Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Cross Dehydrogenative Coupling of N-Aryltetrahydroisoquinolines (sp^3 C-H) with Indoles (sp^2 C-H) Using Heterogeneous Mesoporous Manganese Oxide Catalyst

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Chemicals

Manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2.4H_2O$, ≥ 97.0), Manganese (II) acetate, copper (II) chloride, potassium permanganate, 1-butanol (anhydrous, 99.8%), and poly (ethylene glycol)-block- Poly(propylene glycol)-block- Poly (ethylene glycol) PEO20-PPO70-PEO20 (Pluronic P123), indole, 6-chloroindole, 2-methylindole, 5-methylindole, 5-methoxyindole, 5-carboxylateindole, N-methylindole, 7-nitroindole, pyrrole, 3,4-dihydroisoquinoline, 1,2,3,4-tetrahydroisoquinoline, 4-methyliodobenzene, 4-methoxyiodobenzene, 4-nitroiodobenzene, ethylene glycol, potassium phosphate (tribasic), isopropanol, toluene, 1,4-dioxane, ethanol, methanol, benzonitrile, Acetonitrile, Tert-butyl hydroperoxide, hydrogen peroxide, sodium borodeuteride, C-Mn_2O_3 were purchased from Sigma-Aldrich. Concentrated nitric acid (HNO_3, 68-70 %) was purchased from J. T. Baker. All chemicals were used as received without further purification.

Preparation of meso MnOx

The catalyst was synthesized following the procedure described in the literature.[1] In a typical synthesis 5 g (0.02 mol) of manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$) and 10 g (0.134 mol) of 1-butanol were added into a 120 mL beaker. To this solution 2g (0.0034 mol) of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluoronic P123, $PEO_{20}PPO_{70}PEO_{20}$, molar mass 5750 g mol^{-1}) and 2 g (0.032 mol) of concentrated nitric acid (HNO_3) were added and stirred at room temperature until the solution became clear (light pink). The resulting clear solution was then kept in an oven at 120°C for 3 h. The product was collected and washed with excess ethanol, centrifuged, and dried in a vacuum oven overnight. At the end, the dried black powders were subjected to a heating cycle. First, they were heated at 150°C for 12 h and cooled down to room temperature under ambient conditions. The material was then subjected to a heating cycle. The material was then heated to 250°C for 3 h, 350°C for 2 h, 450°C for 2 h, 550°C for 1 h and 650°C for 1 h, respectively.

Preparation of AMO (Amorphous Manganese Oxide)

The catalyst was synthesized following the procedure described in the literature,[2] by the reduction of $KMnO_4$ with oxalic acid at room temperature. Potassium permanganate solution (1.58 g, 0.01 mol of $KMnO_4$ dissolved in 60 mL of distilled deionized water (DDW)) was added dropwise to the oxalic acid solution (2.28 g, 0.025 mol of oxalic acid dissolved in 100 mL of DDW) and kept stirring for 2 h at room temperature. The brown slurry obtained from the reaction was filtered to get the product. It was washed several times with deionized water and dried at 90 °C overnight to obtain the amorphous manganese oxide.

Reaction procedure of 1,2,3,4-tetrahydroisoquiniline to indole coupling

In a typical reaction, N substituted 1,2,3,4-tetrahydroisoquinoline (THIQ) (0.133 g,1.0 mmol), meso Mn_2O_3 (50 mg) and toluene (0.5 mL) were added successively in a 25 mL round bottom flask equipped with a condenser.

The reaction mixture was heated to reflux under vigorous stirring (700 rpm) for the required time under an air balloon. After reaction, the reaction mixture was cooled and the catalyst was removed by filtration. The product analysis was done using GC-MS (gas chromatography mass

spectrometry). The conversion was determined based on the concentration of N substituted 1,2,3,4-tetrahydroisoquinoline. Most reactions were repeated twice and the average values were used. The products were isolated by silica gel column chromatography (5:95 Ethyl acetate/petroleum ether was used as an eluent).

Preparation of *N*-phenyl-3,4-dihydroisoquinolinium dichlorocuprate

The substrate (1-Deutero-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-d_1) was synthesized following the procedure described in the literature.[3] To a solution of N-phenyl tetrahydroisoquinoline (500 mg, 2.39 mmol) in methanol (20 mL), $CuCl_2 \cdot 2H_2O$ (814.6 mg, 4.78 mmol) was added at room temperature. After stirring for 1 h, the stirring bar was removed and the methanol solution was layered with pentane. Yellow crystals were obtained after standing overnight at room temperature, which was isolated by filtration and washed with a small amount of methanol.

Preparation of 1-Deutero-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-d_1

The substrate (1-Deutero-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-d_1) was synthesized following the procedure described in the literature.[3] To a solution of *N*-Phenyl-3,4-dihydroisoquinolinium dichlorocuprate (473 mg, 1.38 mmol) in methanol (31.4 mL), $NaBD_4$ (69 mg, 1.66 mmol) was added portion wise at 0°C. After stirring for 10 min at room temperature, the reaction mixture was then quenched with aq. $NaHCO_3$, and extracted with CH_2Cl_2 (3 x 20 mL). The organic fractions were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure and purified by column chromatography (ethyl actetate/pentane).

Table S1. Summarization of XPS data of meso MnOx at different calcination temperature.

Entry	**Calcination temp. (°C)**	**Mn^{3+} (641.8 eV)**	**Mn^{4+} (643.9 eV)**	**$O_{lattice}$**	**$O_{adsorbed}$**	**$O_{adsorbed\ water}$**
1.	250	68.25	31.75	55.91	29.09	15
2.	350	68.83	31.17	62.8	25.86	11.3
3.	450	69.63	30.37	65.38	23.22	11.4
4.	550	70.61	29.39	63.83	26.72	9.45
5.	650	73.84	26.16	77.84	22.16	0
6.	AMO	51.41	14.52	62.09	28.77	9.13
7.[a]	550	23.82	43.14	06.62	65.13	28.25

[a] XPS was performed on the sample after separating and washing from a reaction.

Table S2. Structural characterizations of meso MnOx at different calcination temperatures.

Calcination temp. (°C)	**Surface area [a] (m^2g^{-1})**	**Pore diameter [b] (nm)**	**Crystal Str. [c]**
250	200	4.2	Amorphous
350	198	2.6	Amorphous
450	100	5.7	Mn_2O_3
550	71	6.6	Mn_2O_3
650	77	9.6	Mn_2O_3

[a] Calculated by BET method. [b] Calculated by BJH method from the desorption branch of the isotherm. [c] From powder XRD.

Table S3. The catalytic results using different **oxidants**.[a]

Entry	Oxidant	Conversion (%)[b]	Selectivity (%)[b]	GC Yield (%)	TON[c]
1.	Air	42	> 99	42	0.6
2.	H_2O_2	20	76	15	0.24
3.	TBHP	30	76	23	0.36
4.	N_2	25	100	25	0.39
5.	O_2	41	> 99	41	0.64
6.[d]	O_2	63	n.d	N/A	N/A
7.[e]	O_2	82	n.d	N/A	N/A

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.) toluene (0.5 mL), 25 mg of catalyst (Meso MnOx-550), 100°C, 3 hours. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst. [d] 1.5 bar, [e] 20 bar.

Table S4. The catalytic results using different **solvents**. [a]

Entry	Solvent	Conversion (%) [b]	Selectivity (%) [b]	Yield (%) [b]	TON [c]
1.	Toluene	42	>99	42	0.65
2.	1,4-dioxane	<1	>99	<1	0.02
3.	Acetonitrile	4	>99	4	0.06
4.	Benzonitrile	33	>99	33	0.51
5.	Ethanol	9	>99	9	0.14

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.) toluene (0.5 mL), 25 mg of catalyst (Meso MnOx-550), 100°C, 3 hours. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst.

Table S5. The catalytic results using different **solvent volumes**.[a]

Entry	Toluene (mL)	Concentration [g/ L]	Conversion (%) [b]	Selectivity (%) [b]	Yield (%) [b]	TON [c]
1.	neat	n/a	45	> 99	45	0.70
2.	0.25	100	68	> 99	68	1.06
3.	0.5	50	42	> 99	42	0.65
4.	1	25	37	> 99	37	0.58
5.	2	12.5	15	> 99	15	0.23
6.	5	5	7	> 99	7	0.11

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.), toluene, 25 mg of catalyst (Meso MnOx-550), 100°C, 3h. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst.

Table S6. The catalytic results using different **N-phenyl tetrahydroisoquinoline** to **Indole** ratio.[a]

Entry	N-phenyl tetrahydroisoquinoline to Indole ratio	Conversion (%)[b]	Selectivity (%)[b]	Yield (%)[b]	TON[c]
1.	1:0.5	11	> 99	11	0.17
2.	1:1	28	> 99	28	0.44
3.	1:1.2	42	> 99	42	0.65
4.	1:1.5	40	> 99	40	0.62

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.), toluene (0.5 mL) 25 mg of catalyst (Meso MnOx-550), 100°C, 3h. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst.

Table S7. The catalytic results using different **catalyst support**.[a]

Entry	Catalyst support	Conversion (%)[b]	Selectivity (%)[b]	Yield (%)[b]	TON[c]
1.	Meso-CeO_2	2	> 99	2	0.17
2.	Meso-TiO_2	< 1	> 99	< 1	0.16
3.	Meso-Fe_2O_3	9	> 99	9	0.21
4.	Meso-Co_3O_4	18	> 99	18	0.43
5.	Meso-Mn_2O_3	42	> 99	42	0.66

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.), toluene (0.5 mL) 25 mg of catalyst, 100°C, 3h. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst.

Table S8. Aerobic oxidative cross coupling of *N*-Phenyltetrahydroisoquinoline with indole under different **reaction conditions**.[a]

Entry	Catalyst	Oxidant	Conversion (%) [b]	Selectivity (%) [b]	GC Yield (%)	TON [c]
1.	Meso-250-MnOx	Air	26	> 99	26	0.40
2.	Meso-250-MnOx	N_2	17	> 99	17	0.26
3. [d]	Meso-250-MnOx	Air	15	> 99	15	0.23
4.	Meso-350-MnOx	Air	35	> 99	35	0.54
5.	Meso-350-MnOx	N_2	23	> 99	23	0.36
6. [d]	Meso-350-MnOx	Air	25	> 99	25	0.39
7.	Meso-450-MnOx	Air	39	> 99	39	0.61
8.	Meso-450-MnOx	N_2	26	> 99	26	0.40
9. [d]	Meso-450-MnOx	Air	33	> 99	33	0.51
10.	Meso-550-MnOx	Air	42	> 99	42	0.65
11.	Meso-550-MnOx	N_2	27	> 99	25	0.42
12. [d]	Meso-550-MnOx	Air	38	> 99	38	0.59

[a] Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.), Toluene (0.5 mL), 25 mg of catalyst, 100˚C, 3 hours. [b] Conversions and selectivities were determined by GC-MS. [c] TON = no of moles of limiting reagent converted to product per mole of catalyst. [d] 1st Reuse.

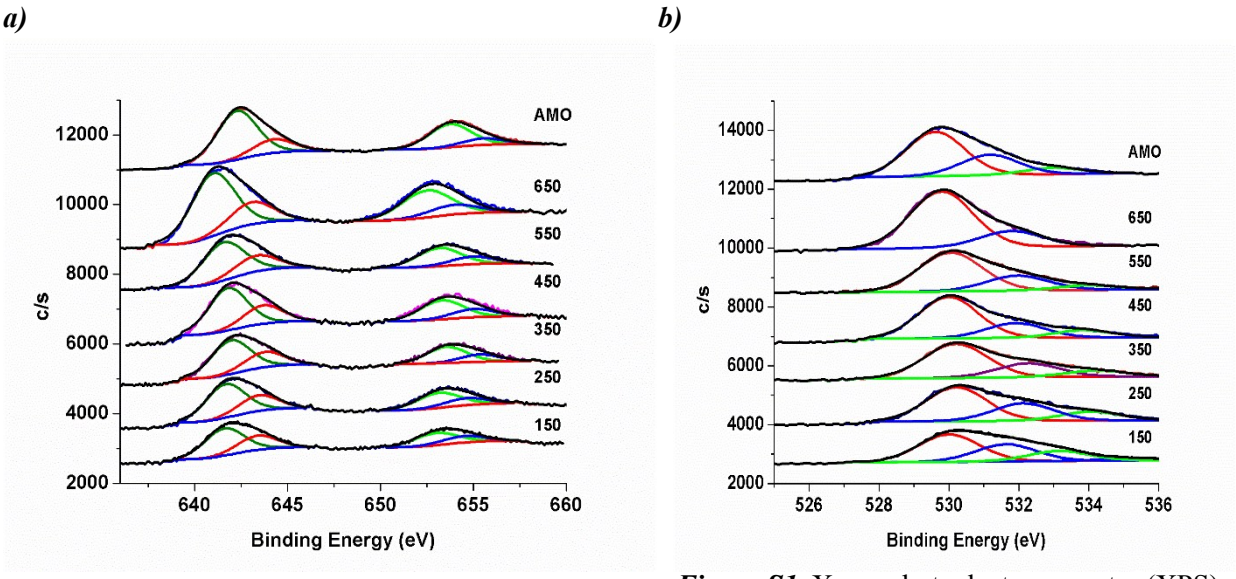


Figure S1. X-ray photoelectron spectra (XPS) of a) Mn 2p [of Meso-MnOx at different calcination temperatures, 150, 250, 350, 450, 550, 650 and AMO] and (b) O 1S [of Meso-MnOx at different calcination temperatures, 150, 250, 350, 450, 550, 650 and AMO] of meso MnOx.

