

Supporting Information

Dual Role of MoS₂ Quantum Dots in a Cross-Dehydrogenative Coupling Reaction

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1. General considerations:

All the chemicals were purchased from commercial suppliers (Spectrochem, SRL, Alfa Aesar, TCI and Sigma Aldrich) and used as delivered. Solvents were obtained from S.D. Fine-Chem Ltd, India. Reactions were carried out in oven dried glassware equipped with magnetic stir-bar. All the LEDs were available commercially. For quenching purpose, distilled water was used. Thin-layer chromatography was performed using silica gel 60 F254 precoated plates (0.25 mm). Column chromatography was performed using silica gel (100-200 mesh). Commercially available lamps were used for irradiation during the course of the experiment.

2. Instrumentation:

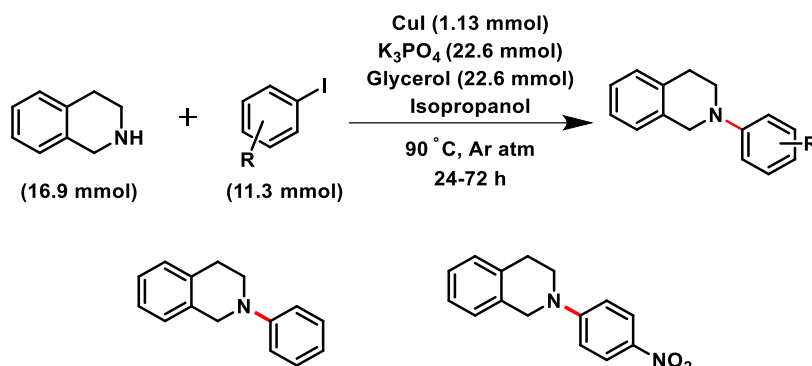
NMR spectra was recorded on JEOL LA-300, BRUKER-AV400 spectrometer at 400 MHz (^1H) and 100 MHz (^{13}C). For ^1H -NMR, data are reported as follows: chemical shift (multiplicity, coupling constant (Hz) and integration). HRMS analysis was done on a MicroMass QTOF Mass Spectrometer. TEM images were acquired using a JOEL JEM-2100F (accelerating voltage of 200 kV). The d-spacing was evaluated using Image J software. Bruker X-ray diffractometer with D8 Advance was used to record the PXRD spectrum using X-ray source of 2.2 kW Cu anode long fine focus ceramic X-ray tube. FT-IR Spectra was recorded in a Shimadzu IR Affinity-1S instrument. The absorption spectra was recorded on a UV-3600 Shimadzu UV-Vis-NIR Spectrophotometer (Japan Analytical Instruments). Fluorescence spectrum was obtained on a Varian Cary Eclipse Fluorescence Spectrophotometer. Zeta Potential was measured using a Malvern Zetasizer Nano ZS System. Cyclic Voltammetry was carried out on Electrochemical Analyser (HCH Instruments CHI604E) and the electrodes were procured from CH Instruments, Inc.

3. Preparation of substrates:

3.a) General procedure for preparation of 2-aryl-1,2,3,4-tetrahydroisoquinoline

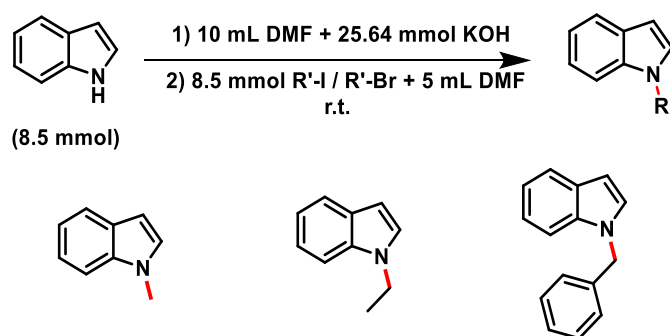
In a two-mouthed RB flask, copper (I) iodide (1.13 mmol) and potassium phosphate (22.6 mmol) were taken. The flask was degassed under argon atmosphere. Isopropanol (10 mL), glycerol (22.6 mmol), 1,2,3,4-tetrahydroisoquinoline (16.9 mmol) and iodobenzene/1-iodo-4-nitrobenzene (11.3 mmol) were added using a syringe. The reaction mixture was refluxed with stirring for 24-72 h at 90 °C. After cooling to room temperature, extraction was carried out using dichloromethane (10 mL X 3). The organic layer was dried over anhydrous sodium

sulphate. The crude mixture was concentrated and purified by column chromatography on silica gel (100-200 mesh) using 0.5-4.5 % EtOAc (ethyl acetate)/Hexane as eluent to give the desired product in 60-70 % isolated yield.

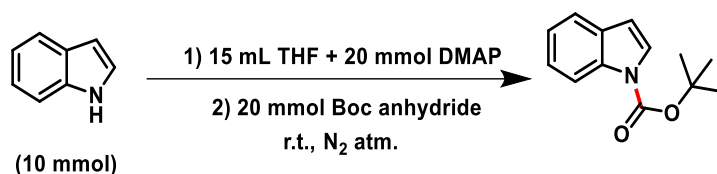


3.b) General procedure for the preparation of N-substituted indole(s)

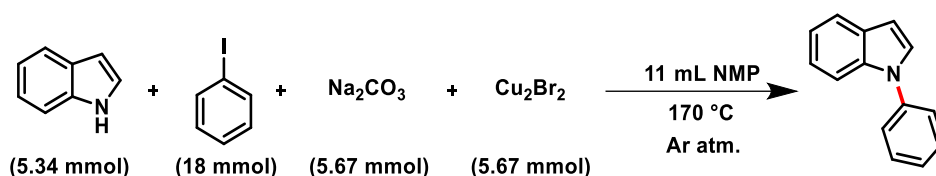
3.b.i) Potassium hydroxide (25.64 mmol) was taken in 10 mL DMF and stirred at room temperature for 15 mins. Indole (8.5 mmol) was added. The mixture was stirred for 40 mins. A solution of the iodide/bromide analogue of the alkyl moiety (8.5 mmol) in DMF (5 mL) was added drop wise with stirring. The reaction mixture was allowed to stir and monitored by TLC. The mixture was poured into cold water and the precipitate was filtered, washed with cold water and purified by silica gel (100-200 mesh) column chromatography in 0.1-0.5 % EtOAc/Hexane to give the N-substituted indole in 70-85 % isolated yield.



