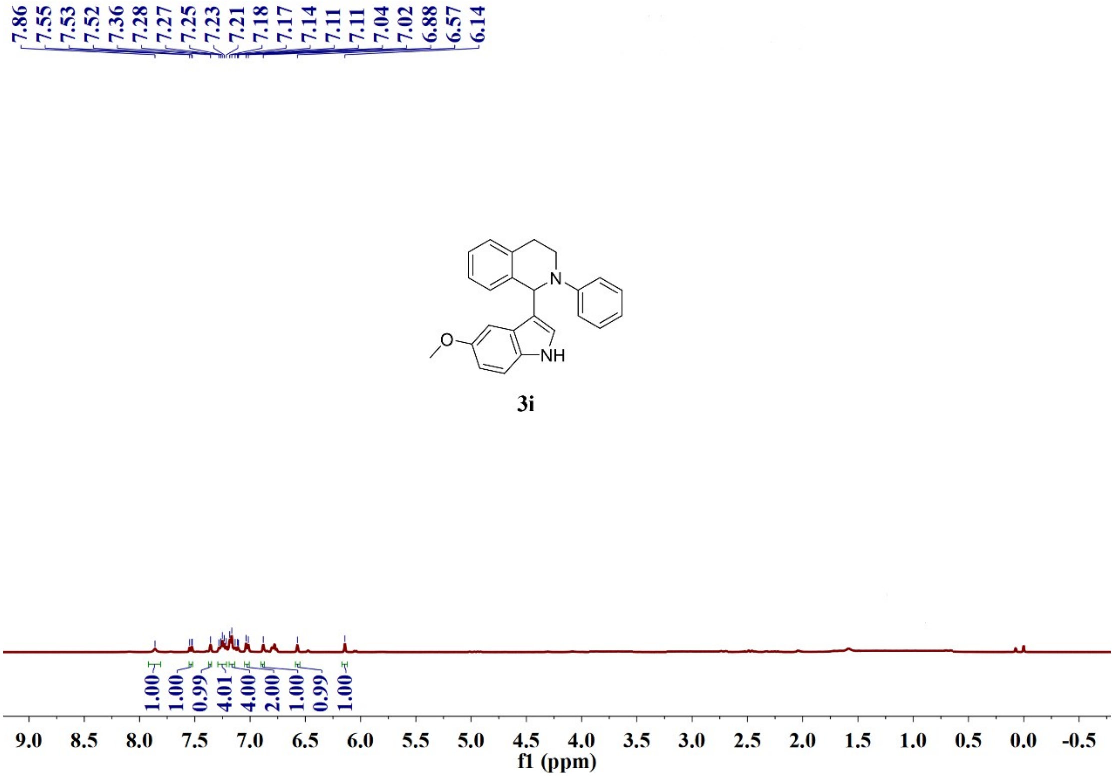
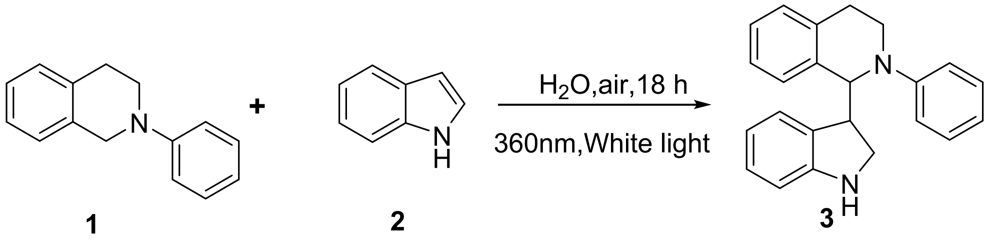


Figure S13. ^{1}HNMR spectra of 3i in $CDCl_3$.

Table S1. Condition optimization for the aerobic CDC reaction of N-phenyl-1,2,3,4-tetrahydroisoquinoline and indole [a].



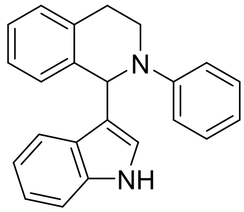
Entry	Conditions	Light irradiation	Yield[b][%]
1	None	Yes	12
2	RSS	Yes	46
3	RhB	Yes	52
4	4PyTPE-RSS	Yes	68
5	4PyTPE-RSS+RhB (0.8 mol%)	Yes	60
6	4PyTPE-RSS+RhB (1.0 mol%)	Yes	90
7	4PyTPE-RSS+RhB (1.2 mol%)	Yes	75
8[c]	4PyTPE-RSS+RhB	no	no reaction

a Reaction conditions: N-phenyl-1,2,3,4-tetrahydroisoquinoline (20 mg, 0.1 mmol), indole (23.4mg, 0.2mmol), 4PyTPE-RSS+Rh B aqueous solution (2 mL), 10 W white light, room temperature,18 h;

b Isolated yields;

c Without a white light.

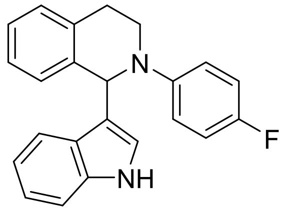
Characterization of all products:



3a

1-(1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a)

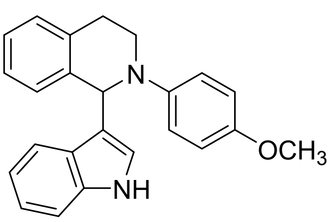
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 25:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.27 (m, 2H), 7.26 – 7.14 (m, 6H), 7.02 (d, *J* = 7.9 Hz, 3H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 6.17 (s, 1H), 3.62 (t, *J* = 6.3 Hz, 2H), 3.06 (dt, *J* = 15.8, 7.7 Hz, 1H), 2.86 – 2.74 (m, 1H).