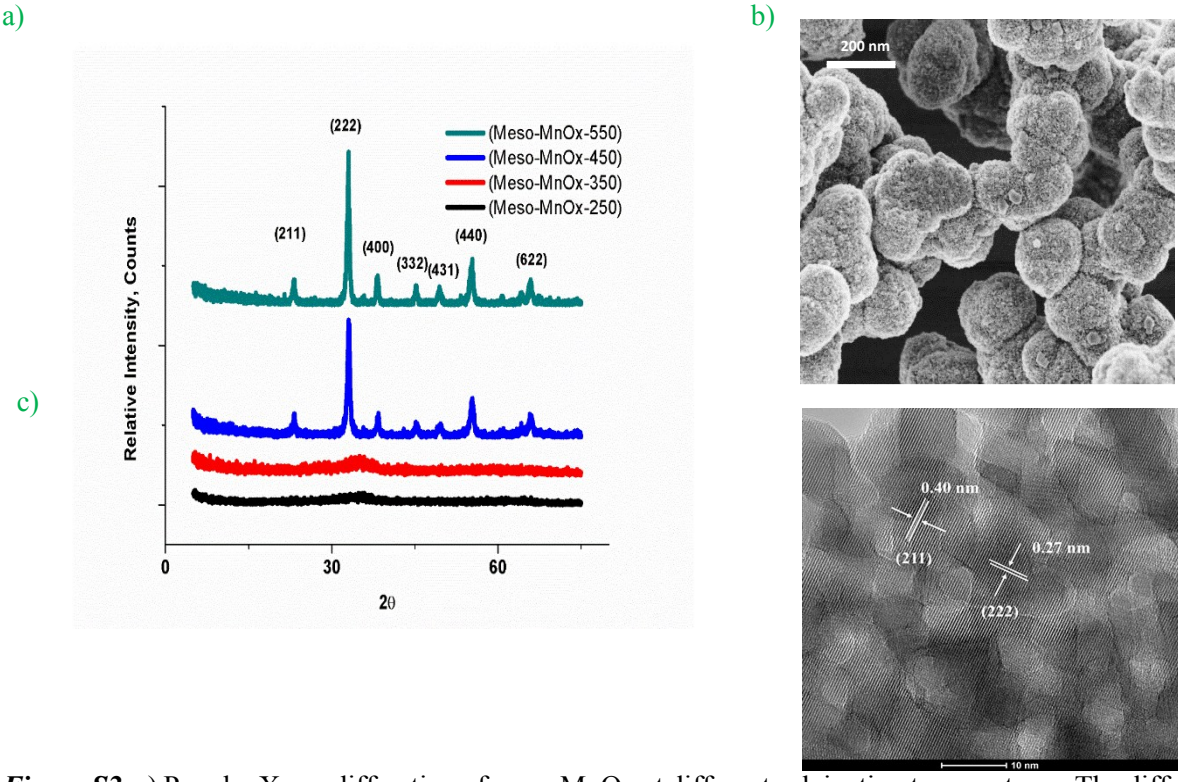


Figure S2. a) Powder X-ray diffraction of meso MnOx at different calcination temperatures. The diffraction patterns at 450°C and 550°C calcinations can be indexed to Mn_2O_3 phase, whereas calcination temperatures at 250°C and 350°C displayed an amorphous nature. b) Scanning electron microscopy (SEM) showed the spherical morphology of the meso-MnOx-550. c) Transmission electron microscopy (TEM) displayed the lattice fringes of the meso-MnOx-550.

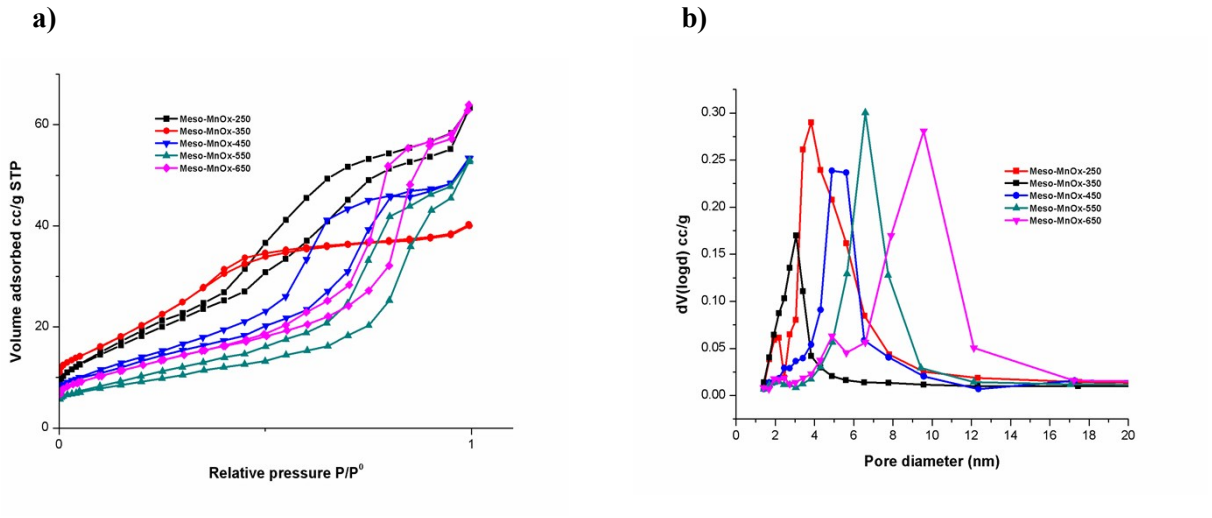


Figure S3. a) Nitrogen adsorption isotherms of meso MnOx at different calcination temperatures. A type IV adsorption isotherm followed by a type I hysteresis loop were observed for all the materials, which confirmed the mesoporous structure. b) BJH pore size distribution of the same materials show a constant increase in pore diameter with increasing calcination temperatures.

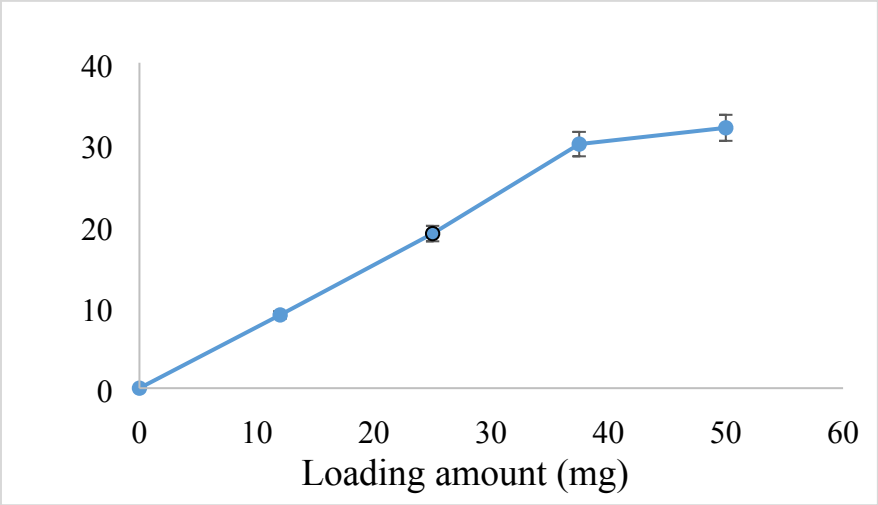


Figure S4. Effect of catalyst loading. Reaction conditions: N-phenyl tetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.) toluene (0.5 mL), 25 mg of catalyst, 2 hrs. Selectivity for the cross coupled compound was > 99% in all cases.

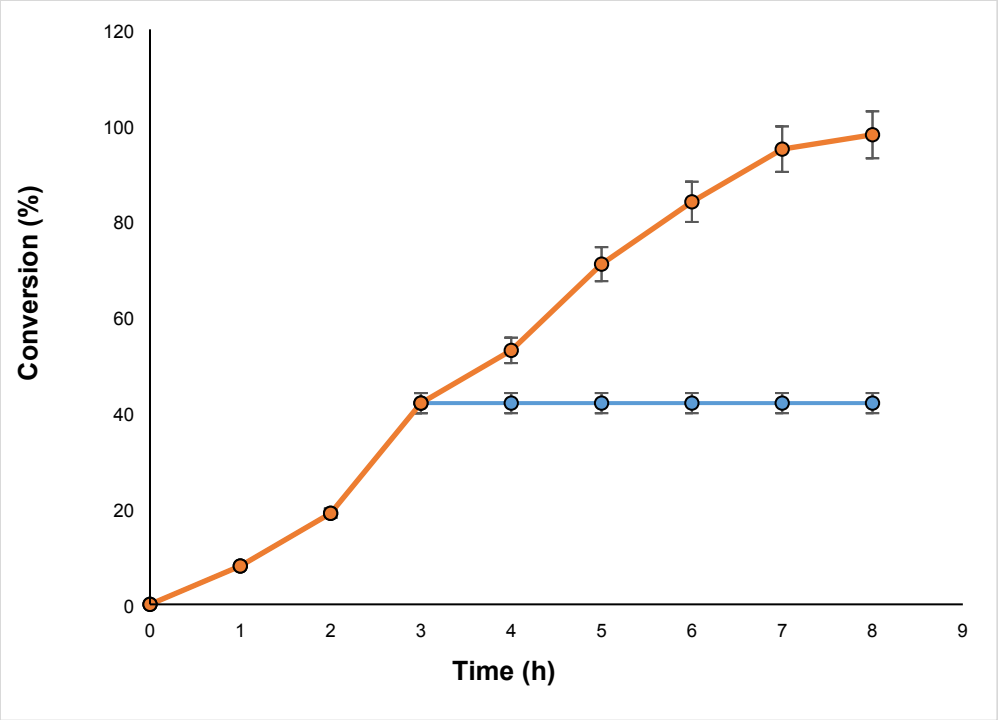
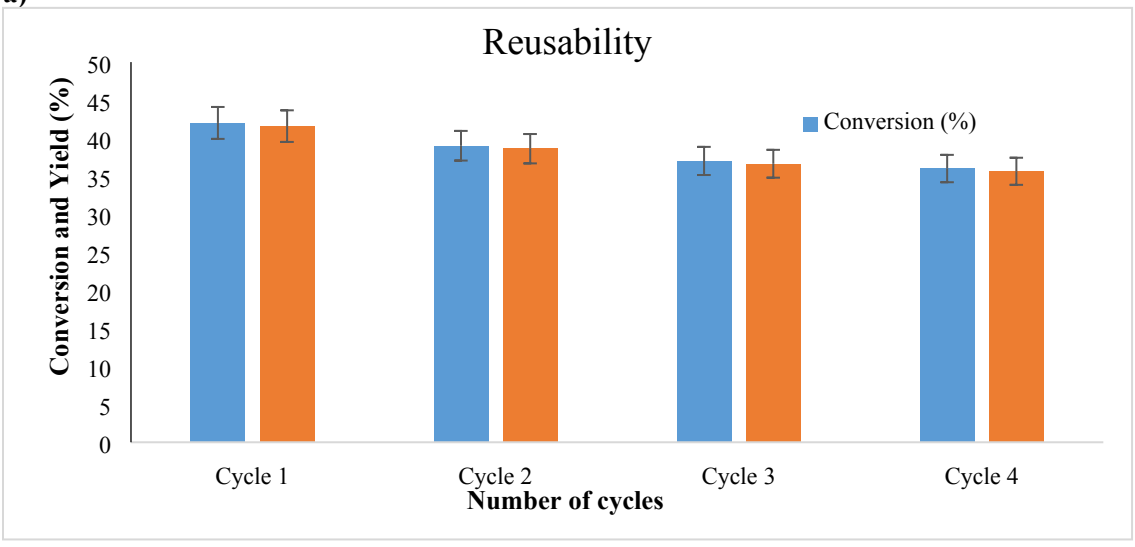


Figure S5. Effect of removal of catalyst on the cross dehydrogenative coupling of ***N*- phenyl tetrahydroisoquinoline** and **indole**: ***N*- phenyl tetrahydroisoquinoline** (0.25 mmol), indole (1.2 eqv.), 100 °C, 0.50 mL toluene, 25 mg catalyst. After **3** h, meso-Mn_2O_3 was removed by hot filtration (at about **42** % conversion).

a)



b)