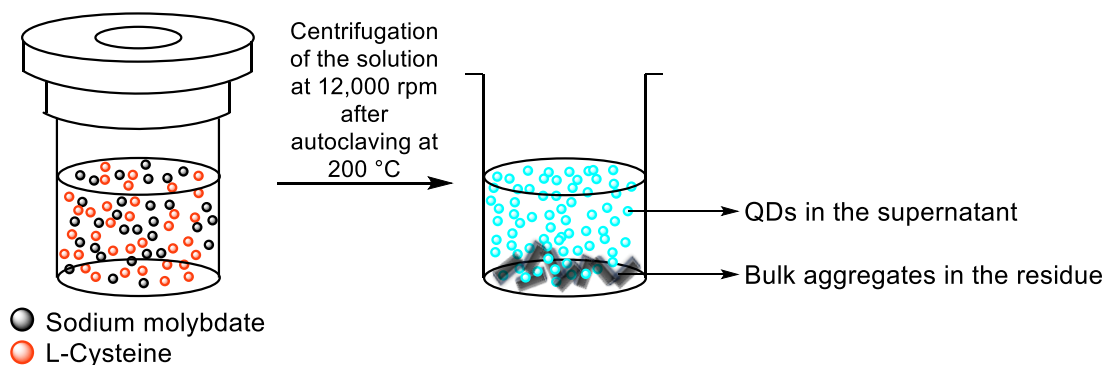
3.b.ii) In a stir-bar equipped round-bottom flask, indole (10 mmol) and DMAP or 4-dimethylaminopyridine (20 mmol) was taken. The flask was degassed under N₂. 15 mL of THF was added and the mixture was stirred at room temperature for 15-20 mins. di-tert-butyl dicarbonate or Boc anhydride (20 mmol) was injected into the flask and stirred overnight. The organic layer was extracted using EtOAc (10 mL X 3), concentrated and purified using silica gel (100-200 mesh) column chromatography in 0.1-0.2 % EtOAc/Hexane to give the product in 80 % isolated yield.



3.b.iii) In a stir-bar equipped round-bottom flask, indole (5.34 mmol), copper (II) bromide (5.67 mmol) and sodium carbonate (5.67 mmol) was taken. The flask was degassed under argon. Iodobenzene (18 mmol) and NMP (11 mL) was added further. The mixture was stirred at 170 °C for 6-7 h. After cooling to room temperature, 5 mL of 5 % HCl and 10 mL of EtOAc was added. The organic layer was concentrated and purified using silica gel (100-200 mesh) column chromatography in Hexane to give the product in 50-60 % isolated yield.



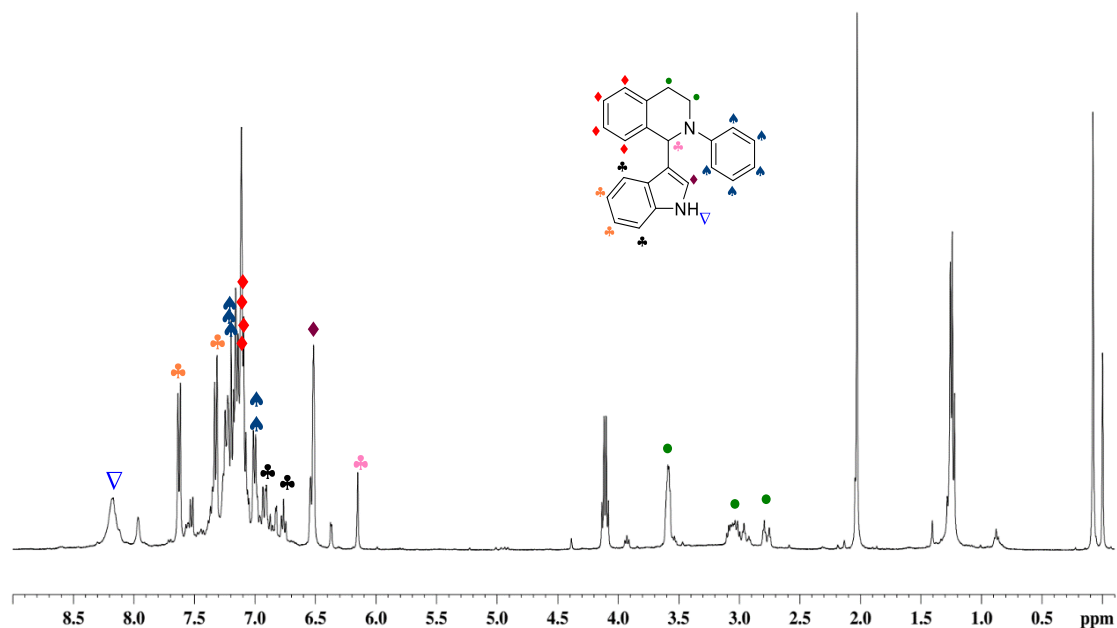
4. Schematic representation for the preparation of MoS₂ QDs:



We also attempted to prepare WS₂ QDs via an organic solvent-mediated top-down approach, but failed to obtain identical properties in various batches. MoSe₂ and WSe₂ QDs were difficult to fabricate.









5. NMR Spectrum of crude reaction mixture:

We analysed the crude reaction mixture and observed the formation of the cross-coupled product exclusively. Stated otherwise, our protocol does not lead to any side product. The peaks have also been assigned in the spectrum.



