Suplemental Information

C-H functionalization of heterocycles with triplet carbenes via an unexpected 1,2-alkyl radical migration

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General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Chempur, Fluorochem, Activate Scientific, abcr and Carl Roth. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR were recorded on a Varian AV600/AV400 or an Agilent DD2 400 NMR spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated brs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV. Low-resolution mass spectra were recorded on an Applied Biosystems API 365 mass spectrometer using electrospray ionization (ESI) technique. GC/MS were recorded on a Shimadzu GCMS-QP2010 SE Gas chromatograph mass spectrometer. GC column: Optima 5 MS column, 30 m. Carrier gas: Helium. IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). UV-Vis spectra were measured on a Shimadzu UV-2600 UV-Vis spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence Spectrophotometer. Cyclic voltammetry was measured on a Metrohm Autolab analyzer. EPR spectra were measured on an ADANI SPINSCAN X EPR Spectrometer.

Blue LEDs used in this manuscript were Kessil PR160L, 467 nm, 40 W. Green LEDs used in this manuscript were Kessil PR160L, 525 nm, 40 W. UV LEDs used in this manuscript were Kessil PR160L, 370 nm, 40 W. Reactions were irradiated from 3 cm with two LEDs (each from one side of the reaction tube), temperature was maintained at room temperature by cooling with a fan.

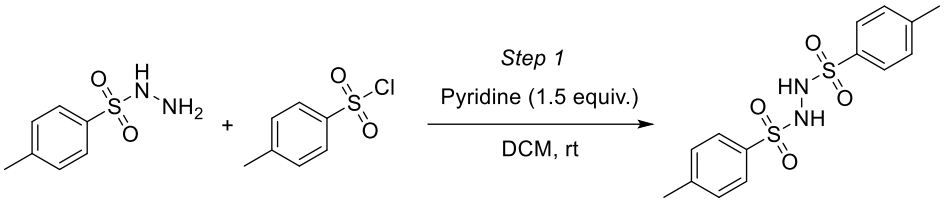
Important Safety Note

Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

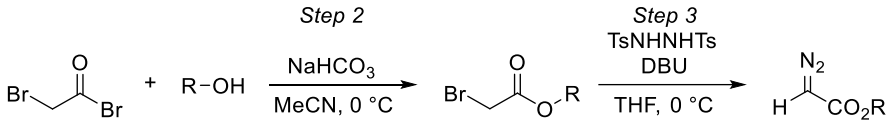
General Procedures

General Procedure for the synthesis of diazoalkanes (GP-D)

All the diazoalkanes used in this manuscript were synthesized according to the literature procedure.[1]



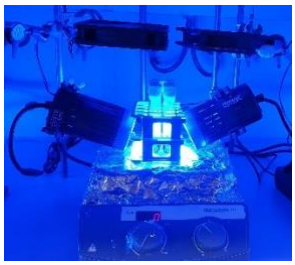
Step 1: A dry 500 mL, round-bottomed flask fitted with a magnetic stir bar was charged with *p*-toluenesulfonyl hydrazide (15 g, 80.5 mmol) and *p*-toluenesulfonyl chloride (23.5 g, 121 mmol) in 80 mL of dry, degassed DCM. The suspension was stirred at room temperature while pyridine (9.77 mL, 121 mmol) was added dropwise. During the addition, the reaction mixture became homogenous and turned yellow. Colorless precipitate was observed within a few minutes and the reaction mixture was stirred for 1.5 h. Et_2O (300 mL) and H_2O (150 mL) were added and stirred at 0 °C for 15 min. The colorless solid precipitate was collected and washed with Et_2O (150 mL). The solid thus obtained was dissolved in boiling MeOH (400 mL). After cooling to room temperature, precipitate appeared. About 300 mL of MeOH was removed by rotary evaporation and cooled to 0 °C. The precipitate was collected in a Büchner funnel using suction filtration and washed with cold MeOH (30 mL) and Et_2O (150 mL) to give *N,N'*-ditosylhydrazine (21.1 g, 77%) as a colorless solid.