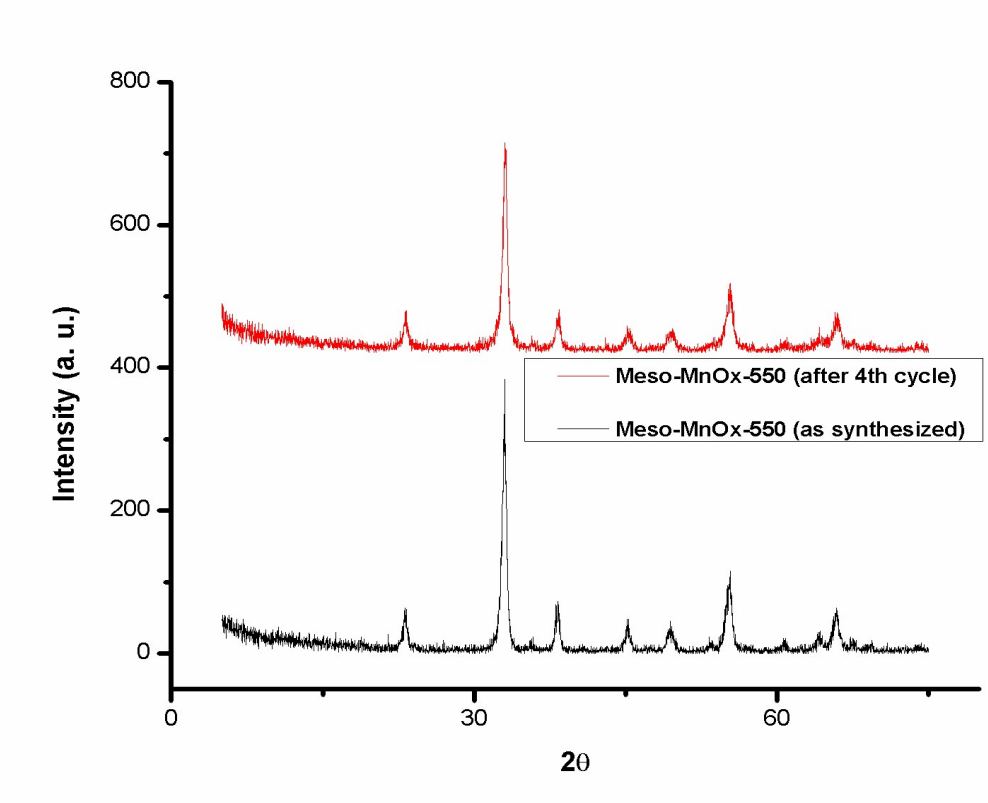


Figure S6. **a)** Reusability test of the catalyst. Reaction condition: ***N*-phenyl tetrahydroisoquinoline** (0.25 mmol), indole (1.2 eqv.), 100 °C, 0.50 mL toluene, 25 mg catalyst. Air balloon, **3** h, Turnover number (TON) = [reacted mol *N*- phenyl tetrahydroisoquinoline]/[total mol catalyst]. **b)** PXRD of meso MnOx-550 before and after fourth reuse. No noticeable changes were observed in the diffraction patterns after fourth reuse.

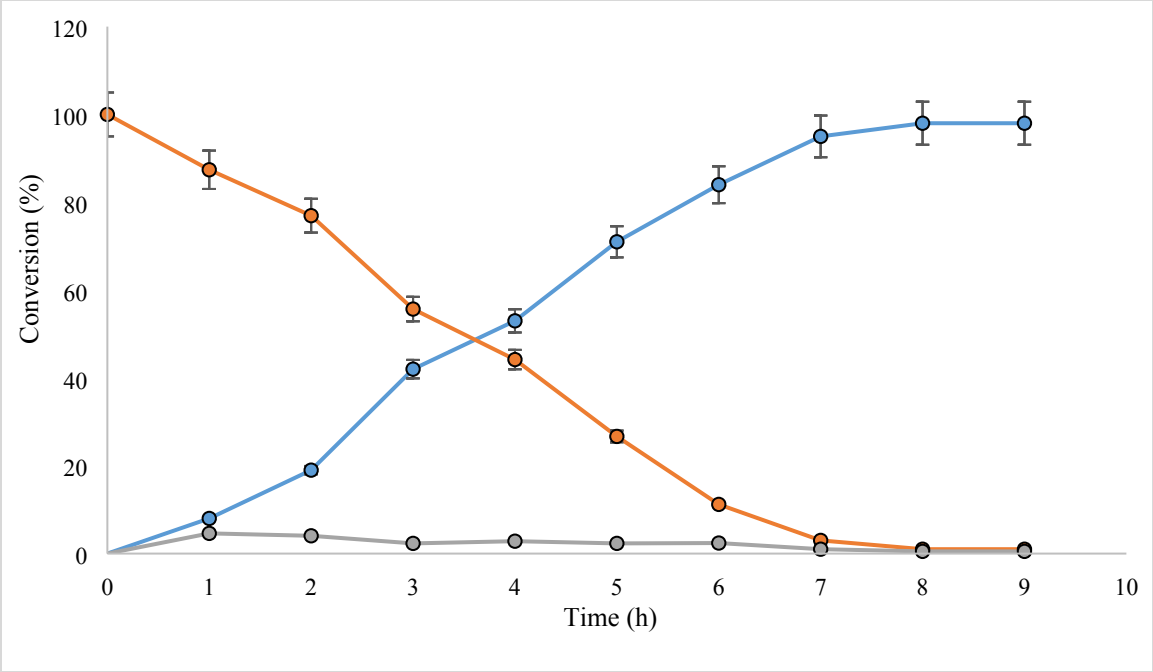


Figure S7. Time Dependent Study. Reaction procedures were the same as discussed in Table S1. Formation of minute amount of imine intermediate was observed.

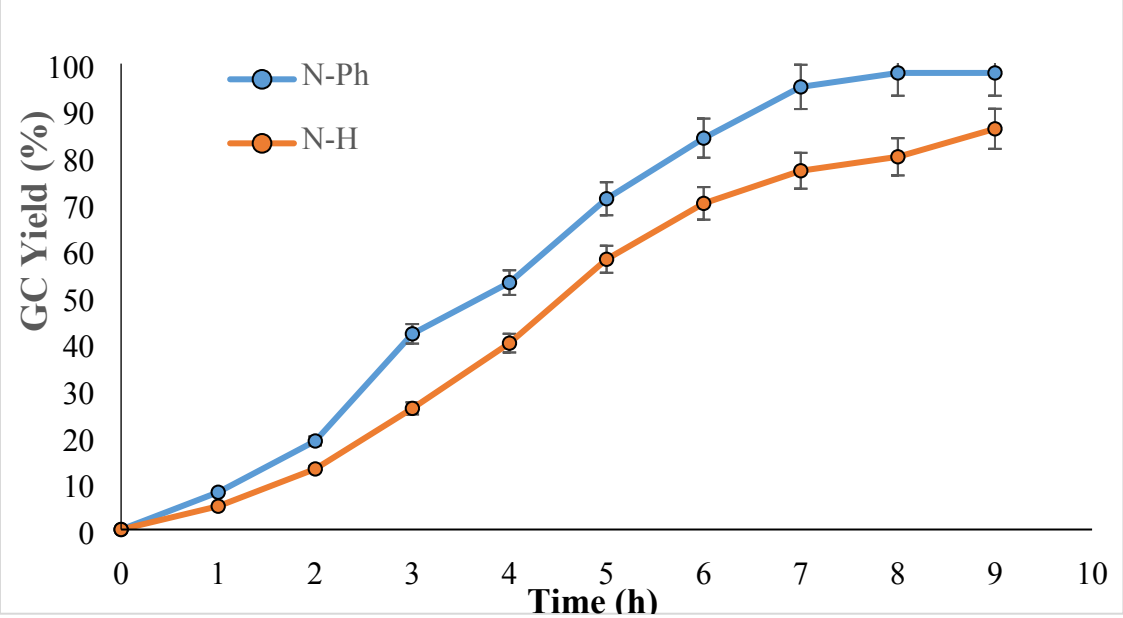


Figure S8: Evidence of charge stability by the incorporation of aryl groups.

Reaction conditions were same as in **Table *S*1.** Reaction kinetics for both *N*-substituted (with Phenyl) and unsubstituted 1,2,3,4-tetrahydroisoquinolines were compared. Faster reaction kinetics was observed in case of *N*-aryltetrahydroisoquinoline. This probably caused, due to the better stability of the charged intermediate **B (Scheme 2)**.

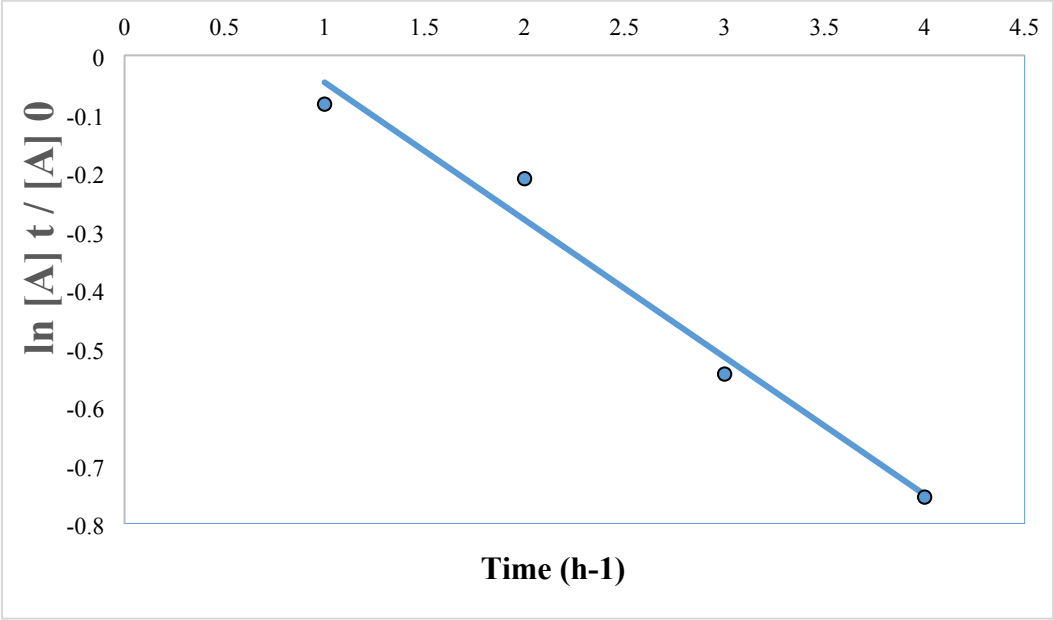


Figure S9. Kinetic study of the oxidative cross coupling of *N*-phenyltetrahydroisoquinoline with indole by meso-Mn_2O_3: The reaction exhibited a first order rate dependence with respect to N-phenyltetrahydroisoquinoline, having the rate constant of 0.235 h^{-1}.

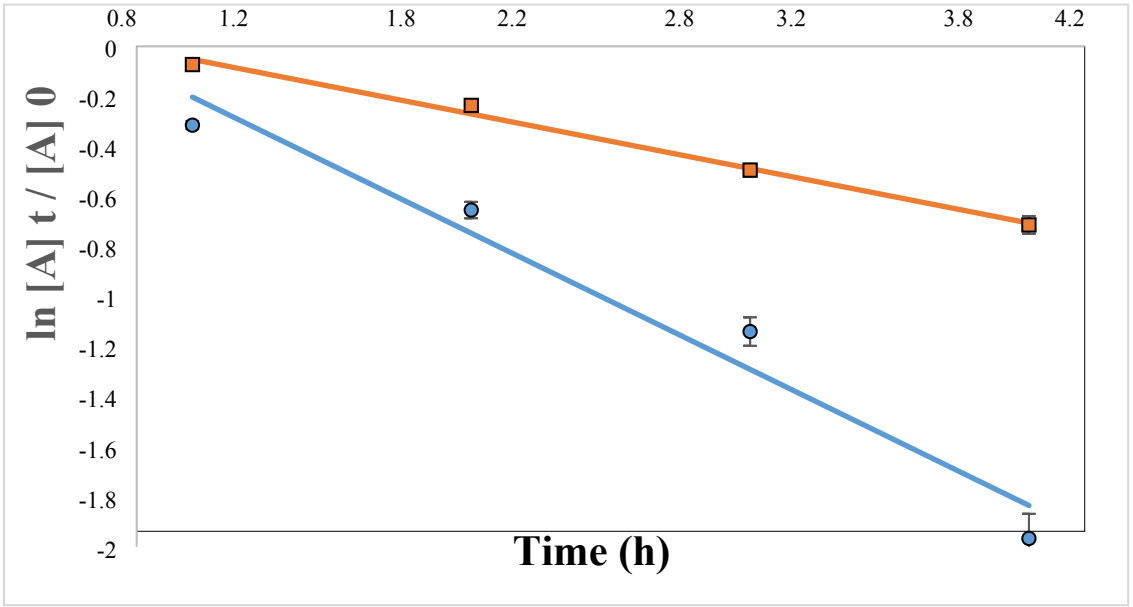


Figure S10. Kinetic study of the oxidative cross coupling of *N*-phenyltetrahydroisoquinoline with indole by meso-Mn_2O_3: The reaction exhibited a first order rate dependence with respect to N-phenyltetrahydroisoquinoline, having the rate constant of 0.544 h^{-1}.

Reaction conditions: N-phenyltetrahydroisoquinoline (0.25 mmol), indole (1.2 eqv.) toluene (0.25 mL), 25 mg of catalyst (Meso MnOx-550), 100°C.
A_0: original concentration of substrate. A_t: concentration of substrate at time t. K: rate constant.