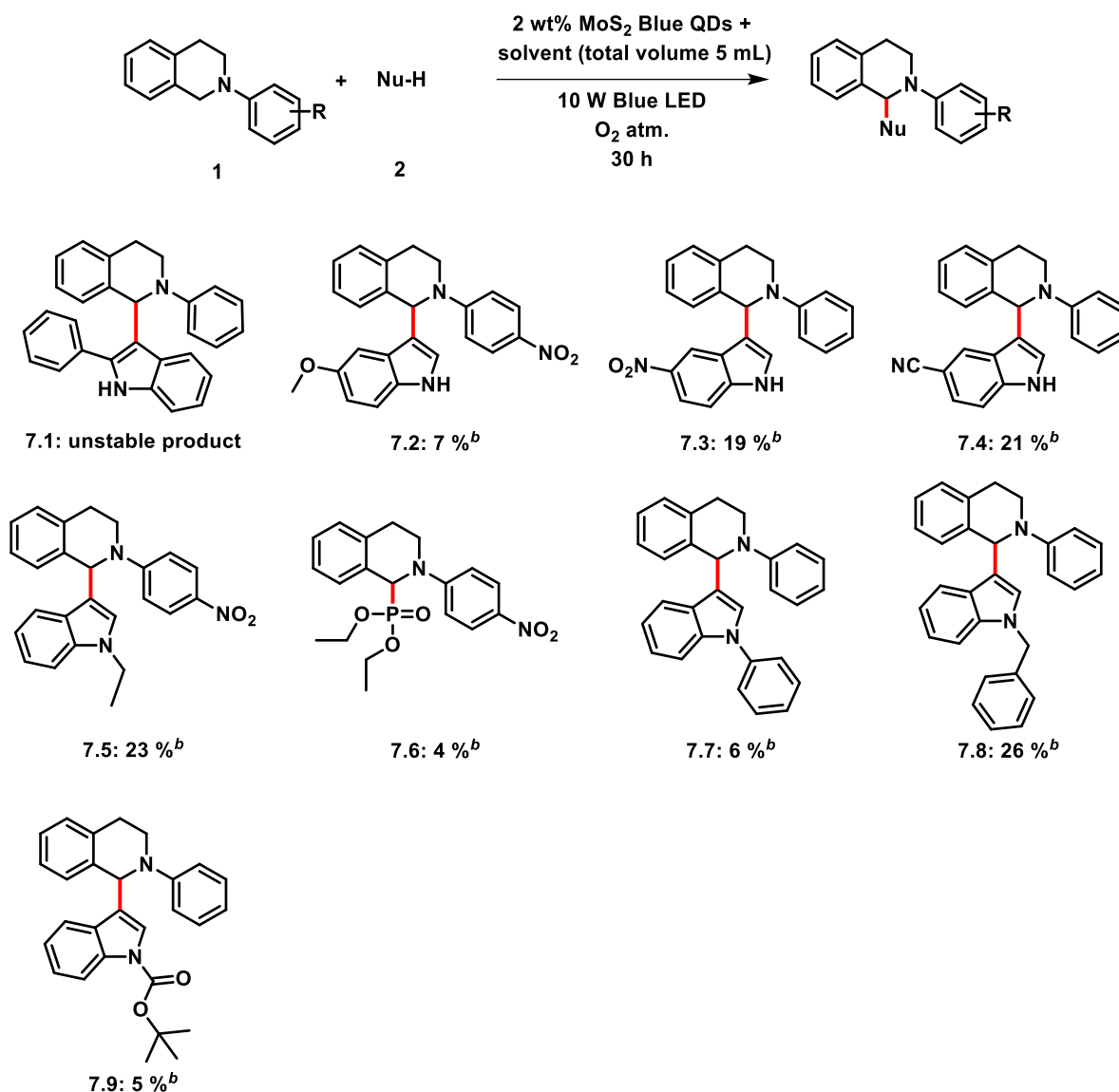
6. Light On-Off experiments:

To investigate the importance of light in the current reaction, we carried out a number of experiments where the setup was subjected to the light source for a certain period of time. Upon removal of the source, the yield did not increase much. The slight increase could be attributed to thermal collisions. Thus, light proved to be indispensable for the coupling reaction. This also ruled out the possibility of a radical propagation pathway in the mechanism.

Sr. No.	Experiment	NMR Yield (%)
1.	0 h  30 h	86
2.	0 h  30 h	06
3.	0 h  20 h	53
4.	0 h  20 h  30 h	60
5.	0 h  10 h	35
6.	0 h  10 h  30 h	45

Reaction conditions: 0.1 mmol of 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a**, 0.25 mmol of indole **2a**, 2 wt% (relative to **1a**) of hydrothermally prepared MoS₂ QDs of strength 4 mg/mL with total volume adjusted to 5 mL with water; reaction mixture was ultra-sonicated and exposed to a 10 W Blue LED at room temperature under O₂ atm.; NMR Yields were measured using Terephthalaldehyde as the reference after concentrating the crude reaction mixture extracted with EtOAc.

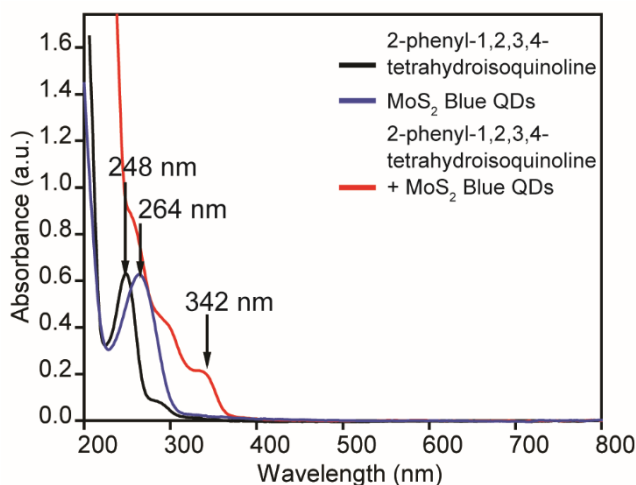
7. Products formed in relatively lower yields:



Reaction conditions: 0.1 mmol of 2-phenyl-1,2,3,4-tetrahydroisoquinoline or its analogue **1**, 0.25 mmol of indole or phosphite derivative **2**, 2 wt% of hydrothermally prepared MoS₂ QDs (relative to **1**) of strength 4 mg/mL with total volume adjusted to 5 mL with H₂O (last 3 entries) or H₂O:CH₃CN (= 4.5:0.5); reaction mixture was ultra-sonicated and exposed to a 10 W Blue LED for 30 h at room temperature under O₂ atm.; ^b: NMR Yields were measured using Terephthalaldehyde as the reference after concentrating the crude reaction mixture extracted with EtOAc.

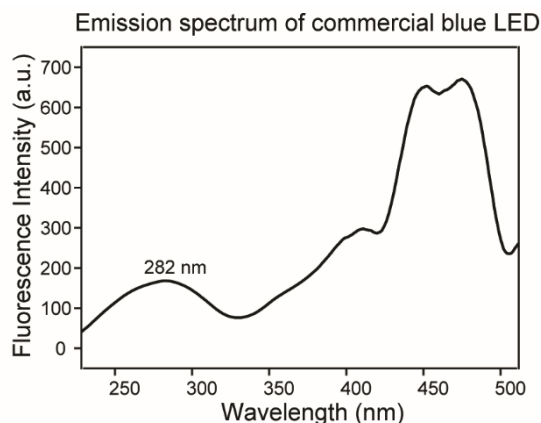
8.a) Examining the change in λ_{max} of the mixture of MoS₂ QDs and 2-phenyl-1,2,3,4-tetrahydroisoquinoline **1a**:

We were interested to know whether the MoS₂ QDs exhibit any change in the λ_{max} in presence of the substrate **1a**. Physical mixture of **1a** (0.1 mmol) and MoS₂ QDs (2 wt% relative to **1a**) in water was ultra-sonicated and the UV-Visible Spectrum was recorded. A new peak was observed for the mixture above 300 nm which was absent in the absorption spectra of the individual components. Thus, the mixture showed a bathochromic shift compared to the individual components which enabled it to absorb blue light more efficiently.