3b

2-(4-fluorophenyl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (3b)

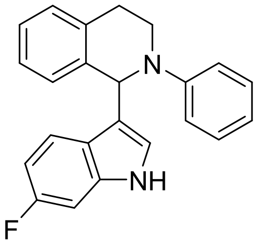
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 25:1), white soli. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.14 (m, 6H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.93 (s, 2H), 6.59 (s, 1H), 6.01 (s, 1H), 3.60 – 3.47 (m, 2H), 3.04 (dt, *J* = 14.8, 6.9 Hz, 1H), 2.82 (d, *J* = 16.1 Hz, 1H).



3c

1-(1H-indol-3-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline(3c)

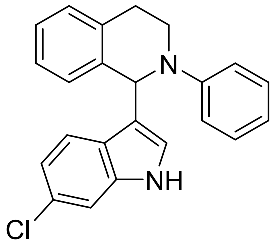
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 25:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.18 (q, J = 12.3, 9.8 Hz, 5H), 7.01 – 6.91 (m, 3H), 6.82 – 6.75 (m, 2H), 6.57 (s, 1H), 5.96 (s, 1H), 3.76 – 3.73 (m, 3H), 3.57 – 3.44 (m, 2H), 3.03 (d, J = 7.5 Hz, 1H), 2.80 (d, J = 16.6 Hz, 1H).



3d

1- (4-fluoro-1h-indole-3-yl) - 2-phenyl-1,2,3,4-tetrahydroisoquinoline (3d)

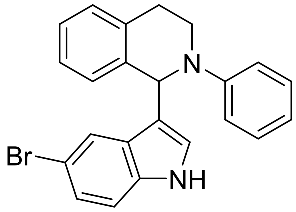
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.59 – 7.48 (m, 1H), 7.24 – 7.20 (m, 2H), 7.20 – 7.07 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 9.6 Hz, 1H), 6.77 (s, 1H), 6.58 (s, 1H), 6.13 (s, 1H), 3.63 – 3.56 (m, 2H), 3.05 (d, *J* = 8.2 Hz, 1H), 2.78 (d, *J* = 16.2 Hz, 1H).



3e

1-(6-chloro-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e)

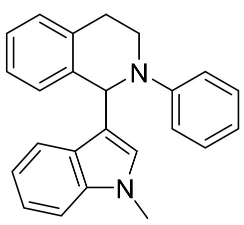
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.53 (dd, J = 8.6, 2.1 Hz, 1H), 7.23 (s, 3H), 7.20 – 7.14 (m, 4H), 6.99 (dd, J = 16.2, 8.4 Hz, 3H), 6.80 (t, J = 7.2 Hz, 1H), 6.62 (s, 1H), 6.12 (s, 1H), 3.67 – 3.56 (m, 2H), 3.07 (dd, J = 16.2, 7.9 Hz, 1H), 2.82 – 2.75 (m, 1H).



3f

1-(5-bromo-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f)

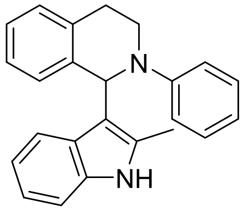
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.56 – 7.45 (m, 1H), 7.25 (d, J = 3.0 Hz, 2H), 7.24 (s, 2H), 7.21 – 7.15 (m, 5H), 7.01 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 7.3 Hz, 1H), 6.61 (s, 1H), 6.07 (s, 1H), 3.59 (s, 1H), 3.08 – 3.00 (m, 1H), 2.79 (d, J = 16.3 Hz, 1H).



3g

1-(1-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3g)

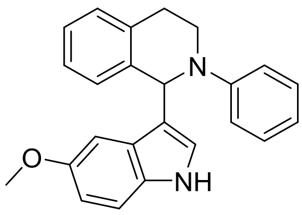
Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.29 (d, J = 3.0 Hz, 1H), 7.26 – 7.14 (m, 7H), 7.02 (dd, J = 8.4, 2.9 Hz, 3H), 6.77 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 2.2 Hz, 1H), 6.18 (s, 1H), 3.65 (t, J = 4.8 Hz, 5H), 3.07 (dt, J = 16.0, 7.8 Hz, 1H), 2.81 (d, J = 16.2 Hz, 1H).



3h

1-(2-methyl-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3h)

Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.16 (s, 5H), 7.08 – 7.03 (m, 3H), 7.00 (dd, J = 8.4, 2.5 Hz, 3H), 6.89 (td, J = 7.7, 1.9 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 5.96 (s, 1H), 3.68 – 3.57 (m, 2H), 3.11 – 2.95 (m, 2H).



3i

1-(5-methoxy-1H-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3i)

Isolated by column chromatography on silica gel (eluting with hexane/ethyl acetate = 20:1), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.86 (s, 1H), 7.55 – 7.52 (m, 1H), 7.36 (s, 1H), 7.29 – 7.21 (m, 4H), 7.17 (d, J = 7.3 Hz, 4H), 7.03 (d, J = 8.1 Hz, 2H), 6.88 (s, 1H), 6.57 (s, 1H), 6.14 (s, 1H).