K_H/K_D for the deprotonation of d-THIQ-N-Ph (THIQ-N-Ph *to* d-THIQ-N-Ph) = 0.544/ 0.218 = 2.49

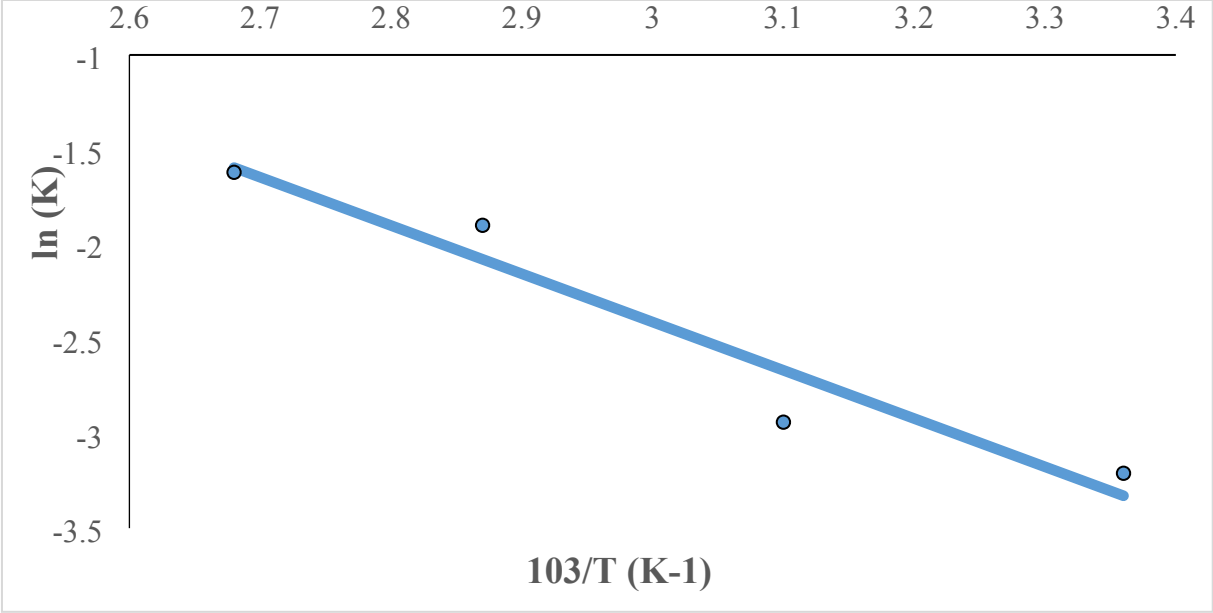
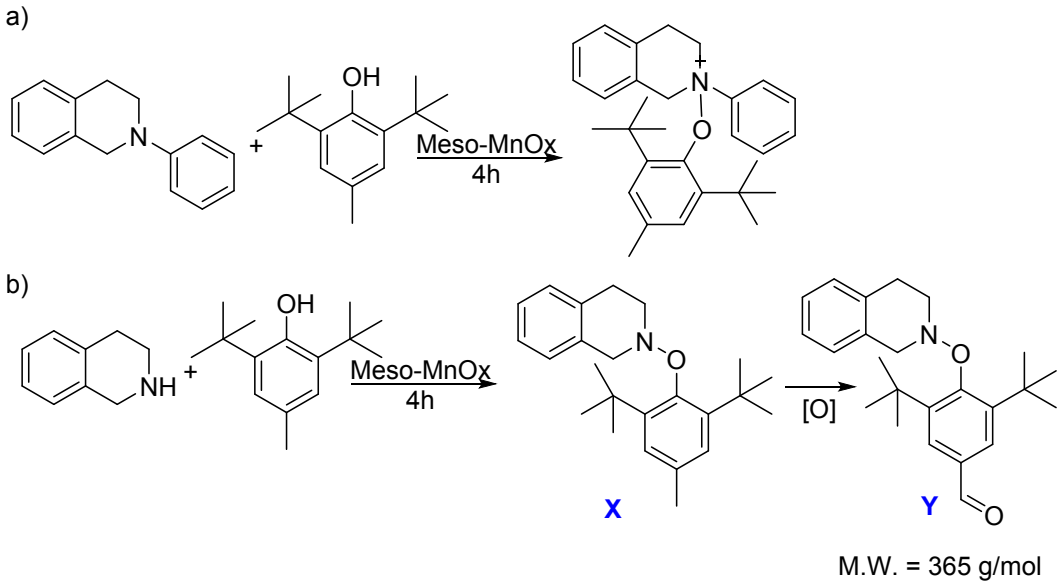


Figure S11. Arrhenius plot for oxidative coupling of N-phenyltetrahydroisoquinoline by meso Mn_2O_3: The apparent activation energy was estimated as 21.12 $KJmol^{-1}$. Reaction conditions: *N*-phenyltetrahydroisoquinoline (0.25 mmol), catalyst (25 mg), solvent (0.5 mL), air balloon. K: rate constant.



c)

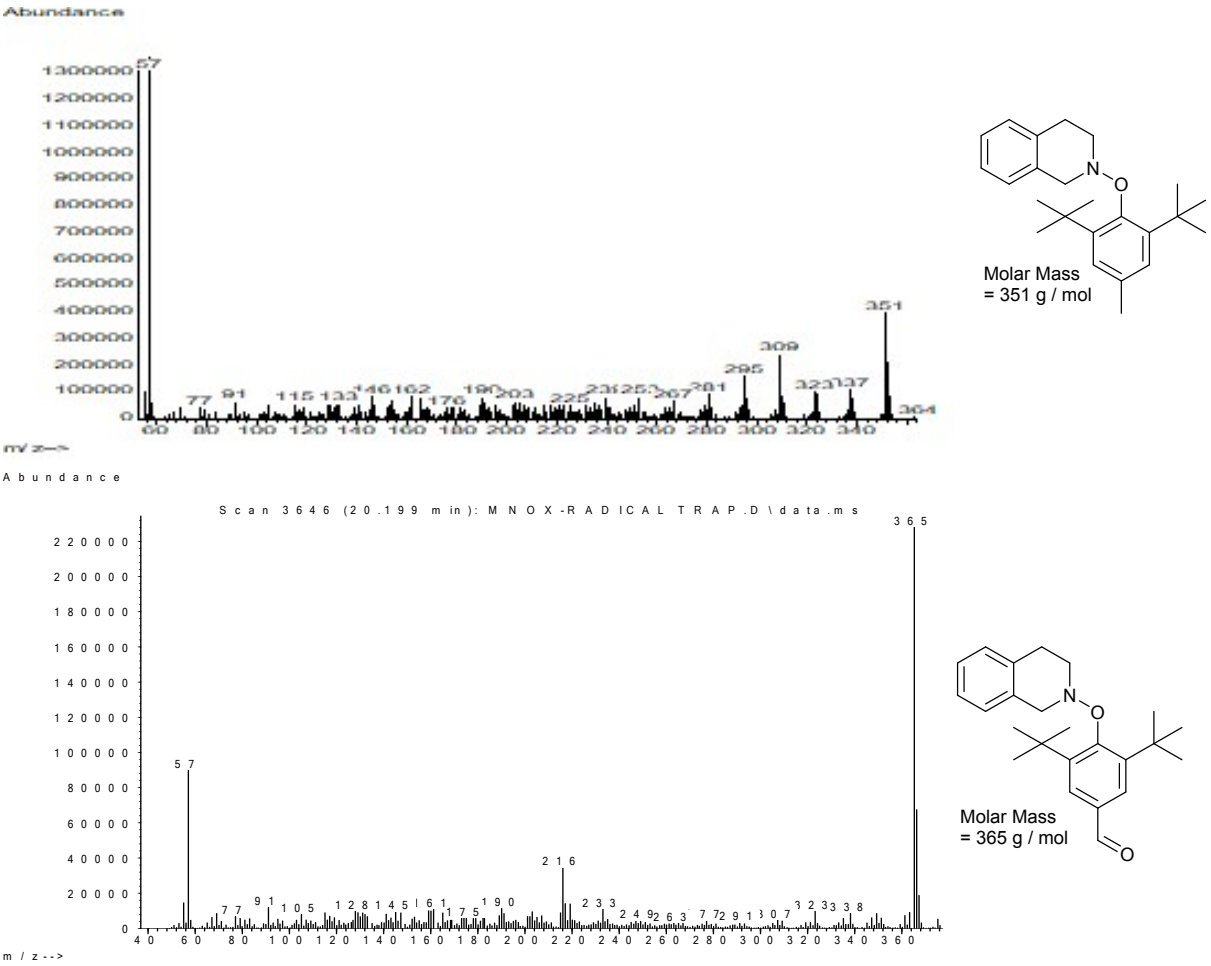


Figure S12. Intermediate Trapping: Reaction procedure: a) *N*-phenyltetrahydroisoquinoline **1a** (0.25 mmol), indole (1.2 eqv.), radical inhibitor (1.2 eqv.), and meso-Mn_2O_3 (25 mg, 0.16 mmol) were successively placed and mixed with toluene (0.5 mL) and refluxed at 100^0C under air balloon. The reaction mixture was analyzed by GC-MS after cooling to room temperature. b) instead of using N-phenyltetrahydroisoquinoline, 1, 2, 3, 4-tetrahydroisoquinoline was used under previously mentioned reaction condition. c) Mass-spectra of the trapped intermediates.

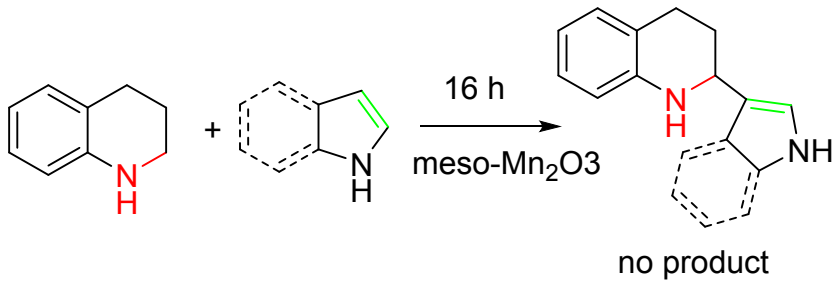


Figure S13. Intermediate Trapping: Reaction procedure: 1, 2, 3, 4-tetrahydroisoquinoline **1a** (0.25 mmol), indole (1.2 mmol), and meso-Mn_2O_3 (25 mg, 0.16 mmol) were successively placed and mixed with toluene

(0.25 mL) and refluxed at 100^{0}C under air balloon. The reaction mixture was analyzed by GC-MS after cooling to room temperature.

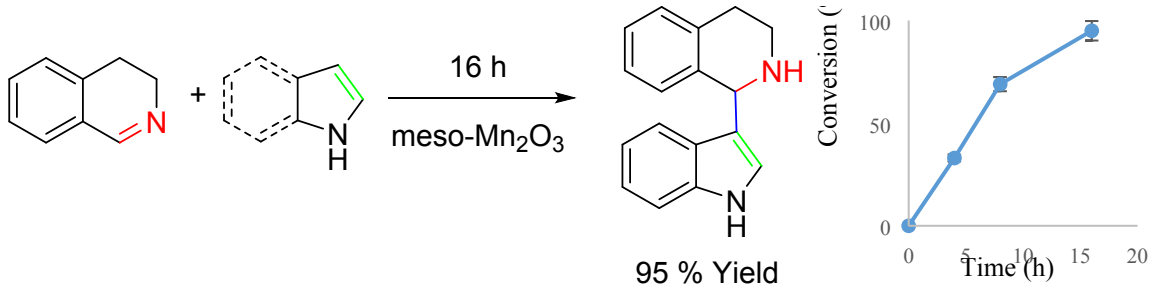


Figure S14. Intermediate as a substrate. Reaction procedure: 3,4-dihydroisoquinoline (0.25 mmol), indole (1.2 mmol) and meso-Mn_2O_3 (25 mg, 0.16 mmol) were successively placed and mixed with toluene (0.25 mL) and refluxed at 100^{0}C under air balloon. The reaction mixture was analyzed by GC-MS after cooling to room temperature.

