Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Water Enabled, Nickel-Catalyzed Highly Chemoselective C-Allylation of (NH)-Indoles Employing Alcohols

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1. General Method

Unless otherwise noted, all manipulations (reactions) were carried out in oven-dried glasswares in glovebox under an atmosphere of dinitrogen (O_2 and H_2O level of <0.1 ppm) without using standard Schlenk-line techniques and monitored by thin layer chromatography (TLC). Concentration of reaction mixtures were done under reduced pressure by rotary evaporation at 25–40 °C at an appropriate pressure. Purified compounds were further dried under vacuum. Yields refer to purified and spectroscopically pure compounds, unless otherwise stated.

Chemicals

All the catalysts, ligands were purchased from Sigma-Aldrich®. All the other reagents like starting materials, additives, bases were used as received from commercial suppliers, unless otherwise stated and were mainly purchased from Alfa Aesar®, Sigma-Aldrich®.

Solvents

Ethyl acetate, Hexane, Diethyl ether were purchased from Fisher Scientific, Qualigen and used as received. Anhydrous solvents (Toluene, THF, DMSO, DMF, MeCN, NMP, 1,4-Dioxane, Nitromethane, MeOH, *t*-BuOH) were obtained from Sigma Aldrich and used as received. All deuterated solvents were purchased from Sigma Aldrich.

Surfactant

All the surfactants were obtained from Sigma Aldrich. SPGS-550M (2% w/w) and TPGS-750M (2% w/w) were used as received while PTS (15% w/w) was diluted using MiliQ water at 2% w/w concentration. Other surfactant including SDOSS (% w/w) concentrations mentioned were made using MiliQ water before using them for the reactions.

Chromatography

Thin layer chromatography (TLC) was performed using Merck TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. All the compounds were purified using column chromatography with 100-200 mesh size silica or with flash chromatography on CombiFlash®Rf$^+$ Lumen™, Teledyne ISCO using RediSep® Rf prepacked columns (24g, CV 33 mL-35 mL/min) and eluted using either EtOAc: Hexane as mobile phase.

Spectroscopy and Instruments:

NMR: ^{1}H NMR and ^{13}C NMR spectra were recorded on Brukar 500 MHz and 125 MHz spectrometers respectively using tetramethylsilane (1% v/v solution in the respective solvent) as an internal standard. Both ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million downfield from tetramethylsilane (δ= 0) with the solvent residual peak. For ^{1}H NMR: $CDCl_3$, δ7.26; For ^{13}C NMR: $CDCl_3$, δ77.16; ^{19}F NMR spectra were referenced

using a unified chemical shift scale based on the ^{1}H resonance of tetramethylsilane (1% v/v solution in the respective solvent). Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet) and m (multiplet).

High-resolution mass spectra (HRMS): spectra of compounds were obtained at Agilent Q-TOF spectrometer in positive (ESI^{+}) ion mode.

GC-MS: Gas Chromatography-Mass Spectrometry data (GC-MS) was recorded on an Agilent Technologies 8890 GC system coupled with Agilent Technologies 7010B mass spectrometer (GC/TQ) using Agilent 19091S-433UI: 0602217H (30m x 250 μm x 0.25 μm) purchased from Agilent Technologies.

Zeta-sizer: Dynamic light scattering (DLS) for particle size and PDI was utilised through zetasizer (NanoZS90, Malvern Instruments, Cambridge, UK).

2. List of chemicals/reagents

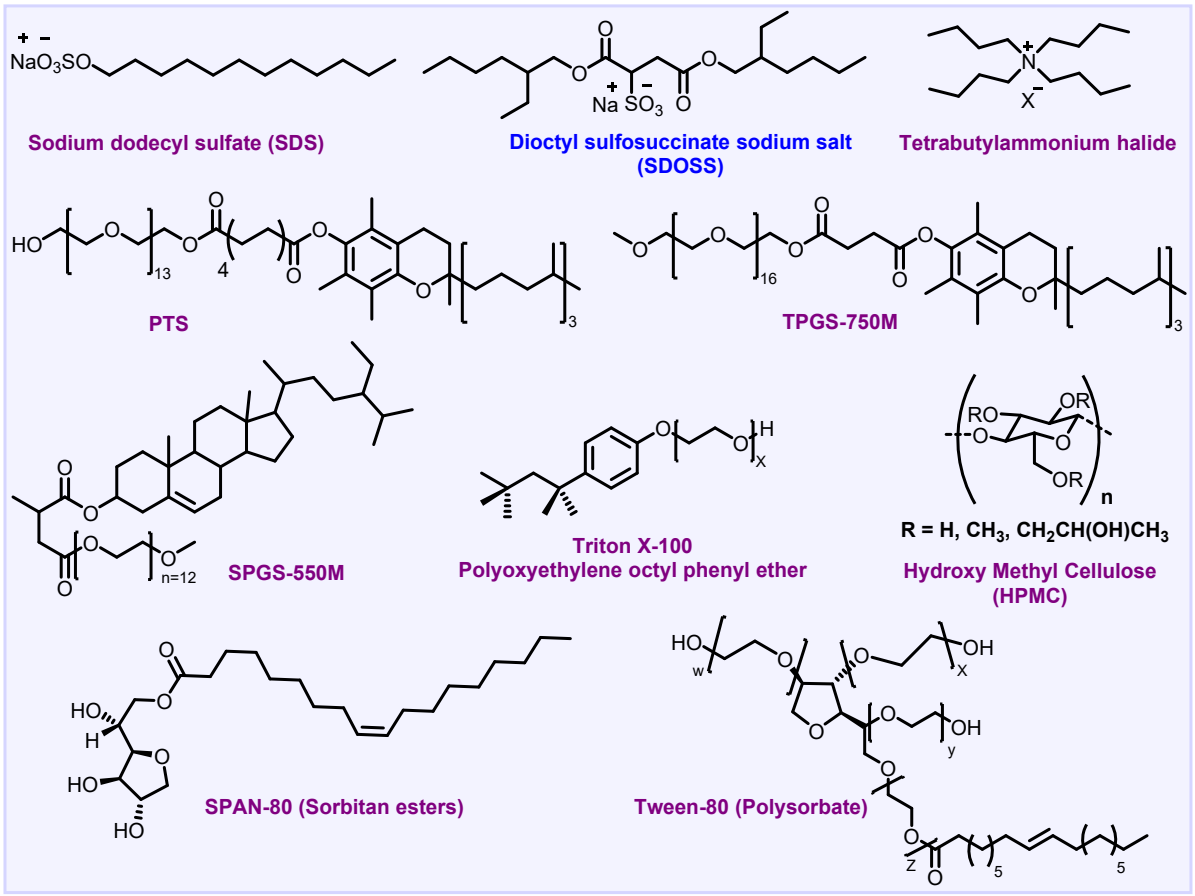


Figure S1. List of Surfactant

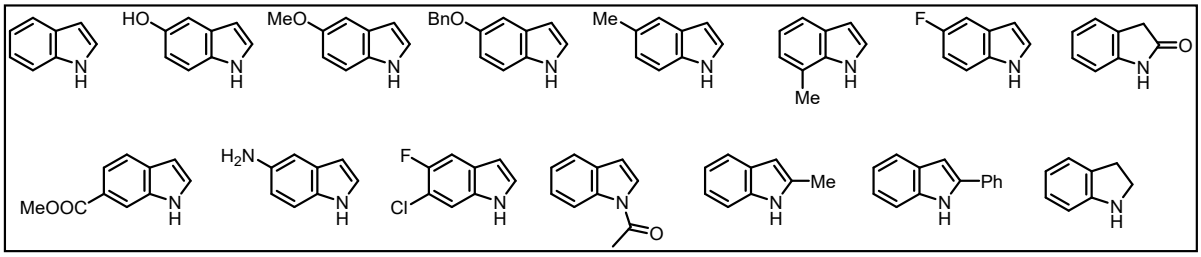


Figure S2. List of indoles

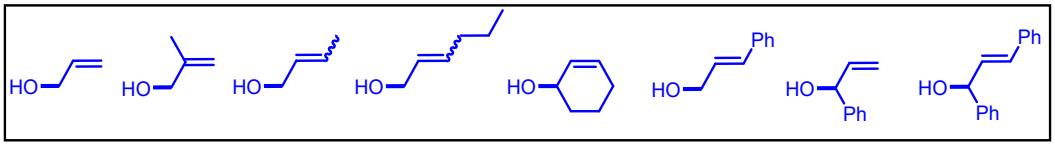
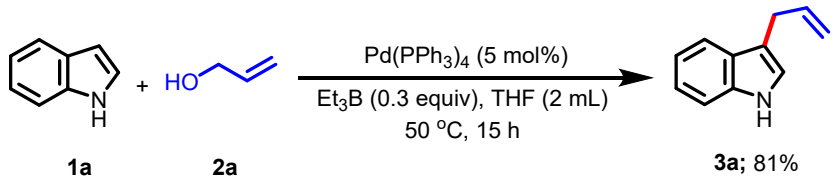


Figure S3. List of Allylic Alcohols

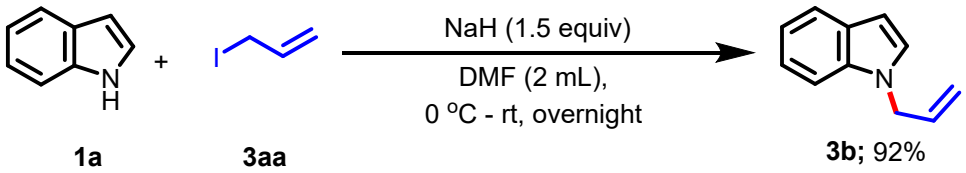
3. Synthesis of authentic samples (Standard reference for GC-MS studies)

3.1. Synthesis of 3-Allyl-*1*H-indole (3a)[1]:



To a well cleaned tube equipped with a stir bar, $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol, 5 mol%), indole **1a** (117.1 mg, 1 mmol), followed by successive addition of THF (2 mL), allyl alcohol **2a** (87.12 mg, 102 μL, 1.5 mmol, 1.5 equiv), Et_3B (0.3 mL of 1 M hexane solution, 0.3 mmol) via syringe. The resultant mixture was stirred 50 °C for 15 h. The reaction mixture was diluted with EtOAc and vortexed the resultant mixture. Final washing was done with sat. $NaHCO_3$ and with brine. The recovered organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (R*f* = 0.47; EtOAc:Hexane = 1:10, v/v) to get analytically pure product **3a** (127.3 mg, 81%) as pale yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (s, 1H), 6.13 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.22 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.13 (dq, *J* = 10.0, 1.5 Hz, 1H), 3.58 (dq, *J* = 6.5, 1.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.4, 127.4, 122.0, 121.6, 119.2, 119.1, 115.2, 114.5, 111.0, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0968.

3.2. Synthesis of 1-Allyl-1*H*-indole (3b)[2]:



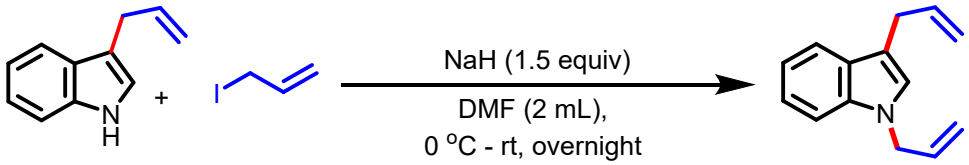
To a well cleaned tube equipped with a stir bar containing DMF (2 mL) solution of indole (117.15 mg, 1 mmol) was added NaH (60% dispersion in mineral oil, 60 mg, 1.5 mmol, 1.5 equiv) at 0 °C. The reaction mixture was allowed to stirred at the same temperature for 20 min, followed by addition of allyl iodide (251.97 mg, 137.2 μL, 7.5 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature until consumption of starting material (detected by TLC). The reaction mixture was quenched with ammonium chloride solution and diluted with EtOAc. Final washing was done with brine. The recovered organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (EtOAc:Hexane = 1:20, v/v) The recovered organic layer was dried

[1]*J. Am. Chem. Soc*. **2005**, *127*, 4592-4593; [2]*Org. Lett*. **2019**, *21*, 3067-3071.

over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were

adsorbed on silica gel and pass through the column (EtOAc:Hexane = 1:20, v/v) to get analytically pure product **3b** (144.63 mg, 92%) as orange liquid; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 – 7.12 (m, 2H), 6.56 (d, J = 3.2 Hz, 1H), 6.08 – 5.99 (m, 1H), 5.23 (dt, J = 10.3, 1.5 Hz, 1H), 5.12 (dt, J = 17.1, 1.5 Hz, 1H), 4.80 – 4.75 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.1, 133.5, 128.7, 127.8, 121.5, 121.0, 119.4, 117.3, 109.6, 101.4, 48.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0970.

3.3 Synthesis of 1,3-Diallyl-1*H*-indole (3c)[2]:



1a **3a** **3c**; 95%

To a well cleaned tube equipped with a stir bar containing DMF (1 mL) solution of indole (157.21 mg, 1 mmol) was added NaH (60% dispersion in mineral oil, 60 mg, 1.5 mmol, 1.5 equiv) at 0 °C. The reaction mixture was allowed to stirred at the same temperature for 20 min, followed by addition of allyl iodide (251.97 mg, 137.2 μL, 7.5 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature until complete consumption of starting material (detected by TLC). The reaction mixture was quenched with ammonium chloride solution and diluted with EtOAc. Final washing was done with brine. The recovered organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (EtOAc:Hexane = 1:20, v/v) The recovered organic layer was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (EtOAc:Hexane = 1:20, v/v) to get analytically pure product **3b** (187.4 mg, 95%) as orange liquid; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 (dd, J = 8.0, 1.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.19 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.09 (ddd, J = 7.9, 6.8, 1.0 Hz, 1H), 6.88 (s, 1H), 6.11 – 5.93 (m, 2H), 5.21 – 5.03 (m, 4H), 4.67 (dt, J = 5.4, 1.7 Hz, 2H), 3.52 (dq, J = 6.5, 1.4 Hz, 2H).; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.4, 136.6, 133.7, 128.0, 125.4, 121.6, 119.2, 118.8, 117.1, 115.1, 113.3, 109.5, 48.7, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{14}H_{16}N^+$ 198.1277, Found 198.1280.

[2] *Org. Lett.* **2019**, *21*, 3067-3071.

4. GC-MS studies

Sample preparation:

Reactions were kept on 0.2 mmole scale and after 18 h, 500 µL of EtOAc was added and vigorously vortex. The biphasic layers were allowed to separate. From the upper organic layer, 20 µL containing reaction mixture was pipetted out and mixed with 1 mL of LC-MS grade methanol. The solution was vortexed for uniformity and then filtered through Fluoropore Membrane Filter (MF-Millipore™, 0.22 µm pore size, hydrophobic PTFE, 47 mm membrane). The filtrate collected was transferred into 1.5 ml GC-glass vial and was analyzed on the developed method. The blank vial containing LC-MS grade methanol was filtered in similar manner before injecting.

Method development:

The method development was done using GC-MS (Agilent Technologies; see General Methods) by optimising the critical parameter such as detector, column, carrier gas, chromatographic conditions and mass specifications which are discussed below.

1. Injection/Inlet conditions: SSL (Split Splitless) was selected with Split ratio: 20:1. The sample was passed through injector temperature (Heater temperature) 250 °C with help of helium (He) carrier gas having gas flow of 1 mL/ min.
2. Selection of column: Agilent 19091S-433UI: 0602217H. Dimensions (30m x 250 µm x 0.25 µm) containing (5%-phenyl)-methylpolysiloxane column was used. The oven condition is as below:

	Rate (°C/ min)	Value (°C)	Hold time (Min)	Run Time (Min)
Initial	-	50	2	2
Ramp 1	35	200	3	9.2857
Ramp 2	20	225	1	11.536

   Total program time 11.536 min; Post run: 2 min at 260 °C was done to remove any impurities from the column with high boiling point.
   Aux Heater: MSD Transfer line Temperature: 270 °C was kept.
3. Detector: FID (Flame Ionization Detector) was utilized with H_2: Air (1:10) as ignition fuel
4. Mass Parameter:
   Electron energy: 70 eV
   Source Temperature: 260 °C
   Scan Type: MS1 scan
   Solvent delay: 1.5 min
   Scanning mass range: 30-400 m/z
5. Data Acquisition/Interpretation: Agilent qualitative analysis Mass Hunter 10.0 was used

Chromatogram:

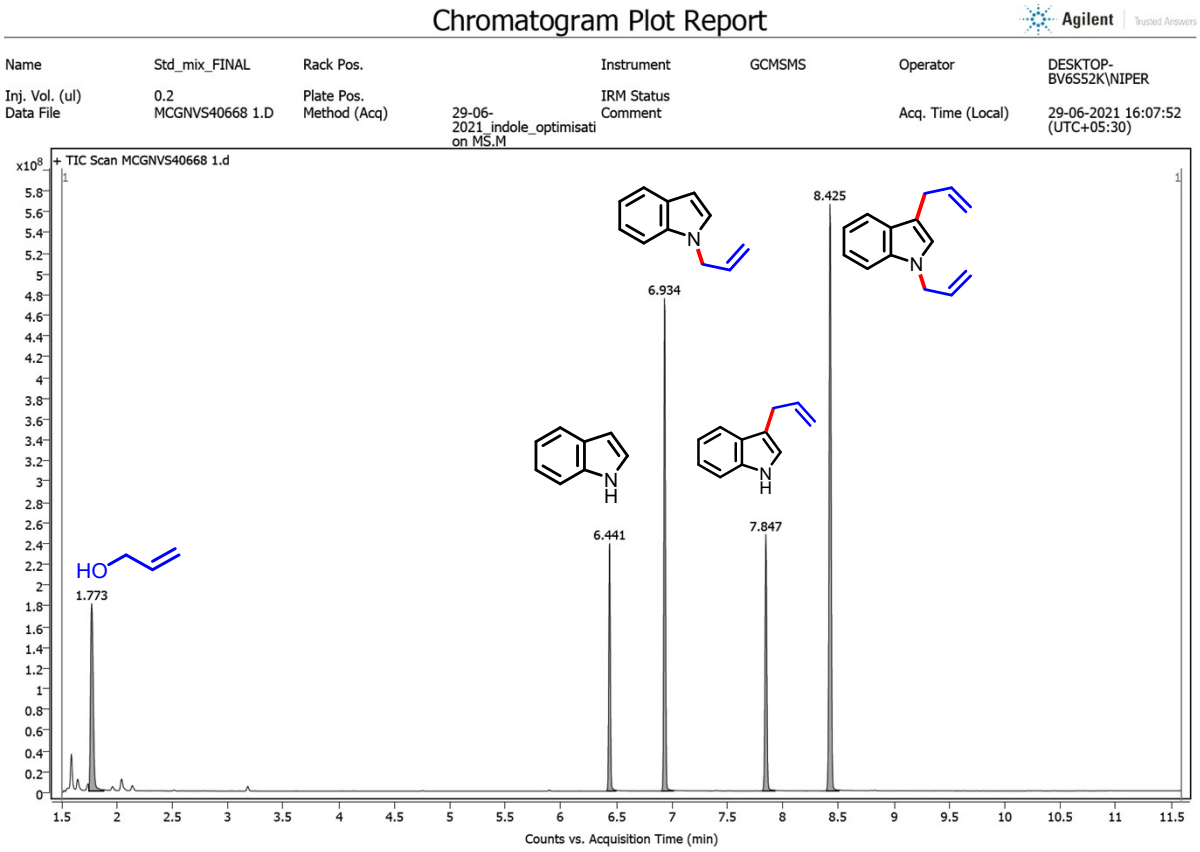


Figure S4. Representative chromatograms with developed method on GC-MS having all the desired peak with their retention time (physical mixture of individual standards)

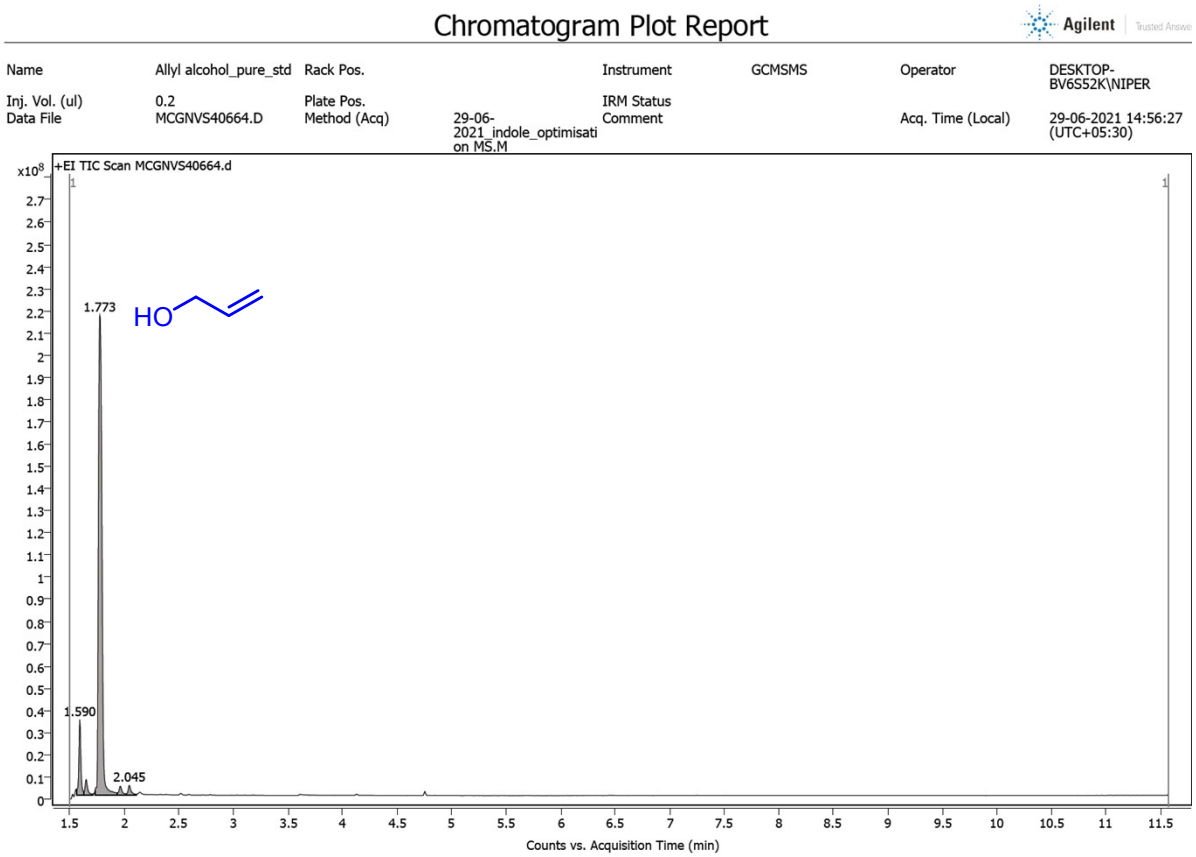


Figure S5. Chromatogram with the retention time of allyl alcohol (2a)

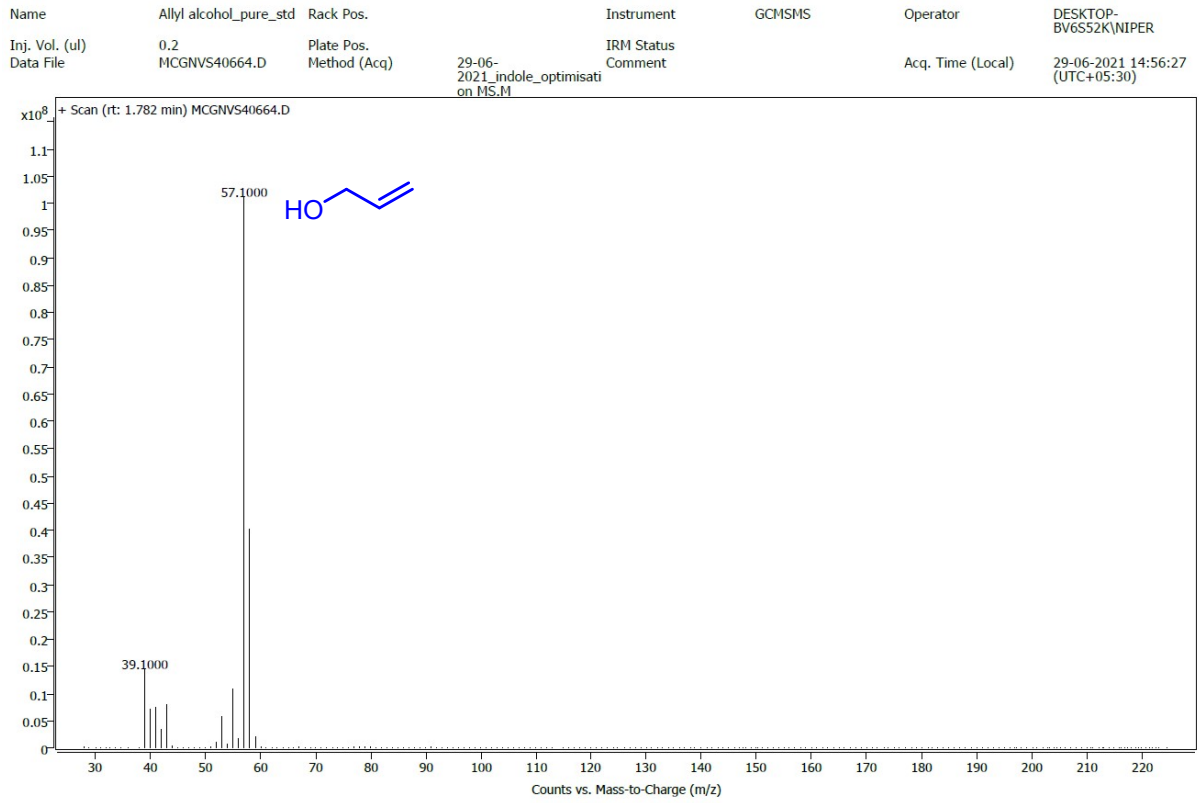


Figure S6. Mass spectra of allyl alcohol (2a)

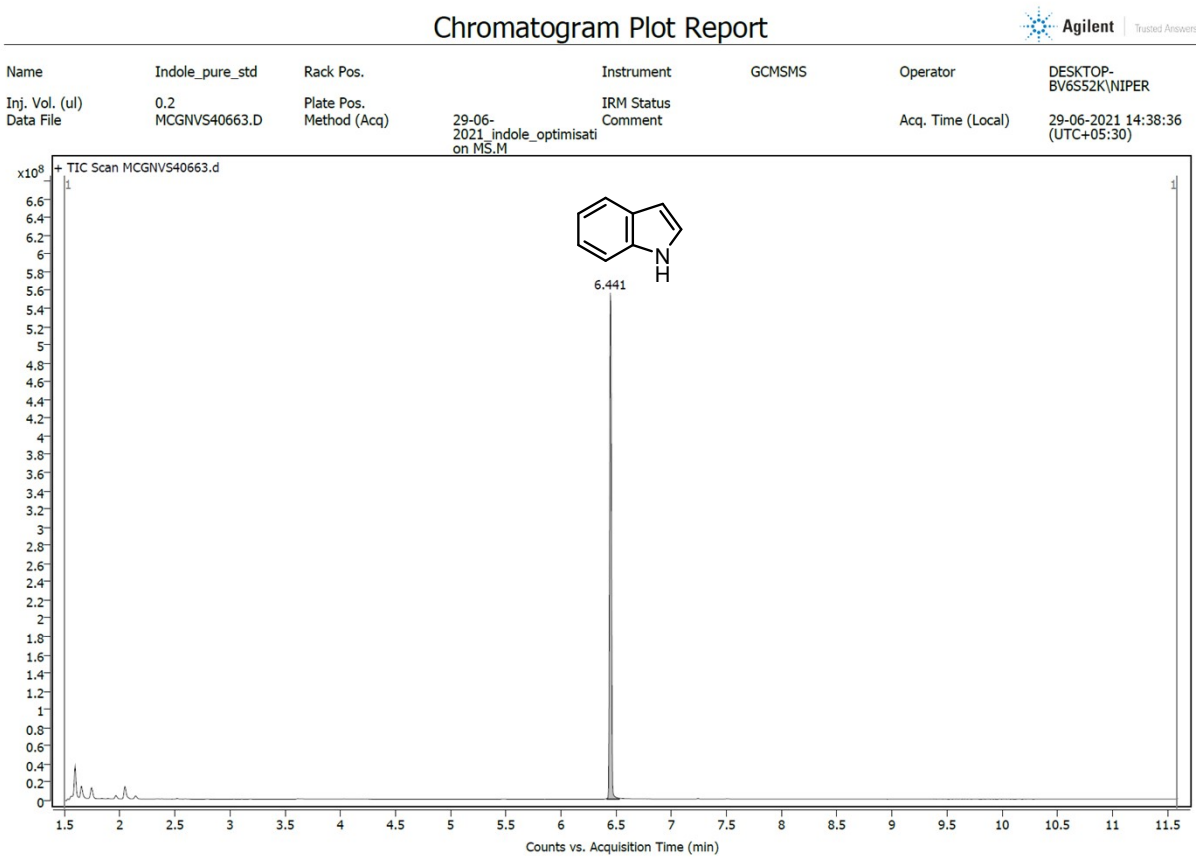


Figure S7. Chromatogram with the retention time of allyl alcohol (1a)

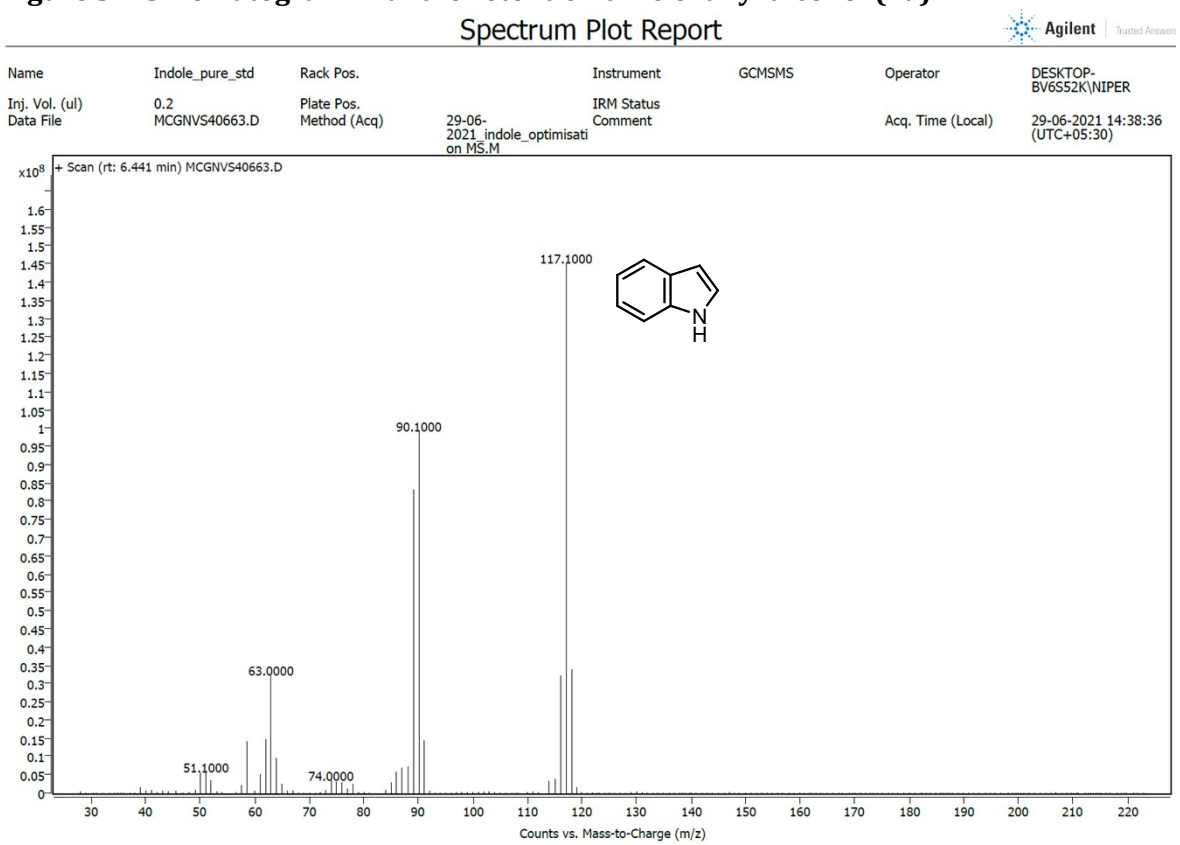


Figure S8. Mass spectra of indole (1a)