8.b) Emission Spectrum of the commercial blue LED lamp used during the experiment:

We recorded the emission spectrum of the blue lamp used for irradiation during the course of our experiment and observed a broad peak centred at 282 nm, which explains the facile absorption of light by the QDs during the reaction.



9. Determining the quantum yield of MoS₂ QDs:

The quantum yield (QY) was determined using 7-Hydroxycoumarin as the reference. The UV-visible and fluorescence spectra was recorded for the reference and sample. Water was used as the solvent. QY was determined using the following formula:

$$QY_{\text{sample}} = QY_{\text{ref.}} \times (\eta/\eta_{\text{ref.}})^2 \times (A_{\text{ref.}}/A) \times (I/I_{\text{ref.}})$$

where: $QY_{\text{ref.}}$ = QY of reference

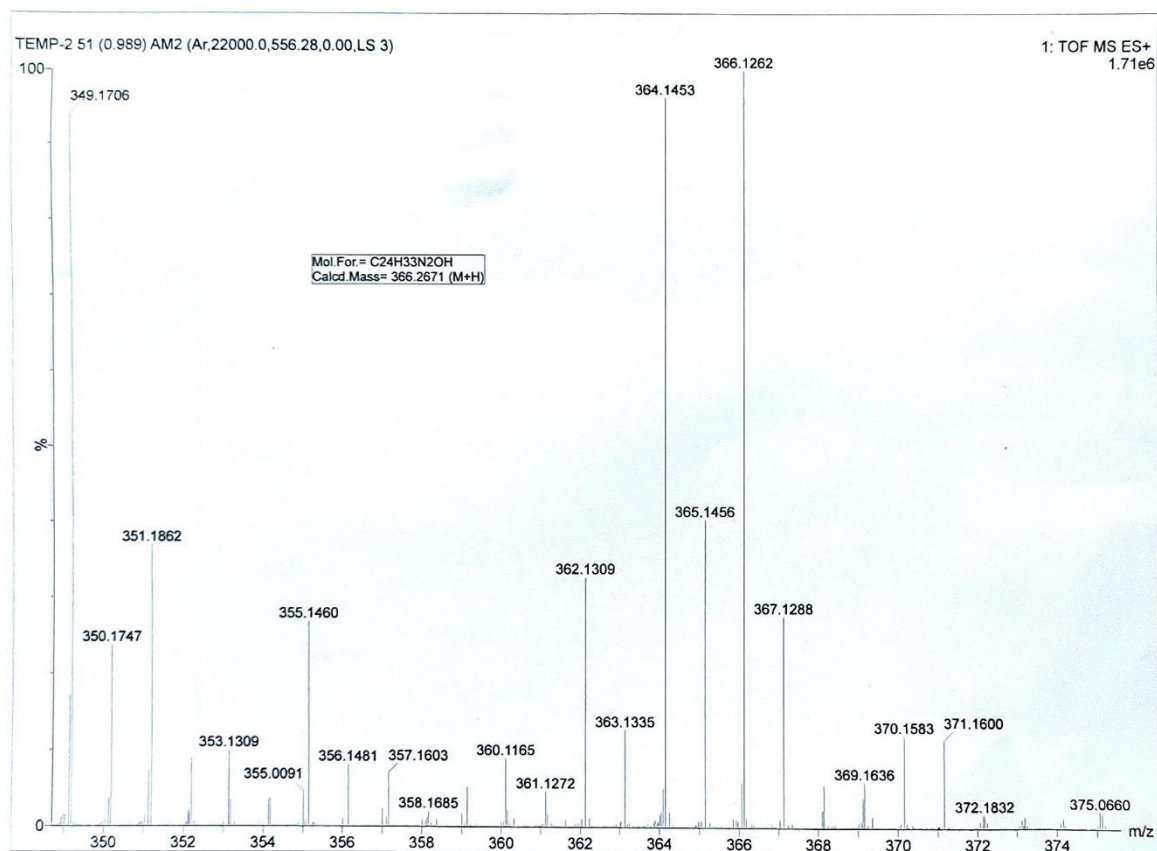
$\eta = \eta_{\text{ref.}} = 1.33$ (refractive index of medium)

$A_{\text{ref.}}$ = Absorbance of reference at $\lambda_{\text{max.}}$; A = Absorbance of sample at λ_{max}

$I_{\text{ref.}}$ = Integrated intensity of reference ; I = Integrated intensity of sample

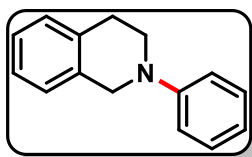
10. HRMS Spectrum for 1a-TEMP:

The crude reaction mixture obtained with TEMPO (experimental details in **Table 2**, Main Text) was analysed by HRMS to detect any possible intermediate that could justify the reduction in yield. The peak corresponding to **1a-TEMP** was observed in the spectra.



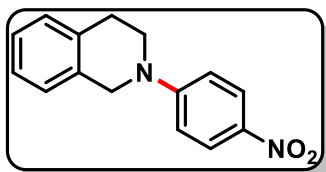
11. Characterization Data:

2-phenyl-1,2,3,4-tetrahydroisoquinoline: Yellowish-white solid; isolated using silica gel



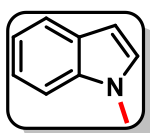
(100 - 200 mesh) column chromatography in 0.5 - 1 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.31 – 7.26 (m, 2H), 7.20 – 7.14 (m, 4H), 7.00 – 6.98 (d, J = 7.8 Hz, 2H), 6.85 – 6.82 (t, J = 7.3 Hz, 1H), 4.42 (s, 2H), 3.58 – 3.55 (t, J = 5.8 Hz, 2H), 3.01 – 2.98 (t, J = 5.8 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 150.35, 134.68, 134.27, 129.02, 128.34, 126.35, 126.14, 125.84, 118.48, 114.96, 50.55, 46.34, 28.93; HRESI-MS (m/z): Calculated for $\text{C}_{15}\text{H}_{15}\text{N}$ ($M + \text{H}$) $^+$: 210.1283, Found ($M + \text{H}$) $^+$: 210.1282.