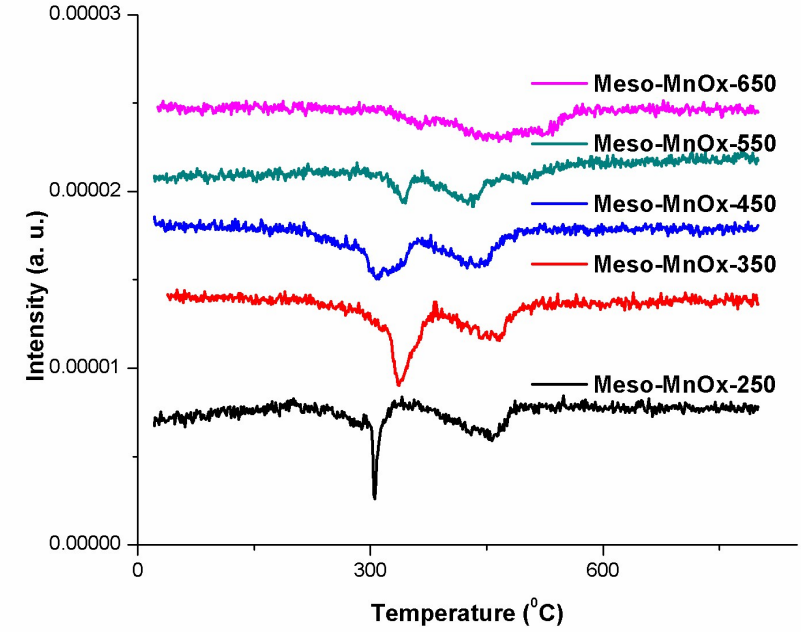
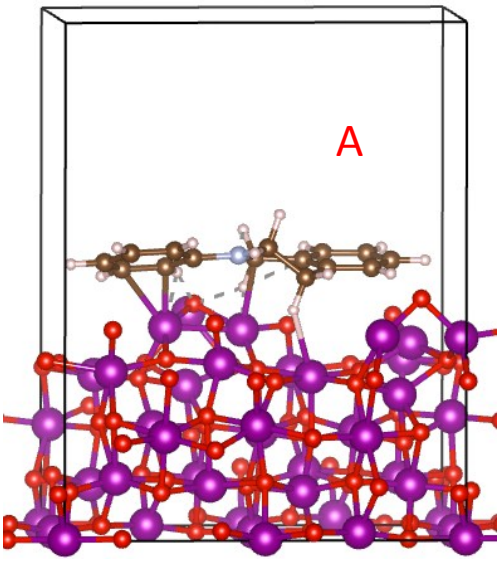
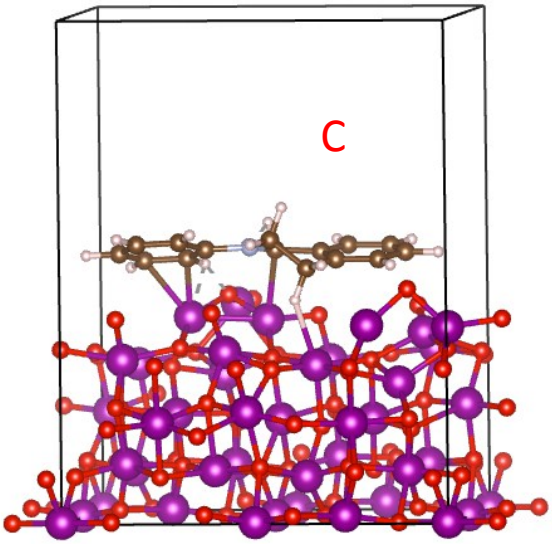
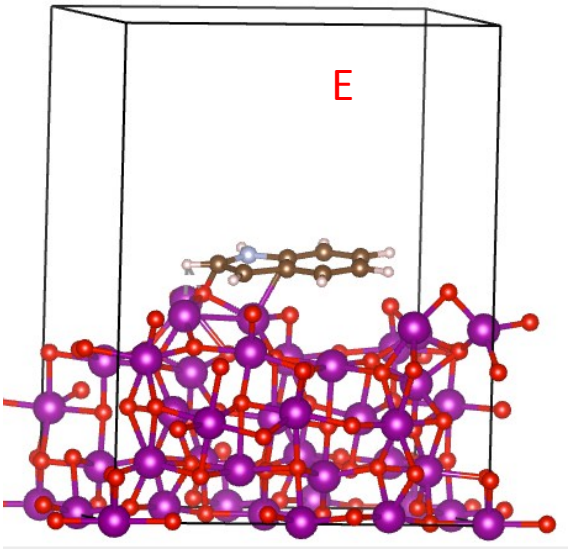


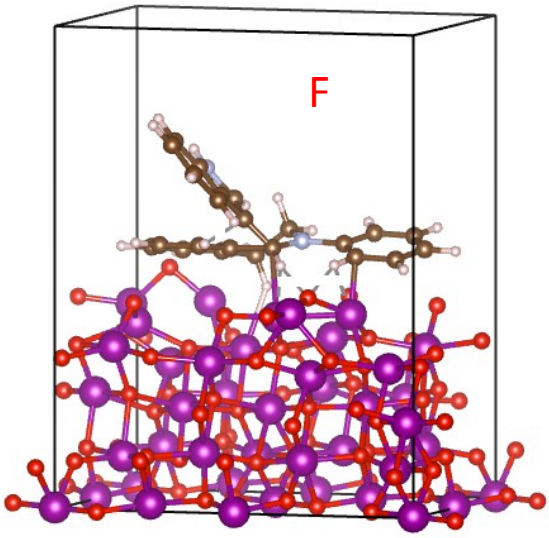
Figure S15. H_2-TPR of Meso-MnOx materials at different calcination temperatures.

Intermediates and their corresponding DFT calculated structures:



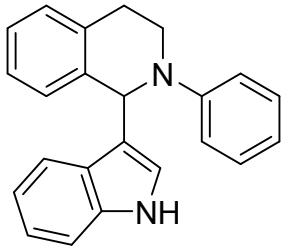




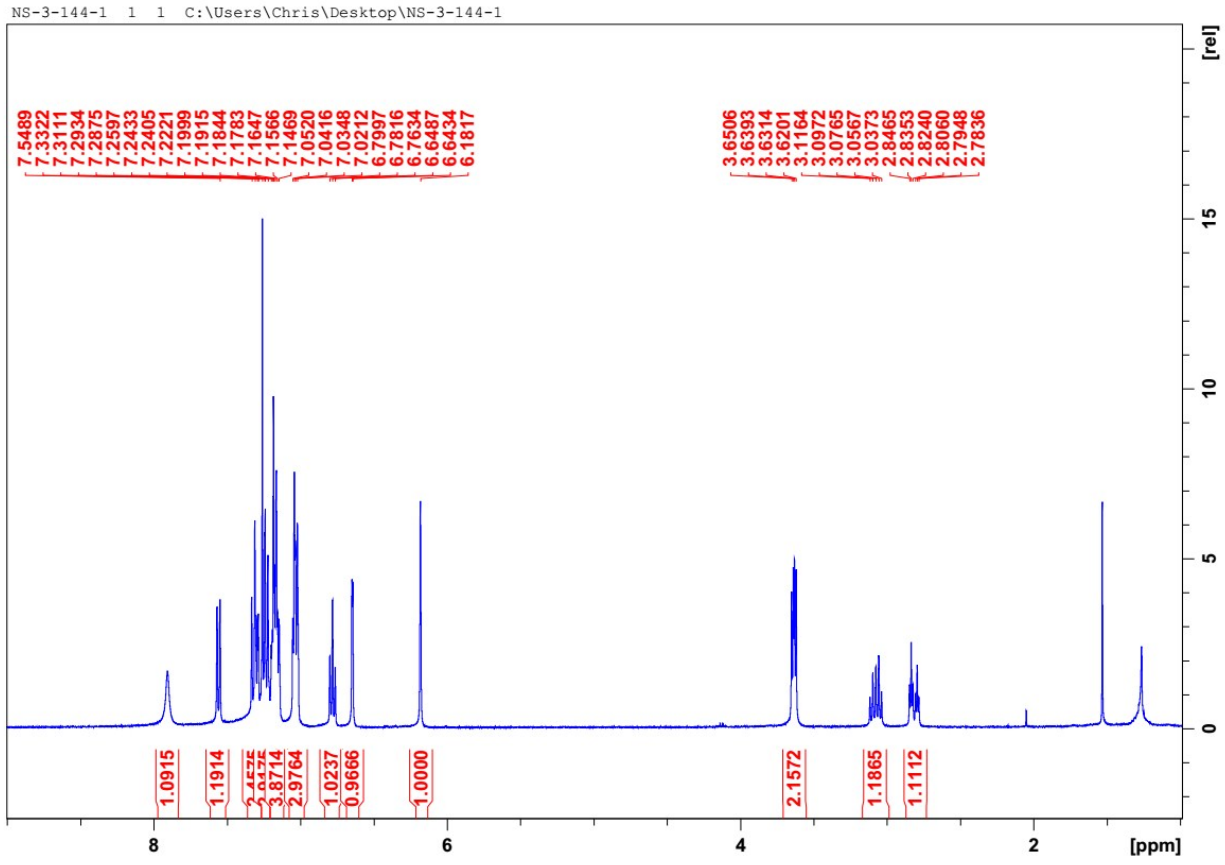


Characterization of typical products:

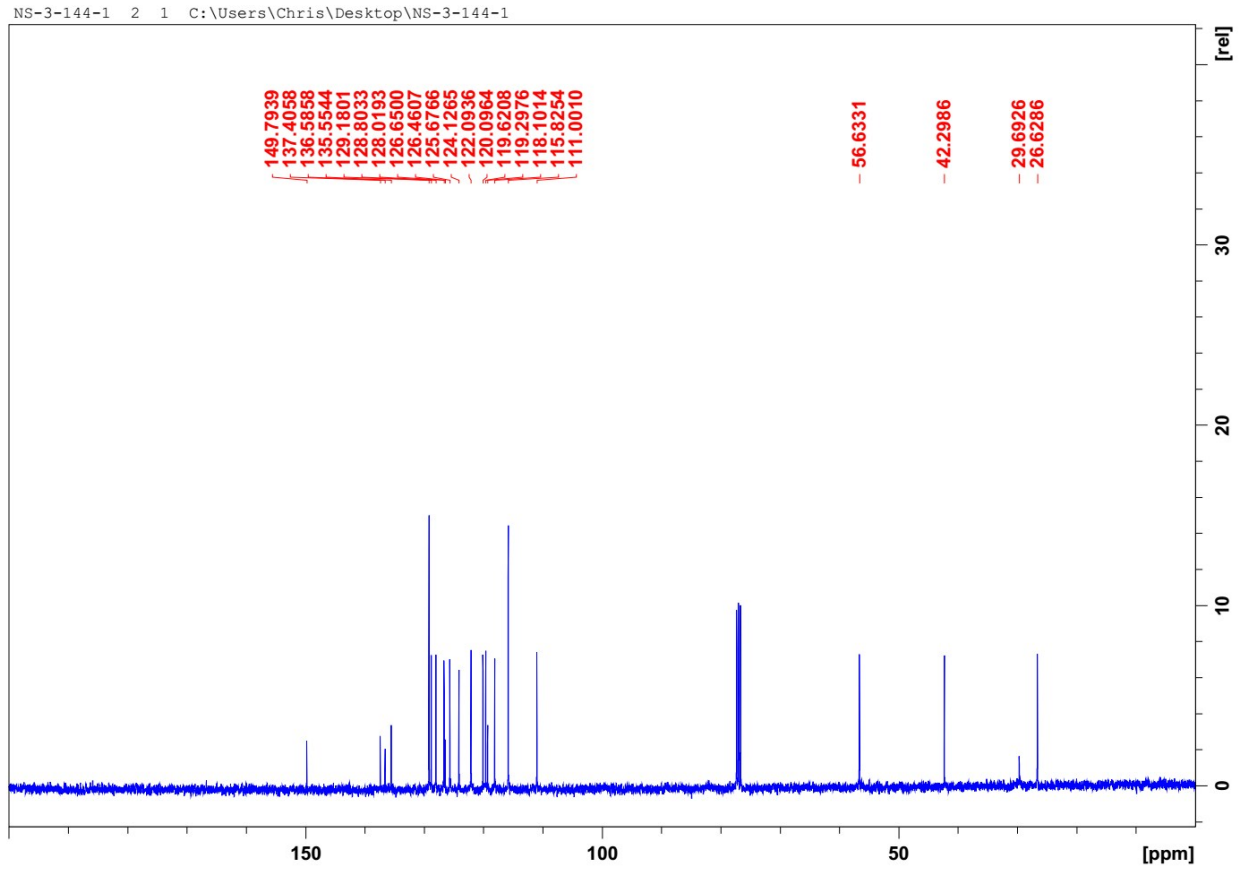
1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline



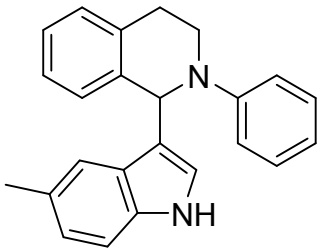
Pale yellow solid; Yield - 71%; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.92 (br s, 1H), 7.55 (d, J = 7.1 Hz, 1H), 7.40 (m, 1H), 7.31 (m, 2H), 7,23 (m, 2H), 7.15 (m, 4H), 7.04 (m, 2H), 7.01 (m, 1H), 3.63 (dd, J = 7.7, 4.6 Hz, 2H), 3.07 (m, 1H), 2.81 (ddd, J = 16.2, 4.4 Hz, 1H);