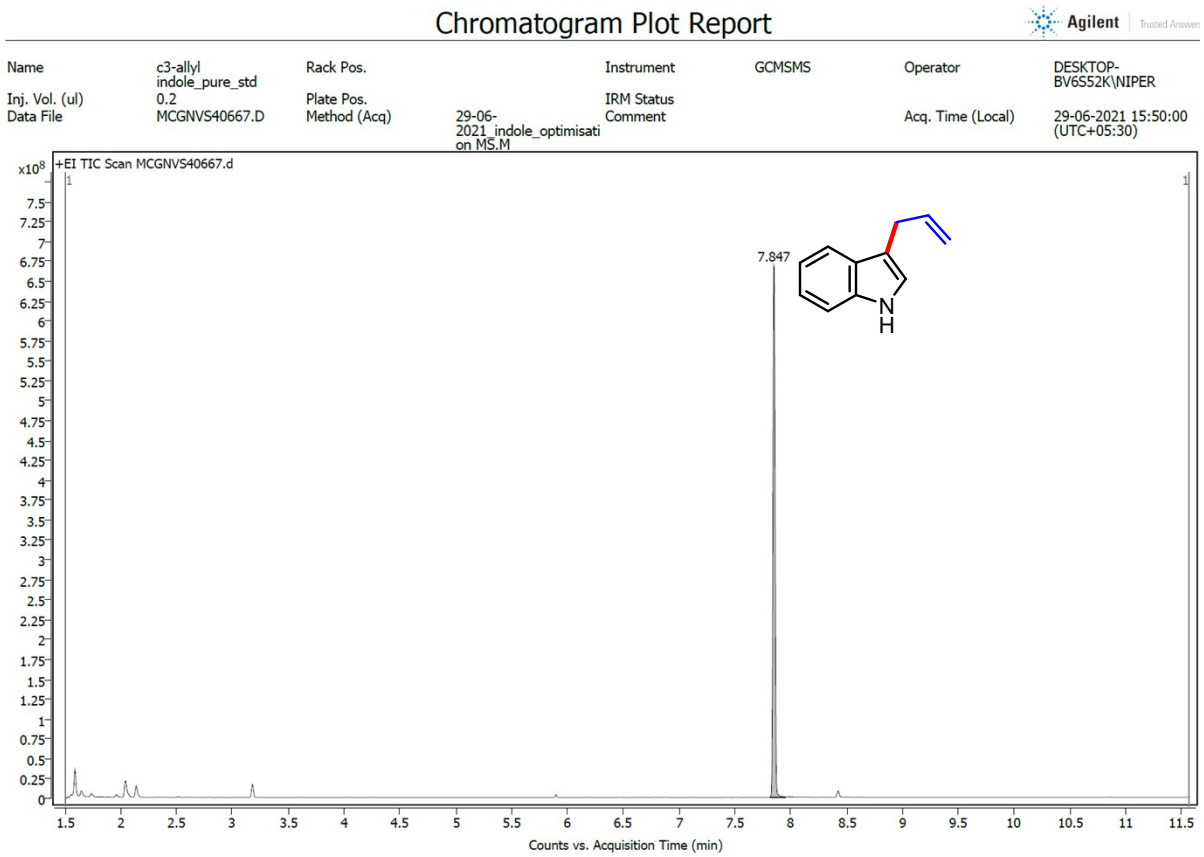


Figure S9. Chromatogram with the retention time of 3-Allyl-1*H*-indole (3a)

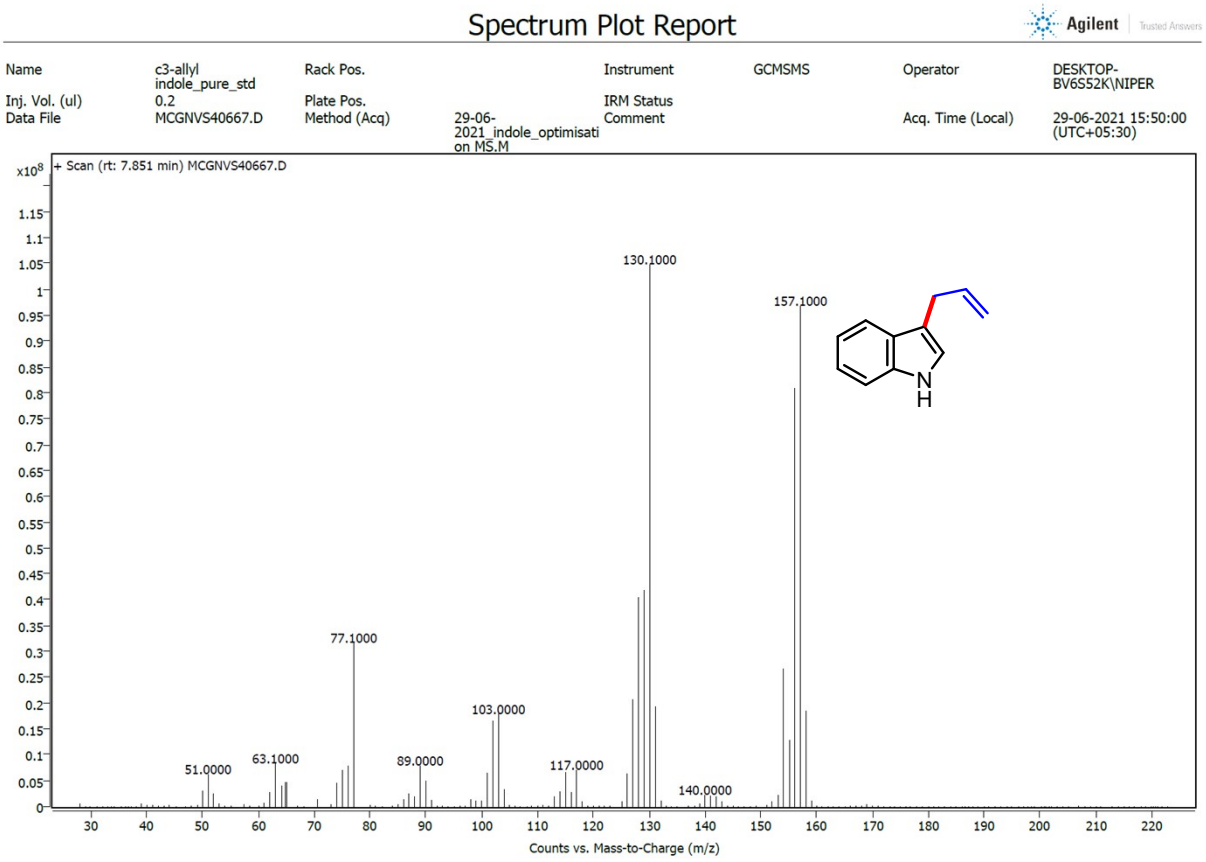


Figure S10. Mass spectra of 3-Allyl-1*H*-indole (3a)

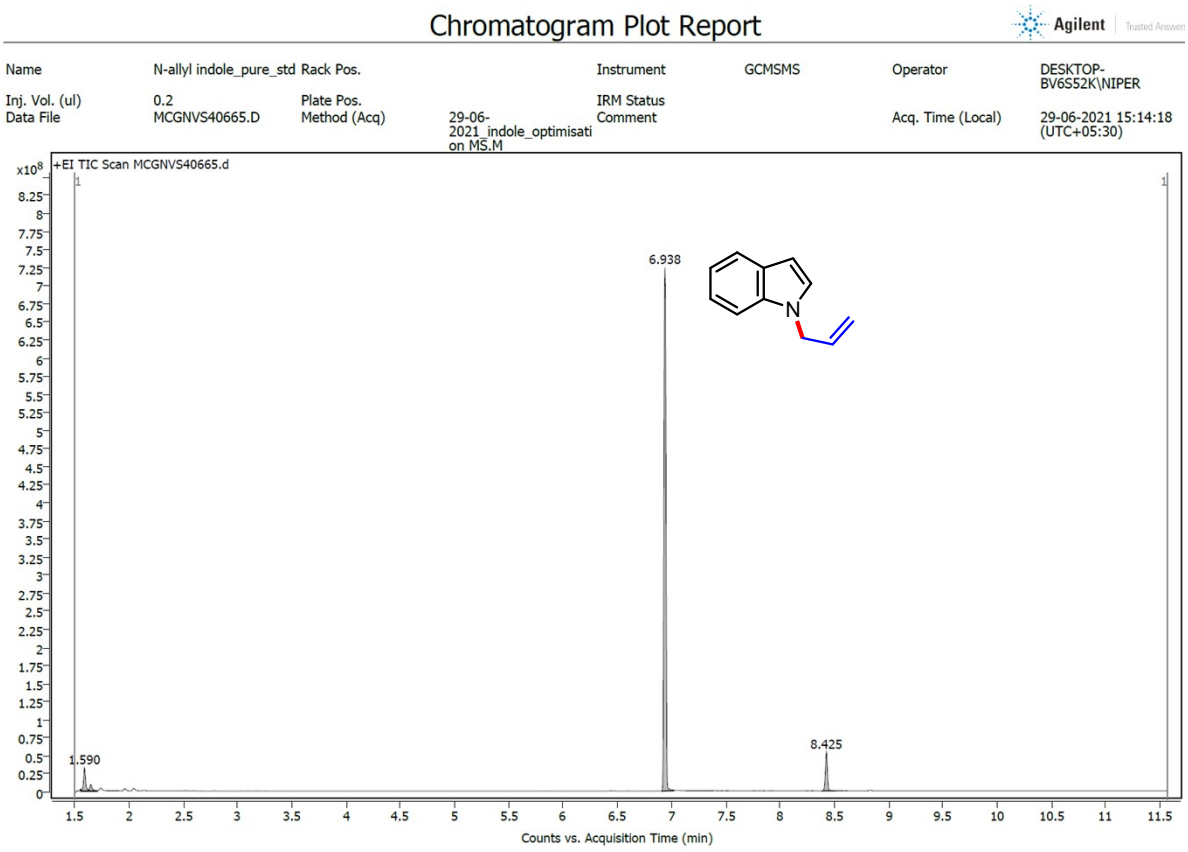


Figure S11. Chromatogram with the retention time of 1-Allyl-1*H*-indole (3b)

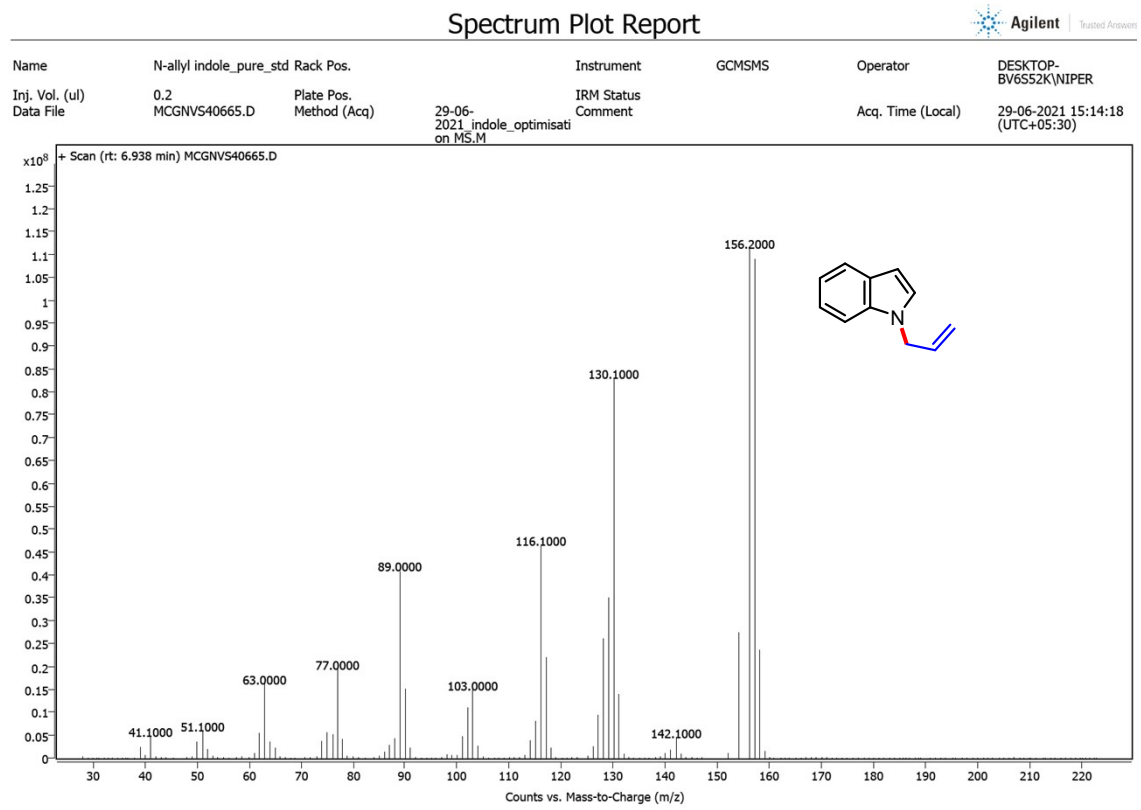


Figure S12. Mass spectra of 1-Allyl-1*H*-indole (3b)

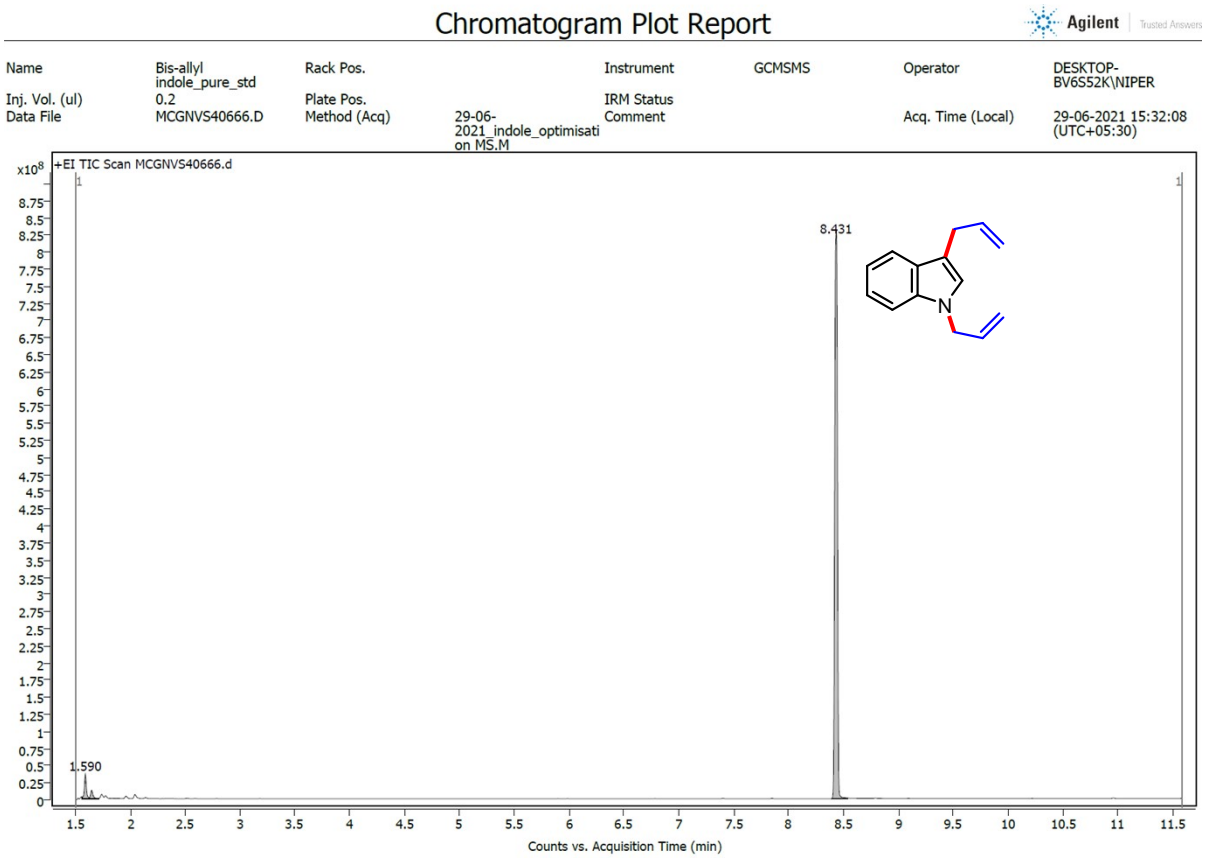


Figure S13. Chromatogram with the retention time of 1,3-Diallyl-1*H*-indole (3c)

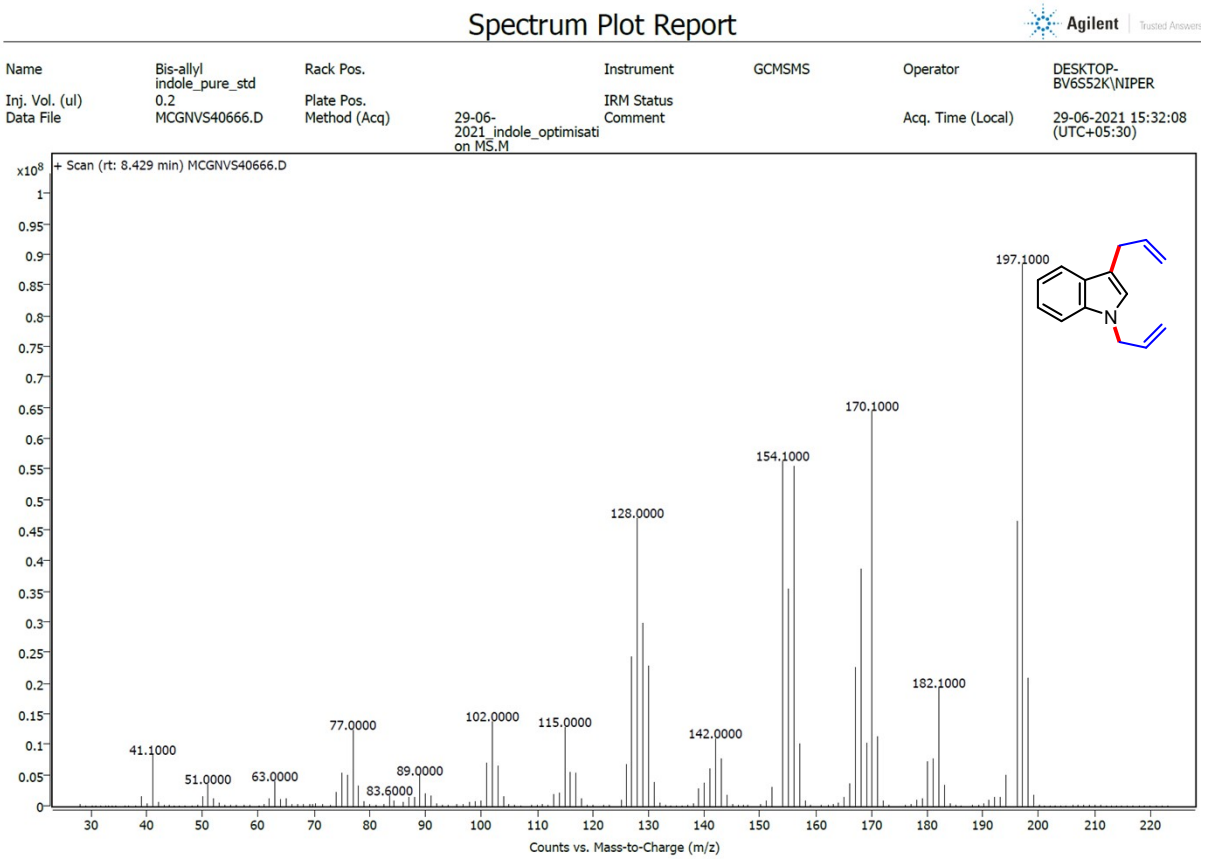


Figure S14. Mass spectra of 1,3-Diallyl-1*H*-indole (3c)

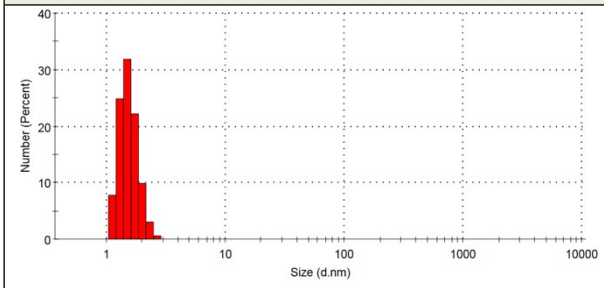
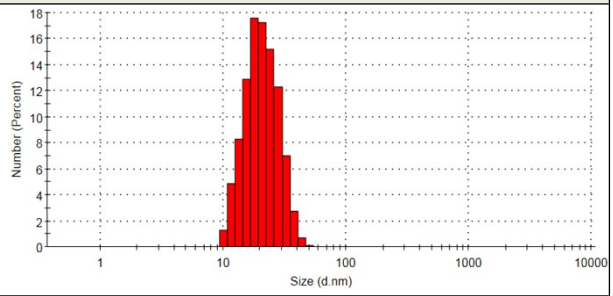
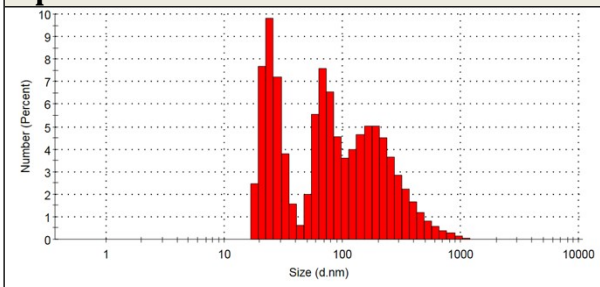
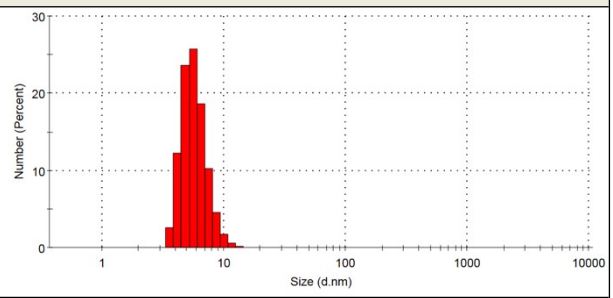
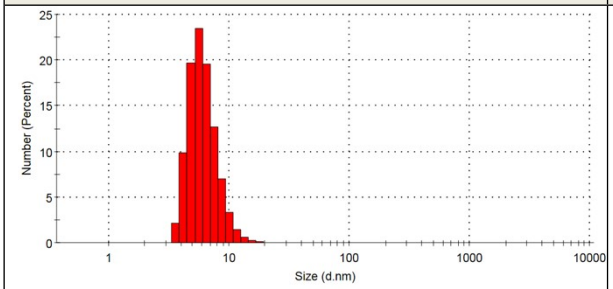
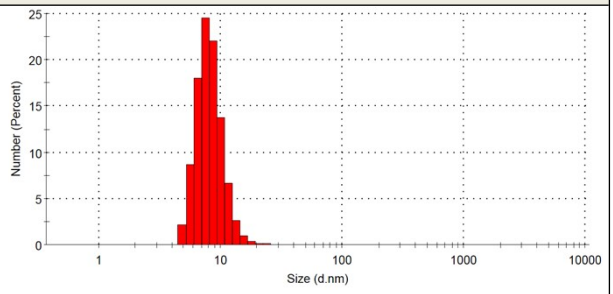
5. Zeta-sizer study: Average micellar size for different surfactants

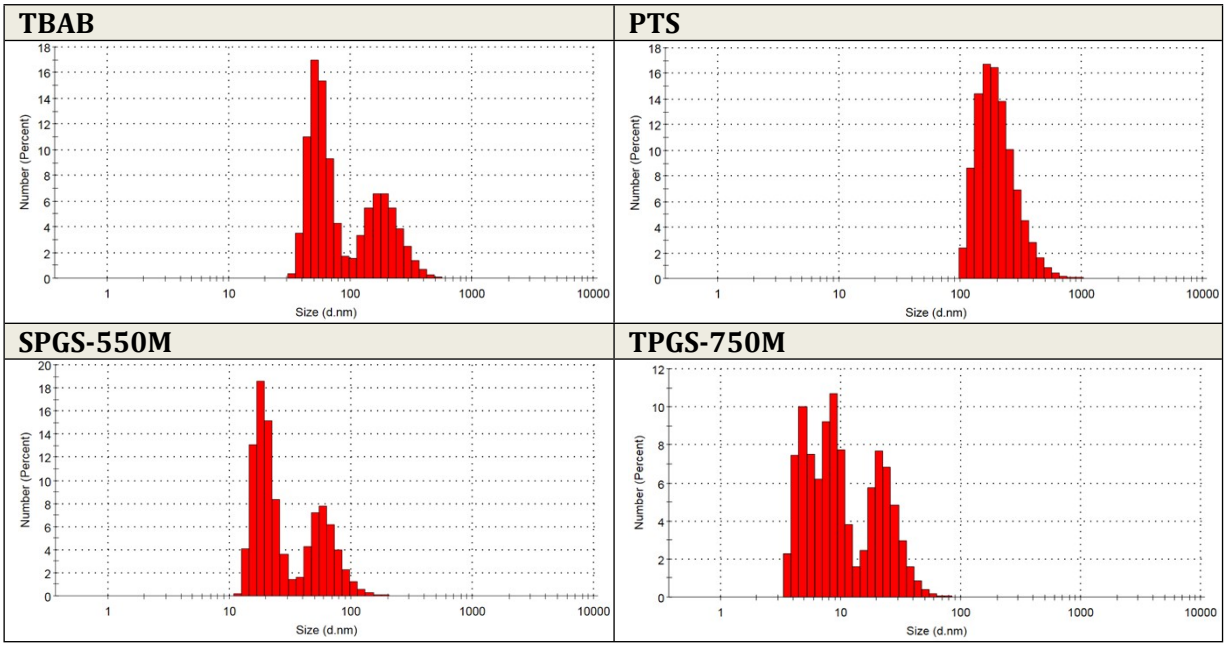
Average particle size and Particle Distribution Index (**PDI,** a representation of the distribution of size populations within a given sample) of the reaction mixture containing the micellar solution was determined using the Zetasizer (See, General Methods)

Sample preparation:

About 0.5 mL of freshly prepared aqueous solutions (2% w/w) of different surfactants were pipetted out and diluted one time (1x) with miliQ water in microcentrifuge tube. This was further filtered through Fluoropore Membrane Filter (MF-Millipore™, 0.22 µm pore size, hydrophobic PTFE, 47 mm membrane). The filtrate collected were used as final sample. All the sample measurements were made at 25 ± 2 °C in triplicate using disposable cuvette, and the results were analyzed using Zetasizer 633 nm and angle (173°).

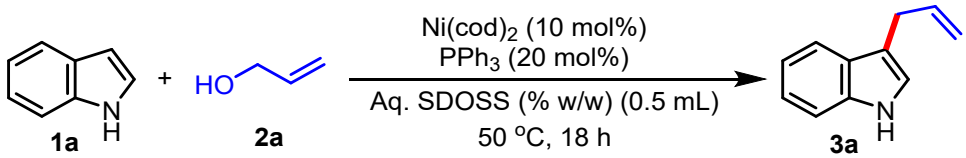
Table S1. Particle size distribution (PSD) of various surfactants (2% w/w)

SDS	**SDOSS**
	
Span-80	**Tween-80**
	
TritonX100	**HPMC**
	



6. Effect of SDOSS concentration

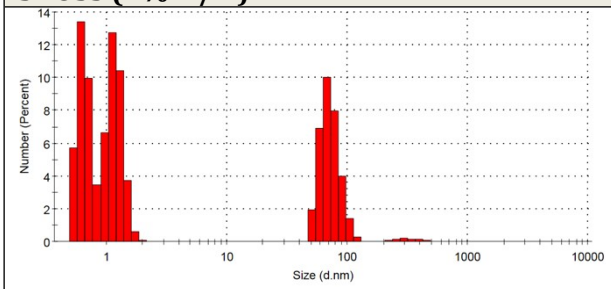
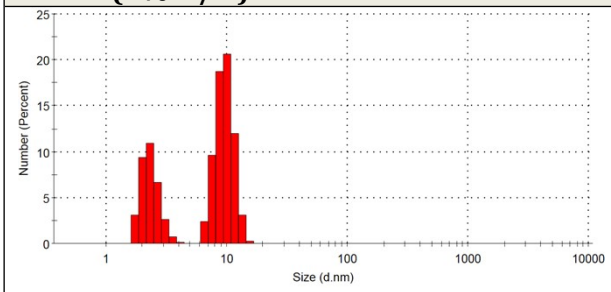
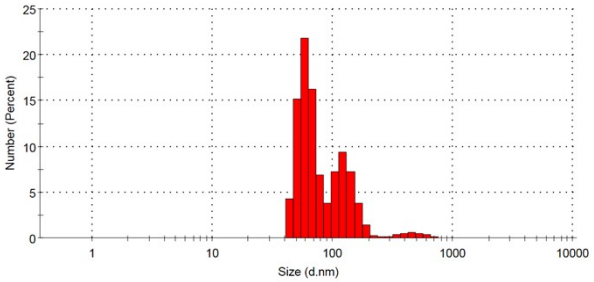
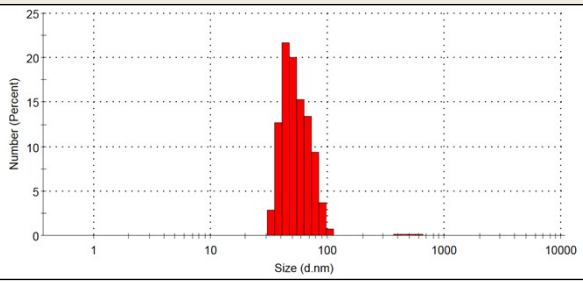
Table S2: **Concentration-dependent SDOSS study**.[a]



Entry	SDOSS (w/w%)	Av. Micellar size [b] (nm)	Yield (%)[c] **3a**
1	1	809	63
2	2	402.0	98
3	4	2116	93
4	6	1136	74
5	8	1621	84

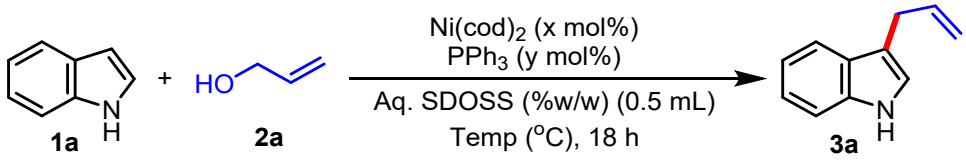
[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in different concentrations of Aq. SDOSS (% w/w) (0.5 mL) in presence of $Ni(cod)_2$ (10 mol%), PPh_3 (20 mol%) at 50 °C for 24 h. [b]Average micellar size (nm) was determined from three runs on zeta sizer. [c]GC-MS yields.

Table S3. Particle size distribution (PSD) of SDOSS at different concentrations (% w/w)

SDOSS (1% w/w)	SDOSS (2% w/w)
	
SDOSS (4% w/w)	**SDOSS (6% w/w)**
	
SDOSS (8% w/w)	
	

7. Optimization study

Table S4. Optimization of reaction conditions.[a]



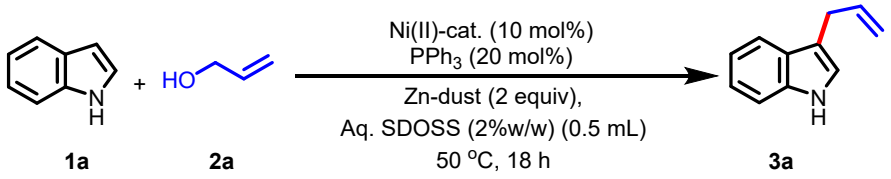
1a **2a** **3a**

Entry	$Ni(cod)_2$ (mol%)	PPh_3 (mol%)	Temperature (°C)	Yield (%)[b] **3a**
1	10	20	50	98(86)[c]
2	8	20	50	84
3	7.5	20	50	70
4	5	20	50	49
5	10	18	50	85
8	10	16	50	72
9	10	14	50	67
10	10	12	50	62
11	10	20	rt	traces[d]

[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in Aq. SDOSS (2% w/w, 0.5 mL) in presence of $Ni(cod)_2$ – PPh_3 under different reaction conditions. [b]GC-MS yield of **3a**. [c]Isolated yield after 18 h.

8. Screening of Ni(II)-Catalyst for C_3-allylation

Table S5. Screening Ni(II)-catalyst under optimized condition [a]

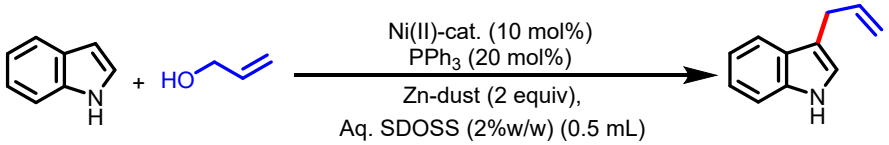


1a **2a** **3a**

Entry	Ni(II)-cat. (10 mol%)	Yield (%)[b] **3a**
1	NiF_2	0[c]
2	$NiCl_2$	0[c]
3	$NiBr_2$	0[c]
4	NiI_2	0[c]
5	$NiCl_2$ glyme	0[c]
6	$Ni(acac)_2$	0[c]
7	$dppeNiCl_2$	0[c]
8	$Ni(PPh_3)_2Cl_2$	0[c]

[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in Aq. SDOSS (2% w/w, 0.5 mL) in presence of Ni(II)-cat (10 mol%), PPh_3 (20 mol%) and zinc dust (2 equiv) at 50 °C for 18 h. [b]GC-MS yield of **3a**. [c]**1a** remained intact.

Table S6. Screening Ni(II)-catalyst under optimized condition at elevated temperature condition [a]

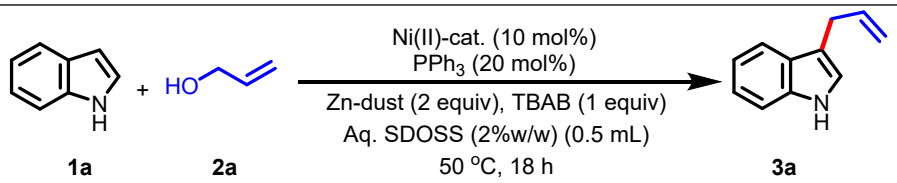


1a **2a** **3a**

Entry	Ni(II)-cat. (10 mol%)	Yield (%)[b] **3a**
1	NiF_2	0[c]
2	$NiCl_2$	0[c]
3	$NiBr_2$	0[c]
4	NiI_2	0[c]
5	$NiCl_2$ glyme	0[c]
6	$Ni(acac)_2$	0[c]
7	$dppeNiCl_2$	0[c]
8	$Ni(PPh_3)_2Cl_2$	0[c]

[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in Aq. SDOSS (2% w/w, 0.5 mL) in presence of Ni(II)-cat (10 mol%), PPh_3 (20 mol%) and zinc dust (2 equiv) at 100 °C for 18 h. [b]GC-MS yield of **3a**. [c]**1a** remained intact.