2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline: Bright yellow solid; isolated using silica



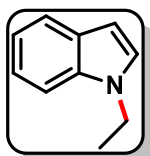
gel (100 - 200 mesh) column chromatography in 4 - 4.5 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 8.18 – 8.16 (d, J = 9.4 Hz, 2H), 7.26 – 7.19 Hz (m, 4H), 6.84 – 6.81 (d, J = 9.7 Hz, 2H), 4.58 (s, 2H), 3.71 – 3.69 (t, J = 5.9 Hz, 2H), 3.04 – 3.01 (t, J = 6.0 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 153.69, 134.75, 132.98, 127.96, 127.03, 126.57, 126.35, 126.04, 111.08, 48.71, 44.64, 28.85; HRESI-MS (m/z): Calculated for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$ ($M + \text{H}$) $^+$: 255.1134, Found ($M + \text{H}$) $^+$: 255.1134.

1-methyl-1H-indole: Yellow liquid; isolated using silica gel (100 - 200 mesh) column



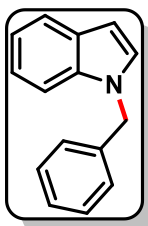
chromatography in 0.1 - 0.5 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.63 – 7.61 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.31 – 7.29 (d, J = 8.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.12 – 7.08 (dt, J = 7.4, J = 1 Hz, 1H), 7.02 – 7.01 (d, J = 3.0 Hz, 1H), 6.47 – 6.46 (d, J = 2.9 Hz, 1H), 3.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 136.55, 128.63, 128.33, 121.33, 120.71, 119.11, 109.03, 100.74, 32.63; HRESI-MS (m/z): Calculated for $\text{C}_9\text{H}_9\text{N}$ ($M + \text{H}$) $^+$: 132.0813, Found ($M + \text{H}$) $^+$: 132.0816.

1-ethyl-1H-indole: Yellow liquid; isolated using silica gel (100 - 200 mesh) column



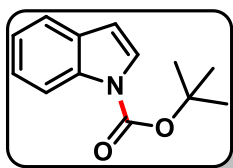
chromatography in 0.1 - 0.4 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.64 – 7.62 (d, J = 7.7 Hz, 1H), 7.36 – 7.34 (d, J = 8.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.12 – 7.07 (m, 2H), 6.49 – 6.48 (d, J = 3.0 Hz, 1H), 4.20 – 4.14 (q, J = 7.4 Hz, 2H), 1.48 – 1.44 (t, J = 7.3 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 135.82, 128.78, 127.14, 121.46, 121.11, 119.34, 109.42, 101.13, 41.04, 15.59; HRESI-MS (m/z): Calculated for $\text{C}_{10}\text{H}_{11}\text{N}$ ($M + \text{H}$) $^+$: 146.0970, Found ($M + \text{H}$) $^+$: 146.0971.

1-benzyl-1H-indole: Pale yellow liquid; isolated using silica gel (100 - 200 mesh) column



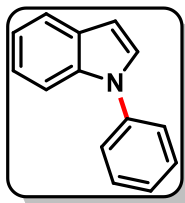
chromatography in 0.1 - 0.3 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.60 – 7.58 (m, 1H), 7.06 – 7.02 (m, 6H), 6.84 – 6.81 (m, 3H), 6.45 – 6.44 (d, J = 3.3 Hz, 1H), 4.85 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 138.18, 136.91, 129.40, 129.27, 128.90, 128.09, 127.31, 122.33, 121.65, 120.24, 110.41, 102.29, 50.33; HRESI-MS (m/z): Calculated for $\text{C}_{15}\text{H}_{13}\text{N}$ ($M + \text{H}$) $^+$: 208.1126, Found ($M + \text{H}$) $^+$: 208.1128.

tert-butyl 1H-indole-1-carboxylate: Pale yellow liquid; isolated using silica gel (100 - 200



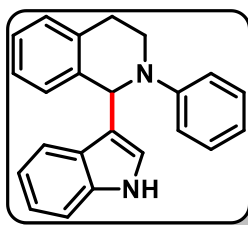
mesh) column chromatography in 0.1 - 0.2 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 8.14 – 8.12 (d, J = 8.8 Hz, 1H), 7.58 – 7.57 (d, J = 3.6 Hz, 1H), 7.54 – 7.53 (d, J = 7.8 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.22 – 7.18 (m, 1H), 6.55 – 6.54 (d, J = 3.7 Hz, 1H), 1.65 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 149.85, 135.21, 130.60, 125.91, 124.21, 122.65, 120.96, 115.19, 107.30, 83.65, 28.23; HRESI-MS (m/z): Calculated for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($M + \text{H}$) $^+$: 218.1181, Found ($M + \text{H}$) $^+$: 218.1180.

1-phenyl-1H-indole: Yellow liquid; isolated using silica gel (100 - 200 mesh) column



chromatography in Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.69 – 7.67 (d, J = 7.6 Hz, 1H), 7.57 – 7.55 (d, J = 8.2 Hz, 1H), 7.50 – 7.49 (d, J = 4.4 Hz, 4H), 7.36 – 7.31 (m, 2H), 7.23 – 7.14 (m, 2H), 6.68 – 6.67 (d, J = 3.1 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 139.87, 137.52, 135.89, 130.28, 129.64, 129.35, 127.98, 126.47, 124.41, 122.38, 121.16, 120.38, 110.54, 103.59; HRESI-MS (m/z): Calculated for $\text{C}_{14}\text{H}_{11}\text{N}$ ($M + \text{H}$) $^+$: 194.0970, Found ($M + \text{H}$) $^+$: 194.0969.

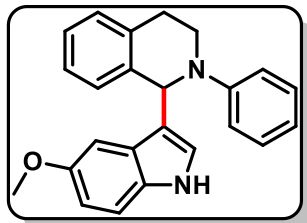
1-(1H-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid; isolated



using silica gel (100 - 200 mesh) column chromatography in 1 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.96 (s, 1H), 7.51 – 7.49 (d, J = 8.2 Hz, 1H), 7.32 – 7.13 (m, 8H), 7.05 – 7.00 (q, J = 7.6 Hz, 3H), 6.82 – 6.78 (t, J = 7.2 Hz, 1H), 6.65 – 6.64 (d, J = 2.1 Hz, 1H), 6.18 (s, 1H), 3.66 – 3.63 (q, J = 4.7 Hz, 2H), 3.14 – 3.06 (m, 1H), 2.88 – 2.82 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 149.74, 137.39, 136.63, 135.52, 129.20, 128.82, 128.05, 126.68, 126.52, 125.71, 124.21, 122.12, 120.11, 119.66,

119.24, 118.28, 115.97, 111.02, 56.78, 42.41, 26.66; HRESI-MS (m/z): Calculated for $C_{23}H_{20}N_2$ ($M + H$)⁺: 325.1705, Found ($M + H$)⁺: 325.1702.