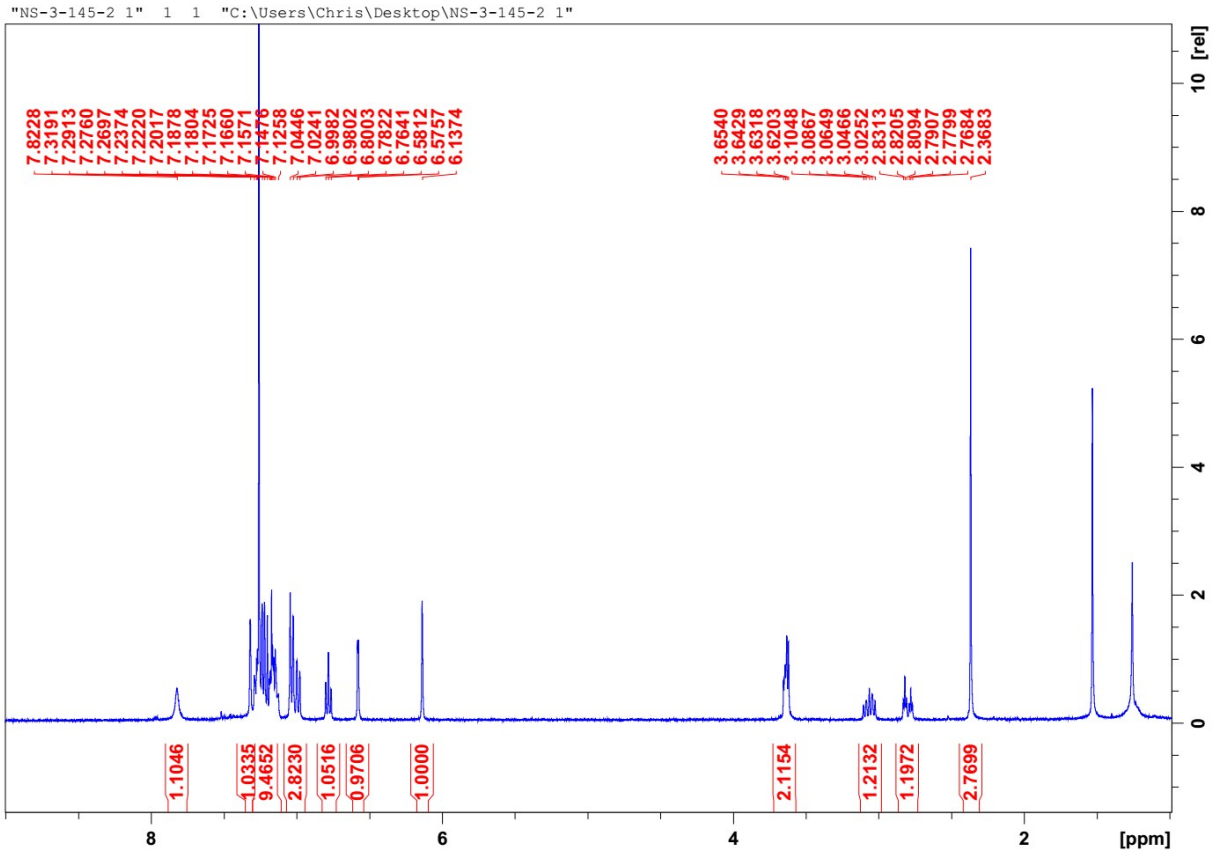
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 149.8, 137.4, 136.6, 135.6, 129.2, 128.8, 128.0, 126.7, 1265, 125.7, 124.1, 122.1, 120.1, 119.6, 119.3, 118.1, 115.8, 111.0, 56.6, 42.3, 29.7, 26.6;



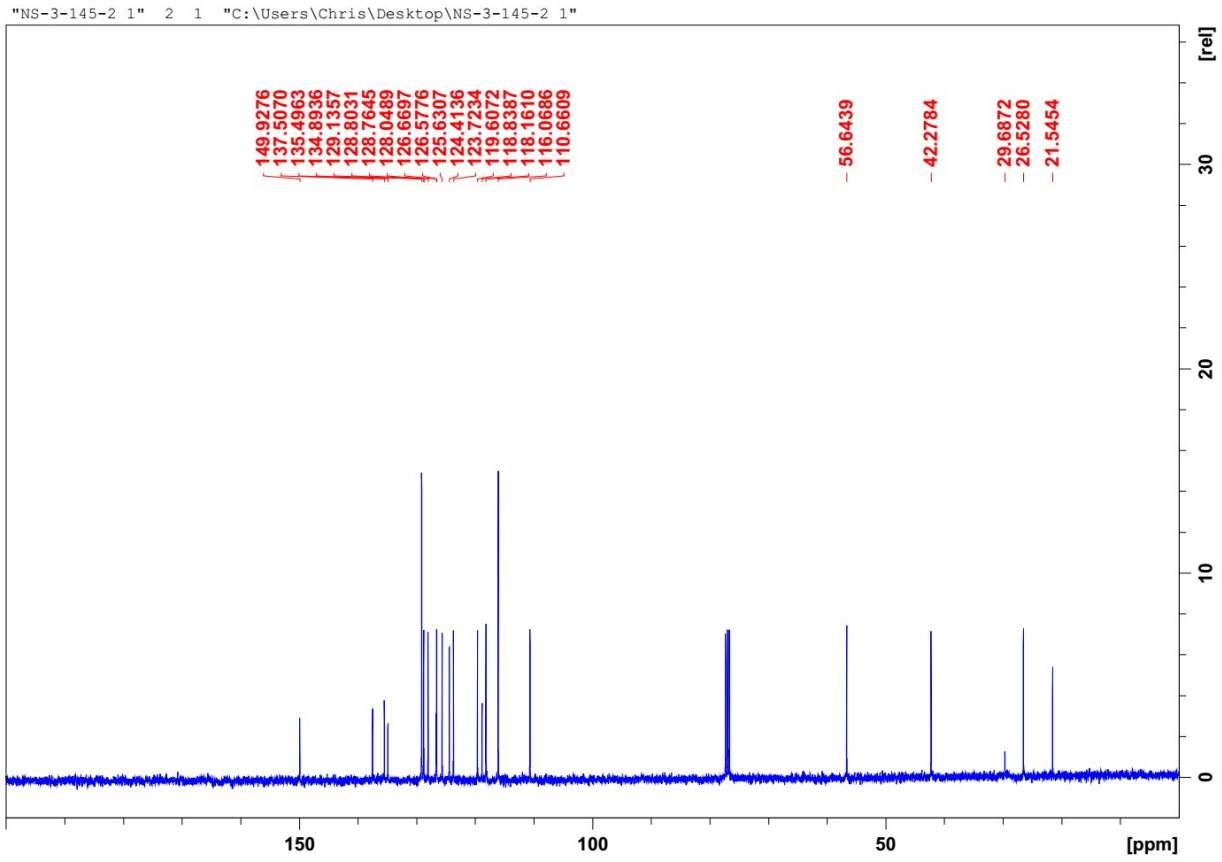
1-[4-(2-Methyl-propenyl)-1*H*-pyrrol-3-yl]-2-phenyl-1,2,3,4-tetrahydro-isoquinoline



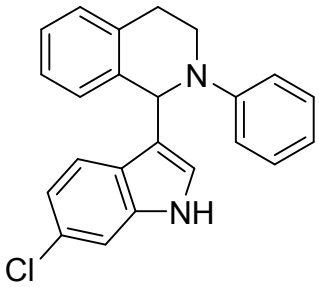
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.82 (br s, 1H), 7.26 9m, 4H), 7.17 (m, 3H), 7.04 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.2 Hz, 1H), 6.78 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 2.2 Hz, 1H), 6.14 (s, 1H), 3.64 (m, 2H), 3.07 (m, 1H), 2.80 (ddd, J = 16.3, 4.4, 4.4 Hz, 1H), 2.37 (s, 3H);



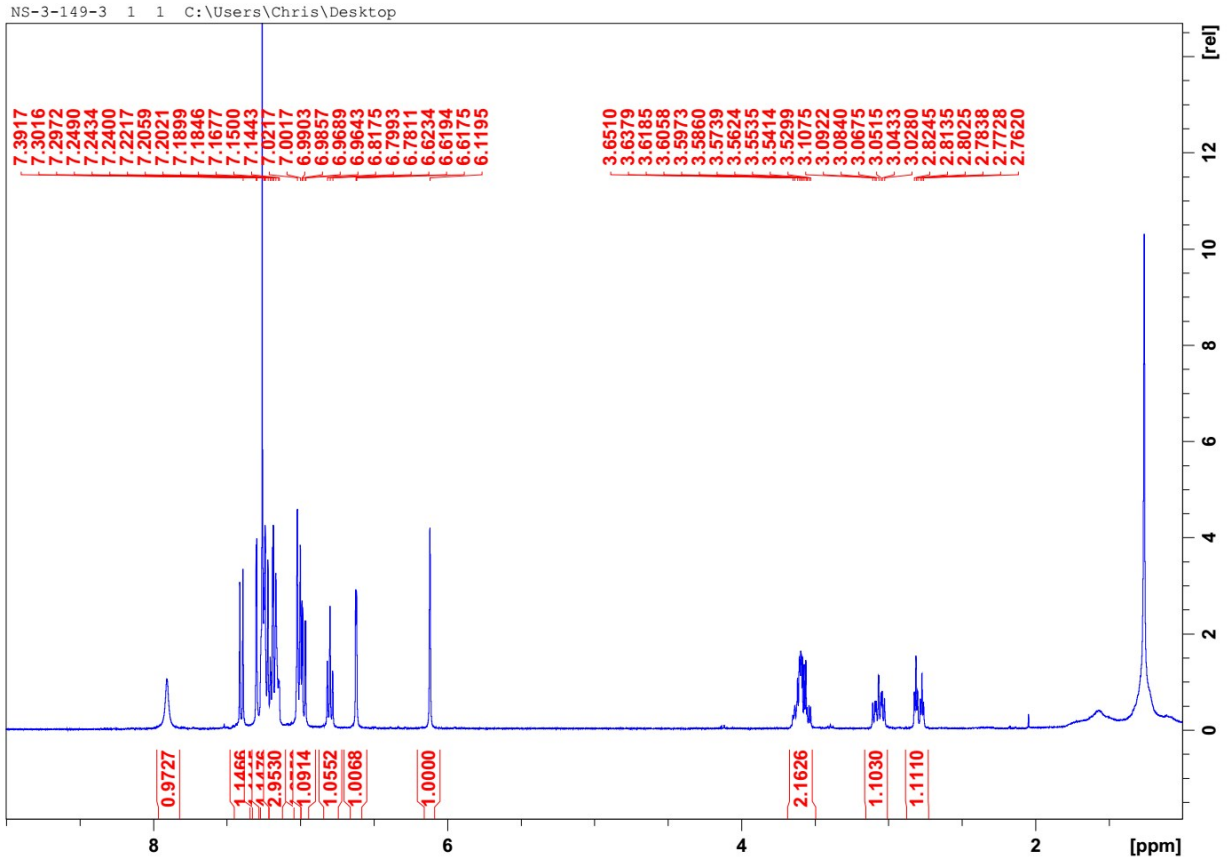
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ, 150.0, 137.5, 135.5, 134.9, 129.1, 128.8, 128.8, 128.1, 126.7, 126.6, 125.6, 124.4, 123.8, 119.6, 118.9, 118.2, 116.1, 56.6, 42.3, 29.7, 26.5, 21.6;



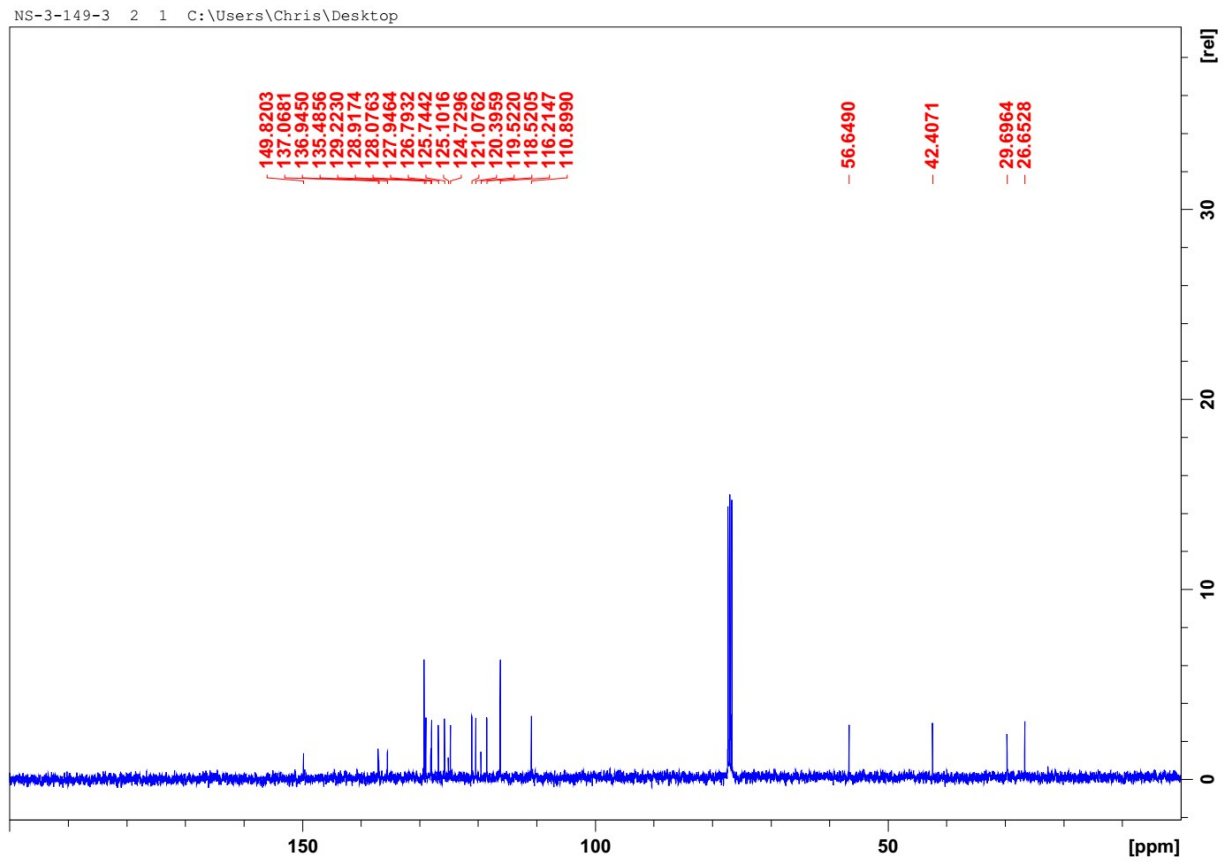
1-(6-Chloro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline



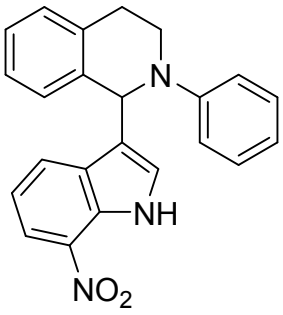
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.90 (br s, 1H), 7.40 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 1.7 Hz, 1H), 7.21 (m, 4H), 7.01 (d, J = 8.2 Hz, 2H), 6.98 (dd, J = 8.6, 1.8 Hz, 1H), 6.80 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 3.59 (m, 2H), 3.07 (ddd, J = 16.0, 9.4, 6.1 Hz, 1H), 2.79 (ddd, J = 16.3, 4.4, 4.4 Hz, 1H),



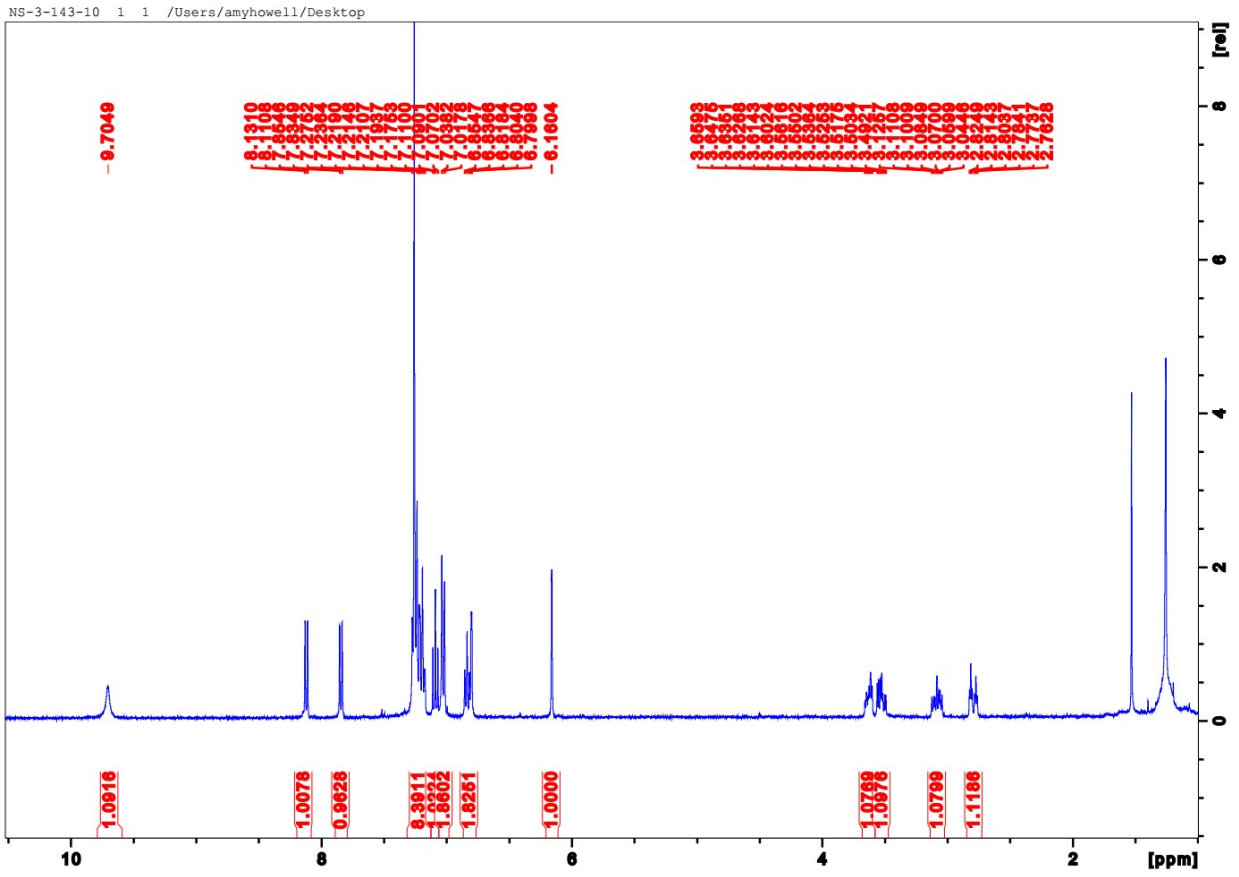
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 149.8, 137.1, 136.9, 135.5, 129.2, 128.9, 128.1, 127.9, 126.8, 125.7, 125.1, 124.7, 121.1, 120.4, 119.5, 118.5, 116.2, 110.9, 56.6, 42.4, 29.7, 26.6;



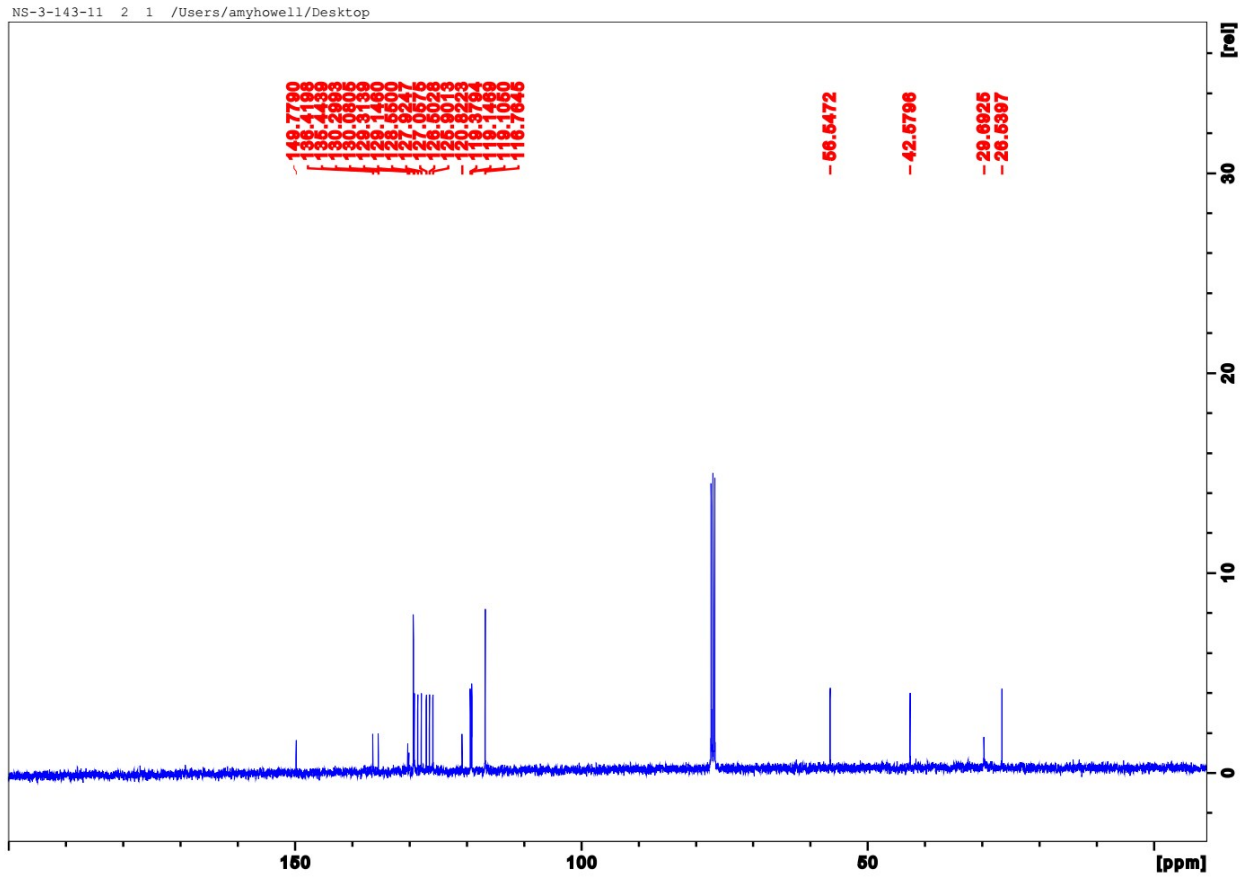
1-(7-Nitro-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydro-isoquinoline.



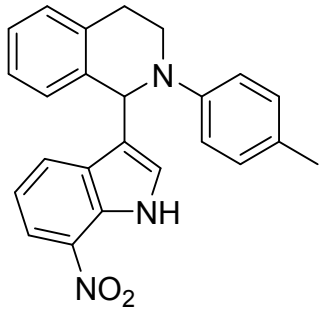
^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 9.71 (s,1H), 8.11, (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.24 (m, 6H), 7.09 (t, J = 8.0 Hz, 1H), 7.04 (d, J = 8.2 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.80 (d, J = 1.4 Hz, 1H), 6.17 (s, 1H), 3.64 (ddd, J = 13.0, 9.8, 4.9 Hz, 1H), 3.54 (ddd, J = 14.4, 10.0, 4.6 Hz, 1H), 3.10 (ddd, J = 16.2, 9.9, 3.3 Hz, 1H), 2.80 (ddd, J = 16.4, 8.2, 4.1 Hz, 1H),



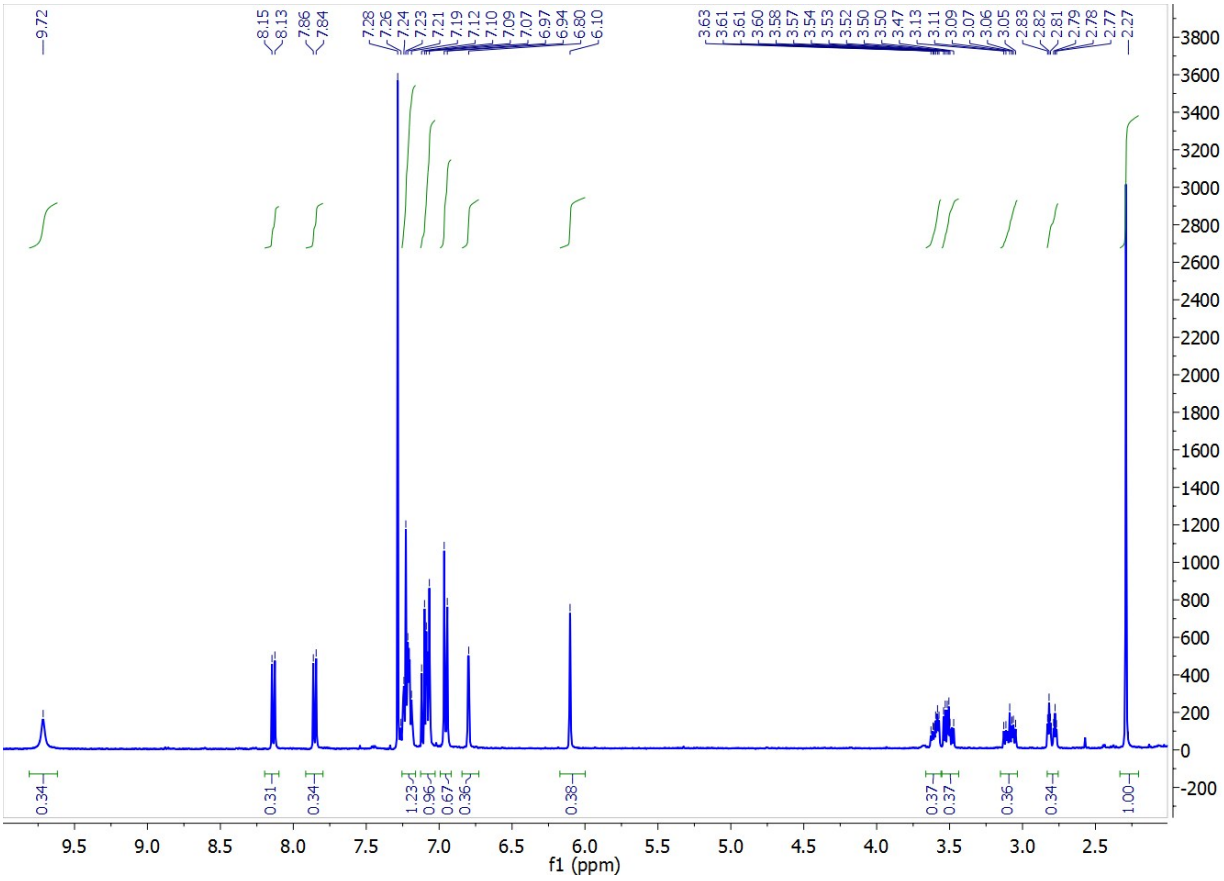
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 149.7, 136.4, 135.4, 132.8, 130.3, 130.0, 129.3, 128.5, 127.9, 127.0, 126.5, 125.9, 120.8, 119.3, 119.1, 119.1, 116.7, 56.5, 42.5, 29.7, 26.5;