Table S7. Screening Ni(II)-catalyst under optimized condition in presence of TBAB [a]

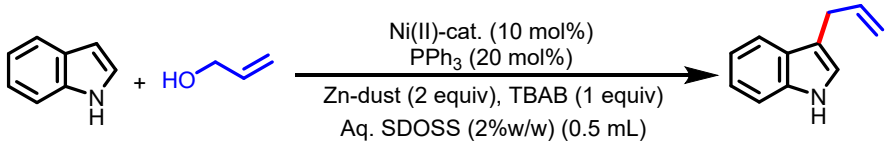


1a **2a** **3a**

Entry	Ni(II)-cat. (10 mol%)	Yield (%)[b] **3a**
1	NiF_2	0[c]
2	$NiCl_2$	0[c]
3	$NiBr_2$	0[c]
4	NiI_2	0[c]
5	$NiCl_2$ glyme	0[c]
6	$Ni(acac)_2$	0[c]
7	$dppeNiCl_2$	0[c]
8	$Ni(PPh_3)_2Cl_2$	0[c]

[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in Aq. SDOSS (2% w/w, 0.5 mL) in presence of Ni(II)-cat (10 mol%), PPh_3 (20 mol%), zinc dust (2 equiv) and TBAB (1 equiv) at 50 °C for 18 h. [b]GC-MS yield of **3a**. [c]**1a** remained intact..

Table S8. Screening Ni(II)-catalyst under optimized condition at elevated temperature condition in presence of TBAB [a]



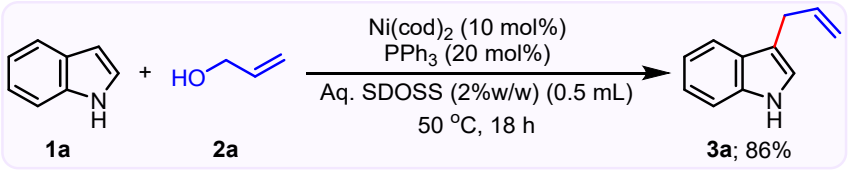
1a **2a** **3a**

Entry	Ni(II)-cat. (10 mol%)	Yield (%)[b] **3a**
1	NiF_2	0[c]
2	$NiCl_2$	0[c]
3	$NiBr_2$	0[c]
4	NiI_2	0[c]
5	$NiCl_2$ glyme	0[c]
6	$Ni(acac)_2$	0[c]
7	$dppeNiCl_2$	0[c]
8	$Ni(PPh_3)_2Cl_2$	0[c]

[a]**1a** (0.2 mmol) was treated with **2a** (0.3 mmol, 1.5 equiv) in Aq. SDOSS (2% w/w, 0.5 mL) in presence of Ni(II)-cat (10 mol%), PPh_3 (20 mol%), zinc dust (2 equiv) and TBAB (1 equiv) at 100 °C for 18 h. [b]GC-MS yield of **3a**. [c]**1a** remained intact.

9. Representative experimental procedure

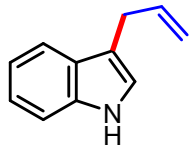
General procedure for the *N*-allylation using allyl alcohols under aqueous micellar nickel-catalysis:



To a well cleaned tube equipped with a stir bar, $Ni(cod)_2$ (5.1 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), indole **1a** (23.5 mg, 0.2 mmol), allyl alcohol **2a** (17.4 mg, 20.1 μL, 0.3 mmol, 1.5 equiv), and Aq. SDOSS (2% w/w, 0.5 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with EtOAc (2 X 0.5 mL), vortexed and subjected to aqueous workup. Final washing was done using brine solution. The organic liquid containing product and other organic residue was removed carefully and was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (R*f* = 0.47; EtOAc:Hexane = 1:10, v/v) to get analytically pure product **3a** as pale yellow liquid (27.0 mg, 86%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ δ 7.94 (br s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (s, 1H), 6.13 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.22 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.13 (dq, *J* = 10.0, 1.5 Hz, 1H), 3.58 (dq, *J* = 6.5, 1.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.4, 127.4, 122.0, 121.6, 119.2, 119.1, 115.2, 114.5, 111.0, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0968.

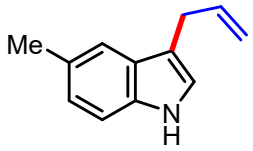
10. Spectroscopic characterization data

3-Allyl-1*H*-indole (3a): Pale yellow liquid (27.0 mg, 86%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ



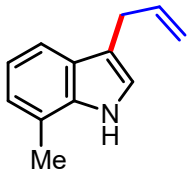
δ 7.94 (br s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.39 (dt, J = 8.2, 0.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (s, 1H), 6.13 (ddt, J = 16.6, 10.0, 6.5 Hz, 1H), 5.22 (dq, J = 17.0, 1.7 Hz, 1H), 5.13 (dq, J = 10.0, 1.5 Hz, 1H), 3.58 (dq, J = 6.5, 1.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.4, 127.4, 122.0, 121.6, 119.2, 119.1, 115.2, 114.5, 111.0, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0968.

3-Allyl-5-methyl-1*H*-indole (4a): Yellow liquid (28.7 mg, 84%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ



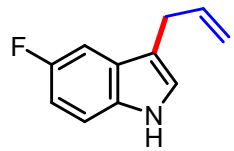
7.83 (br s, 1H), 7.38 (s, 1H), 7.23 (dd, J = 8.4, 1.5 Hz, 1H), 7.01 (dd, J = 8.2, 1.9 Hz, 1H), 6.94 (s, 1H), 6.14 – 5.99 (m, 1H), 5.21 – 5.11 (m, 1H), 5.06 (d, J = 10.0 Hz, 1H), 3.49 (dt, J = 6.5, 1.3 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.4, 134.8, 128.5, 127.7, 123.6, 121.8, 118.7, 115.1, 114.0, 110.8, 29.8, 21.6; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}N^+$ 172.1121, Found 172.1122.

3-Allyl-7-methyl-1*H*-indole (4b): Yellow liquid (29.5 mg, 86%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ



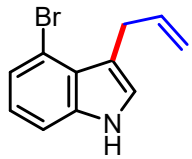
7.83 (br s, 1H), 7.50 – 7.41 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.06 (ddt, J = 16.6, 10.0, 6.5 Hz, 1H), 5.15 (dq, J = 17.0, 1.7 Hz, 1H), 5.06 (dq, J = 10.0, 1.6 Hz, 1H), 3.52 (dq, J = 6.4, 1.4 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.0, 127.0, 122.5, 121.3, 120.2, 119.5, 116.8, 115.1, 115.1, 29.9, 16.6.; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}N^+$ 172.1121, Found 172.1130.

3-Allyl-5-fluoro-1*H*-indole (4c): Dark brown liquid (29.4 mg, 84%); **^{1}H NMR** (500 MHz, $CDCl_3$):



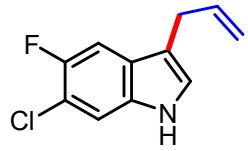
δ 7.97 (br s, 1H), 7.31 – 7.26 (m, 2H), 7.06 (s, 1H), 7.00 – 6.95 (m, 1H), 6.11 – 6.03 (m, 1H), 5.19 (dt, J = 17.1, 1.8 Hz, 1H), 5.12 (dt, J = 10.0, 1.7 Hz, 1H), 3.51 (d, J = 6.4 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.7 (d, J = 234.3 Hz), 136.9, 132.9, 127.8 (d, J = 9.7 Hz), 123.5, 115.5, 114.7 (d, J = 4.9 Hz), 111.7 (d, J = 9.7 Hz), 110.4 (d, J = 26.3 Hz), 104.1 (d, J = 23.4 Hz), 29.8; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -124.76; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{11}NF^+$ 176.0870, Found 176.0870.

3-Allyl-4-bromo-1*H*-indole (4d): Blackish-brown liquid (30.7 mg, 65%); **^{1}H NMR** (500 MHz,

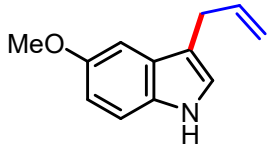


$CDCl_3$): δ 8.05 (br s, 1H), 7.32 – 7.26 (m, 2H), 7.09 – 6.90 (m, 2H), 6.28 – 6.07 (m, 1H), 5.10 (dq, J = 14.0, 1.9 Hz, 2H), 3.84 (dq, J = 6.4, 1.4 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.0, 136.7, 124.4, 122.9, 122.4, 121.8, 114.8, 114.3, 113.4, 109.4, 29.7; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{11}BrN^+$ 236.0069, Found 236.0073.

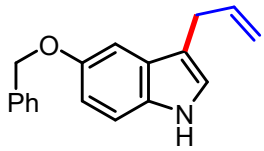
3-Allyl-6-chloro-5-fluoro-1*H*-indole (4e): Yellow liquid (32.3 mg, 77%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.35 (d, J = 6.1 Hz, 1H), 7.30 (d, J = 9.7 Hz, 1H), 7.02 (d, J = 2.3 Hz, 1H), 6.01 (ddt, J = 16.6, 10.0, 6.4 Hz, 1H), 5.14 (dq, J = 17.0, 1.7 Hz, 1H), 5.09 (dq, J = 10.0, 1.5 Hz, 1H), 3.50 – 3.36 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.8 (d, J = 237.6 Hz), 136.6, 132.6, 126.4 (d, J = 8.6 Hz), 123.9, 115.7 (d, J = 21.4 Hz), 115.7, 114.8 (d, J = 4.6 Hz), 112.2, 105.2 (d, J = 23.2 Hz), 29.7; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -127.10; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{10}ClFN^+$ 210.0480, Found 210.0486.



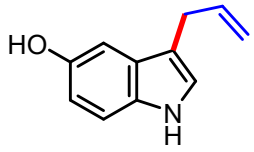
3-Allyl-5-methoxy-1*H*-indole (4f): Pale yellow liquid (32.9 mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (br s, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 2.5 Hz, 1H), 6.96 (dd, J = 2.4, 1.1 Hz, 1H), 6.85 (dd, J = 8.8, 2.5 Hz, 1H), 6.06 (ddt, J = 16.6, 10.0, 6.5 Hz, 1H), 5.20 – 5.12 (m, 1H), 5.16 (dq, J = 17.1, 1.8 Hz, 1H), 5.07 (dq, J = 10.0, 1.5 Hz, 1H), 3.85 (s, 3H), 3.49 (dq, J = 6.5, 1.4 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.9, 137.2, 131.6, 127.8, 122.5, 115.2, 114.2, 112.2, 111.8, 101.0, 55.9, 29.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}NO^+$ 188.1070, Found 188.1071.



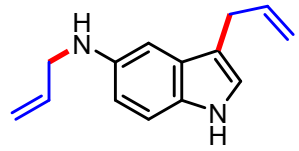
3-Allyl-5-(benzyloxy)-1*H*-indole (4g): Pale yellow liquid (41.6 mg, 79%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (br s, 1H), 7.45 (dd, J = 7.2, 2.3 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.24 (m, 1H), 7.15 – 7.04 (m, 2H), 6.90 (dt, J = 8.7, 2.1 Hz, 1H), 6.82 (s, 1H), 6.10 – 5.93 (m, 1H), 5.17 – 5.10 (m, 1H), 5.12 – 5.00 (m, 2H), 3.49 – 3.39 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.1, 137.8, 137.3, 131.9, 128.7, 127.9 (d, J = 4.6 Hz), 127.8, 122.8, 122.8, 115.3, 114.1, 112.9, 112.0, 102.9, 71.2, 30.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{18}H_{18}NO^+$ 264.1383, Found 264.1387.



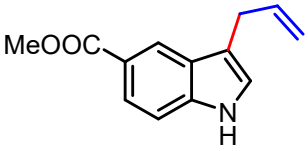
3-Allyl-1*H*-indol-5-ol (4h): Black liquid (23.5 mg, 68%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (br s, 1H), 7.21 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 12.7 Hz, 2H), 6.76 (dd, J = 8.6, 2.4 Hz, 1H), 6.11 – 5.98 (m, 2H), 5.15 (d, J = 17.0 Hz, 1H), 5.07 (d, J = 10.0 Hz, 1H), 4.59 (br s, 1H), 3.53 – 3.38 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.2, 137.2, 131.8, 128.2, 122.9, 115.2, 113.9, 111.7, 111.7, 103.7, 29.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}NO^+$ 174.0913, Found 174.0915.



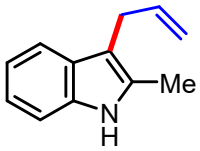
***N*,3-diallyl-1*H*-indol-5-amine (4i):** Brown liquid (27.6 mg, 65%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78 (br s, 1H), 7.15 (d, J = 8.6 Hz, 1H), 6.93 – 6.76 (m, 2H), 6.63 (dd, J = 8.6, 2.2 Hz, 1H), 6.17 – 5.90 (m, 2H), 5.31 (dq, J = 17.2, 1.6 Hz, 1H), 5.21 – 5.12 (m, 2H), 5.05 (dq, J = 10.0, 1.4 Hz, 1H), 3.81 (dt, J = 5.5, 1.6 Hz, 2H), 3.45 (dq, J = 6.4, 1.3 Hz, 2H), 3.15 (br s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 141.7, 137.4, 136.1, 130.8, 128.2, 122.1, 116.1, 115.0, 113.5, 112.2, 111.7, 101.3, 48.2, 29.9; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{14}H_{17}N_2^+$ 213.1386, Found 213.1390.



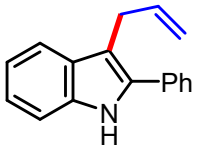
Methyl-3-allyl-1*H*-indole-5-carboxylate (4j): White solid (31.0 mg, 72%); mp: 104 – 106 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.34 (br s, 1H), 8.16 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.83 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.64 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.18 (dd, *J* = 2.2, 1.1 Hz, 1H), 6.09 (ddt, *J* = 16.5, 10.0, 6.4 Hz, 1H), 5.18 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.12 (dq, *J* = 10.0, 1.5 Hz, 1H), 3.96 (s, 3H), 3.56 (dq, *J* = 6.4, 1.4 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 168.3, 136.8, 135.7, 131.0, 125.2, 123.7, 120.3, 118.7, 115.6, 115.0, 113.5, 52.0, 29.6; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{13}H_{14}NO_2^+$ 216.1019, Found 216.1021.



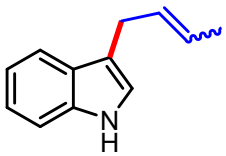
3-Allyl-2-methyl-1*H*-indole (4l): Pale yellow liquid (24.6 mg, 72%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.70 (br s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.25 (dt, *J* = 8.6, 1.2 Hz, 1H), 7.14 – 7.02 (m, 2H), 5.97 (ddt, *J* = 17.2, 10.0, 6.2 Hz, 1H), 5.05 (dq, *J* = 17.0, 1.8 Hz, 1H), 4.99 (dq, *J* = 10.1, 1.7 Hz, 1H), 3.45 (dt, *J* = 6.1, 1.7 Hz, 2H), 2.35 (s, 3H).; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.4, 135.2, 131.3, 128.7, 121.0, 119.1, 118.2, 114.4, 110.1, 109.3, 28.6, 11.6; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}N^+$ 172.1121, Found 172.1112.



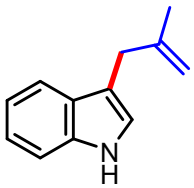
3-Allyl-2-phenyl-1*H*-indole (4m): Pale yellow liquid (32.6 mg, 70%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06 (br s, 1H), 7.63 – 7.54 (m, 3H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 7.7, 5.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.13 (ddt, *J* = 16.3, 10.8, 5.6 Hz, 1H), 5.16 – 5.05 (m, 2H), 3.63 (dt, *J* = 5.7, 1.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.4, 135.9, 134.8, 133.0, 129.4, 128.9, 127.9, 127.7, 122.4, 119.7, 119.4, 115.2, 110.8, 110.5, 29.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{17}H_{16}N^+$ 234.1277, Found 234.1277.



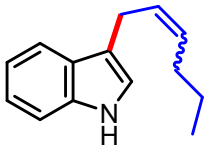
3-(But-2-en-1-yl)-1*H*-indole (5a): (Obtained as mixture: linear: branch in 1.5:1 ratio) Pale yellow liquid (27.4 mg, 80%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (br s, 1H), 7.68 – 7.63 (m, 1H), 7.39 – 7.33 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 (ddt, *J* = 7.0, 6.1, 1.7 Hz, 1H), 6.98 (dt, *J* = 2.3, 1.0 Hz, 1H), 5.81 – 5.69 (m, 1H), 5.68 – 5.60 (m, 1H), 3.49 (dq, *J* = 6.4, 1.3 Hz, 2H), 1.73 (dq, *J* = 6.2, 1.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): 143.3, 136.5, 129.9, 125.7, 122.0, 121.5, 119.2, 112.8, 111.1, 34.9, 28.6, 17.9.; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}N^+$ 172.1121, Found 172.1114.



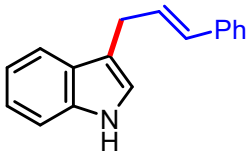
3-(2-Methylallyl)-1*H*-indole (5b): Pale yellow liquid (26.8 mg, 78%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.88 (br s, 1H), 7.61 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.33 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.18 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.10 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 4.82 (ddd, *J* = 7.1, 2.4, 1.2 Hz, 2H), 3.47 (d, *J* = 1.3 Hz, 2H), 1.75 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.1, 136.4, 127.8, 122.3, 121.9, 119.4, 119.2, 114.1, 111.1, 111.1, 34.1, 22.3; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{12}H_{14}N^+$ 172.1121, Found 172.1115.



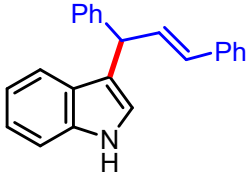
3-(Hex-2-en-1-yl)-1*H*-indole (5c): Pale yellow liquid (31.1 mg, 78%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (br s, 1H), 7.61 (dq, J = 7.9, 0.9 Hz, 1H), 7.33 (dt, J = 8.1, 1.0 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.13 – 7.08 (m, 1H), 6.95 (dt, J = 2.3, 1.0 Hz, 1H), 5.70 – 5.63 (m, 1H), 5.62 – 5.54 (m, 1H), 3.46 (dp, J = 6.6, 1.1 Hz, 2H), 2.04 – 1.97 (m, 2H), 1.39 (h, J = 7.3 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.5, 131.2, 128.7, 127.5, 121.9, 121.4, 119.2, 119.2, 115.7, 111.1, 34.7, 28.7, 22.7, 13.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{14}H_{18}N^+$ 200.1434, Found 200.1431.



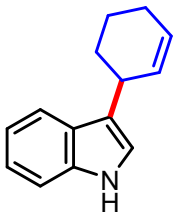
3-Cinnamyl-1*H*-indole (5d): White solid (38.2 mg, 82%); mp: 99 – 101 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.70 – 7.60 (m, 2H), 7.36 (dd, J = 7.5, 1.3 Hz, 3H), 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 2H), 7.14 – 7.08 (m, 1H), 7.02 (dd, J = 2.3, 1.1 Hz, 1H), 3.68 (dt, J = 6.3, 1.1 Hz, 2H).; **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.7, 136.4, 130.4, 129.3, 128.5, 127.5, 127.0, 126.1, 122.1, 121.8, 119.4, 119.2, 114.7, 111.1, 29.0; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{17}H_{16}N^+$ 234.1277, Found 234.1277.



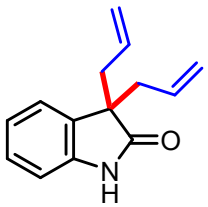
(*E*)-3-(1,3-Diphenylallyl)-1*H*-indole (5e): Orange liquid (42.7 mg, 69%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.82 (br s, 1H), 7.41 (dd, J = 8.0, 1.0 Hz, 1H), 7.36 – 7.31 (m, 4H), 7.30 – 7.24 (m, 5H), 7.23 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 7.01 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.81 (dd, J = 2.5, 1.0 Hz, 1H), 6.70 (dd, J = 15.8, 7.4 Hz, 1H), 6.42 (dd, J = 15.8, 1.3 Hz, 1H), 5.09 (d, J = 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.5, 137.6, 136.7, 132.6, 130.6, 128.6, 128.5, 127.3, 126.9, 126.5, 126.4, 122.7, 122.2, 120.0, 119.5, 118.7, 111.2, 46.3; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{23}H_{20}N^+$ 310.1590, Found 310.1590.



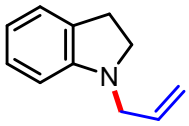
3-(Cyclohex-2-en-1-yl)-1*H*-indole (5f): Pale yellow liquid (31.9 mg, 81%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, J = 7.9 Hz, 1H), 7.60 (br s, 1H), 7.22 (d, J = 8.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.09 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 5.84 (s, 2H), 3.70 (t, J = 6.2 Hz, 1H), 2.12 – 1.98 (m, 3H), 1.85 – 1.55 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 135.5, 129.3, 126.5, 125.5, 120.7, 120.4, 119.7, 118.1, 118.0, 110.1, 31.6, 29.1, 24.2, 19.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{14}H_{16}N^+$ 198.1277, Found 198.1277.



3,3-Diallylindolin-2-one (6b): White solid (17.9 mg, 42%); mp: 97 – 99 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.30 (br s, 1H), 7.23 – 7.14 (m, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 5.46 (ddt, J = 17.4, 10.1, 7.3 Hz, 2H), 5.01 (dd, J = 17.1, 2.0 Hz, 2H), 4.91 (dd, J = 10.1, 2.0 Hz, 2H), 2.59 (h, J = 7.1, 6.7 Hz, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 181.9, 141.0, 132.1, 131.8, 127.8, 123.6, 122.2, 118.8, 109.8, 53.3, 41.2; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{14}H_{16}NO^+$ 214.1226, Found 214.1222.

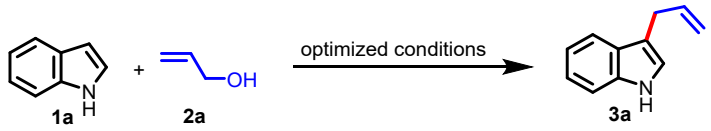


1-Allylindoline (7a): Pale yellow liquid (28.0 mg, 88%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.14 – 6.98 (m, 1H), 6.65 (td, J = 7.3, 1.0 Hz, 1H), 6.51 (d, J = 7.8 Hz, 1H), 5.91 (ddt, J = 17.2, 10.2, 6.0 Hz, 1H), 5.28 (dq, J = 17.1, 1.7 Hz, 1H), 5.19 (dq, J = 10.2, 1.5 Hz, 1H), 3.70 (dt, J = 6.0, 1.5 Hz, 2H), 3.33 (t, J = 8.3 Hz, 2H), 2.96 (t, J = 8.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.2, 134.2, 130.3, 127.2, 124.4, 117.7, 117.3, 107.3, 53.2, 52.2, 28.5; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{14}N^+$ 160.1121, Found 160.1125.



11. Role of water toward the activation of allylic alcohols

Supporting fact 1. Reaction does not proceed in organic solvent lacking H-bond donor property

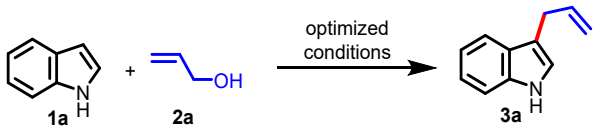


Reaction medium	α-value	3a (%yield)	Reaction medium	α-value	3a (%yield)
Toluene	0.00	0	MeOH	0.93	41
THF	0.00	0	*t*-BuOH	0.68	37
DCE	0.00	0			
Dioxane	0.00	6			

Yield based on GCMS, α scale: Hydrogen bond donor property
Yield in Aq. SDOSS micelles: 9!% (**α-value 1.17**)

NOTE: Hydrogen bond donor (HBD) property (α-scale) of MeOH (0.97) and ^{t}-BuOH (0.68) is relatively poor compared to water (1.17) [*Green Chem*., **2013**,*15*, 798].

Supporting fact 2. The reaction does not proceed in Trifluoroethanol (TFE) and hexafluoroisopropanol (HFP) due to the lack of stabilization of the resulting hydroxide ion.

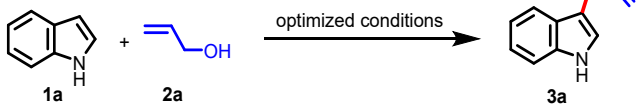


Reaction medium	β-value	3a (%yield)
TFE	0.00	0
HFP	0.00	0
Aq. micelles	0.18	94

Yield based on GCMS
β scale: Hydrogen bond acceptor property

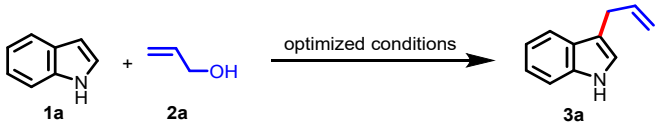
NOTE: While the hydrogen bond donor (HBD) property (a-scale) is expected to be the major/critical factor, the β value would also contribute to the overall outcome of the reaction. Thus, despite having better α values compared to that of water [α scale: 1.51 (TFE), 1.96 (HFP), 1.17 (water)], no product formation was observed in TFE and HFP due to their poor β values [β scale: 0.00 (TFE), 0.00 (TFP), 0.18 (water)].

Supporting fact 3. Reaction kinetics, H_2O *vs* MeOH, clearly indicates the role of H-bonding towards the activation of allylic alcohol



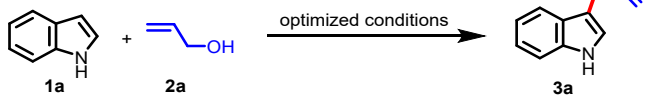
Time	**3a** (%yield) (GCMS)	
	Aq. micelles	**MeOH**
15 min	42	0
30 min	49	0
45 min	53	0
1 h	56	0
18 h	95	41

Supporting fact 4. Reaction kinetics, H_2O *vs* D_2O, clearly indicates the role of H-bonding towards the activation of allylic alcohol



Time	**3a** (%yield) (GCMS)	
	Aq. micelles (H_2O)	**Aq. micelles (D_2O)**
15 min	42	13
30 min	49	28
45 min	53	36
1 h	56	42

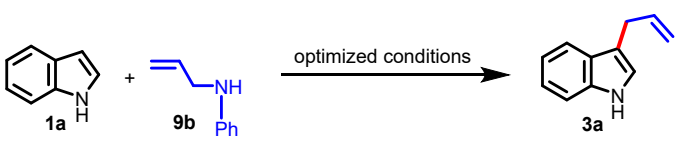
Supporting fact 5. Reaction kinetics, MeOH *vs* CD_3OD *vs* CD_3OH clearly indicates the role of H-bonding towards the activation of allylic alcohol



Time	Reaction media	**3a** (%yield) (GCMS)
18 h	CH_3OH	39
	CD_3OD	0
	CD_3OH	33
	Aq. micelles	95

NOTE: The substitution of deuterium for hydrogen affects the strength of HB. Hence a reduction in the product yield would occur when carrying out the reaction in corresponding deuterated reaction media. This is indicative of the hydrogen bonding (HB) effect on the reaction progress and outcomes. [*J. Am. Chem. Soc.*, **1959**, *81*, 5048].

Supporting fact 6: Reaction proceeds with suitably activated allylic amines in aqueous SDOSS micelles but not in an organic solvent

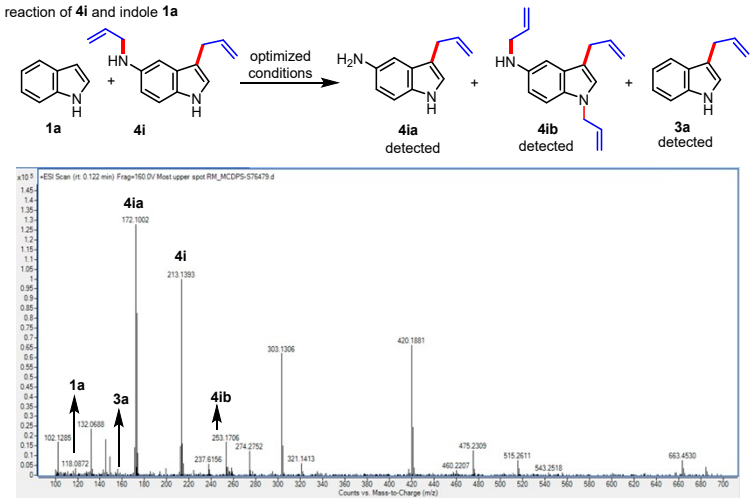


Time	Reaction media	**3a** (%yield)
18 h	Toluene	0
	Aq. micelles	79

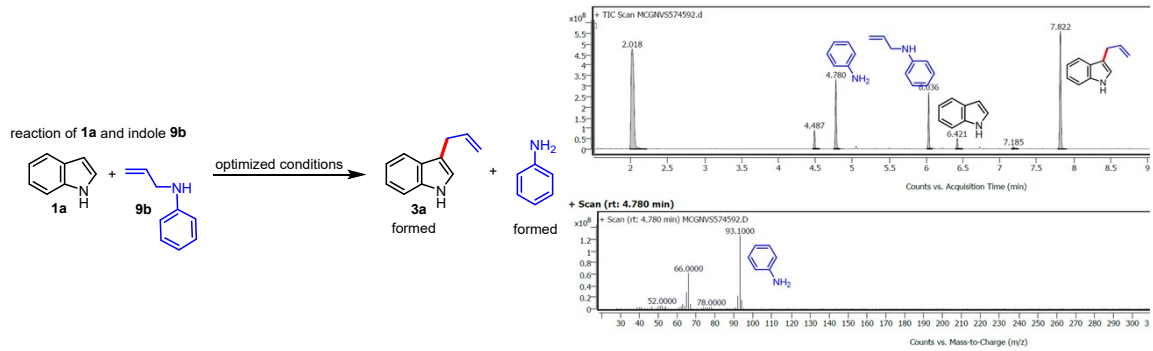
Yield based on GCMS

Supporting fact 7: H-Bond Assisted Intermolecular N→C Allylic Migration via π-AllylNi Complexation

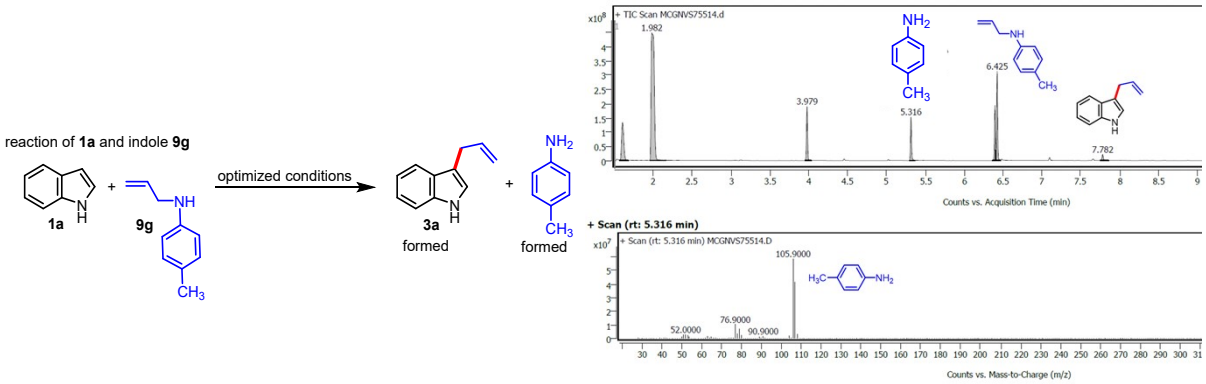
The reaction of **4i** with **1a** was carried out under optimized conditions and the crude reaction mixture was analysed using the mass technique. As expected, the formation of 5-aminoindole **4ia** along with 3-allyl indole **3a** was detected. Additionally, the mass peak corresponding to *N*-allyl indole **4ib** was observed as well.



To make the case clear, analysis of the reaction mixture involving *N*-allyl-aniline **9b** with **1a** under optimized conditions was done. The data revealed the formation of 3-allyl indole **3a** along with aniline, conforming to the intermolecular N→C allylic migration via π-allylNi complexation.



Further, the reaction of *N*-Allyl-4-methyl aniline **9c** with **1a** under optimized conditions resulted in **3a** along with *p*-toluidine (GCMS), strengthening the concept of intermolecular N→C allylic migration via π-AllylNi complexation.



Supporting fact 8: Spectroscopic studies

Working limitations: Since reaction proceeds well in water only, the online NMR monitoring of the optimized reaction excluding **1a** was done in D_2O, however the solubility (miscibility) of the reaction mixture is an issue. We observed the formation of lumps in the NMR tube, and thus experienced limitations in terms of characterization of reaction species and or intermediates. **Reaction does not proceed in deuterated methanol CD_3OD at all; therefore, this option has been ruled out.** Lastly, we tried the above-mentioned reaction in CD_3OH and the data are presented here.

The treatment of allyl alcohol with $Ni(cod)_2$ and PPh_3 in CD_3OH under optimized conditions were monitored at 10 min. intervals. Although not conclusive, it is suggestive of p-allyl nickel complexation.