Step 2: Alcohol (1.0 mmol) and $NaHCO_3$ (3.0 mmol) were dissolved in MeCN (5.0 mL) and bromoacetyl bromide (1.5 mmol) was added slowly at 0 °C. After stirring for 10 min at 0 °C, the reaction was quenched with H_2O. The solution was extracted with DCM three times. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was evaporated, and the residue was used in the next reaction without purification.

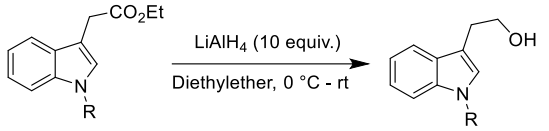
Step 3: The bromoacetate thus obtained and *N,N'*-ditosylhydrazine (2.0 mmol) were dissolved in THF (5.0 mL) and cooled to 0 °C. DBU (5.0 mmol) was added dropwise and stirred at the temperature for 10 minutes. After quenching of the reaction by the addition of saturated $NaHCO_3$ solution, this was extracted with Et_2O three times. The organic phase was washed with brine, dried over $MgSO_4$ and evaporated to give the crude diazoacetate. The diazoacetate was purified by silica gel column chromatography to give the corresponding diazoacetate as a pale-yellow oil.

General Procedure for Photocatalytic C-H Functionalization Reaction (GP-1)



In an oven-dried reaction tube indole **7** (0.6 mmol, 3 equiv.), $Ir(ppy)_3$ (0.5 mol%) and one stirring bar were added. Then the tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1.0 mL dry, degassed DCM in a separate tube under argon atmosphere and the resulting solution was added to the reaction tube by syringe. Then the final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was irradiated with blue LED (2 × Kessil PR160L, 467 nm, 40 W) for 8 h at a distance of ~ 3 cm from the LED, temperature was maintained at room temperature with a cooling fan. After completion of the reaction, the product was purified by column chromatography on silica gel (*n*-Hexane : EtOAc).

General Procedure for the Synthesis of Tryptophol Derivatives (GP-2)

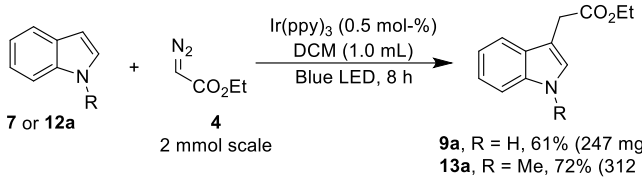


9a or **13a**

17a, R = H, 81%
17b, R = Me, 84%

Compound **9a** or **13a** (0.7 mmol, 1 equiv.), dissolved in diethyl ether (5 mL), was added dropwise over 30 minutes to a stirred suspension of lithium aluminum hydride (292 mg, 7.7 mmol, 11 equiv.) in diethyl ether (5 mL). The resulting mixture was heated refluxed for 1 h. The reaction mixture was allowed to cool to room temperature and excess of lithium aluminum hydride was carefully quenched with ice-water (50 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure. The product was purified by flash column chromatography.

Scale Up Experiment of Photocatalyzed C-H Functionalization Reaction (2 mmol)



In an oven-dried reaction tube $Ir(ppy)_3$ (0.5 mol-%) and indole **7** or **12a** (10 mmol, 3 equiv.) were added. Reaction tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (2 mmol, 1 equiv.) was dissolved in 10 mL dry, degassed DCM and the solution was added via syringe to the reaction tube. Then the final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 8 h under blue LED irradiation (2 × Kessil PR160L, 467 nm, 40 W) at room temperature. After completion of the reaction, the product was purified by column chromatography on silica gel (*n*-Hexane : EtOAc).

Product **9a** was isolated in 61% (247 mg) yield; Product **13a** was isolated in 72% (312 mg) yield.