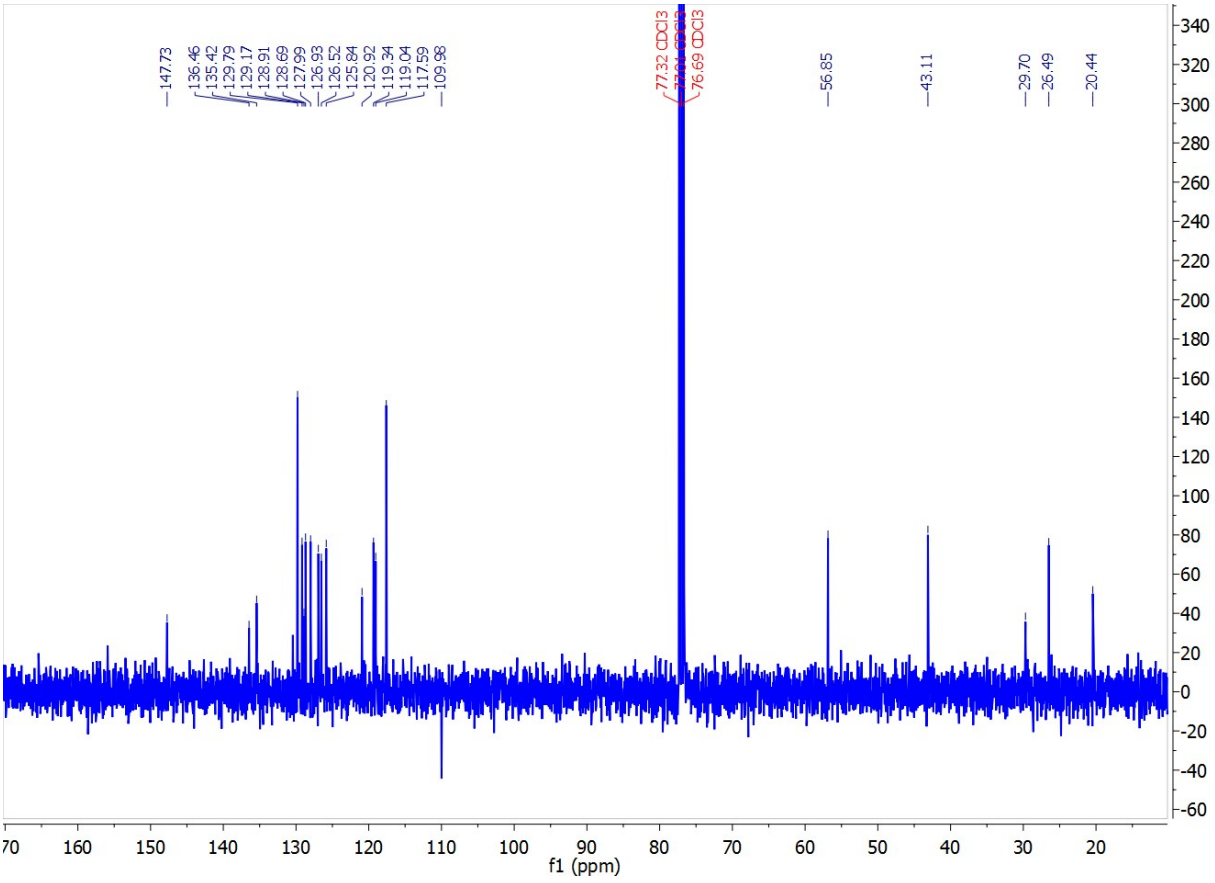
1-(7-Nitro-1*H*-indol-3-yl)-2-(4-methyl phenyl)-1,2,3,4-tetrahydro-isoquinoline.



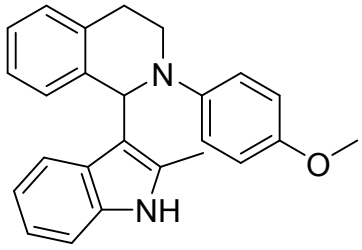
^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 9.70 (s, 1H), 8.15, (d, J = 8.07 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.21 (m, 4H), 7.11 (t, J = 8.01 Hz, 1H), 7.06 (d, J = 7.23 Hz, 1H), 6.95 (t, J = 8.19 Hz, 1H), 6.79 (d, 1H), 6.10 (s, 1H), 3.57 (m, J = 13.2, 9.96, 5.43 Hz, 1H), 3.10 (ddd, J = 16.2, 9.9, 3.3 Hz, 2H), 2.79 (ddd, J = 16.4, 8.2, 4.1 Hz, 2H), 2.25 (s, 3H).



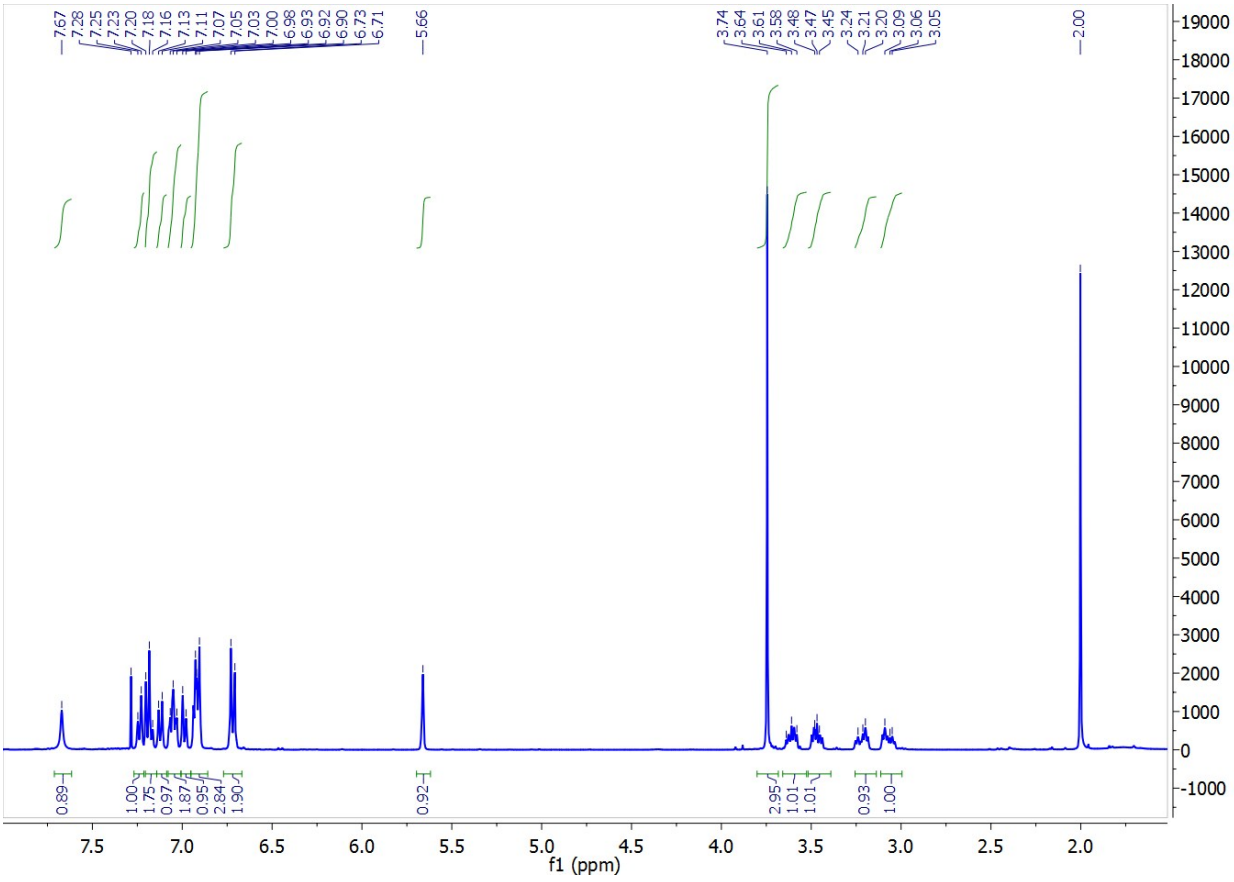
^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 147.73, 136.46, 132.42, 129.79, 129.17, 128.91, 128.69, 127.99, 126.93,126.52, 125.84, 120.92, 119.34, 119.04, 117.59, 109.98, 56.85, 43.13, 29.70, 26.49, 20.44;



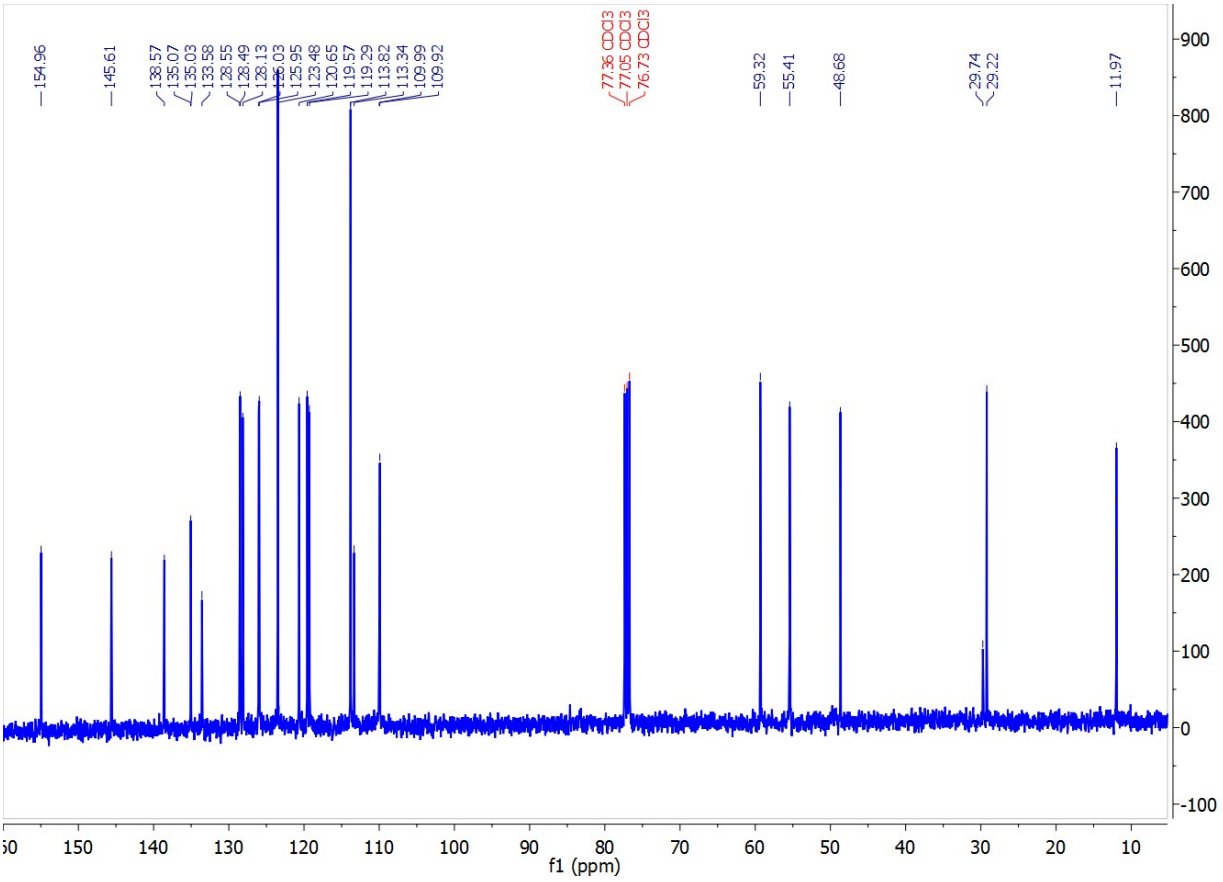
1-(2-Methyl-1*H*-indol-3-yl)-2(4-methoxy-phenyl)-1,2,3,4-tetrahydro-isoquinoline.



^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.67 (s,1H), 7.2 (m, 1H), 7.1 (m, 1H), 7.04 (m, 7H), 6.90 (d, J = 12.4 Hz, 2H), 6.7 (d, J = 8.7 Hz, 2H), 5.64 (s, 1H), 3.59 (m, 1H), 3.45 (m, 1H), 3.21 (m, 1H), 3.34 (m, 1H), 2.00 (s, 3H).



^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 154.96, 145.61, 138.57, 135.07, 135.03, 133.58, 128.55, 128.49, 128.13, 126.03, 125.95, 123.48, 120.65, 119.57, 119.29, 113.82, 113.34, 109.99, 109.92, 59.32, 55.41, 48.68, 29.74 29.22, 11.97;



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