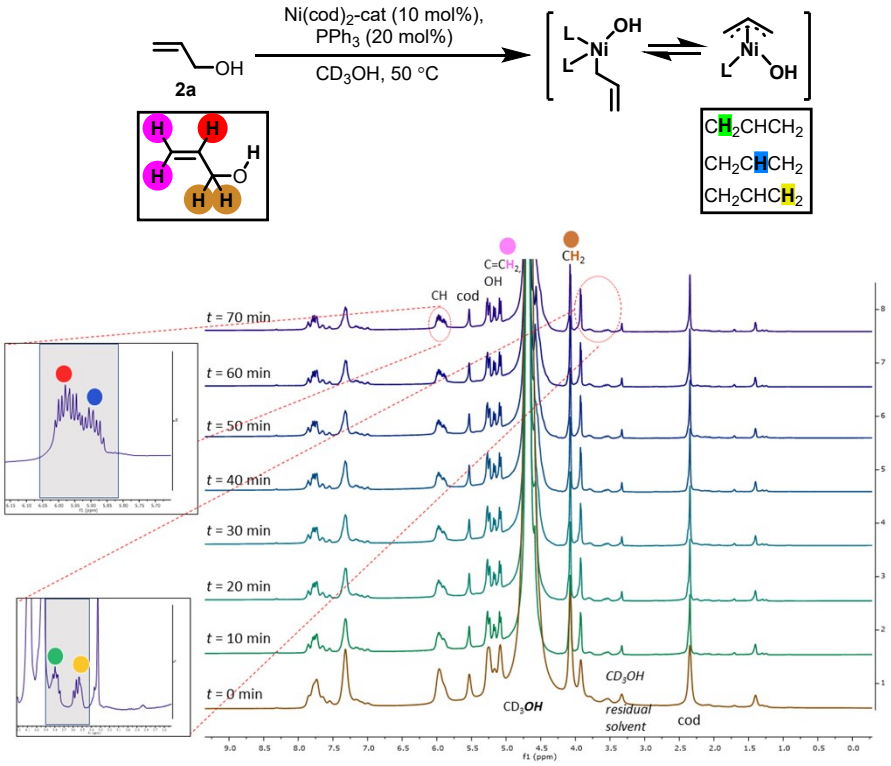


Figure S15. Monitoring of the of 2a under optimized conditions in CD_3OH by ^1H NMR

Further, the appearance of a new peak (other than peak corresponds to PPh_3 and $P(O)PPh_3$) in ^{31}P NMR while monitoring the progress of optimized reaction conditions is the indicative of complexation of PPh_3 with nickel.

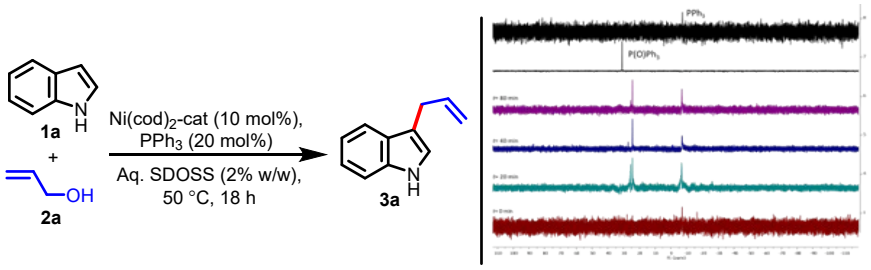
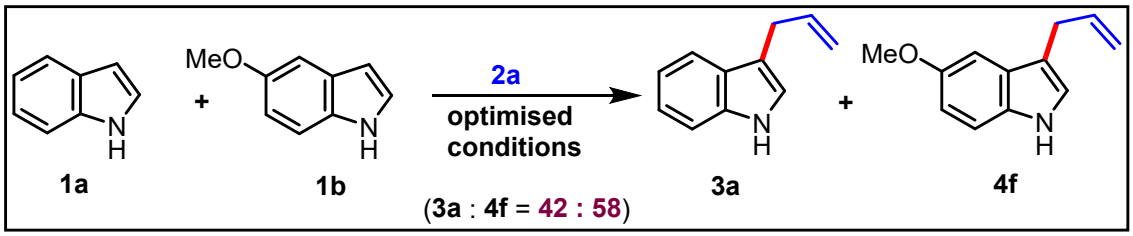


Figure S16. Monitoring of the optimized reaction in CD_3OH by ^1H NMR

12. Selectivity study

Typical procedure for intermolecular competition study involving two different indoles:



In a glove box, to an oven dried sealed tubed equipped with a stirring bar, $Ni(cod)_2$ (5.1 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), indole **1a** (23.5 mg, 0.2 mmol), 5-Methoxy indole (29.4 mg, 0.2 mmol), allyl alcohol **2a** (11.6 mg, 13.6 μL, 0.2 mmol, 1 equiv), and Aq. SDOSS (2% w/w, 0.5 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with EtOAc (0.5 mL) and vortexed. From the organic layer containing crude reaction mixture, an aliquot portion (20 µL) was taken out, diluted with MeOH (upto 1 mL) and subjected to GCMS to observe the selectivity, which reflected an 42:58 selectively in favor of **4f**.

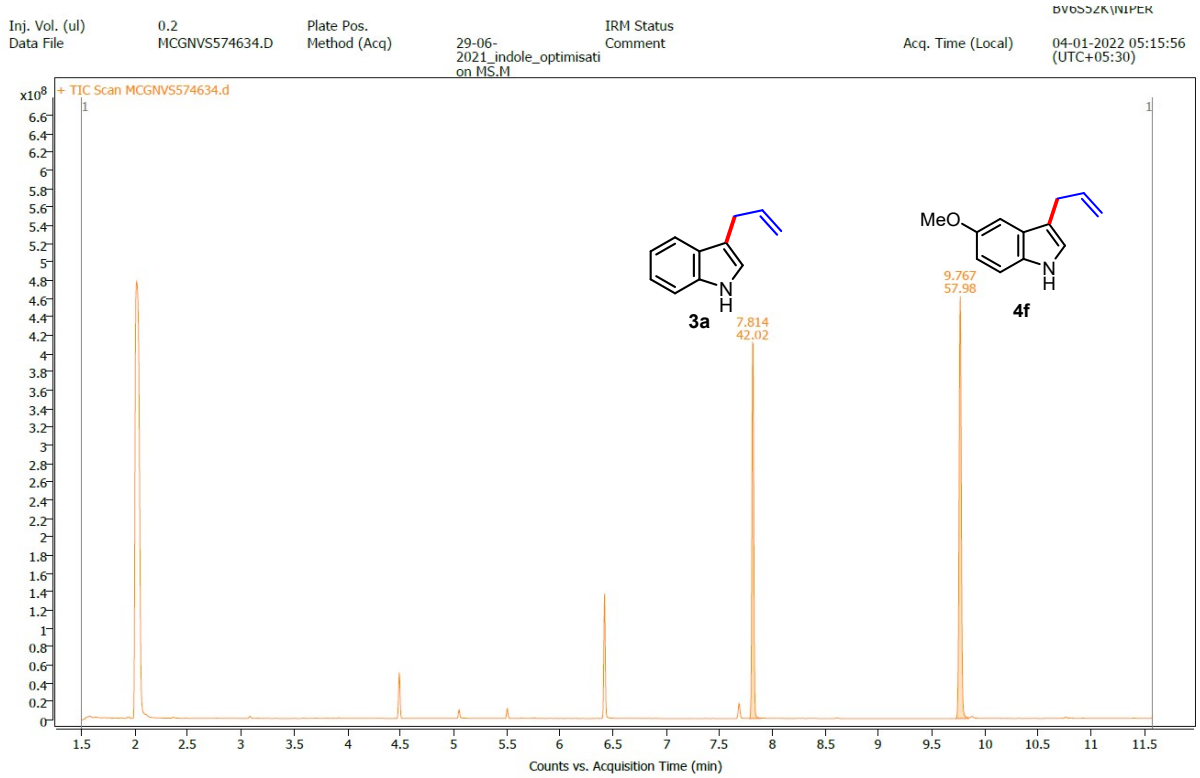
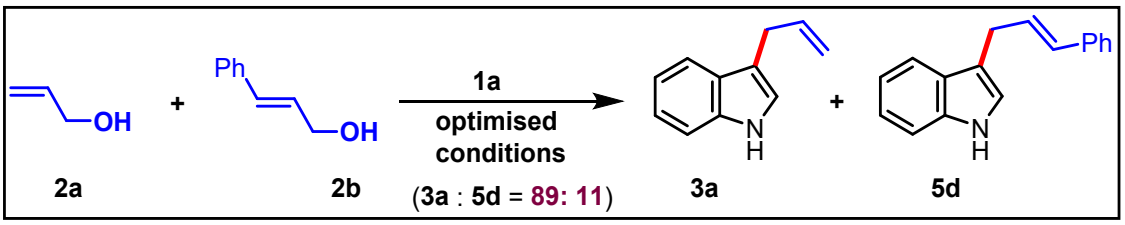


Figure S17. Chromatographic representation

Typical procedure for intermolecular competition study involving two different allyl alcohols:



In a glove box, to an oven dried sealed tubed equipped with a stirring bar, $Ni(cod)_2$ (5.1 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), indole **1a** (23.5 mg, 0.2 mmol), allyl alcohol **2a** (11.6 mg, 13.6 μL, 0.2 mmol, 1 equiv), cinnamyl alcohol **2b** (26.8 mg, 25.8 μL, 0.2 mmol, 1 equiv) and Aq. SDOSS (2% w/w, 0.5 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with EtOAc (0.5 mL) and vortexed. From the organic layer containing crude reaction mixture, an aliquot portion (20 µL) was taken out, diluted with MeOH (upto 1 mL) and subjected to GCMS (on modified method) to observe the selectivity, which reflected an 89:11 selectively in favor of **3a**.

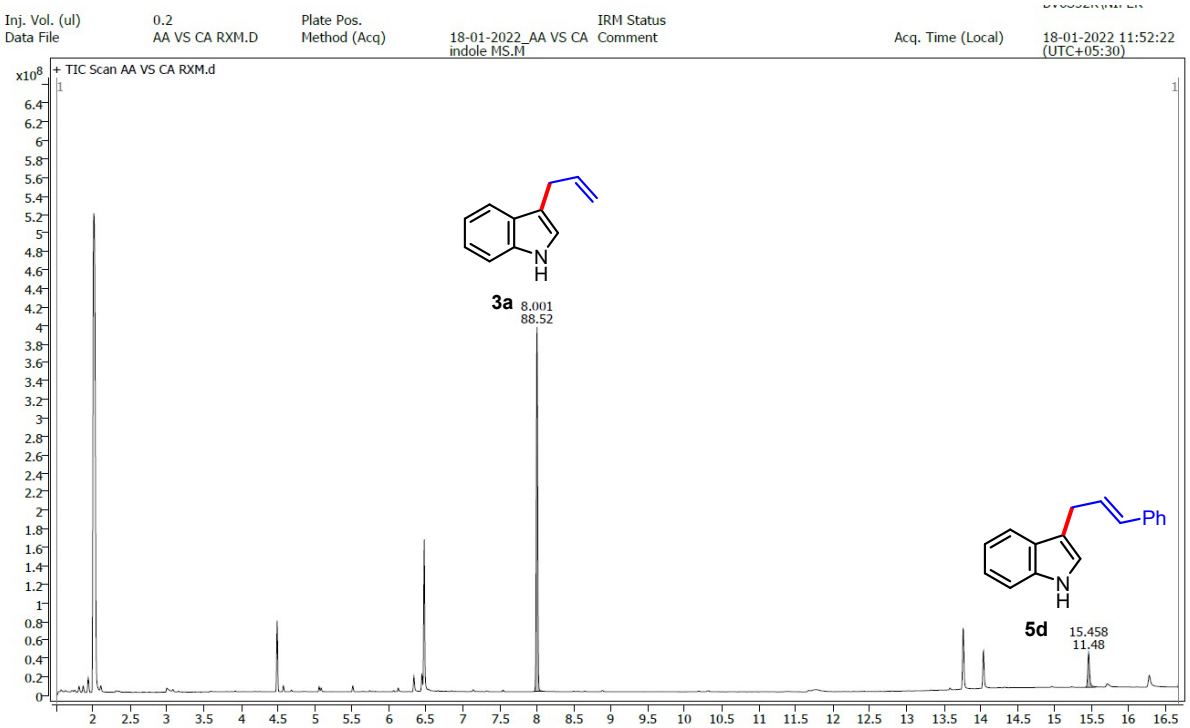
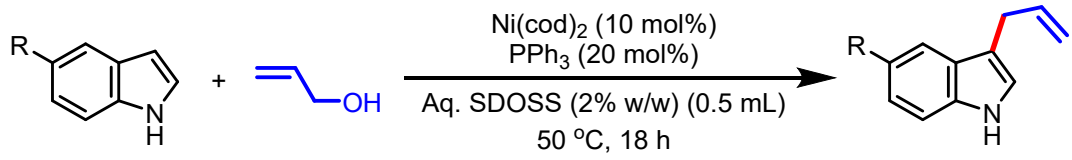


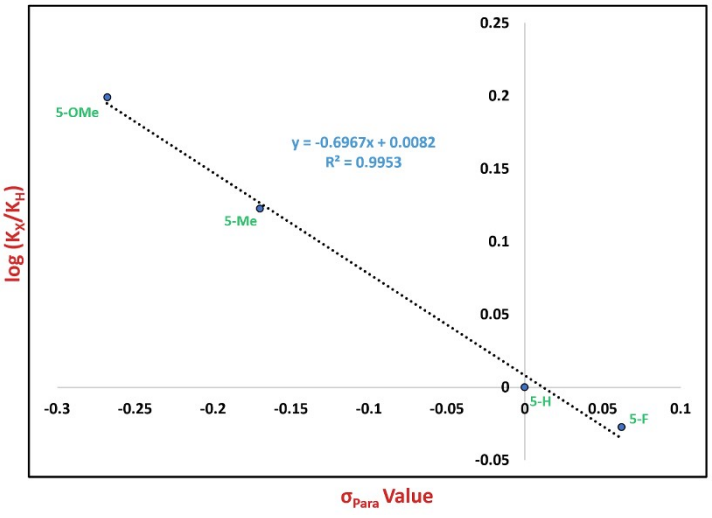
Figure S18. Chromatographic representation

13. Hammett Plot analysis

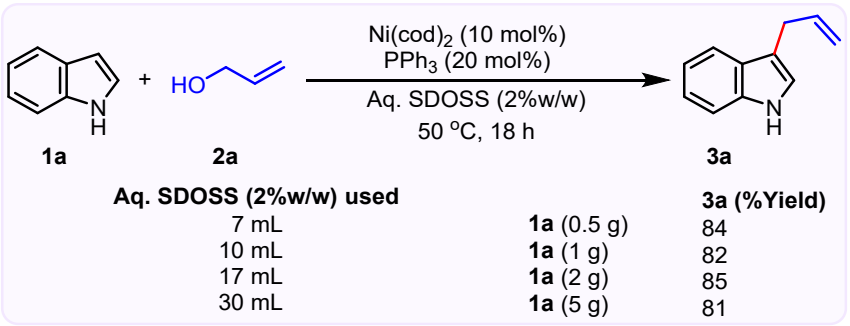
Table S9. Hammett linear free energy relationship study



Indole	Time (min)	% Yield	$\sigma_{(para)}$	Rate (K)	K_X/K_H	Log K_X/K_H
R = H	15	73	0.000	0.3163	1.0000	0
	30	76				
	45	81				
	60	81				
R = Me	15	67	-0.170	0.4197	1.3269	0.1228
	30	82				
	45	95				
	60	96				
R = OMe	15	95	-0.268	0.5003	1.5819	0.1991
	30	95				
	45	100				
	60	98				
R = F	15	32	+0.062	0.2970	0.9392	-0.0272
	30	44				
	45	57				
	60	66				
R = CN	15	0	+0.660	0.0000	0.0000	-
	30	0				
	45	0				
	60	0				
R = NO_2	15	0	+0.778	0.0000	0.0000	-
	30	0				
	45	0				
	60	0				



14. Scale up study



Aq. SDOSS (2%w/w) used		3a (%Yield)
7 mL	**1a** (0.5 g)	84
10 mL	**1a** (1 g)	82
17 mL	**1a** (2 g)	85
30 mL	**1a** (5 g)	81

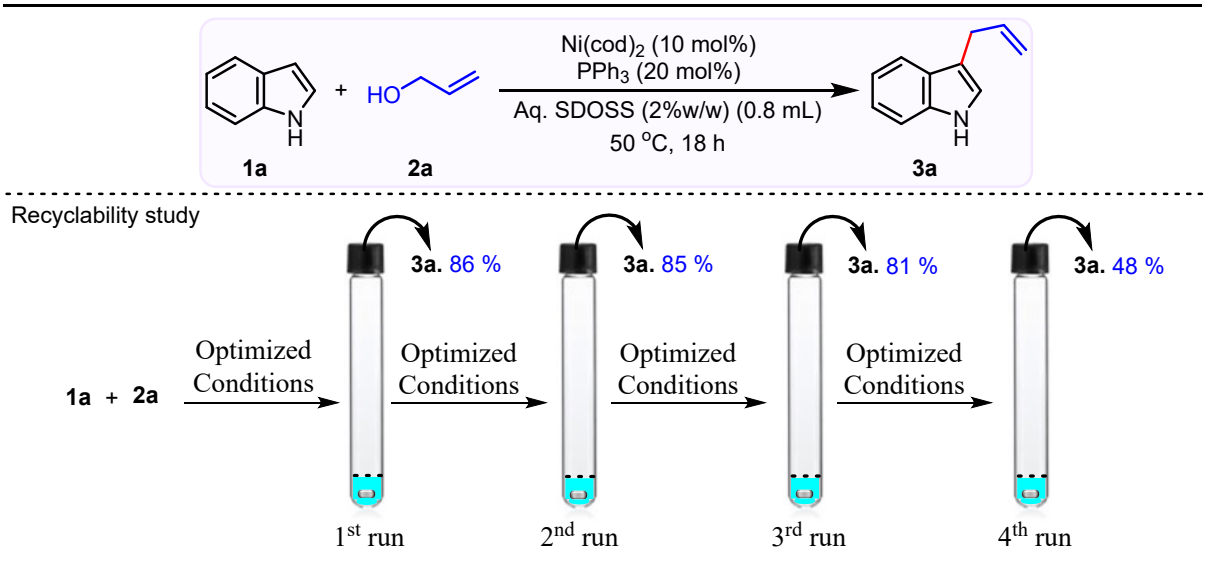
To a well cleaned tube equipped with a stir bar, $Ni(cod)_2$ (115.52 mg, 0.42 mmol, 10 mol%), PPh_3 (223.47 mg, 0.85 mmol, 20 mol%), indole **1a** (500 mg, 4.26 mmol), allyl alcohol **2a** (371.13 mg, 434.6 μL, 6.39 mmol, 1.5 equiv), and Aq. SDOSS (2% w/w, 7 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with EtOAc (2 X 7 mL), vortexed and subjected to aqueous workup. Final washing was done using brine solution. The organic liquid containing product and other organic residue was removed carefully and was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the column (R*f* = 0.47; EtOAc:Hexane = 1:10, v/v) to get analytically pure product **3a** as pale yellow liquid (562.5 mg, 84%); **^{1}H NMR** (500 MHz, $CDCl_3$): δ δ 7.94 (br s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (s, 1H), 6.13 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.22 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.13 (dq, *J* = 10.0, 1.5 Hz, 1H), 3.58 (dq, *J* = 6.5, 1.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.4, 127.4, 122.0, 121.6, 119.2, 119.1, 115.2, 114.5, 111.0, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0968.

15. Recyclability study

Procedure:

To a well cleaned tube equipped with a stir bar, $Ni(cod)_2$ (5.1 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), indole **1a** (23.5 mg, 0.2 mmol), allyl alcohol **2a** (17.4 mg, 20.1 μL, 0.3 mmol, 1.5 equiv), and Aq. SDOSS (2% w/w, 0.8 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with EtOAc (2 X 0.5 mL), vortexed. The organic liquid containing product and other organic residue was removed carefully using microsyringe and was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the burette column (R*f* = 0.47; EtOAc:Hexane = 1:10, v/v) to get analytically pure product **3a** as pale yellow liquid; **^{1}H NMR** (500 MHz, $CDCl_3$): δ δ 7.94 (br s, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (s, 1H), 6.13 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.22 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.13 (dq, *J* = 10.0, 1.5 Hz, 1H), 3.58 (dq, *J* = 6.5, 1.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.3, 136.4, 127.4, 122.0, 121.6, 119.2, 119.1, 115.2, 114.5, 111.0, 29.8; **HRMS** (ESI-TOF) *m/z*: $[M + H]^+$ Calculated for $C_{11}H_{12}N^+$ 158.0964, Found 158.0968.

To the remaining aqueous layer same protocol as mentioned above was repeated except addition of fresh aqueous TPGS-750-M for product formation in the next consecutive cycles as summarized below.



After 3rd run the yield was drastically reduced. In order to the understand the loss of reactivity, zeta sizer analysis on the particle size distribution after the 3rd run (recycled

Aq. SDOSS) was carried out which revealed a dire increase in average particle size (7055.06 nm) as compared to 0th run (402.0 nm), suggesting destruction of required nano-micellar composition, and that could be the reason of yield reduction. (See **Figure 17**)

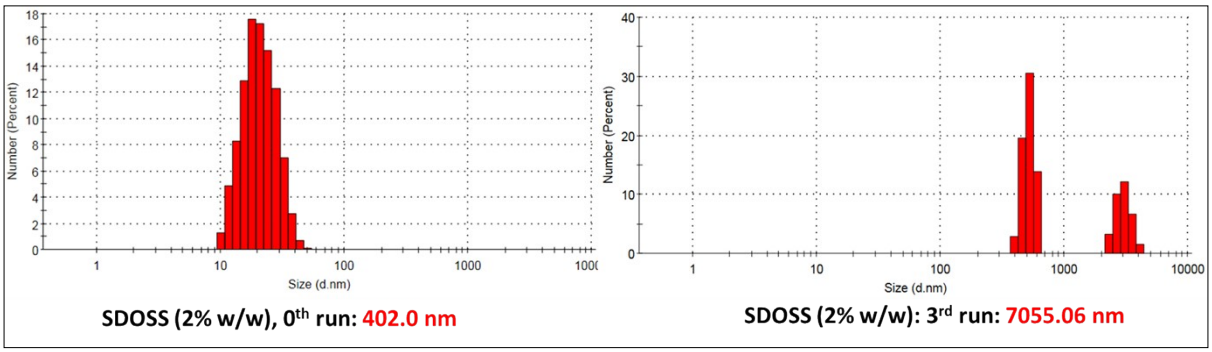
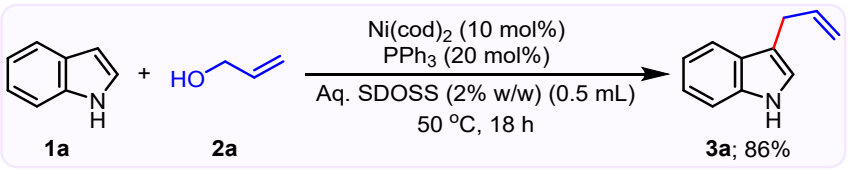


Figure S19. Zeta sizer analysis (Particle size distribution) before 0th run and after 3rd run recyclability

16. E-factor determination for the developed protocol:



To a well cleaned tube equipped with a stir bar, $Ni(cod)_2$ (5.1 mg, 0.02 mmol, 10 mol%), PPh_3 (10.5 mg, 0.04 mmol, 20 mol%), indole **1a** (23.5 mg, 0.2 mmol), allyl alcohol **2a** (17.4 mg, 20.1 μL, 0.3 mmol, 1.5 equiv), and Aq. SDOSS (2% w/w, 0.4 mL) were added. The resultant mixture was stirred at 50 °C for 18 h. The cooled (room temp.) reaction mixture was diluted with minimal amount of EtOAc (0.2 mL), vortexed and subjected to aqueous workup. The organic liquid containing product and other organic residue was removed carefully using microsyringe and subjected and was dried over anhyd. Na_2SO_4 and concentrated under reduced pressure. The crude products were adsorbed on silica gel and pass through the burette column (R*f* = 0.47; EtOAc:Hexane = 1:10, v/v) to get analytically pure product **3a** as pale yellow liquid (27.0 mg, 86%). Consequently, for the 1st Cycle to 3rd Cycle: the collected aqueous surfactant media was subjected to weighing of all the reaction component as described above.

E-factor calculation:

Volume of EtOAc used = 200 μL = 0.2 mL Volume of H_2O used = 400 μL = 0.4 mL
Density of EtOAc = 0.902 g/mL Density of H_2O = 1 g/mL

Organic waste:

$$\text{E Factor} = \frac{\text{organic waste (g)}}{\text{product (g)}} = \frac{\text{Waste of EtOAc used during workup (g)}}{\text{product (g)}}$$

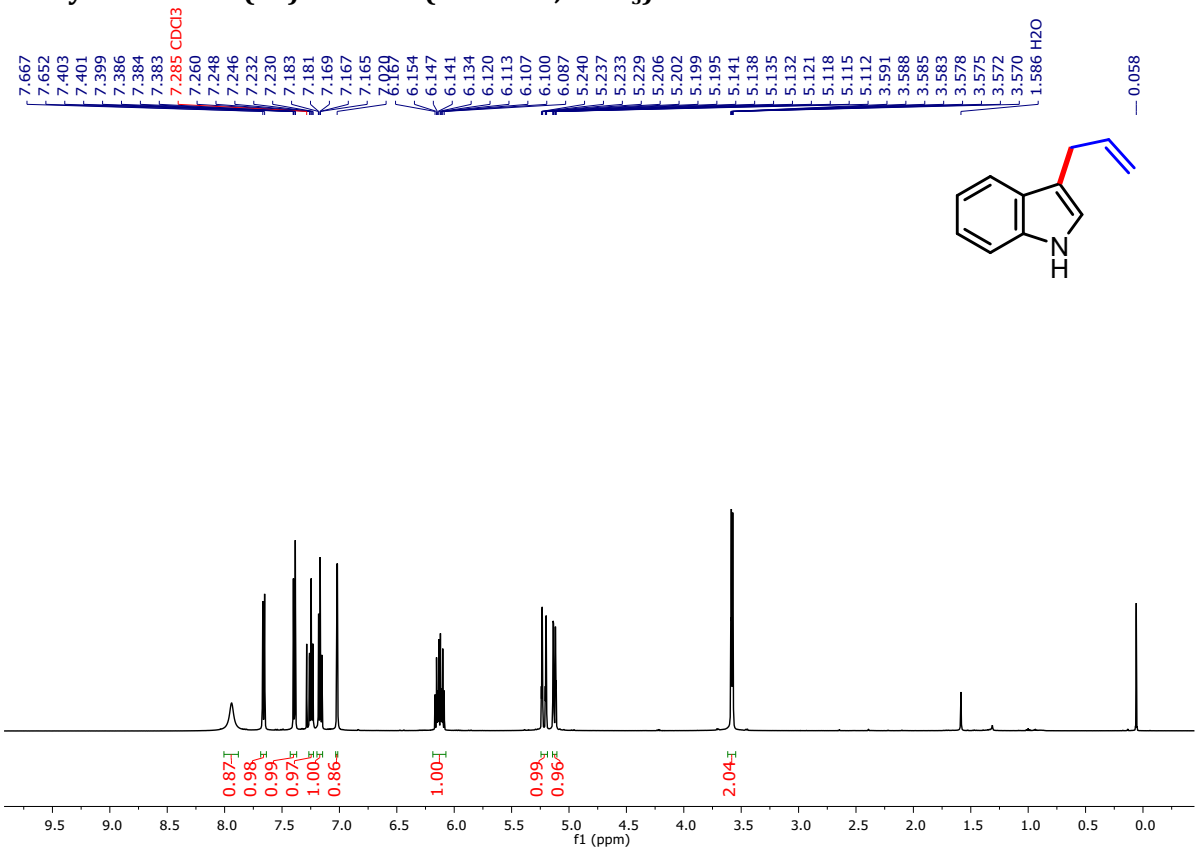
Organic waste + Aqueous waste:

$$\text{E Factor} = \frac{\text{Total waste (g)}}{\text{product (g)}} = \frac{\text{Waste of EtOAc used during workup (g) + Aqueous waste (g)}}{\text{product (g)}}$$

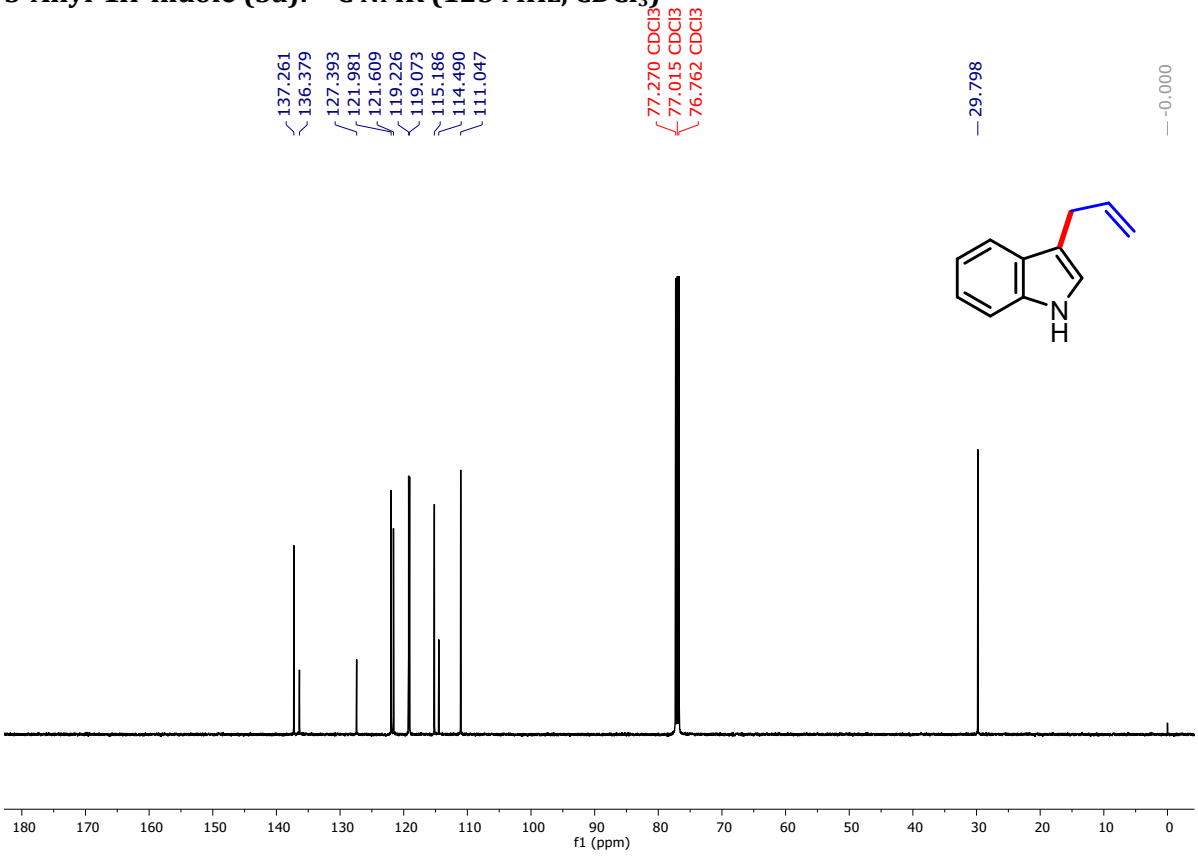
0th Cycle	1st Cycle	2nd Cycle	3rd Cycle
Considering only organic waste			
EtOAc used = 0.18 g Product = 0.027 g E-Factor = 6.66	EtOAc used = 0.18 g Product = 0.0267 g E-Factor = 6.74	EtOAc used = 0.18 g Product = 0.0254 g E-Factor = 7.08	EtOAc used = 0.18 g Product = 0.015 g E-Factor = 12
Avg E-factor (organic waste) = 8.12			
Considering only organic waste + aqueous waste			
Aq. media recycled Product = 0.027 g Aqueous waste = 0 g E-Factor = 6.66	Aq. media recycled Product = 0.0267 g Aqueous waste = 0 g E-Factor = 6.74	Aq. media recycled Product = 0.0254 g Aqueous waste = 0 g E-Factor = 7.08	Aq. media used = 0.5 mL Product = 0.015 g Aqueous waste = 0.4 g E-Factor = 45.3
Avg E-factor (organic waste + aqueous waste) = 16.44			

17. NMR spectra (^{1}H, ^{13}C, ^{19}F NMR):

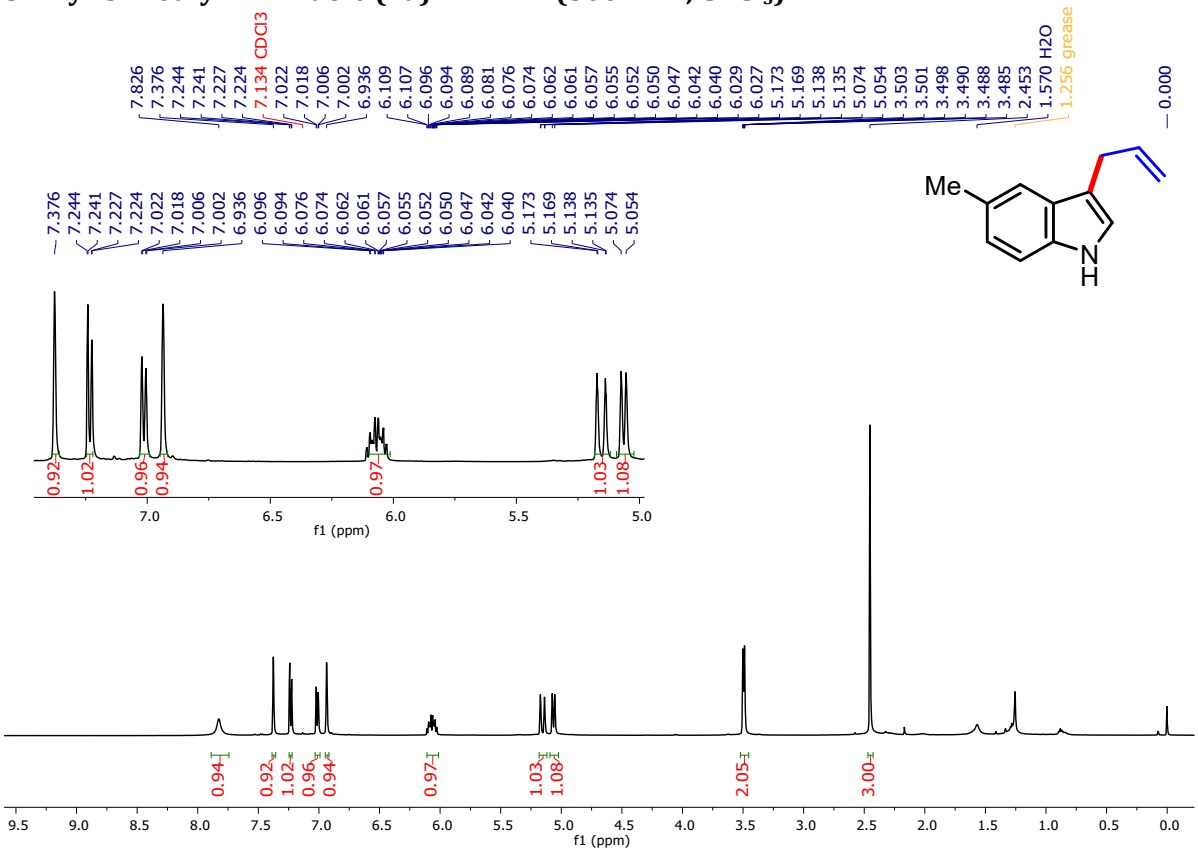
3-Allyl-1*H*-indole (3a): ^{1}H NMR (500 MHz, $CDCl_3$)