Structure of Photocatalysts

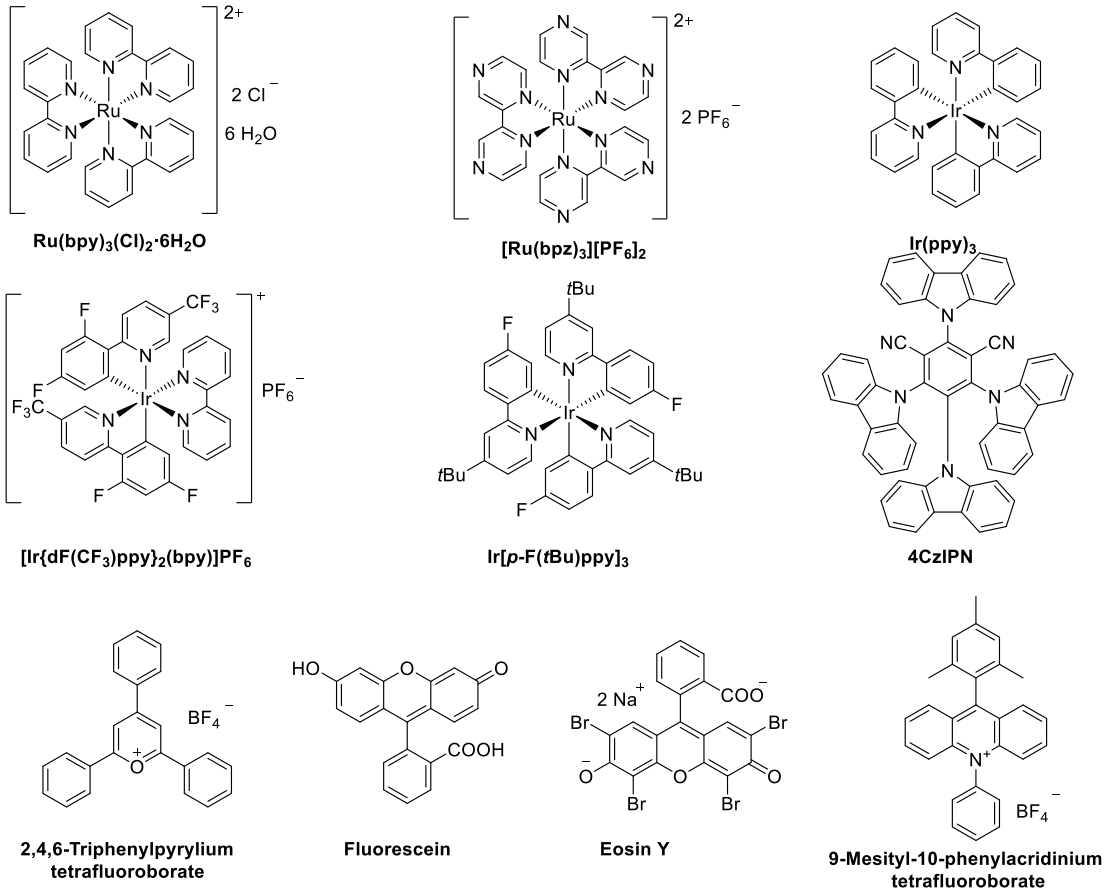
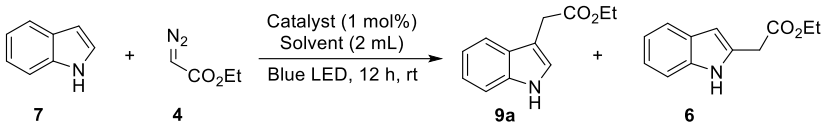