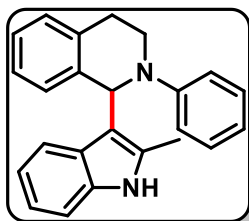
1-(5-methoxy-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid;



isolated using silica gel (100 - 200 mesh) column chromatography in 3.2 % EtOAc/Hexane eluent; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.82 (s, 1H), 7.28 – 7.15 (m, 7H), 7.04 – 7.01 (d, J = 8.2 Hz, 2H), 6.88 – 6.87 (d, J = 2.1 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.58 – 6.57 (d, J = 2.1 Hz, 1H), 6.14 (s, 1H), 3.65 (s, 3H), 3.61 – 3.58

(m, 2H), 3.11 – 3.03 (m, 1H), 2.85 – 2.79 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 153.91, 150.03, 137.54, 135.56, 131.63, 129.19, 128.79, 128.01, 126.96, 126.69, 125.69, 124.99, 118.72, 118.32, 116.23, 112.28, 111.64, 101.92, 56.88, 55.69, 42.16, 26.96; HRESI-MS (m/z): Calculated for $C_{24}H_{22}N_2O$ ($M + H$)⁺: 355.1810, Found ($M + H$)⁺: 355.1808.

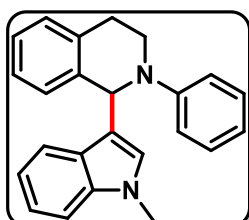
1-(2-methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Orange solid;



isolated using silica gel (100 - 200 mesh) column chromatography in 5.2 % EtOAc/Hexane eluent; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.68 (s, 1H), 7.24 – 7.13 (m, 5H), 7.06 – 6.98 (m, 6H), 6.90 – 6.86 (t, J = 7.6 Hz, 1H), 6.83 – 6.79 (t, J = 7.3 Hz, 1H), 5.94 (s, 1H), 3.70 – 3.56

(m, 2H), 3.11 – 2.95 (m, 2H), 2.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 150.91, 137.97, 135.28, 134.89, 133.31, 128.77, 128.64, 128.60, 128.20, 126.26, 126.03, 120.75, 120.20, 119.47, 119.43, 119.15, 113.38, 109.96, 57.14, 45.83, 27.91, 12.26; HRESI-MS (m/z): Calculated for $C_{24}H_{22}N_2$ ($M + H$)⁺: 339.1861, Found ($M + H$)⁺: 339.1858.

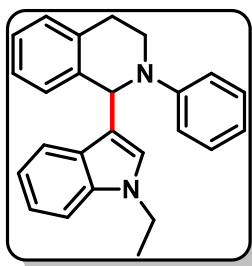
1-(1-methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Yellow solid;



isolated using silica gel (100 - 200 mesh) column chromatography in 1.8 % EtOAc/Hexane eluent; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.51 – 7.49 (d, J = 7.6 Hz, 1H), 7.28 – 7.16 (m, 8H), 7.04 – 6.99 (m, 3H), 6.79 – 6.76 (t, J = 7.3 Hz, 1H), 6.50 (s, 1H), 6.17 (s, 1H), 3.85 – 3.60 (m, 5H), 3.12 – 3.04 (m, 1H), 2.85 – 2.81 (m, 1H); ¹³C NMR (100

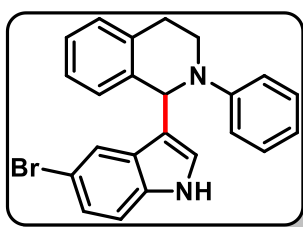
MHz, CDCl₃): δ (ppm) = 149.70, 137.59, 137.36, 135.53, 129.20, 128.80, 128.04, 126.89, 126.63, 125.70, 121.64, 120.15, 119.12, 118.01, 115.70, 109.13, 96.13, 56.64, 42.21, 32.71, 26.63; HRESI-MS (m/z): Calculated for $C_{24}H_{22}N_2$ ($M + H$)⁺: 339.1861, Found ($M + H$)⁺: 339.1859.

1-(1-ethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Yellow solid; isolated



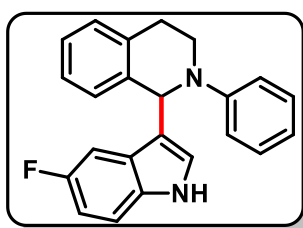
using silica gel (100 - 200 mesh) column chromatography in 1 % EtOAc/Hexane eluent; ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.51 – 7.48 (m, 1H), 7.29 – 7.14 (m, 8H), 7.04 – 6.97 (m, 3H), 6.80 – 6.76 (t, J = 7.2 Hz, 1H), 6.54 (s, 1H), 6.17 (s, 1H), 4.06 – 4.00 (q, J = 7.2 Hz, 2H), 3.65 – 3.62 (m, 2H), 3.13 – 3.05 (m, 1H), 2.84 – 2.80 (m, 1H), 1.36 – 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 150.02, 140.44, 139.30, 136.35, 129.20, 128.81, 128.11, 127.24, 127.13, 126.64, 125.72, 121.50, 120.26, 119.08, 116.03, 109.23, 73.10, 42.35, 40.88, 26.61, 15.43; HRESI-MS (m/z): Calculated for $\text{C}_{25}\text{H}_{24}\text{N}_2$ ($M + \text{H}$) $^+$: 353.2018, Found ($M + \text{H}$) $^+$: 353.2019.

1-(5-bromo-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid;



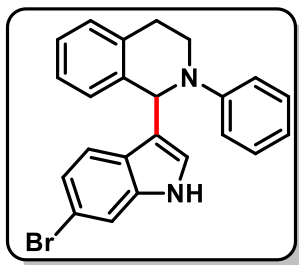
isolated using silica gel (100 - 200 mesh) column chromatography in 2 % EtOAc/Hexane eluent; ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.96 (s, 1H), 7.59 (s, 1H), 7.25 – 7.13 (m, 8H), 7.01 – 6.99 (d, J = 8.0 Hz, 2H), 6.83 – 6.79 (t, J = 7.3 Hz, 1H), 6.62 – 6.61 (d, J = 2.2 Hz, 1H), 6.07 (s, 1H), 3.60 – 3.56 (m, 2H), 3.09 – 3.01 (m, 1H), 2.83 - 2.76 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 149.89, 137.03, 135.45, 135.20, 129.21, 128.91, 128.17, 127.96, 126.82, 125.81, 125.38, 125.04, 122.74, 119.11, 118.82, 116.56, 113.02, 112.43, 56.74, 42.61, 26.63; HRESI-MS (m/z): Calculated for $\text{C}_{23}\text{H}_{19}\text{BrN}_2$ ($M + \text{H}$) $^+$: 403.0810, Found ($M + \text{H}$) $^+$: 403.0809.