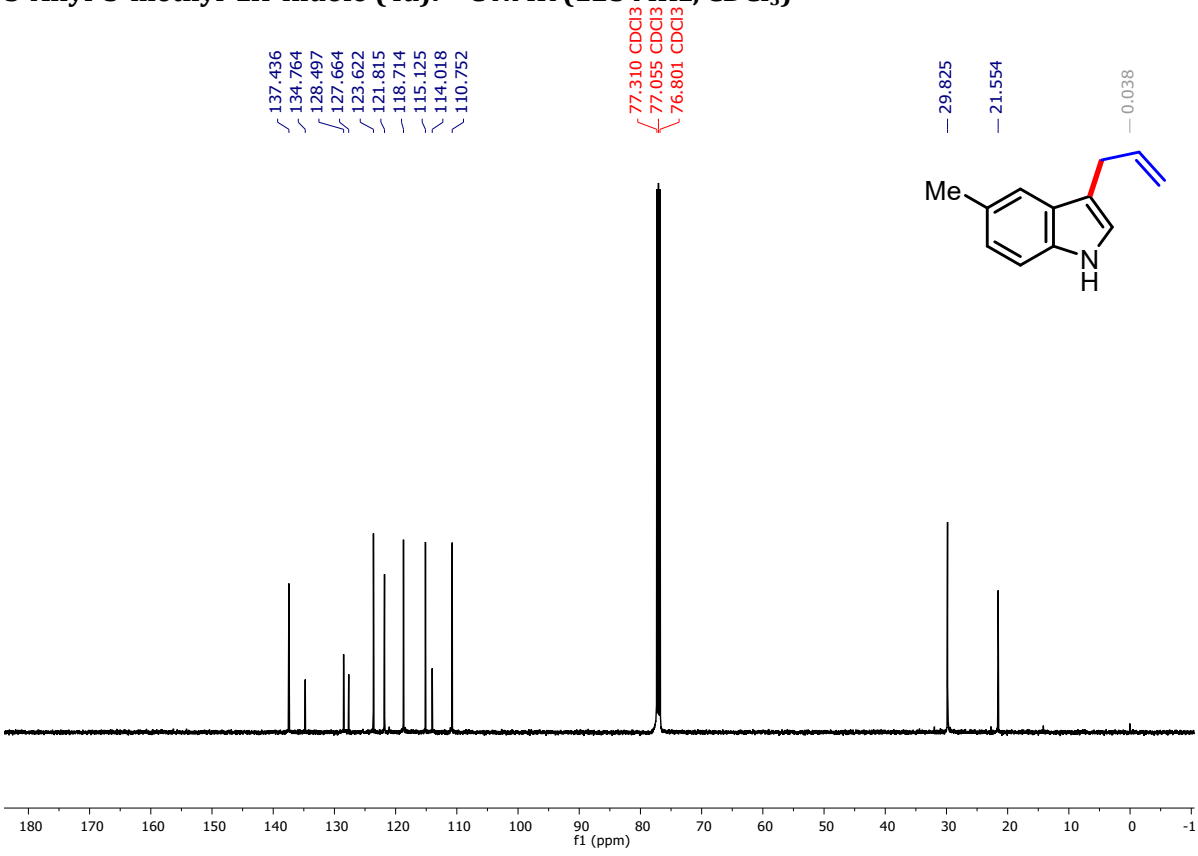
3-Allyl-1*H*-indole (3a): ^{13}C NMR (125 MHz, $CDCl_3$)



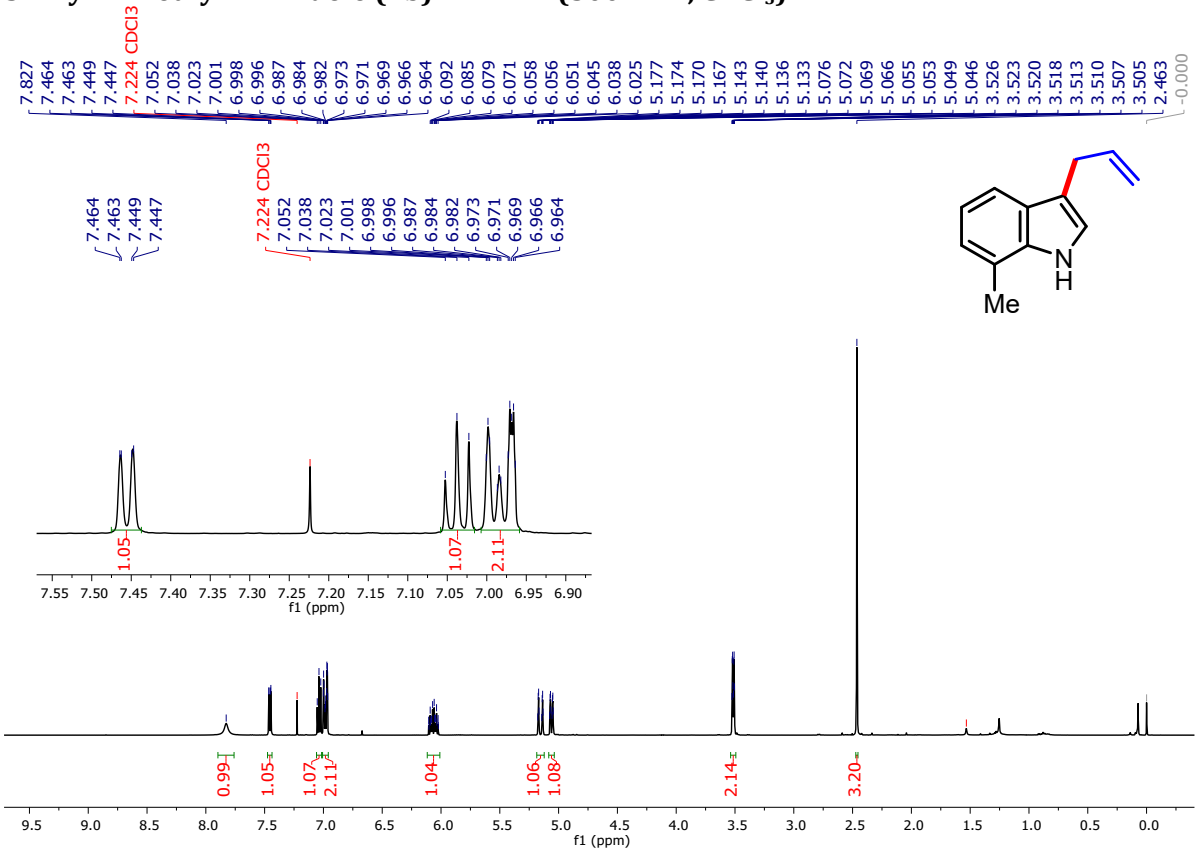
3-Allyl-5-methyl-1*H*-indole (4a): ^{1}H NMR (500 MHz, $CDCl_3$)



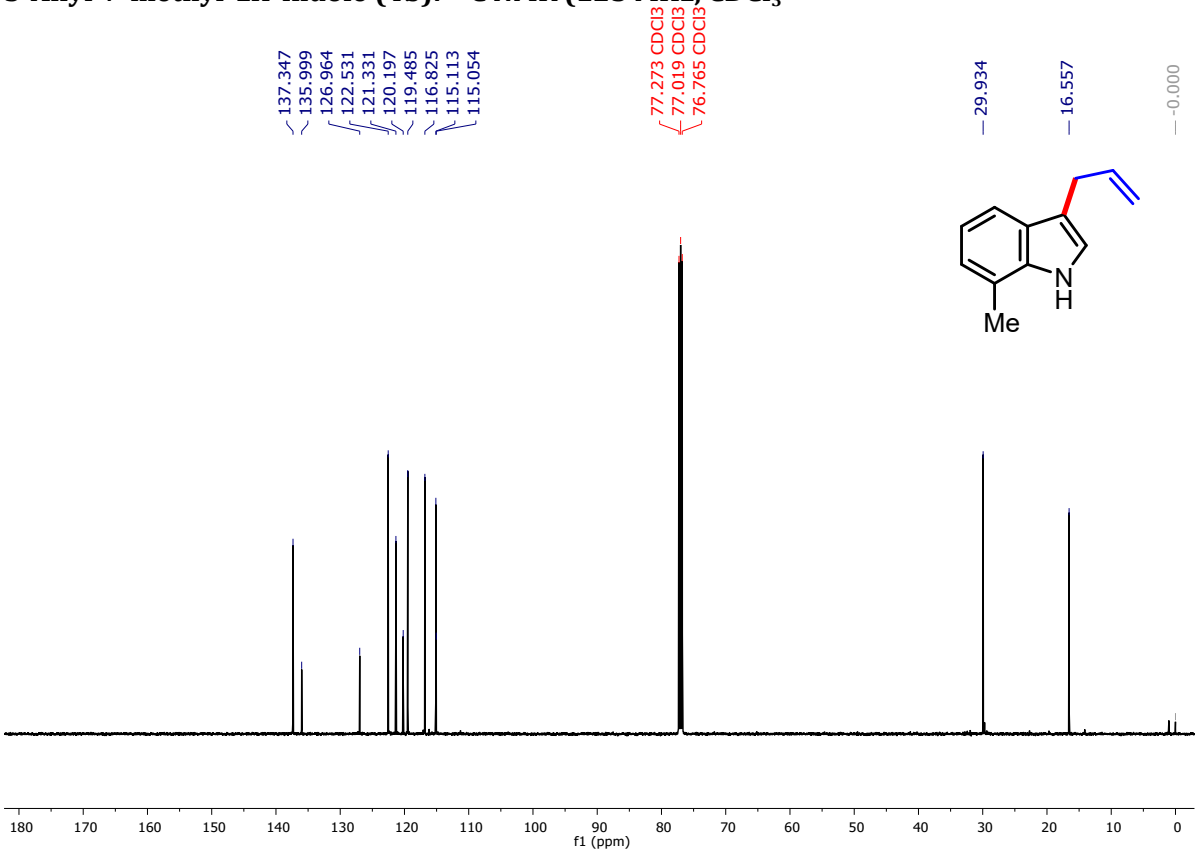
3-Allyl-5-methyl-1*H*-indole (4a): ^{13}C NMR (125 MHz, $CDCl_3$)



3-Allyl-7-methyl-1*H*-indole (4b): ^{1}H NMR (500 MHz, $CDCl_3$)

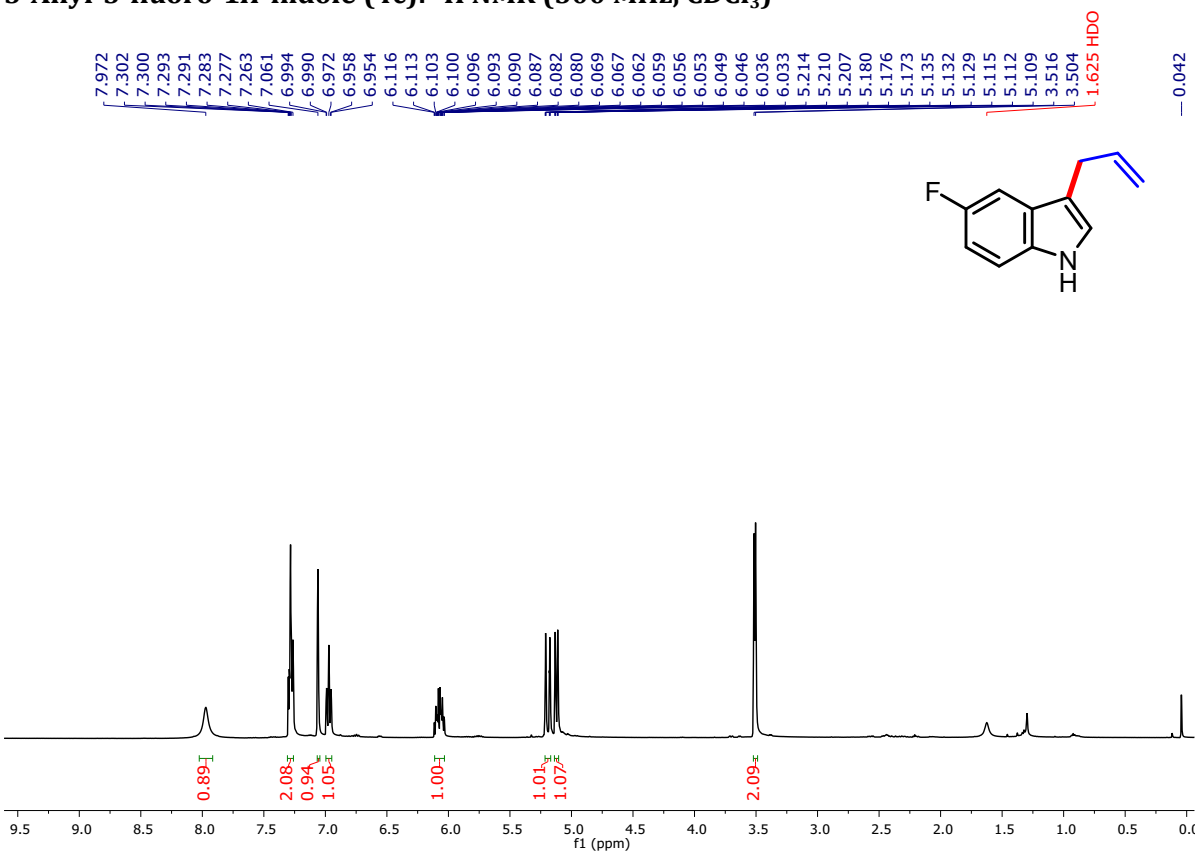


3-Allyl-7-methyl-1*H*-indole (4b): ^{13}C NMR (125 MHz, $CDCl_3$

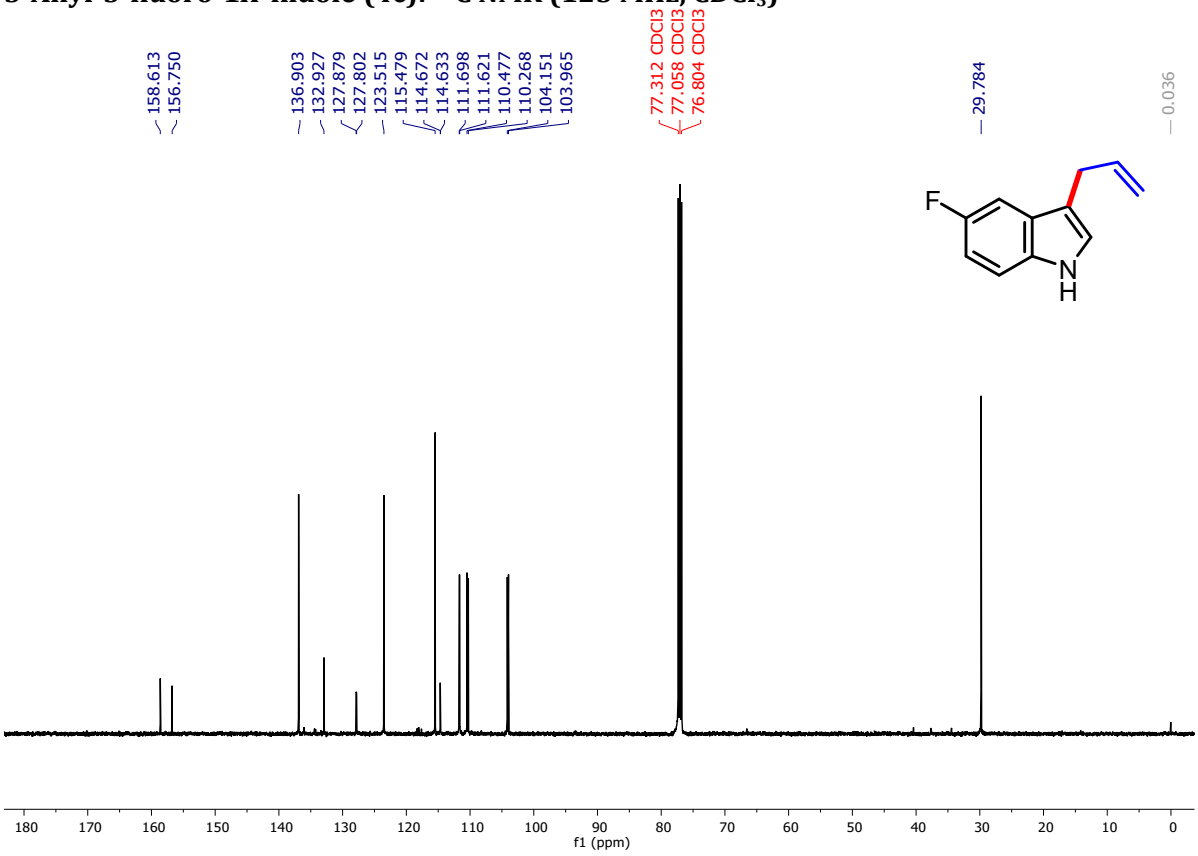


)

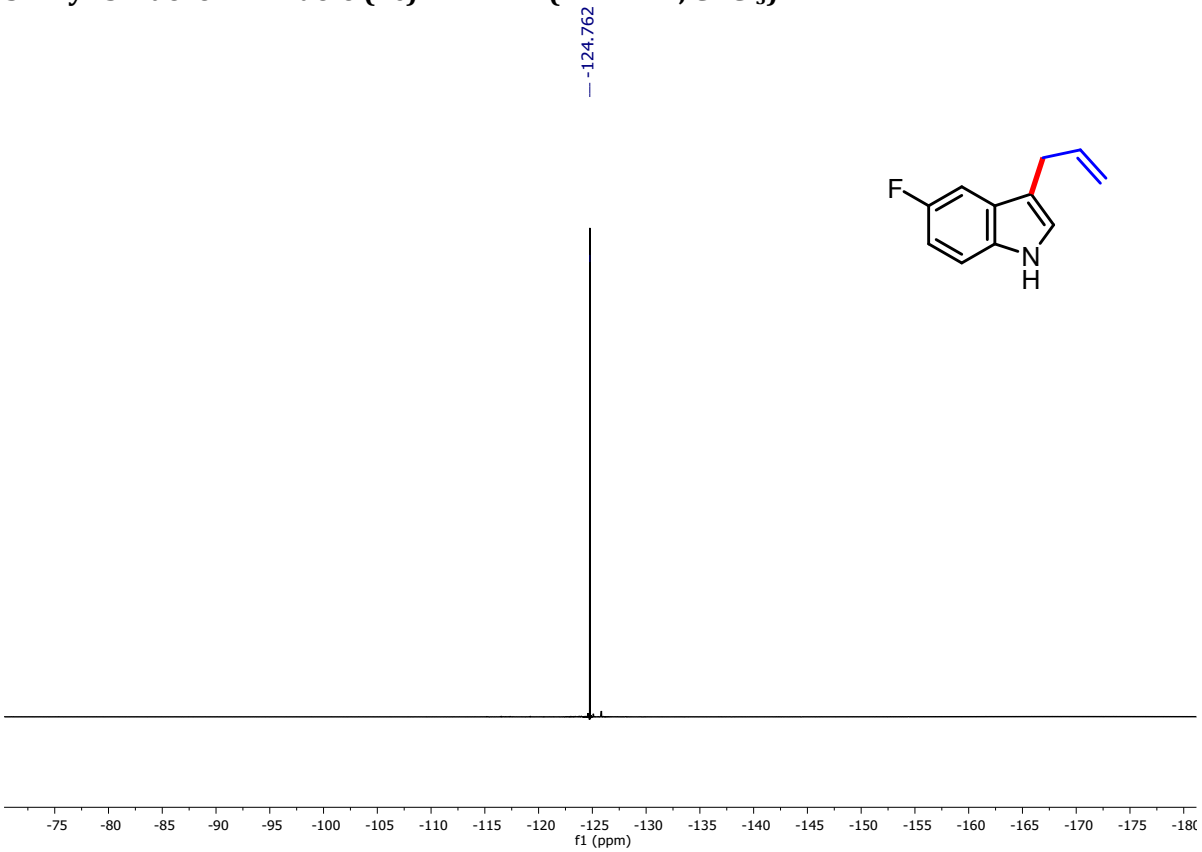
3-Allyl-5-fluoro-1*H*-indole (4c): ^{1}H NMR (500 MHz, $CDCl_3$)



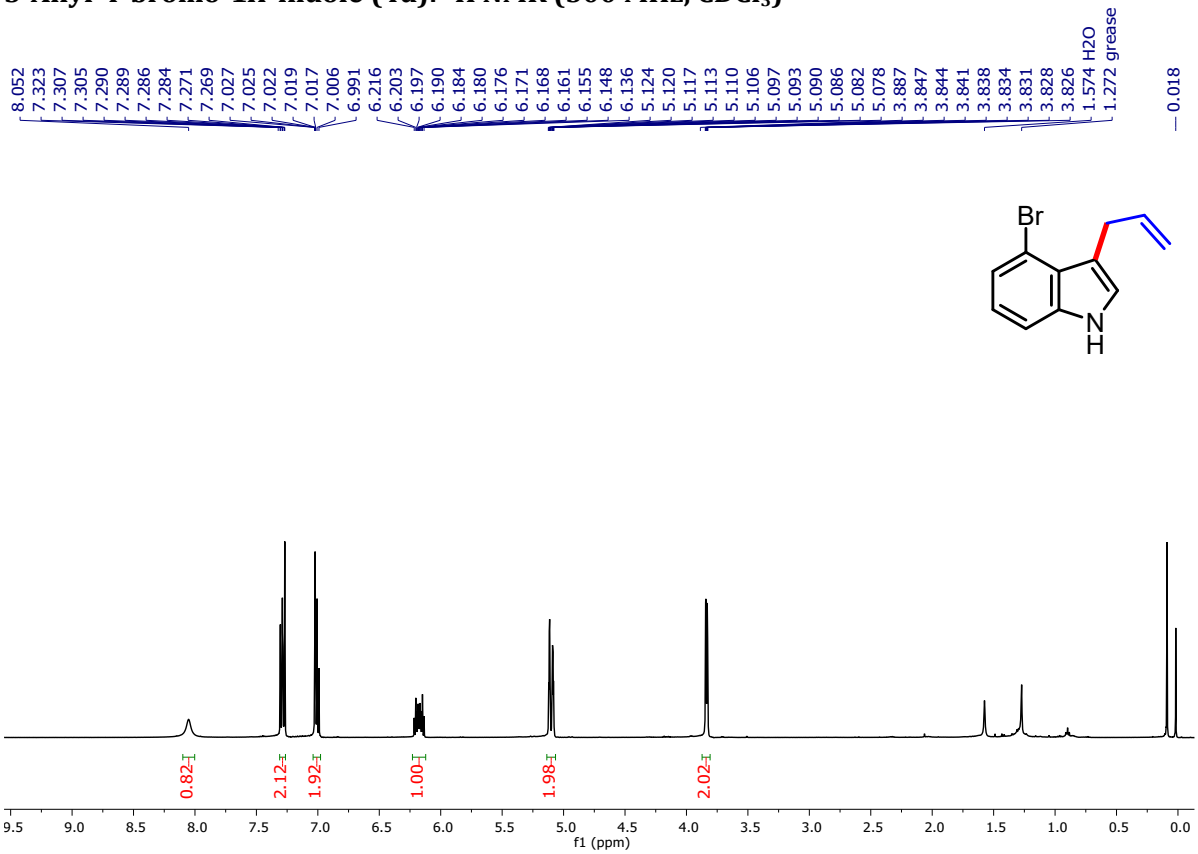
3-Allyl-5-fluoro-1*H*-indole (4c): ^{13}C NMR (125 MHz, $CDCl_3$)



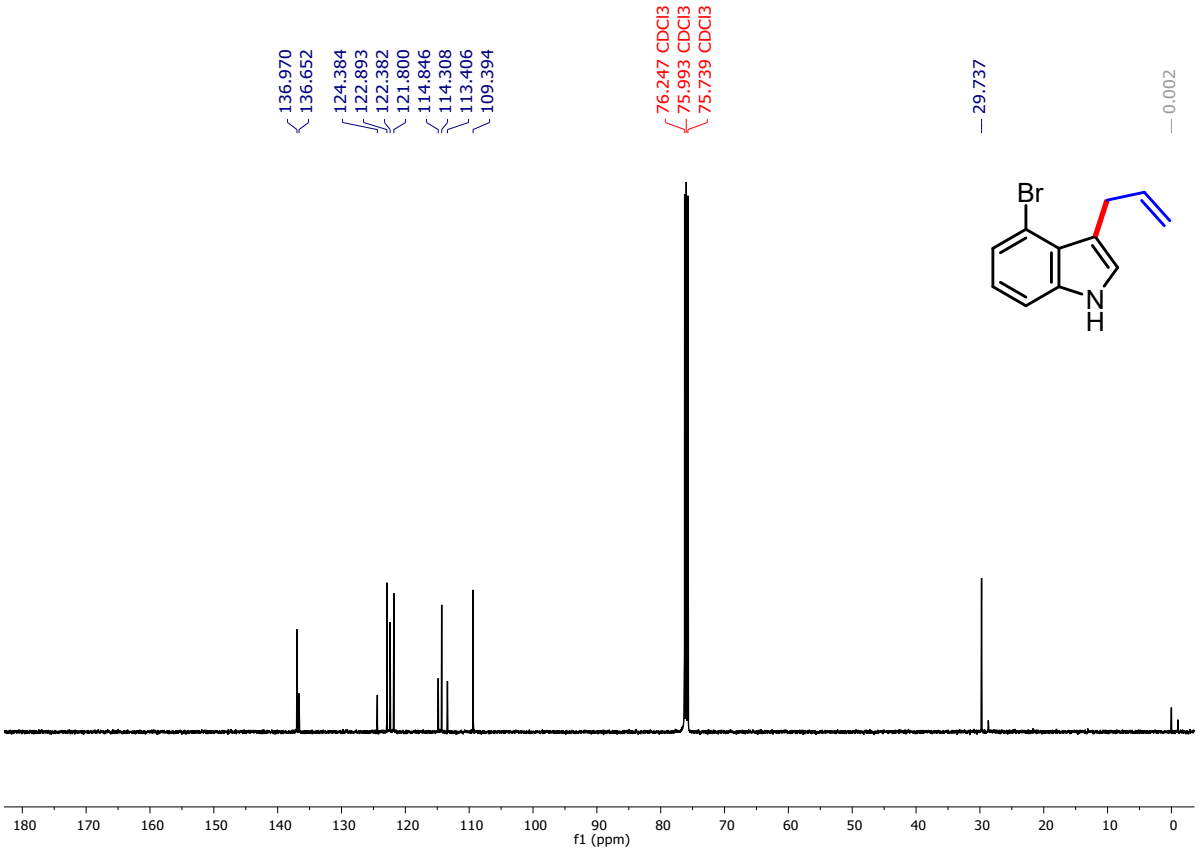
3-Allyl-5-fluoro-1*H*-indole (4c): ^{19}F NMR (471 MHz, $CDCl_3$)



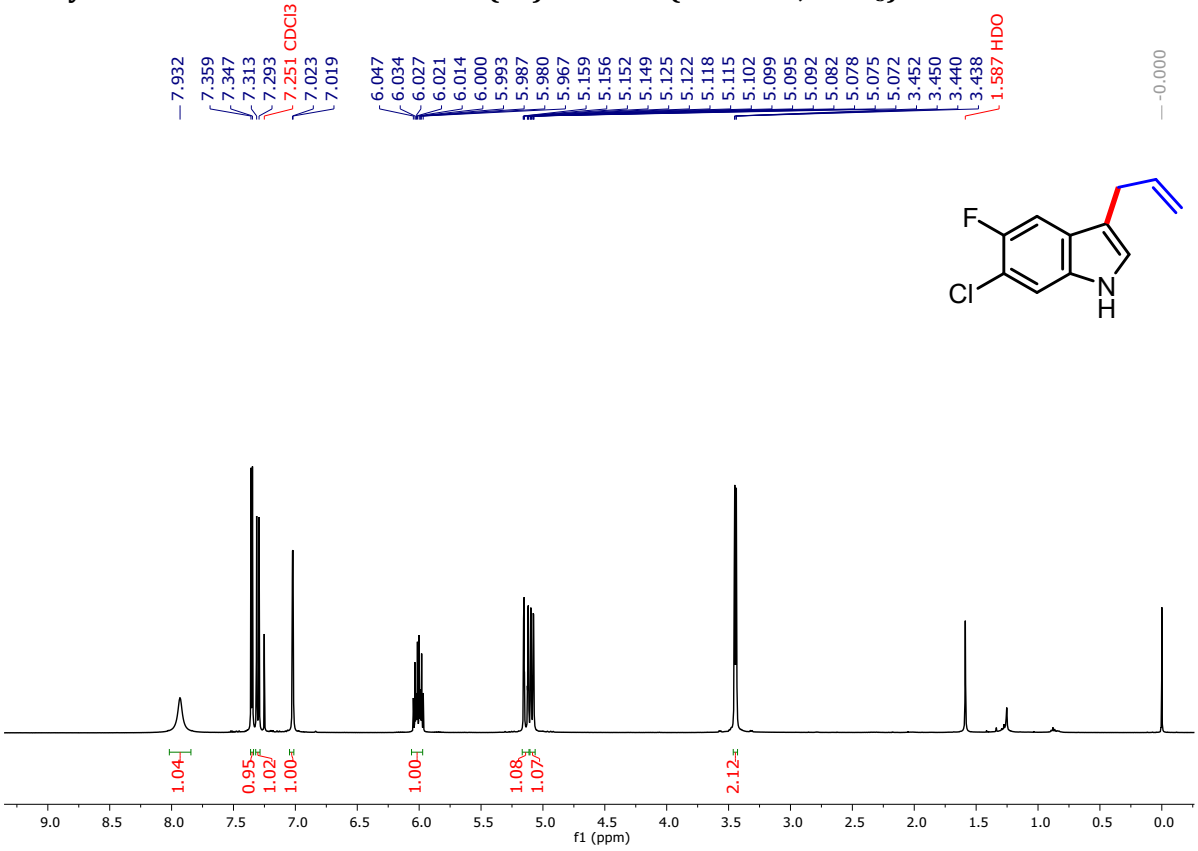
3-Allyl-4-bromo-1*H*-indole (4d): ^{1}H NMR (500 MHz, $CDCl_3$)



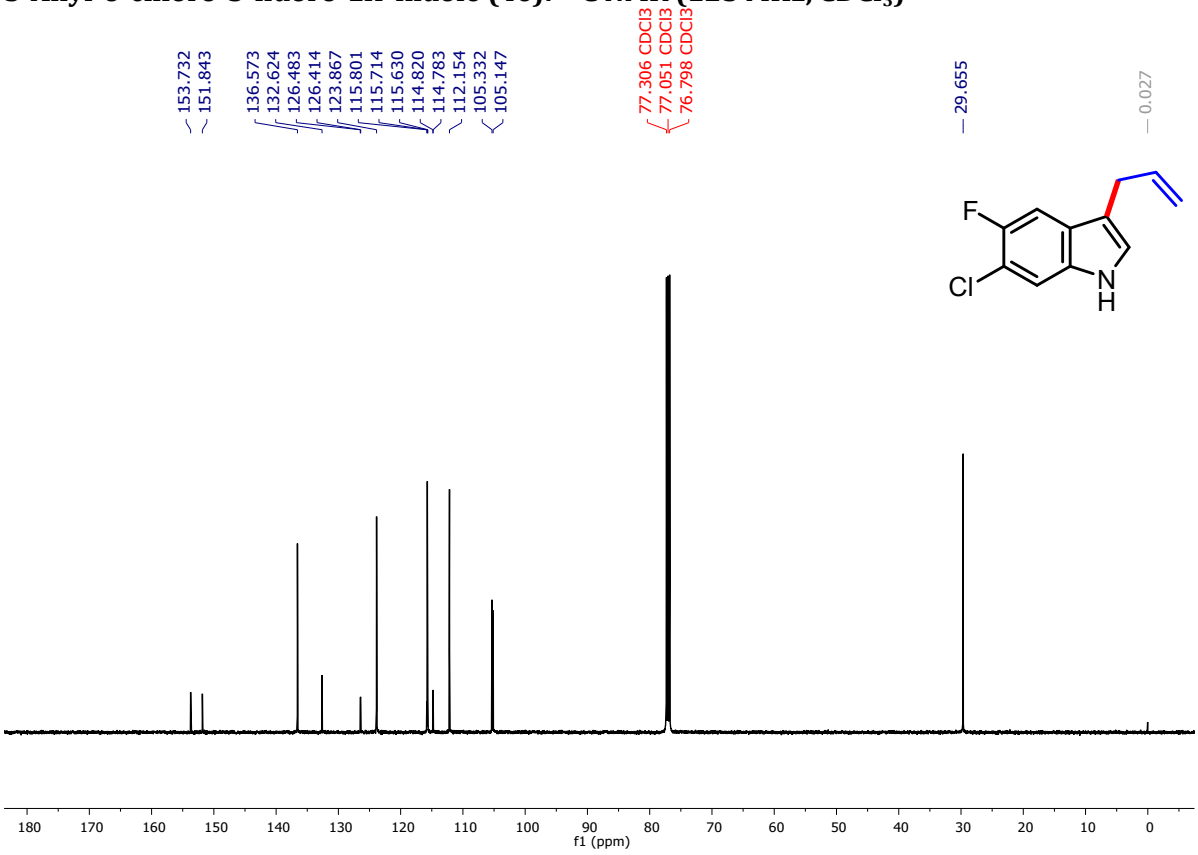
3-Allyl-4-bromo-1*H*-indole (4d): ^{13}C NMR (125 MHz, $CDCl_3$)