Figure S5. Structure of photocatalysts

Reaction Optimization

Table S4. Catalyst screening

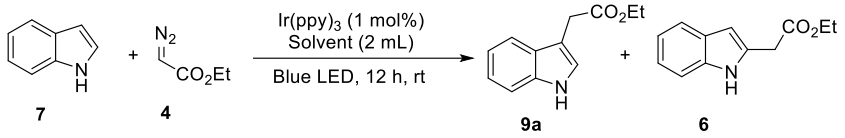


7 4 9a 6

Entry[a]	Catalyst	Solvent	%-Yield 9a / 6[b]
1	4-CzIPN	DCM	13 / 8
2	4-CzIPN	MeOH	diazo decomposed
3	Eosin Y	DCM	trace / -, no reaction
4	Eosin Y	MeOH	diazo decomposed
5	Fluorescein	DCM	trace / -, no reaction
6	Fluorescein	MeOH	diazo decomposed
7	$Ru(bpy)_3Cl_2$	DCM	22 / 10
8	$Ru(bpy)_3Cl_2$	MeOH	8 / 73
9	$Ir(ppy)_3$	DCM	87 / trace
10	$Ir(ppy)_3$	MeOH	14 / 70
11	2,4,6-Triphenylpyrylium tetrafluoroborate	DCM	23 / trace
12	9-Mesityl-10-phenylacridinium tetrafluoroborate	DCM	16 / trace
13	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	DCM	53 / 14
14	$Ir[p\text{-}F(t\text{Bu})ppy]_3$	DCM	76 / traces
15	$[Ru(bpz)_3][PF_6]_2$	DCM	no reaction
16	$[Ru(bpz)_3][PF_6]_2$	MeCN	no reaction

Reaction condition: [a] Photocatalyst (1 mol%), **7** (0.6 mmol, 3 equiv.) and **4** (0.2 mmol, 1 equiv.) in 2 mL solvent under argon atmosphere irradiated with 2 x 40 W blue LED for 12 h at room temperature. [b] Isolated yield.

Table S5. Solvent screening

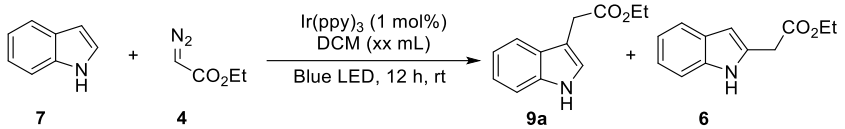


7 4 9a 6

Entry[a]	Solvent	%-Yield 9a / 6[b]
1	EtOAc	46 / trace
2	$CHCl_3$	70 / 18
3	Toluene	19 / trace
4	*n*-Hexane	26 / trace
5	MeCN	30/ 18
6	DCM	87 / trace
7	1,2-DCE	83 /trace
8	MeOH	14 / 70
9	THF	- / -, diazo decomposed
10	Et_2O	- / -, diazo decomposed
11	DMF	- / -, diazo decomposed
12	DMSO	- / -, diazo decomposed

Reaction condition: [a] $Ir(ppy)_3$ (1 mol%), **7** (0.6 mmol, 3 equiv.) and **4** (0.2 mmol, 1 equiv.) in 2 mL solvent as mentioned in table S5 under argon atmosphere irradiated with 2 x 40 W blue LED for 12 h at room temperature. [b] Isolated yield.

Table S6. Stoichiometry and concentration screening

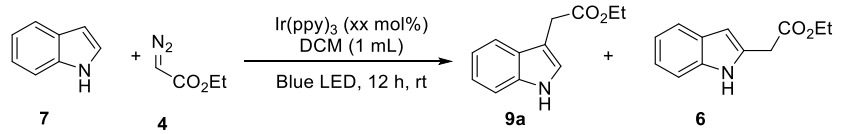


7 4 9a 6

Entry[a]	7 : 4	DCM (mL) / C (M)	%-Yield 9a / 6[d]
1	3:1	2 / 0.1	87 / trace
2	3:1	1 / 0.2	93 / trace
3[b]	3:1	1 / 0.2	74 / trace[e]
4	4:1	1 / 0.2	97 / trace
5	5:1	1 / 0.2	99 / trace
6	2:1	1 / 0.2	69 / trace
7	1:1	1 / 0.2	24 / trace
8	5:1	3 / 0.06	57 / trace
9[c]	1:3	1 / 0.2	23 / trace

Reaction condition: [a] $Ir(ppy)_3$ (1 mol%), **7** (xx mmol, xx equiv.) and **4** (0.2 mmol, 1 equiv.) in xx mL DCM as mentioned in table S6 under argon atmosphere irradiated with 2 x 40 W blue LED for 12 h at room temperature. [b] $Ir(ppy)_3$ (1 mol%), **7** (0.6 mmol, 3 equiv.) in 0.5 mL DCM then EDA **4** (0.2 mmol, 1 equiv.) was dissolved in 0.5 mL DCM and added to the reaction mixture slowly over 5 h to the reaction mixture under argon atmosphere and irradiated with 2 x40 W blue LED at room temperature. [c] **7** (0.2 mmol, 1 equiv.) and **4** (0.6 mmol, 3 equiv.). [d] Isolated yield. [e] ^{1}H NMR yield.