1-(5-fluoro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: white solid; isolated



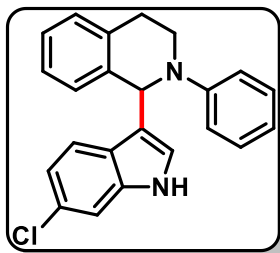
using silica gel (100 - 200 mesh) column chromatography in 2 % EtOAc/Hexane eluent; ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.94 (s, 1H), 7.25 – 7.14 (m, 7H), 7.13 – 7.09 (dd, J = 10.0 Hz, J = 2.4 Hz, 1H), 7.02 – 7.00 (d, J = 8.2 Hz, 2H), 6.91 – 6.86 (dt, J = 9.0 Hz, J = 2.4 Hz, 1H), 6.82 – 6.78 (t, J = 7.2 Hz, 1H), 6.69 – 6.68 (d, J = 2.2 Hz, 1H), 6.09 (s, 1H), 3.62 – 3.58 (m, 2H), 3.11 – 3.03 (m, 1H), 2.84 - 2.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 158.86, 156.53, 149.82, 137.09, 135.50, 133.09, 129.22, 128.91, 127.96, 126.79, 125.87, 125.78, 119.38, 118.56, 116.26, 111.60, 111.51, 110.64, 110.38, 105.25, 105.01, 56.75, 42.49, 30.93, 26.65; HRESI-MS (m/z): Calculated for $\text{C}_{23}\text{H}_{19}\text{FN}_2$ ($M + \text{H}$) $^+$: 343.1611, Found ($M + \text{H}$) $^+$: 343.1610.

1-(6-bromo-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid;



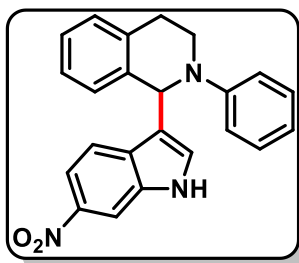
isolated using silica gel (100 - 200 mesh) column chromatography in 1.8 % EtOAc/Hexane eluent; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.92 (s, 1H), 7.45 – 7.44 (d, *J* = 1.4 Hz, 1H), 7.34 – 7.32 (d, *J* = 8.5 Hz, 1H), 7.25 – 7.14 (m, 6H), 7.10 – 7.08 (dd, *J* = 8.5 Hz, *J* = 1.6 Hz, 1H), 7.01 – 6.99 (d, *J* = 8.0 Hz, 2H), 6.81 – 6.78 (t, *J* = 7.3 Hz, 1H), 6.60 – 6.59 (d, *J* = 1.7 Hz, 1H), 6.11 (s, 1H), 3.64 – 3.52 (m, 2H), 3.10 – 3.02 (m, 1H), 2.82 – 2.76 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 149.81, 137.36, 137.06, 135.45, 129.19, 128.89, 127.92, 126.77, 125.73, 125.39, 124.67, 122.92, 121.42, 119.49, 118.55, 116.25, 115.68, 113.89, 56.65, 42.43, 30.87, 26.67; HRESI-MS (*m/z*): Calculated for C₂₃H₁₉BrN₂ (*M* + *H*)⁺: 403.0810, Found (*M* + *H*)⁺: 403.0810.

1-(6-chloro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid;



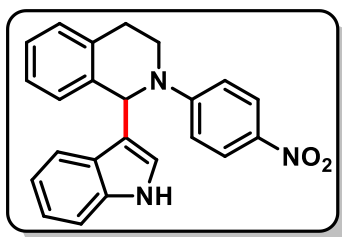
isolated using silica gel (100 - 200 mesh) column chromatography in 1.8 % EtOAc/Hexane eluent; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.91 (s, 1H), 7.40 – 7.37 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.27 (d, *J* = 1.7 Hz, 1H), 7.25 – 7.14 (m, 7H), 7.01 – 6.99 (d, *J* = 8.2 Hz, 2H), 6.98 – 6.95 (dd, *J* = 8.6 Hz, *J* = 1.7 Hz, 1H), 6.81 – 6.78 (t, *J* = 7.3 Hz, 1H), 6.60 – 6.59 (d, *J* = 2.2 Hz, 1H), 6.11 (s, 1H), 3.64 – 3.52 (m, 2H), 3.10 – 3.02 (m, 1H), 2.82 – 2.76 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 149.79, 137.05, 136.94, 135.49, 129.26, 128.94, 128.04, 127.97, 126.82, 125.77, 125.07, 124.80, 121.06, 120.37, 119.43, 118.52, 116.18, 110.94, 56.64, 42.37, 30.99, 26.62; HRESI-MS (*m/z*): Calculated for C₂₃H₁₉ClN₂ (*M* + *H*)⁺: 359.1315, Found (*M* + *H*)⁺: 359.1312.

1-(6-nitro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Pale yellow solid;



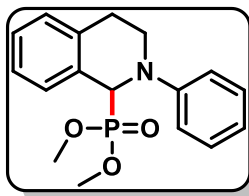
isolated using silica gel (100 - 200 mesh) column chromatography in 12 % EtOAc/Hexane eluent; **¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 8.50 (s, 1H), 8.27 (s, 1H), 7.90 – 7.87 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.49 – 7.47 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.19 (m, 6H), 7.03 – 7.01 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 6.86 – 6.82 (t, *J* = 7.2 Hz, 1H), 6.14 (s, 1H), 3.65 – 3.49 (m, 2H), 3.13 – 3.05 (m, 1H), 2.85 – 2.79 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ (ppm) = 149.80, 143.33, 136.59, 135.44, 135.07, 131.15, 129.75, 129.31, 129.09, 127.87, 127.07, 125.96, 120.34, 120.20, 119.21, 116.79, 115.14, 108.00, 56.72, 42.75, 30.90, 26.80; HRESI-MS (*m/z*): Calculated for C₂₃H₁₉N₃O₂ (*M* + *H*)⁺: 370.1556, Found (*M* + *H*)⁺: 370.1555.