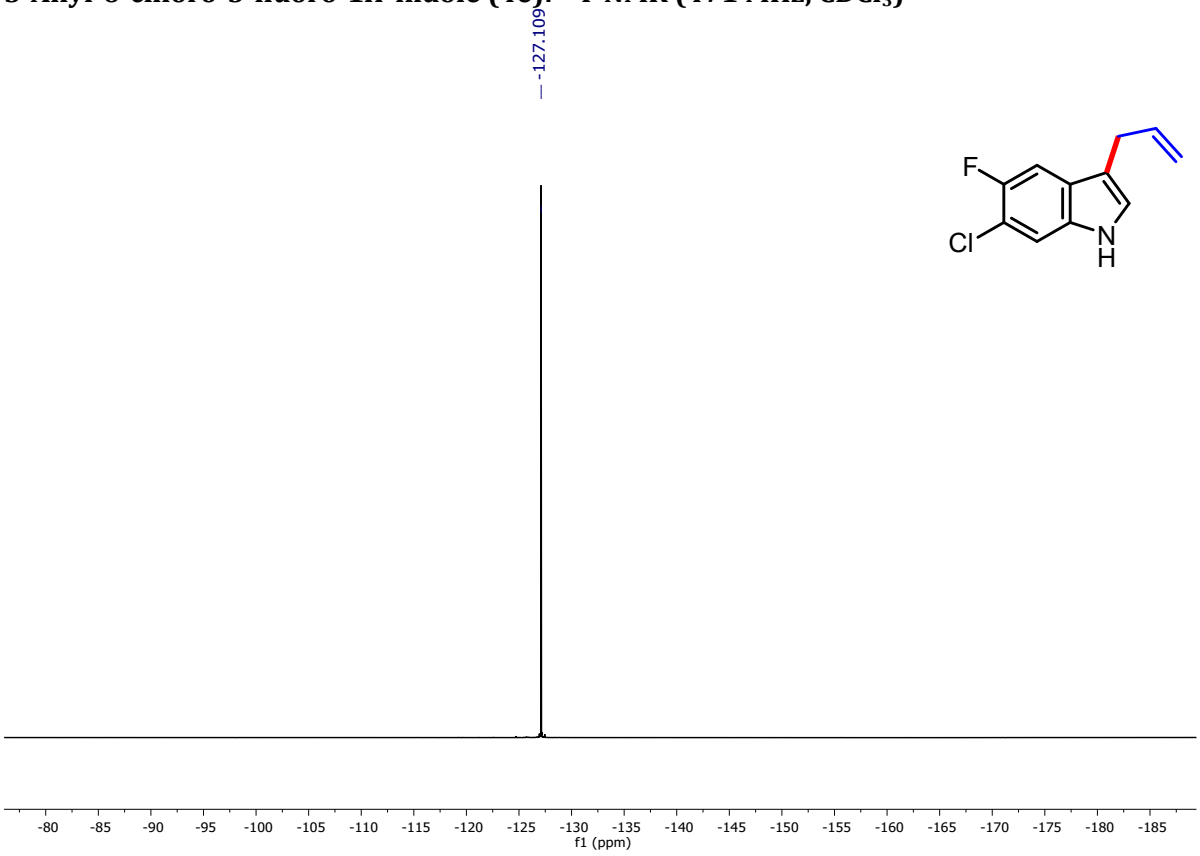
3-Allyl-6-chloro-5-fluoro-1*H*-indole (4e): ^{1}H NMR (500 MHz, $CDCl_3$)



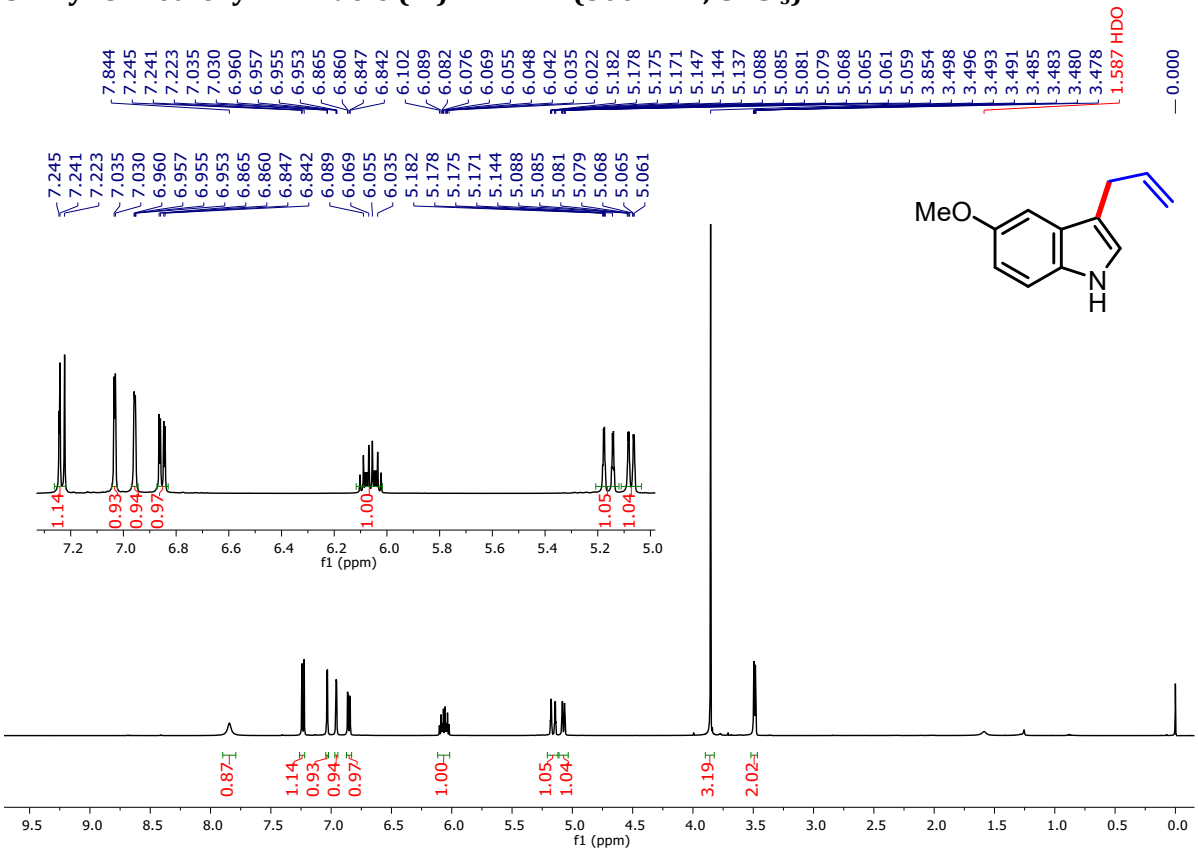
3-Allyl-6-chloro-5-fluoro-1*H*-indole (4e): ^{13}C NMR (125 MHz, $CDCl_3$)



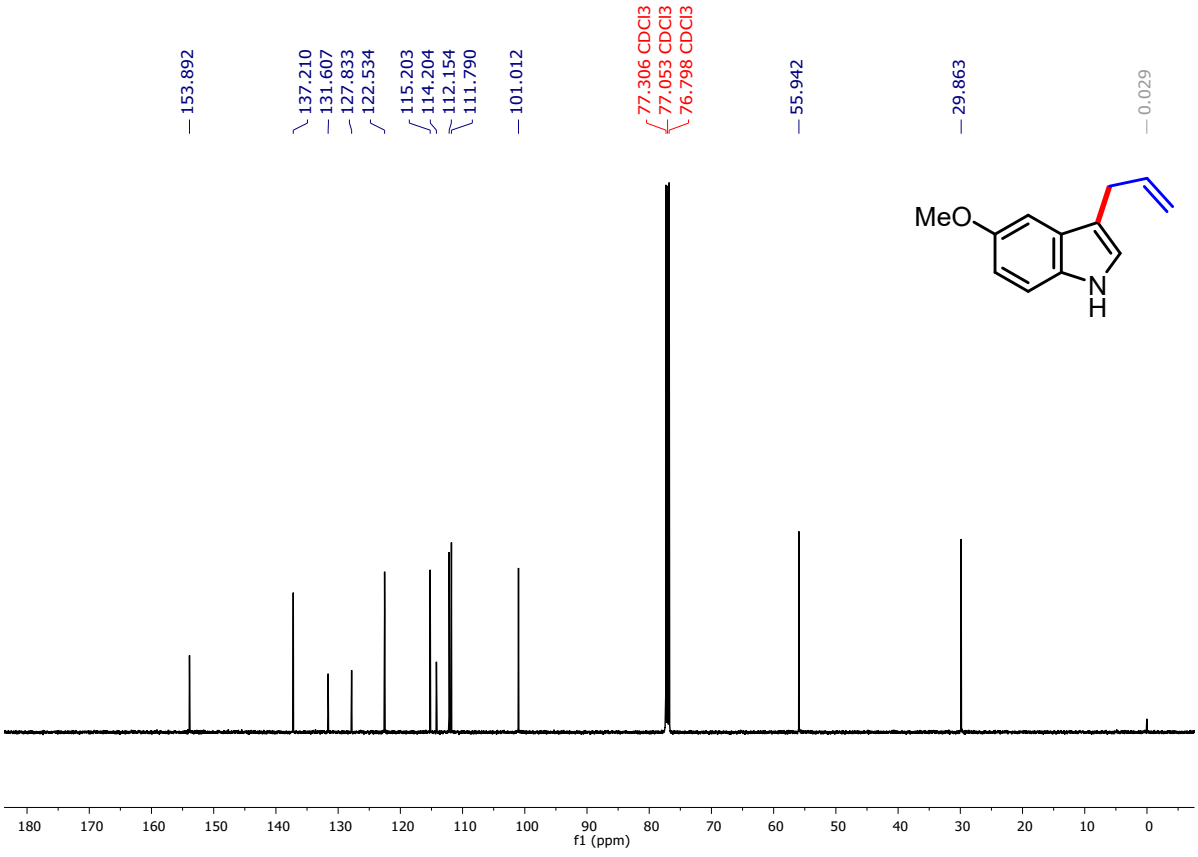
3-Allyl-6-chloro-5-fluoro-1*H*-indole (4e): ^{19}F NMR (471 MHz, $CDCl_3$)



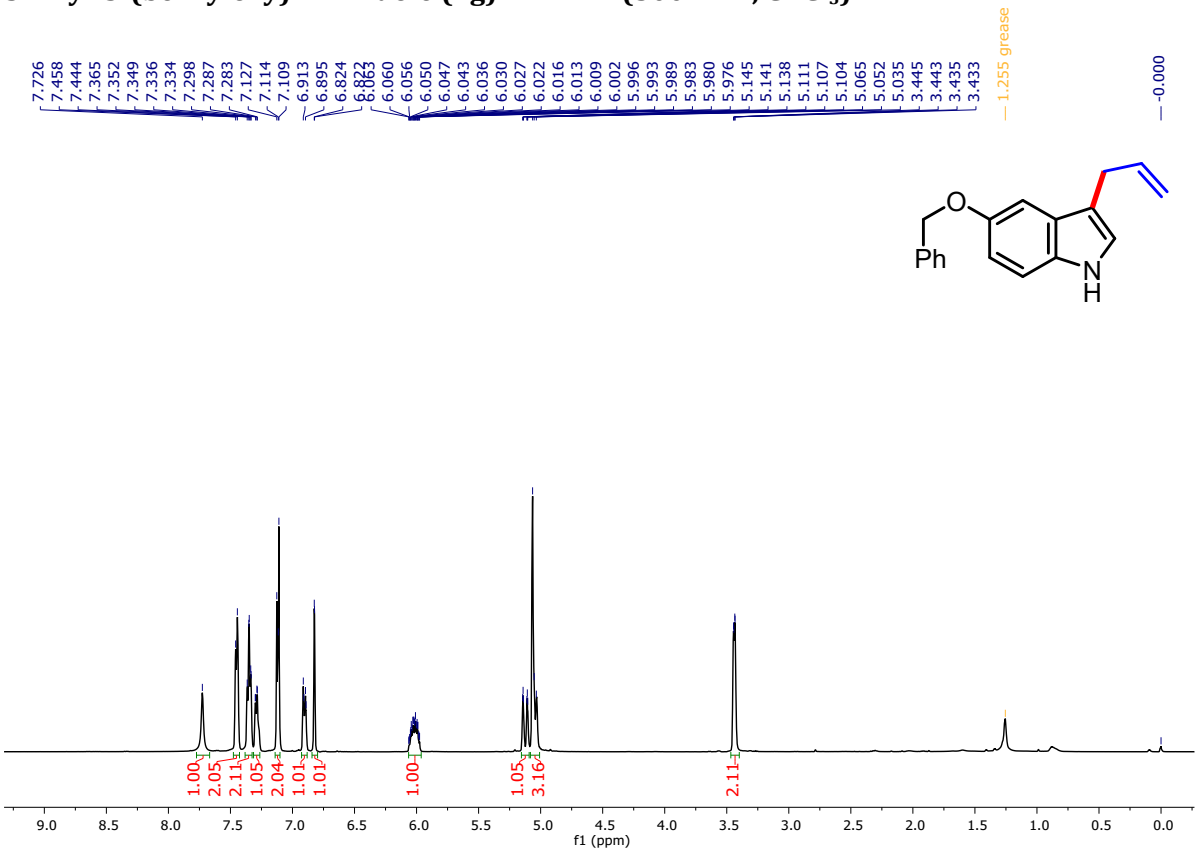
3-Allyl-5-methoxy-1*H*-indole (4f): ^{1}H NMR (500 MHz, $CDCl_3$)



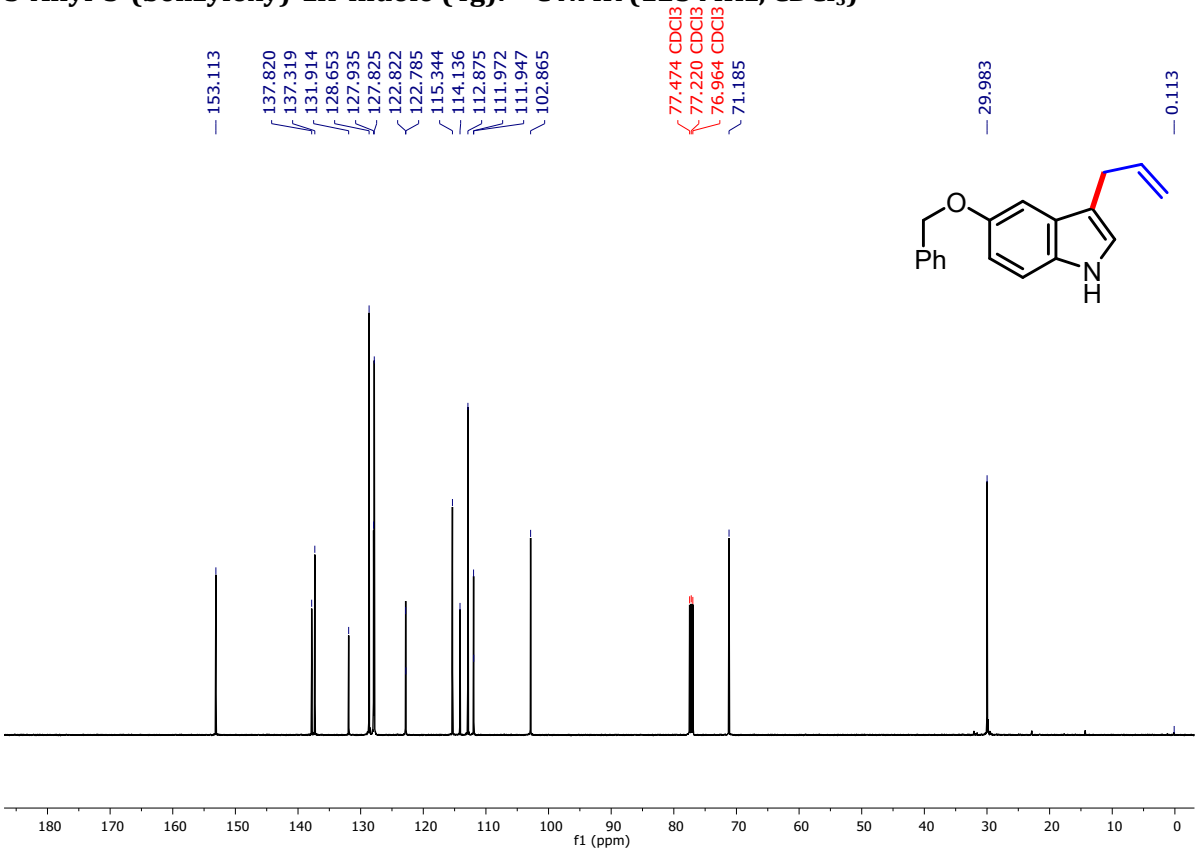
3-Allyl-5-methoxy-1*H*-indole (4f): ^{13}C NMR (125 MHz, $CDCl_3$)



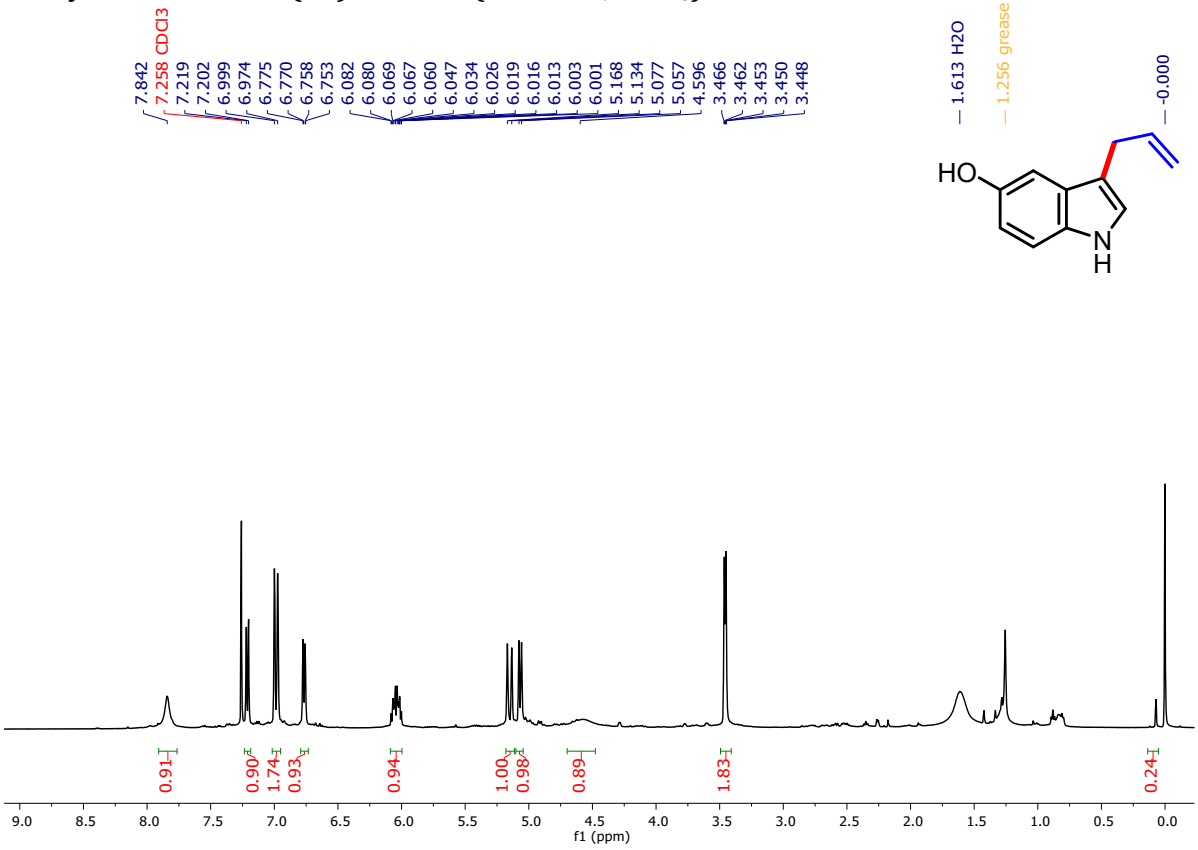
3-Allyl-5-(benzyloxy)-1*H*-indole (4g): ^{1}H NMR (500 MHz, $CDCl_3$)



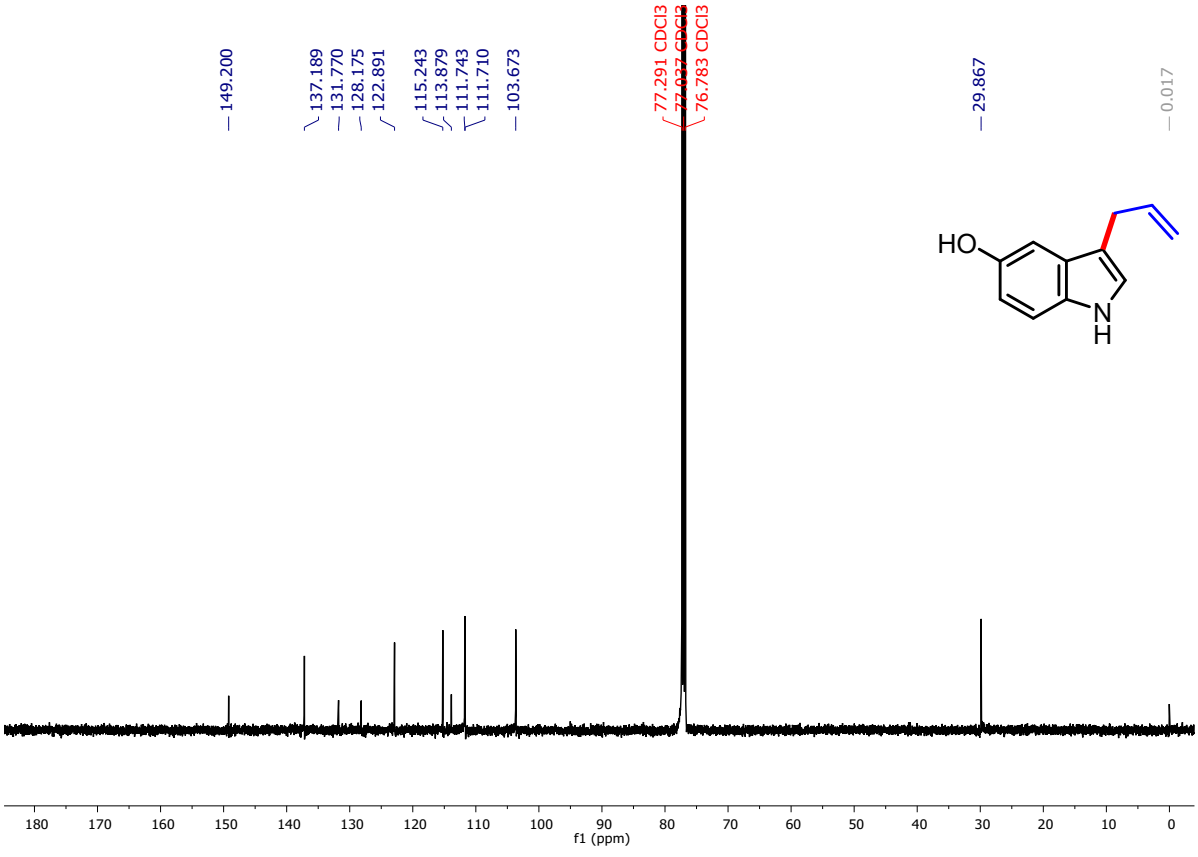
3-Allyl-5-(benzyloxy)-1*H*-indole (4g): ^{13}C NMR (125 MHz, $CDCl_3$)



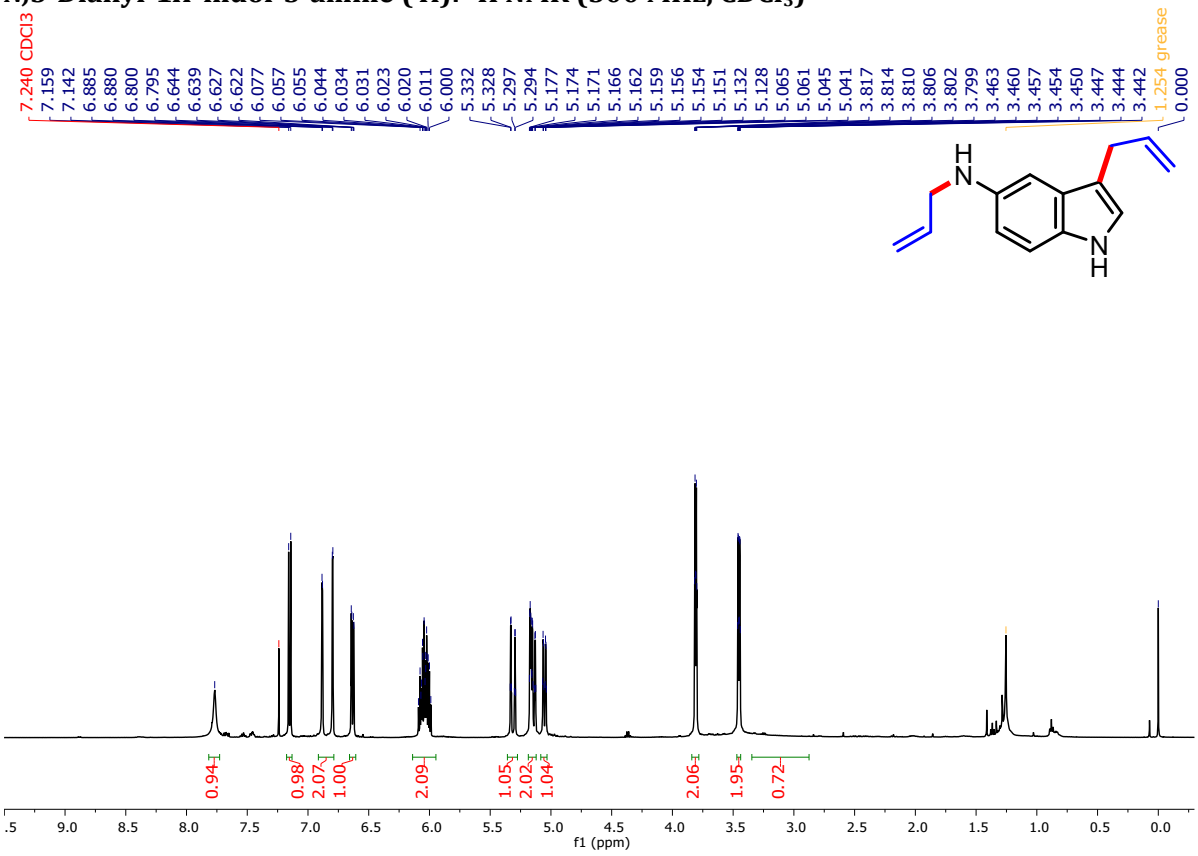
3-Allyl-1*H*-indol-5-ol (4h): ^{1}H NMR (500 MHz, $CDCl_3$)



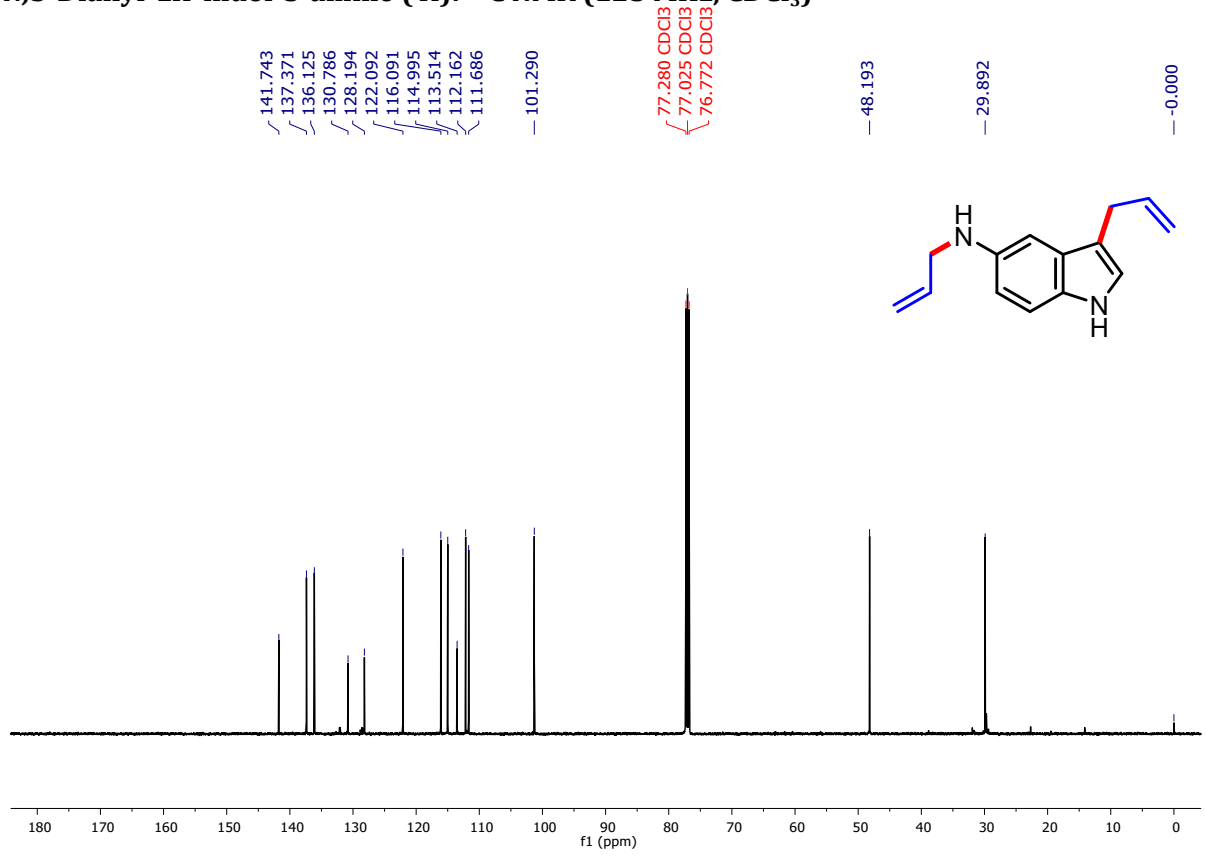
3-Allyl-1*H*-indol-5-ol (4h): ^{13}C NMR (125 MHz, $CDCl_3$)



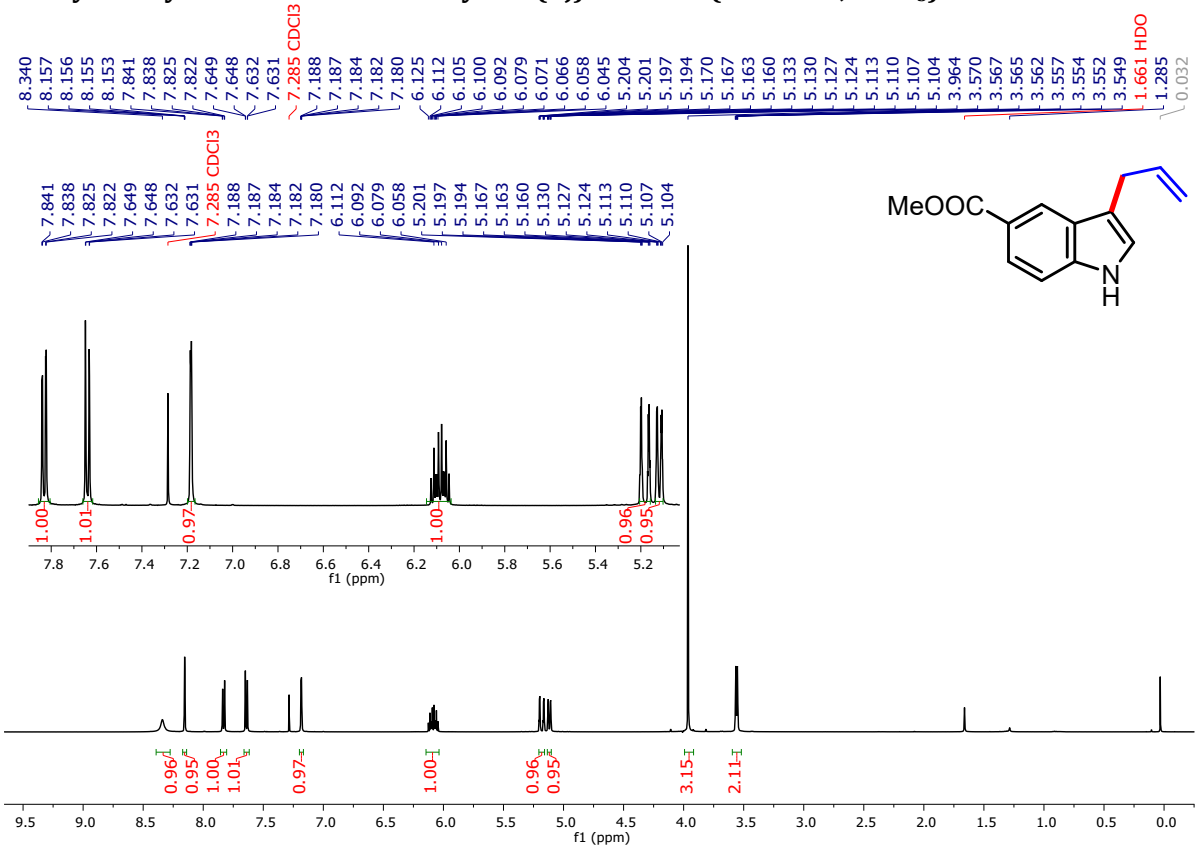
***N*,3-Diallyl-1*H*-indol-5-amine (4i): ^{1}H NMR (500 MHz, $CDCl_3$)**



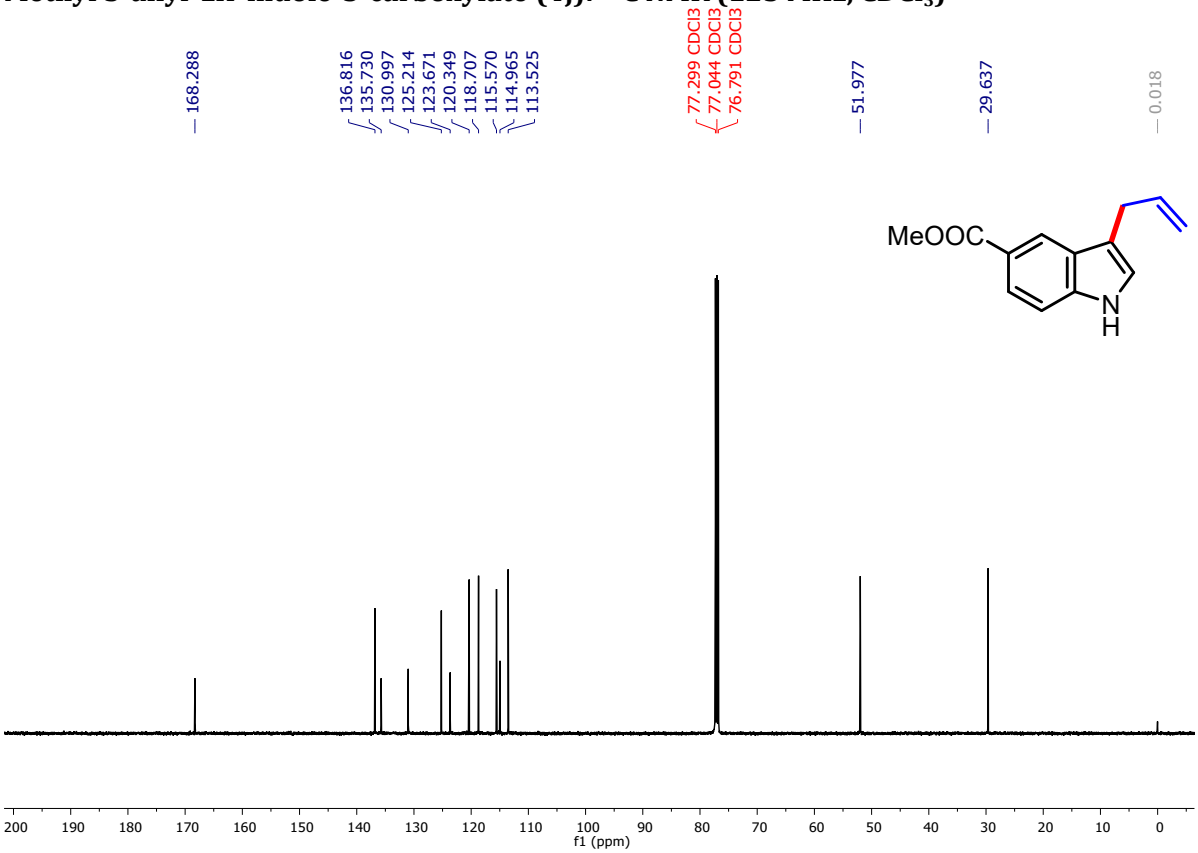
***N*,3-Diallyl-1*H*-indol-5-amine (4i): ^{13}C NMR (125 MHz, $CDCl_3$)**



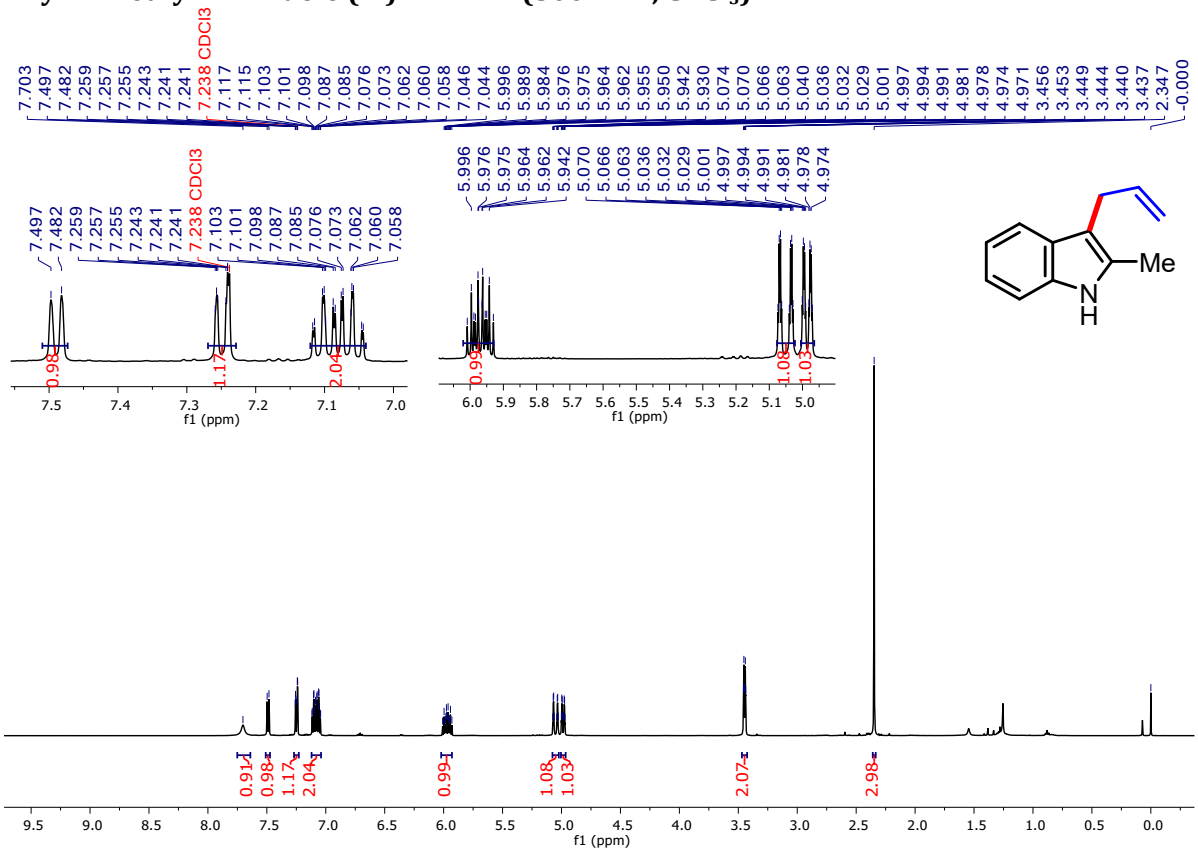
Methyl 3-allyl-1*H*-indole-5-carboxylate (4j): ^{1}H NMR (500 MHz, $CDCl_3$)



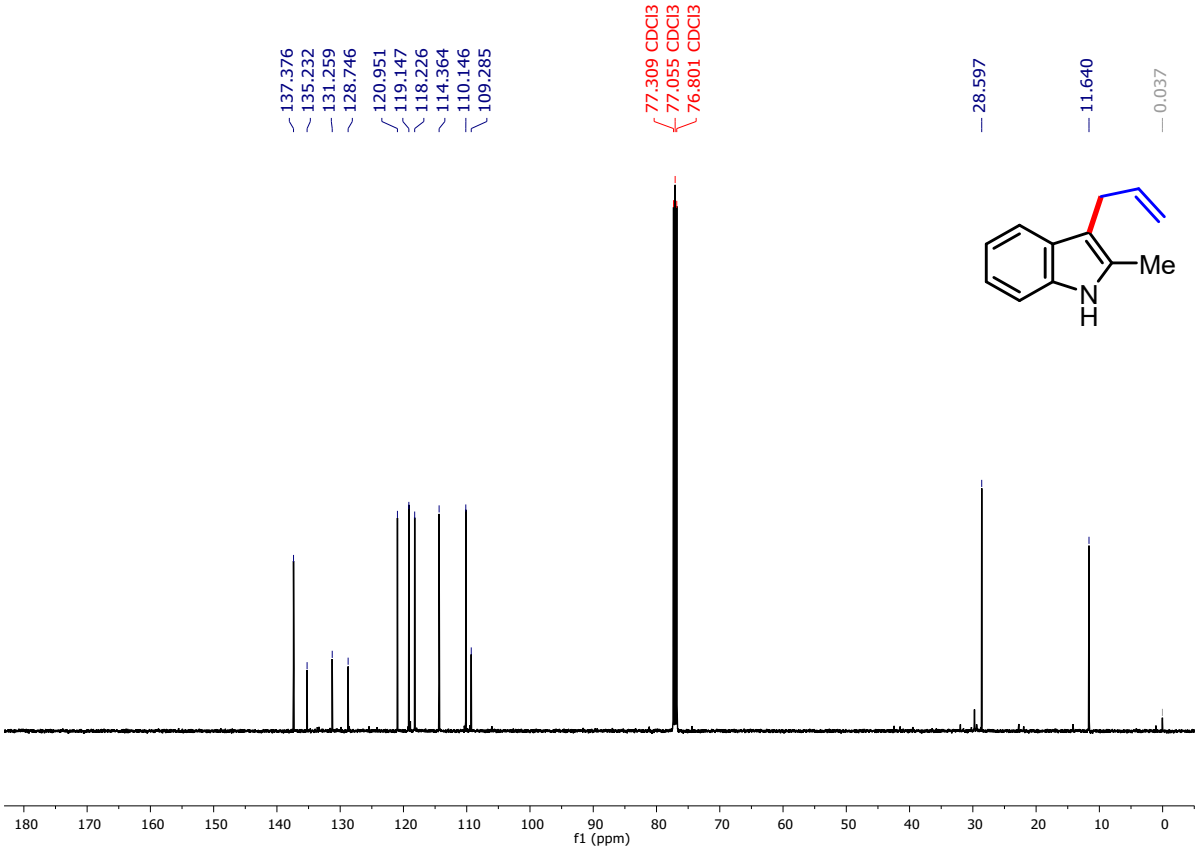
Methyl 3-allyl-1*H*-indole-5-carboxylate (4j): ^{13}C NMR (125 MHz, $CDCl_3$)



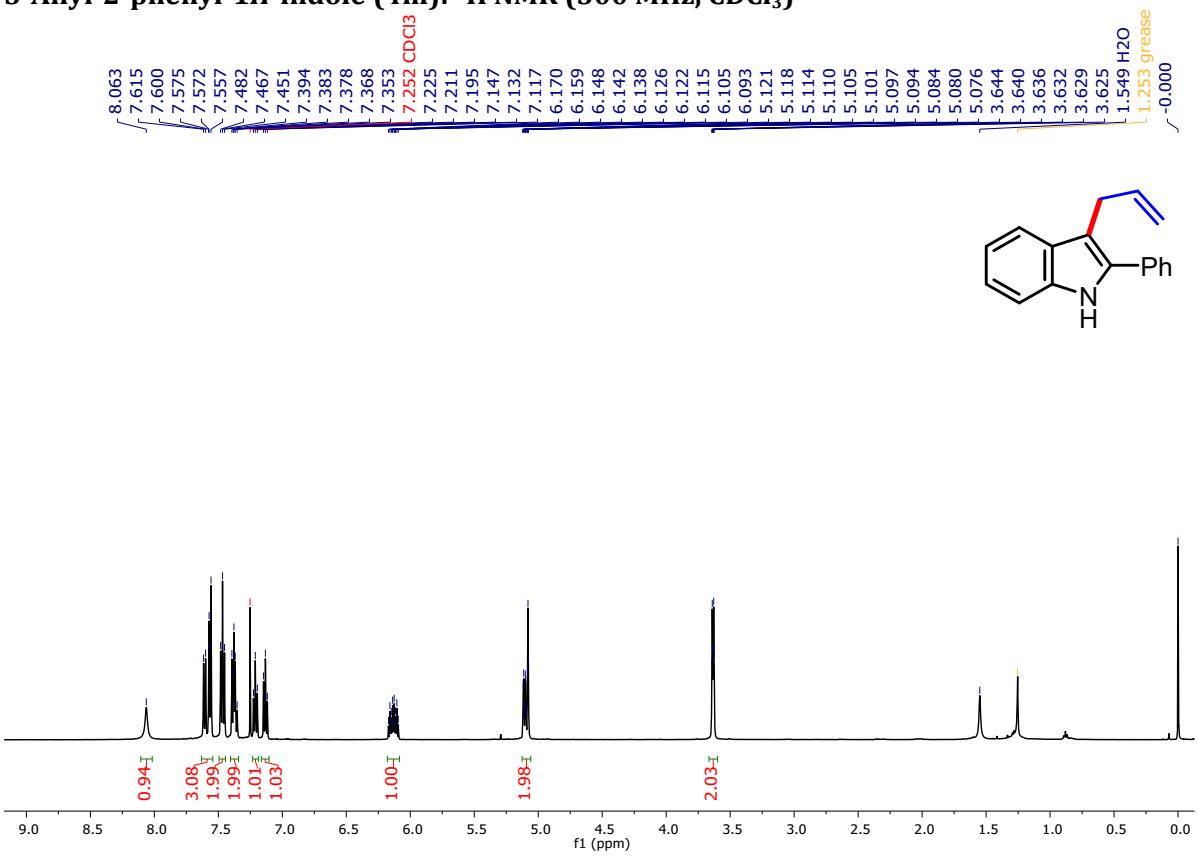
Allyl-2-methyl-1*H*-indole (4l): ^{1}H NMR (500 MHz, $CDCl_3$)



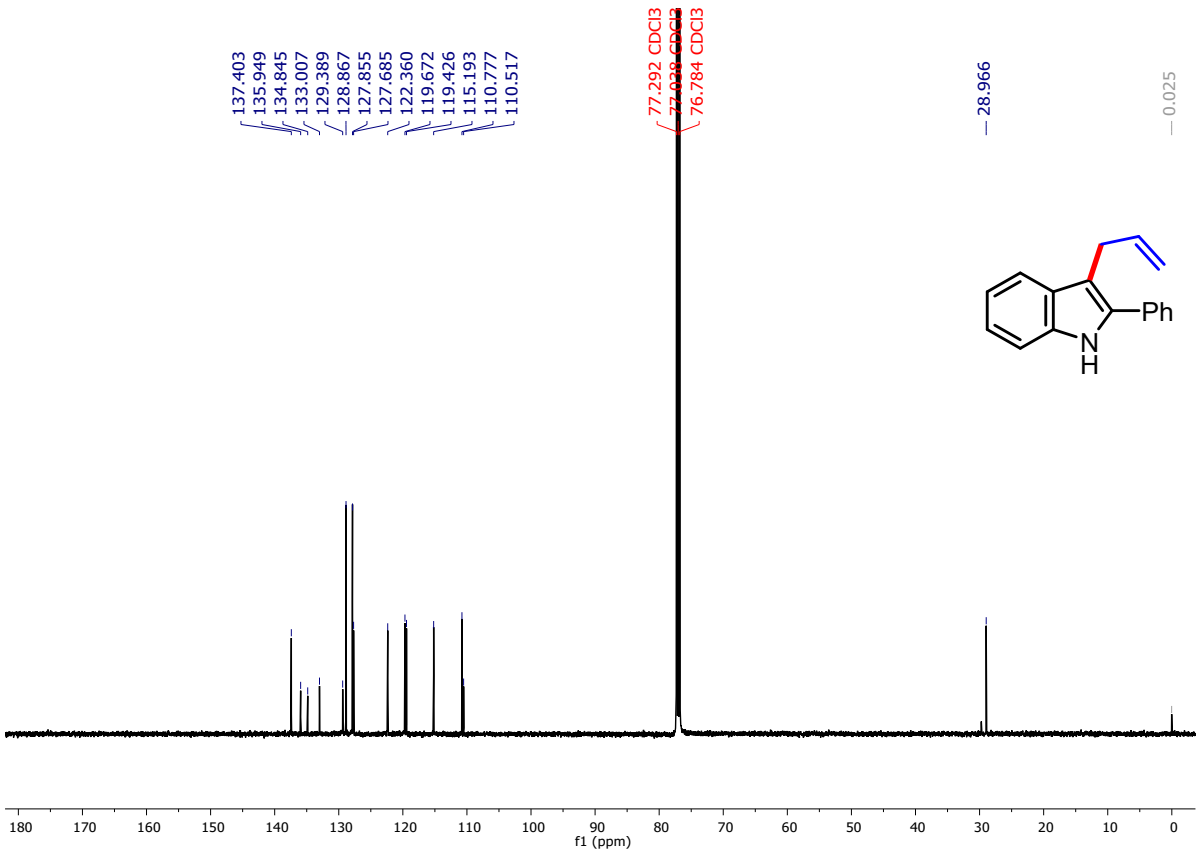
3-Allyl-2-methyl-1*H*-indole (4l): ^{13}C NMR (125 MHz, $CDCl_3$)



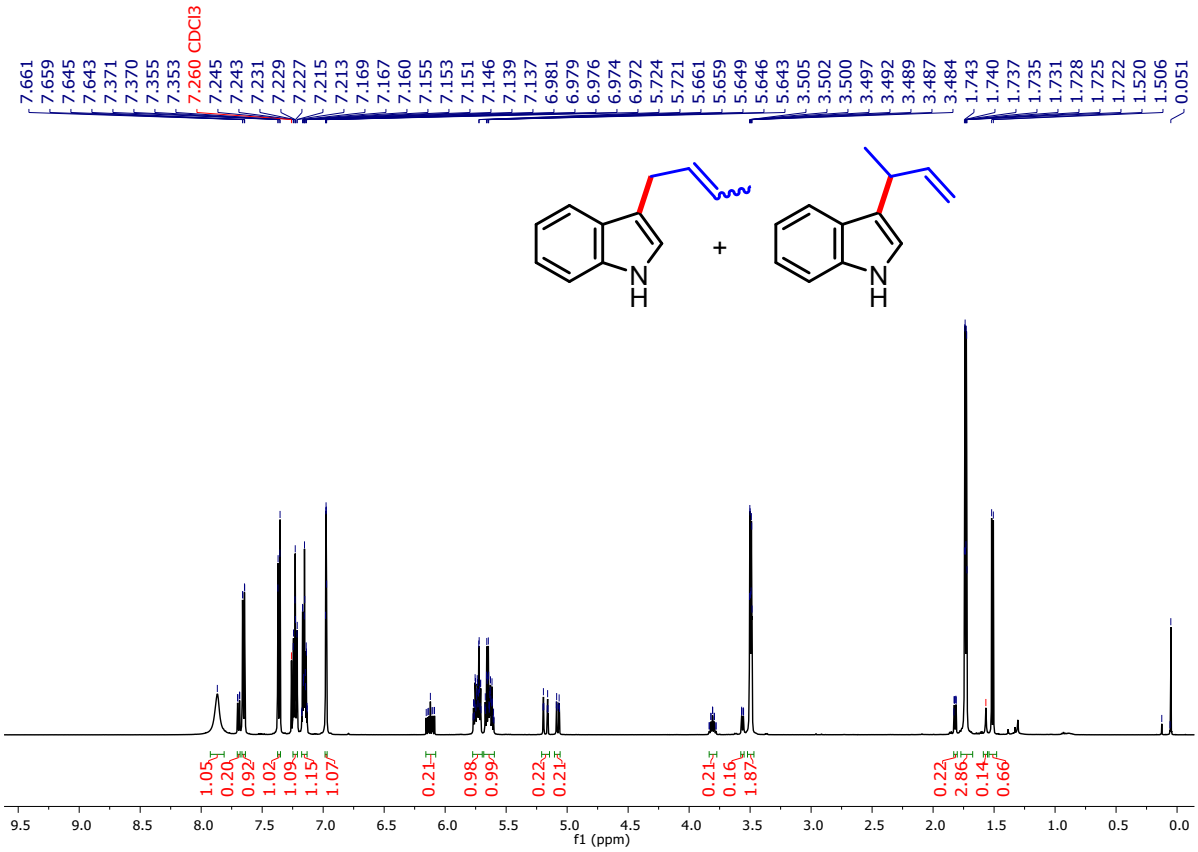
3-Allyl-2-phenyl-1*H*-indole (4m): ^{1}H NMR (500 MHz, $CDCl_3$)



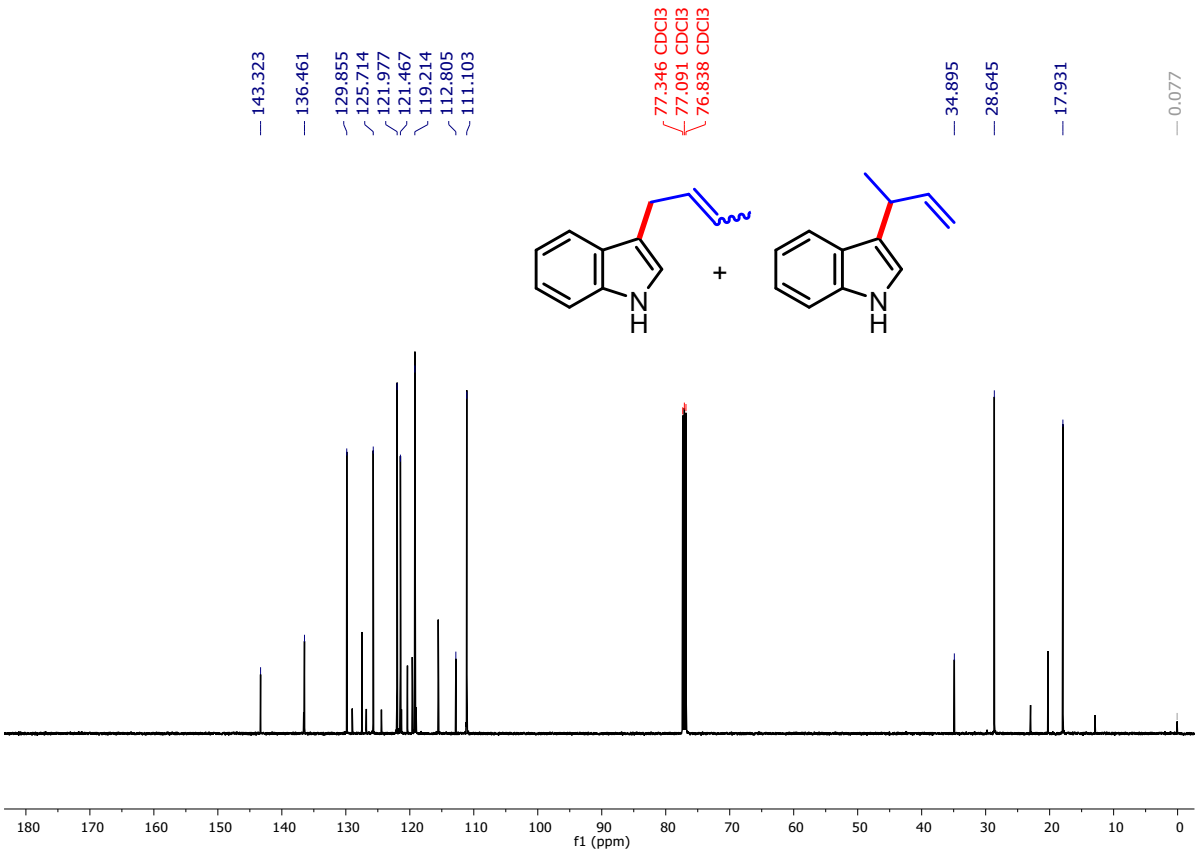
3-Allyl-2-phenyl-1*H*-indole (4m): ^{13}C NMR (125 MHz, $CDCl_3$)


137.403
135.949
134.845
133.007
129.389
128.867
127.855
127.685
122.360
119.672
119.426
115.193
110.777
110.517
77.292 CDCl3
77.038 CDCl3
76.784 CDCl3
28.966
0.025
Ph
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

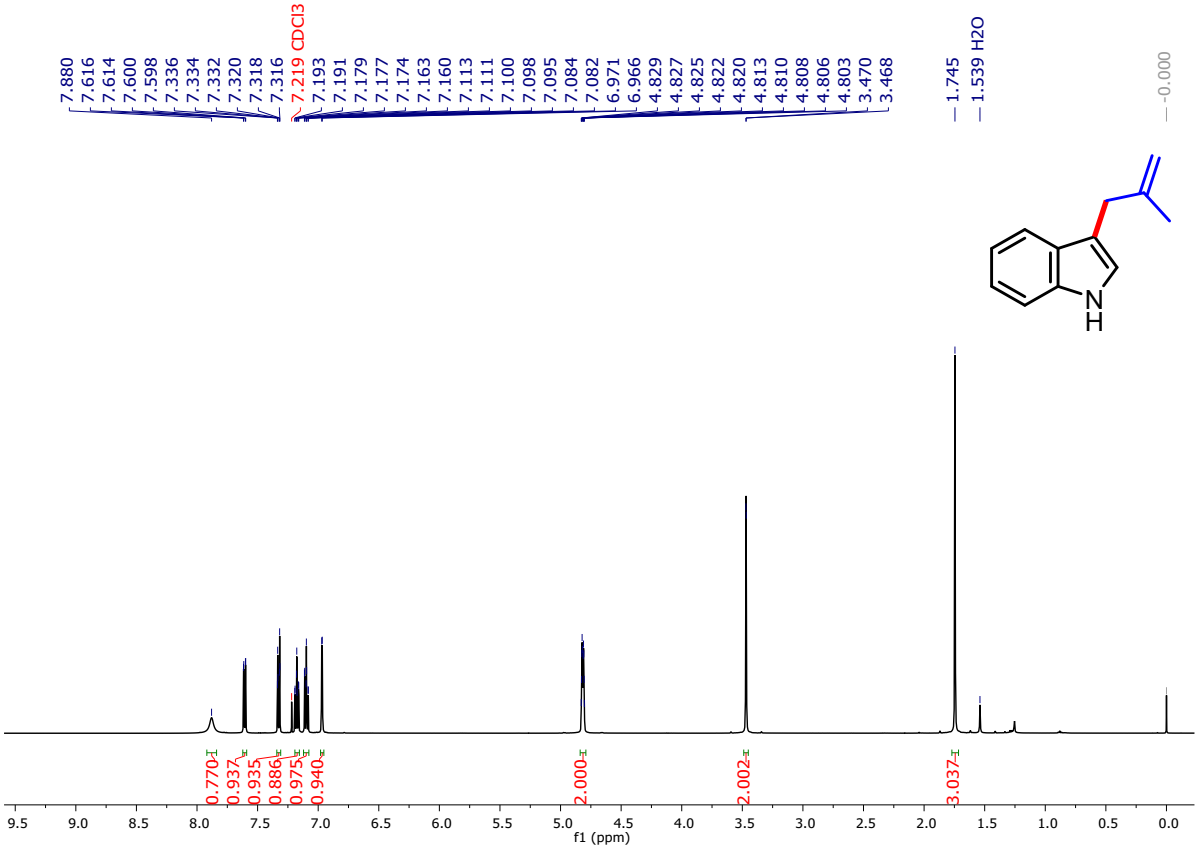
3-(But-2-en-1-yl)-3*H*-indole (5a): ^{1}H NMR (500 MHz, $CDCl_3$)



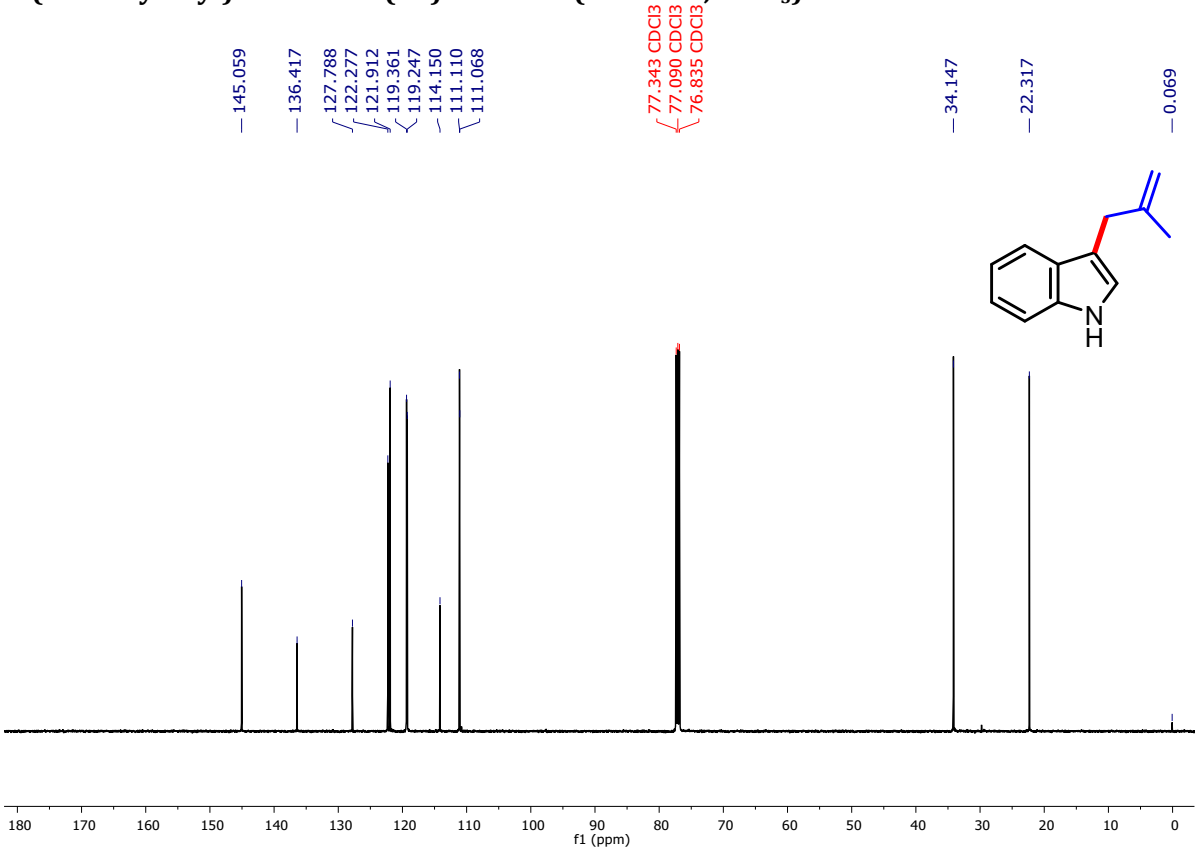
3-(But-2-en-1-yl)-3H-indole (5a): ^{13}C NMR (125 MHz, $CDCl_3$)



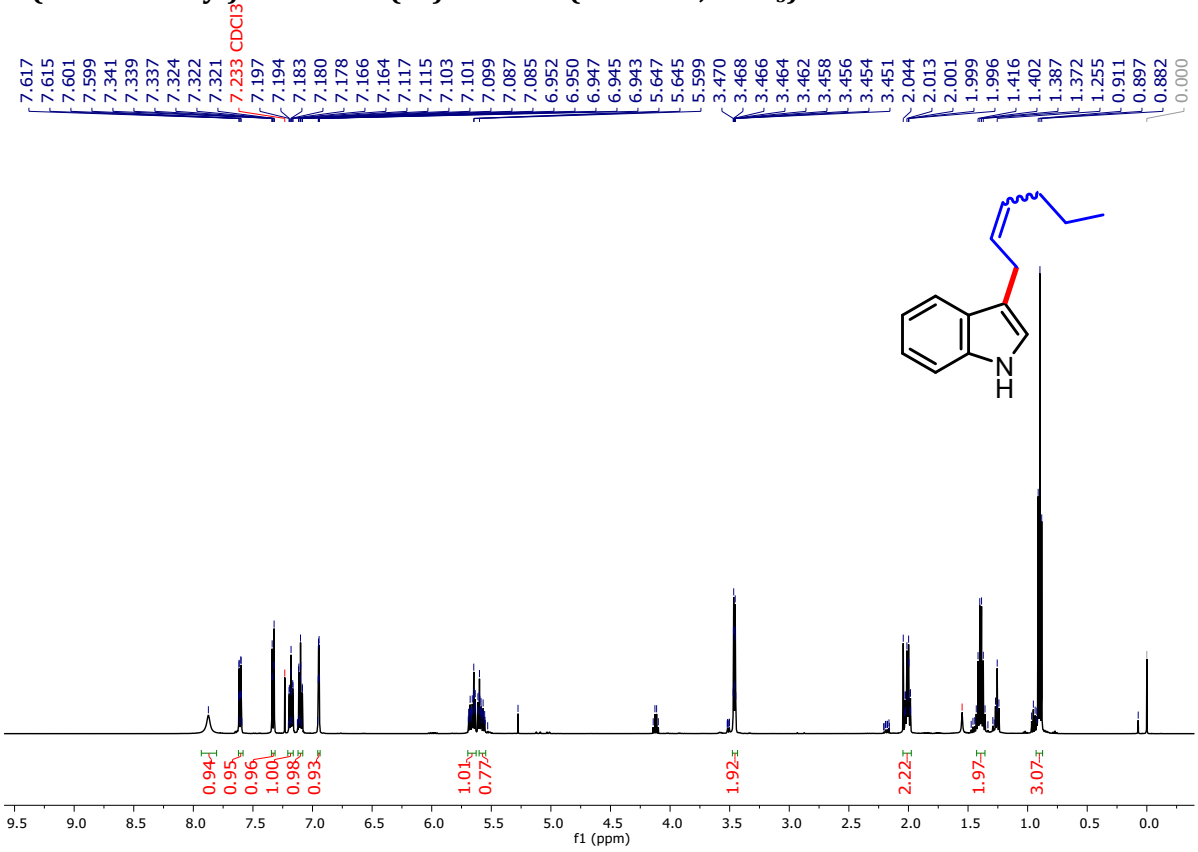
3-(2-Methylallyl)-3*H*-indole (5b): ^{1}H NMR (500 MHz, $CDCl_3$)