1-(1*H*-indol-3-yl)-2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline: Yellow solid; isolated



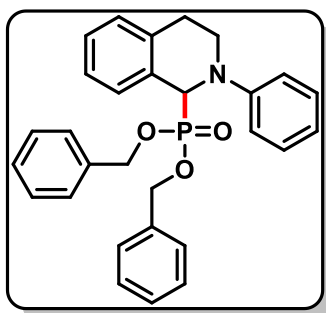
using silica gel (100 - 200 mesh) column chromatography in 4.2 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 8.15 – 8.13 (d, J = 9.5 Hz, 2H), 8.07 (s, 1H), 7.53 – 7.51 (d, J = 8.0 Hz, 1H), 7.42 – 7.40 (t, J = 4.5 Hz, 1H), 7.26 – 7.18 (m, 5H), 7.09 – 7.05 (t, J = 7.5 Hz, 1H), 6.96 – 6.94 (d, J = 9.5 Hz, 2H), 6.77 – 6.76 (d, J = 1.5 Hz, 1H), 6.35 (s, 1H), 3.84 – 3.71 (m, 2H), 3.12 – 2.97 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 153.42, 137.51, 136.77, 136.52, 135.00, 128.67, 127.73, 127.55, 126.39, 126.35, 125.63, 123.88, 122.58, 120.11, 119.46, 117.34, 111.73, 111.43, 56.41, 42.63, 29.71, 27.31, 22.71; HRESI-MS (m/z): Calculated for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_2$ ($M + \text{H}$) $^+$: 370.1556, Found ($M + \text{H}$) $^+$: 370.1553.

dimethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: Yellow liquid;



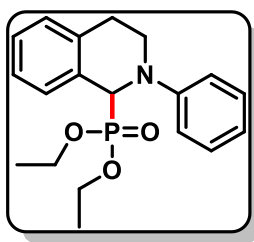
isolated using silica gel (100 - 200 mesh) column chromatography in 1 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.36 – 7.34 (d, J = 6.6 Hz, 1H), 7.28 – 7.14 (m, 6H), 6.98 – 6.96 (d, J = 8.1 Hz, 2H), 6.82 – 6.79 (t, J = 7.3 Hz, 1H), 5.23 – 5.18 (d, J = 20.3 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.67 – 3.62 (m, 7H), 3.09 – 2.97 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 149.30, 136.46, 130.40, 129.27, 128.88, 127.99, 127.94, 127.60, 127.56, 126.10, 118.72, 114.82, 59.56, 57.97, 54.00, 53.93, 53.02, 52.94, 43.59, 29.71, 26.70; HRESI-MS (m/z): Calculated for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{P}$ (M) $^+$: 317.1181, Found (M) $^+$: 317.1183.

dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: Green solid; ; isolated



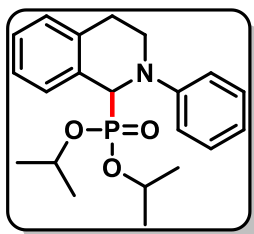
using silica gel (100 - 200 mesh) column chromatography in 8 % EtOAc/Hexane eluent; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm) = 7.35 – 7.20 (m, 13H), 7.16 – 7.10 (m, 4H), 6.97 – 6.95 (d, J = 8.3 Hz, 2H), 6.80 – 6.77 (t, J = 7.2 Hz, 1H), 5.30 – 5.25 (d, J = 19.3 Hz, 1H), 5.05 – 4.74 (m, 4H), 4.02 – 3.97 (m, 1H), 3.63 – 3.60 (m, 1H), 3.04 – 2.97 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ (ppm) = 149.22, 149.17, 136.49, 136.44, 136.35, 136.29, 136.23, 136.17, 130.34, 129.15, 128.77, 128.75, 128.65, 128.50, 128.45, 128.39, 128.31, 128.21, 128.17, 128.12, 127.99, 127.94, 127.89, 127.53, 127.49, 125.95, 125.92, 118.60, 114.86, 68.63, 68.56, 67.74, 67.67, 59.76, 58.19, 43.54, 29.65, 29.61, 26.79; HRESI-MS (m/z): Calculated for $\text{C}_{29}\text{H}_{28}\text{NO}_3\text{P}$ ($M + \text{Na}$) $^+$: 492.1704, Found ($M + \text{Na}$) $^+$: 492.1703.

diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: Red oily liquid;



isolated using silica gel (100 - 200 mesh) column chromatography in 11 % EtOAc/Hexane eluent; ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.38 – 7.36 (d, J = 6.8 Hz, 1H), 7.27 – 7.14 (m, 5H), 6.99 – 6.97 (d, J = 8.0 Hz, 2H), 6.81 – 6.77 (t, J = 7.2 Hz, 1H), 5.21 – 5.16 (d, J = 20.0 Hz, 1H), 4.10 – 3.88 (m, 5H), 3.64 – 3.61 (m, 1H), 3.06 – 3.01 (m, 2H), 1.26 – 1.23 (t, J = 7.0 Hz, 3H), 1.15 – 1.12 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 149.40, 136.39, 130.59, 129.11, 128.74, 128.12, 128.07, 127.44, 127.41, 125.86, 125.84, 118.47, 114.79, 63.38, 63.31, 62.40, 62.32, 59.56, 57.98, 43.46, 26.73, 16.44, 16.36, 16.30; HRESI-MS (m/z): Calculated for $\text{C}_{19}\text{H}_{24}\text{NO}_3\text{P}$ ($\text{M} + \text{Na}$) $^+$: 368.1391, Found ($\text{M} + \text{Na}$) $^+$: 368.1391 (NMR Spectra is same as our previous report: Ref. 6).

diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: Red oily liquid;



isolated using silica gel (100 - 200 mesh) column chromatography in 10 % EtOAc/Hexane eluent; ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.36 – 7.35 (d, J = 6.8 Hz, 1H), 7.24 – 7.13 (m, 5H), 6.97 – 6.95 (d, J = 8.0 Hz, 2H), 6.79 – 6.76 (t, J = 7.2 Hz, 1H), 5.20 – 5.15 (d, J = 20.0 Hz, 1H), 4.09 – 3.97 (m, 2H), 3.91 – 3.85 (m, 1H), 3.64 – 3.58 (m, 1H), 3.05 – 2.98 (m, 2H), 1.41 – 1.39 (d, J = 8.0 Hz, 2H), 1.27 – 1.21 (m, 7H), 1.14 – 1.11 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) = 149.38, 149.32, 136.42, 136.37, 130.58, 129.08, 128.71, 128.69, 128.10, 128.05, 127.40, 127.37, 125.83, 125.81, 118.43, 114.75, 63.33, 63.26, 62.35, 62.27, 59.55, 57.96, 43.43, 31.59, 30.25, 29.64, 26.71, 16.42, 16.36, 16.34, 16.28; HRESI-MS (m/z): Calculated for $\text{C}_{21}\text{H}_{28}\text{NO}_3\text{P}$ ($\text{M} + \text{Na}$) $^+$: 396.1704, Found ($\text{M} + \text{Na}$) $^+$: 396.1706 (NMR Spectra is same as our previous report: Ref. 6).

12. References:

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NMR Spectra