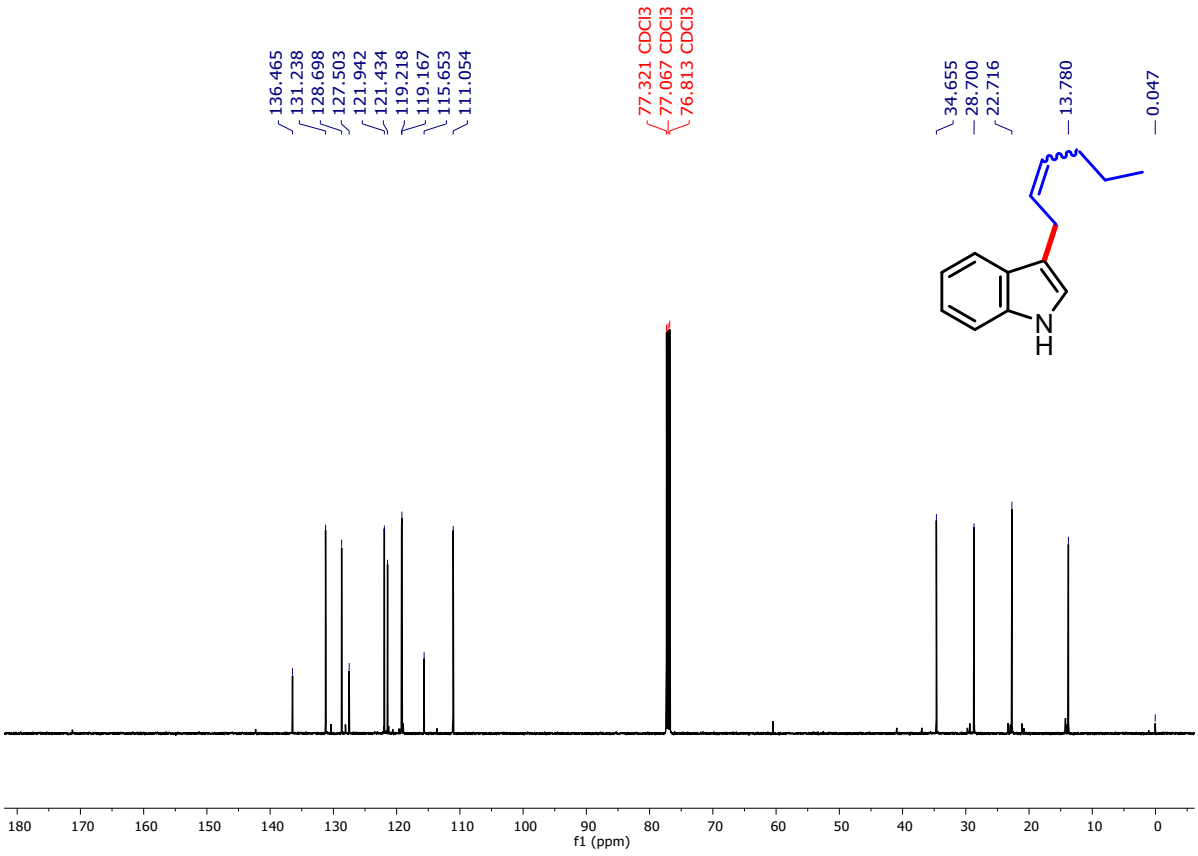
3-(2-Methylallyl)-3*H*-indole (5b): ^{13}C NMR (125 MHz, $CDCl_3$)



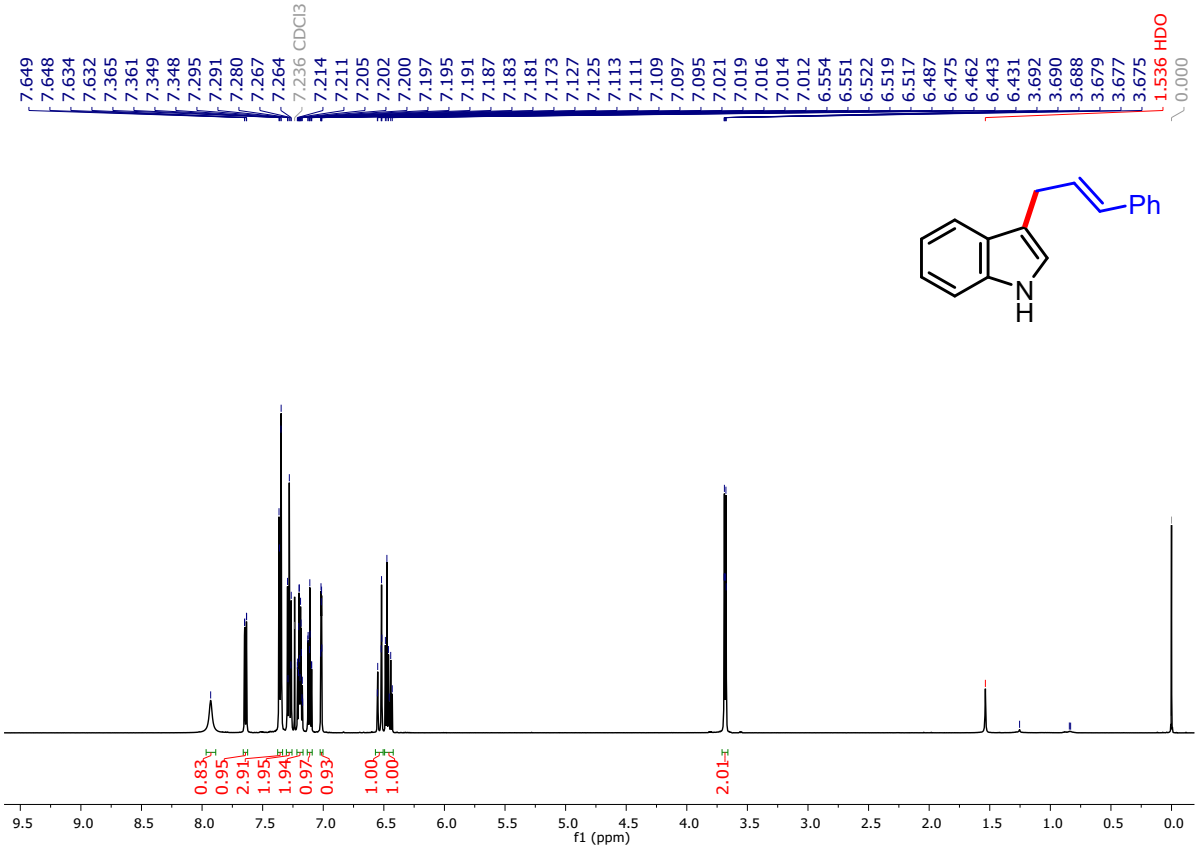
3-(Hex-2-en-1-yl)-1*H*-indole (5c): ^{1}H NMR (500 MHz, $CDCl_3$)



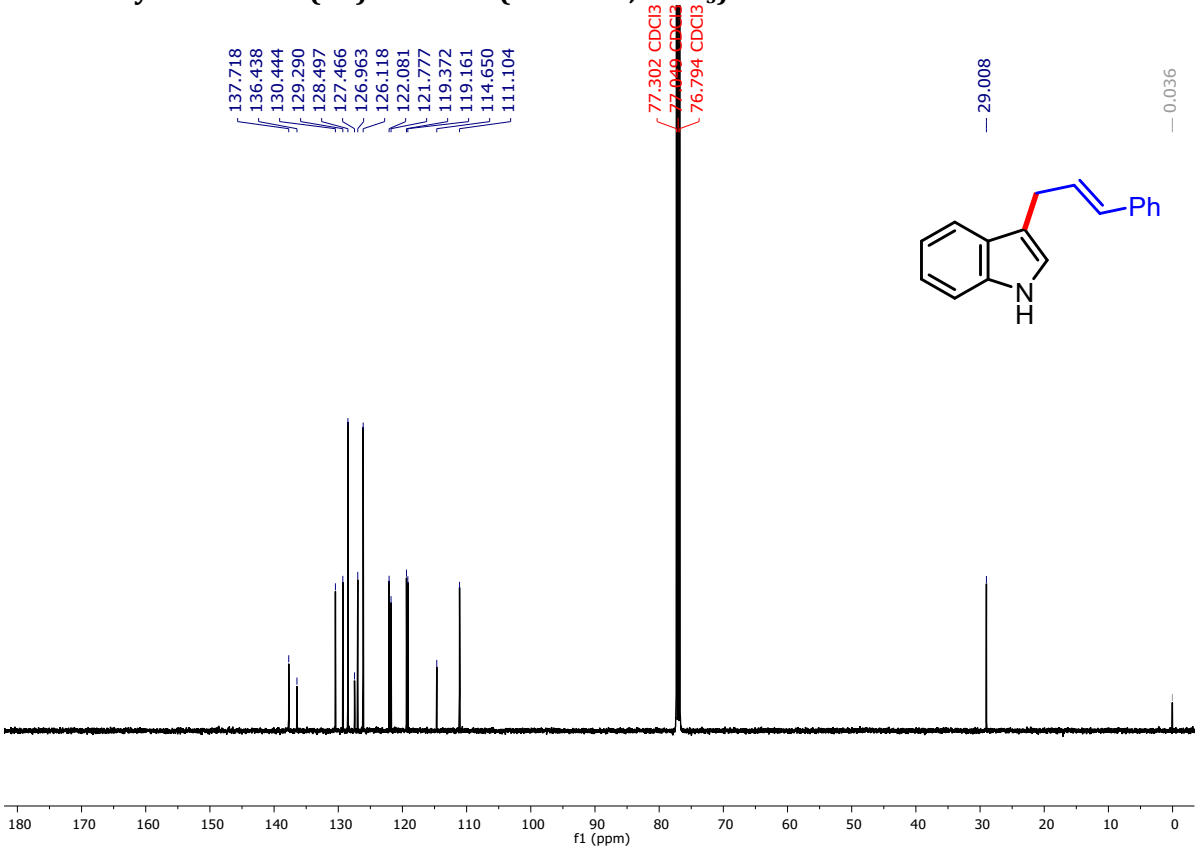
3-(Hex-2-en-1-yl)-1*H*-indole (5c): ^{13}C NMR (125 MHz, $CDCl_3$)



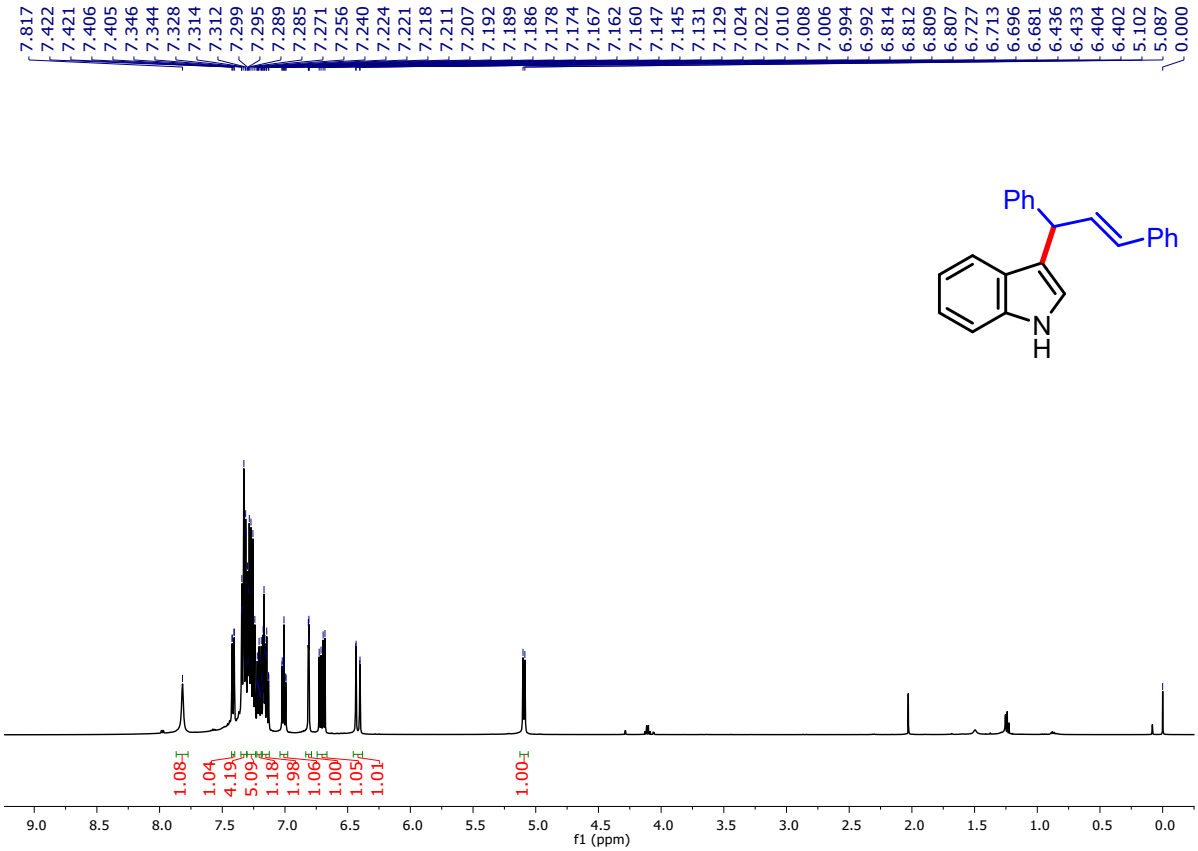
3-Cinnamyl-1*H*-indole (5d): ^{1}H NMR (500 MHz, $CDCl_3$)



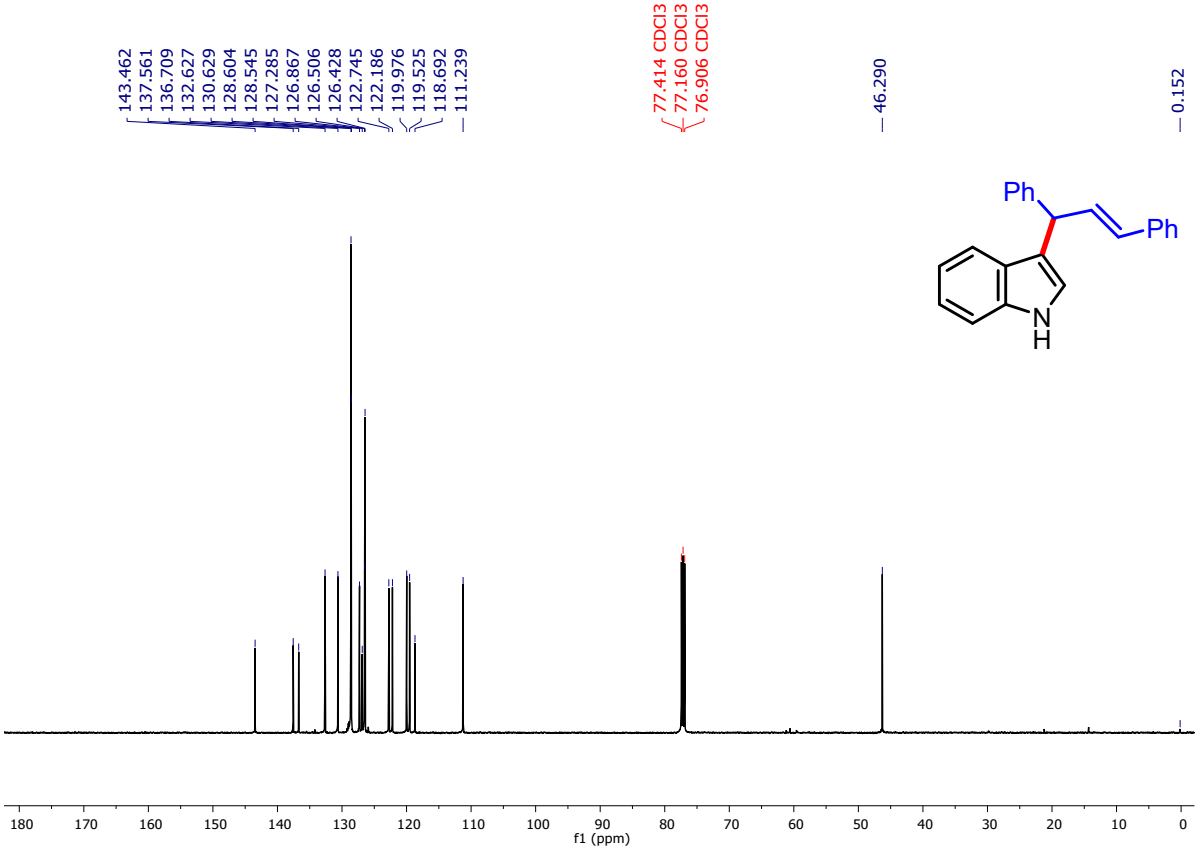
3-Cinnamyl-1*H*-indole (5d): ^{13}C NMR (125 MHz, $CDCl_3$)



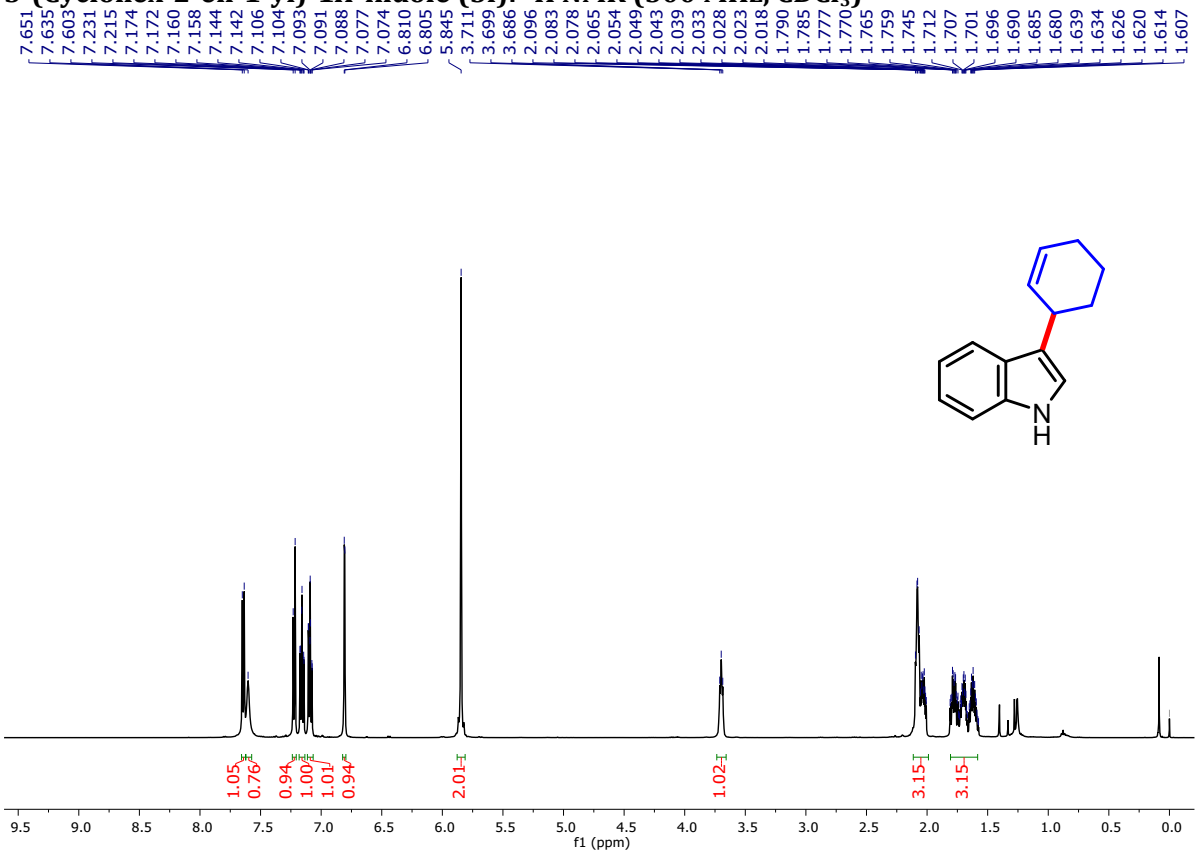
(*E*)-3-(1,3-Diphenylallyl)-1*H*-indole (5e): ^{1}H NMR (500 MHz, $CDCl_3$)



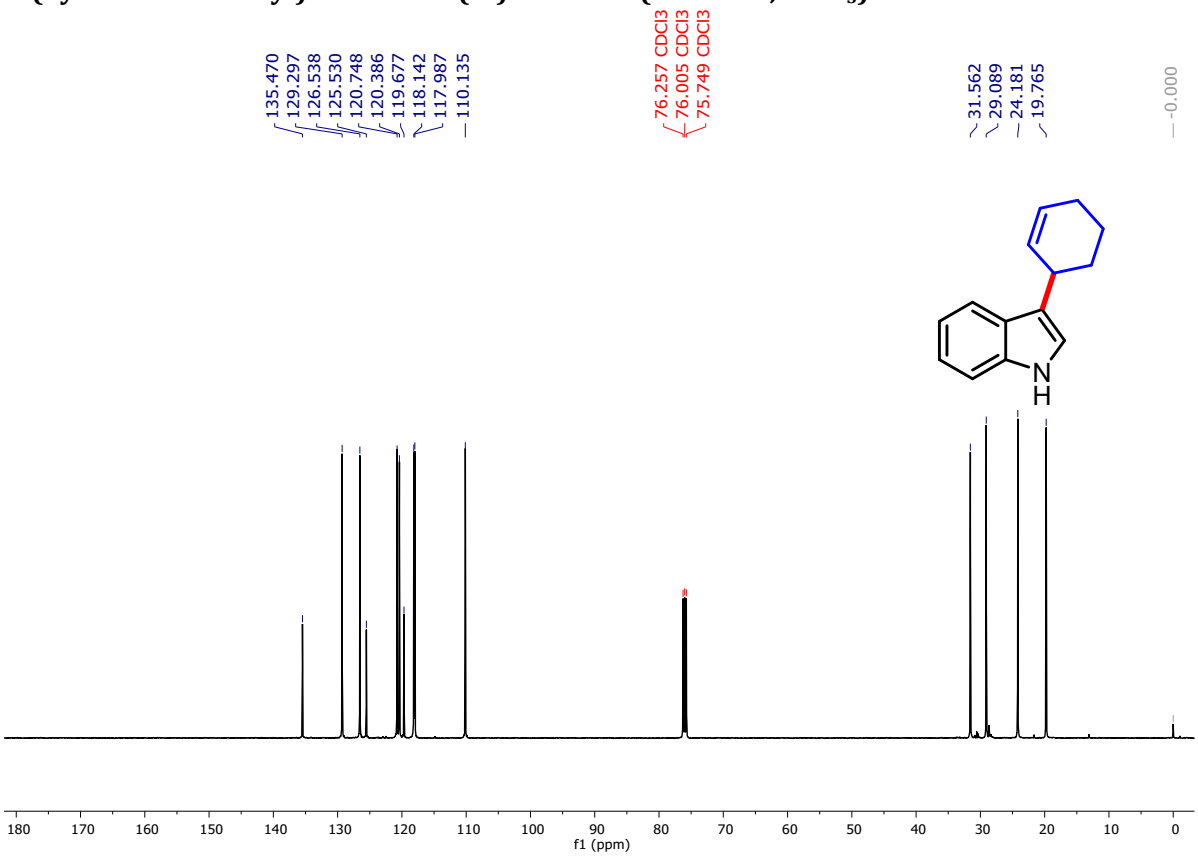
(*E*)-3-(1,3-Diphenylallyl)-1*H*-indole (5e): ^{13}C NMR (125 MHz, $CDCl_3$)



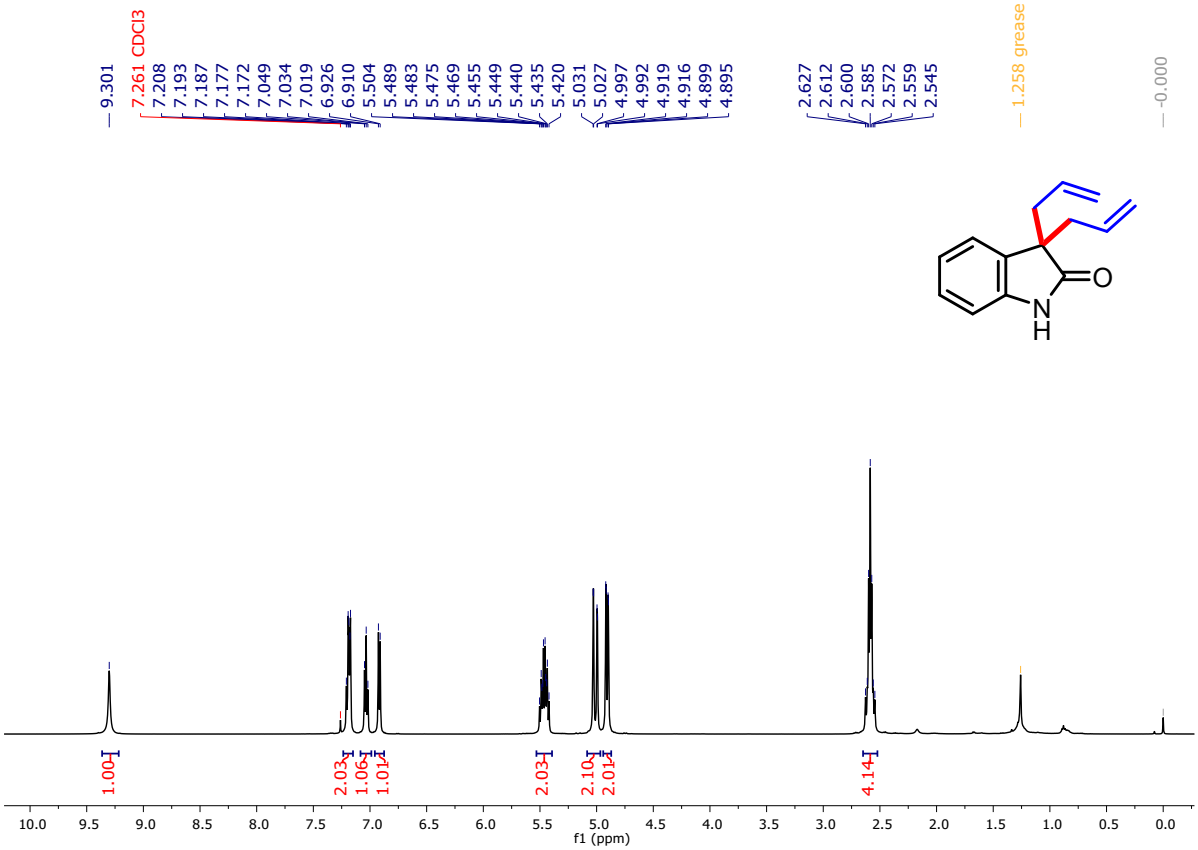
3-(Cyclohex-2-en-1-yl)-1*H*-indole (5f): ^{1}H NMR (500 MHz, $CDCl_3$)



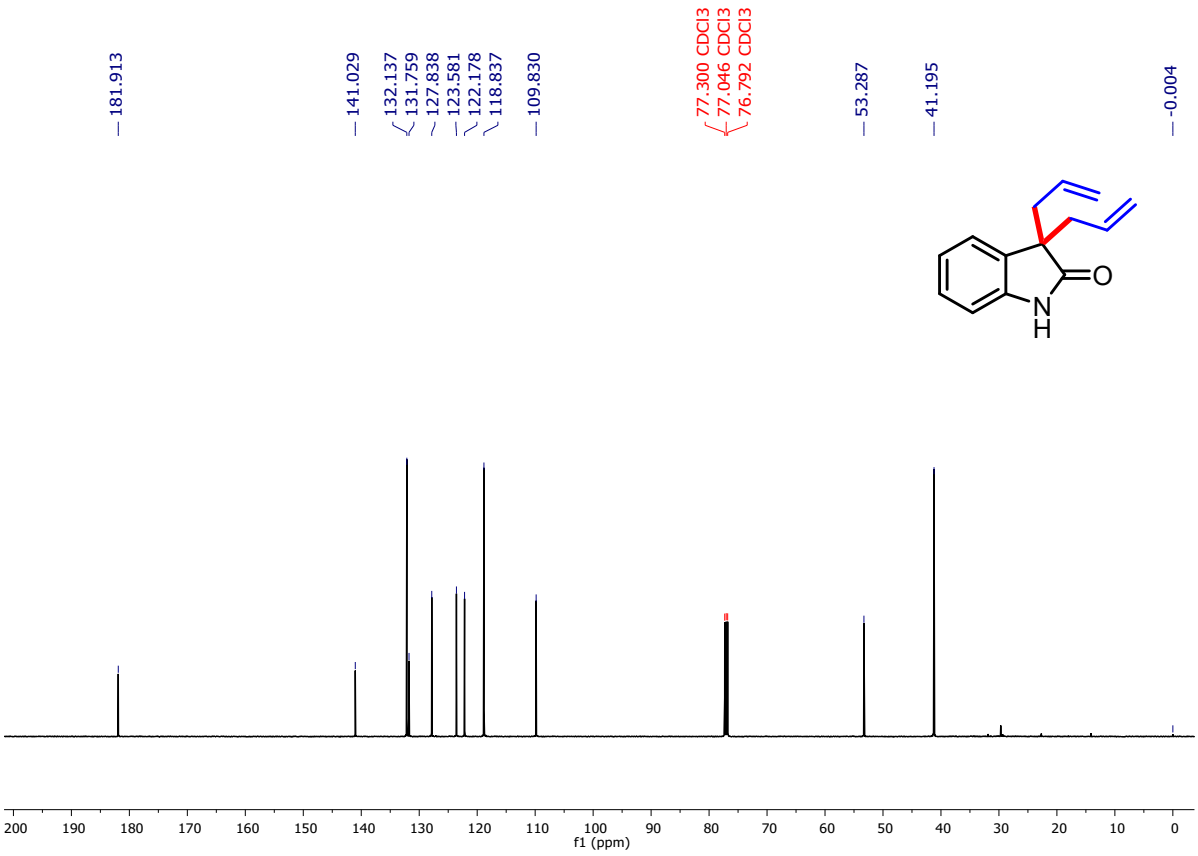
3-(Cyclohex-2-en-1-yl)-1*H*-indole (5f): ^{13}C NMR (125 MHz, $CDCl_3$)



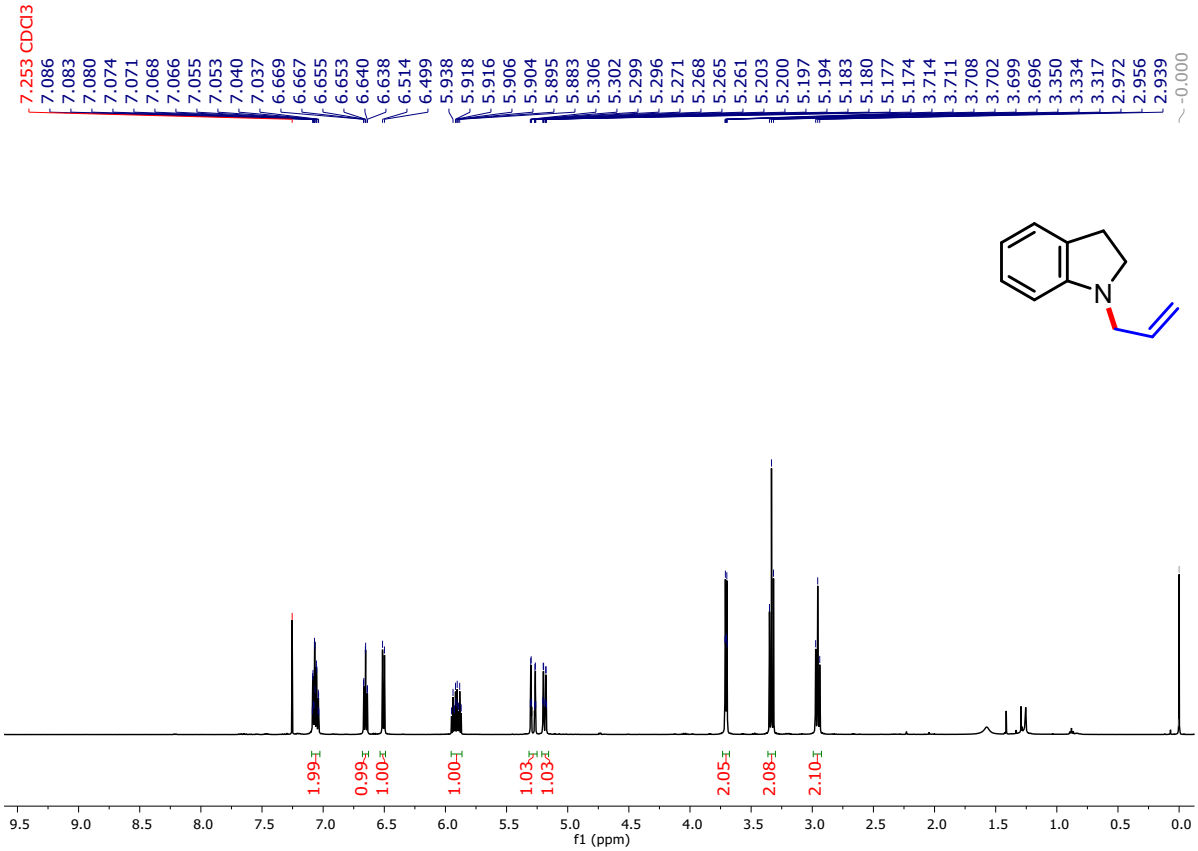
3,3-Diallylindolin-2-one (6b): ^{1}H NMR (500 MHz, $CDCl_3$)



3,3-Diallylindolin-2-one (6b): ^{13}C NMR (125 MHz, $CDCl_3$)



N-Allylindoline (7a): ^{1}H NMR (500 MHz, $CDCl_3$)



N-Allylindoline (7a): ^{13}C NMR (125 MHz, $CDCl_3$)