Table S7. Catalyst loading screening

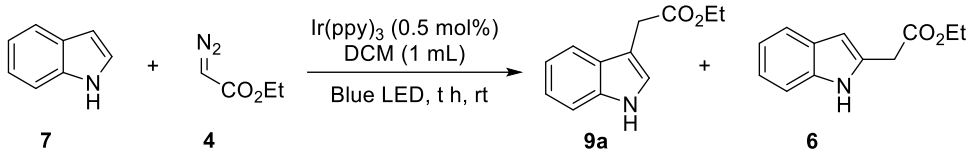


7 4 9a 6

Entry[a]	Catalyst loading (mol-%)	%-Yield 9a / 6[b]
1	1	93 / trace
2	2	85 / trace
3	3	76 / trace
4	0.5	91 / trace
5	0.25	79 / trace

Reaction condition: [a] $Ir(ppy)_3$ (xx mol%) as mentioned in table S7, **7** (0.6 mmol, 3 equiv.) and **4** (0.2 mmol, 1 equiv.) in 1 mL DCM under argon atmosphere irradiated with 2 x 40 W blue LED for 12 h at room temperature. [b] Isolated yield.

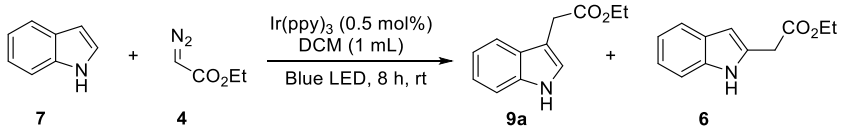
Table S8. Time screening



Entry[a]	Time (h)	%-Yield 9a / 6[b]
1	1	23 / trace
2	2	44 / trace
3	4	67 / trace
4	6	79 / trace
5	8	93 / trace
6	12	92 / trace

Reaction condition: [a] $Ir(ppy)_3$ (0.5 mol%), **7** (0.6 mmol, 3 equiv.) and **4** (0.2 mmol, 1 equiv.) in 1 mL DCM under argon atmosphere irradiated with 2 x 40 W blue LED at room temperature for the mentioned time. [b] Isolated yield.

Table S9. Other experiments

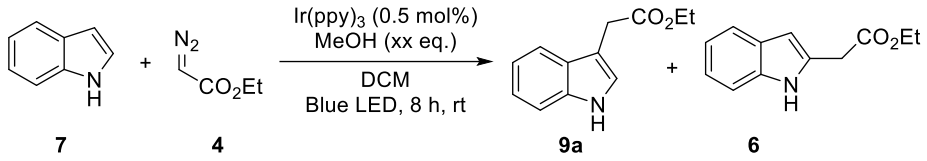


Entry[a]	Deviation from above	%-Yield 9a / 6[b]
1	In the dark	no reaction
2	40 °C, 80 °C in 1,2-DCE	no reaction
3	in UV light	decomposition of diazo
4	in green light	29 (diazo remained)
5	no catalyst, UV light	decomposition of diazo
6	no catalyst	no reaction

Reaction condition: [a] $Ir(ppy)_3$ (0.5 mol%) as mentioned in table S9, **7** (0.6 mmol, 3 equiv.) and **4** (0.2 mmol, 1 equiv.) in 1 mL DCM under argon atmosphere irradiated with the light source indicated at either room temperature or elevated temperature. [b] Isolated yield.

Solvent Dependency of Photocatalytic C-H Functionalization Reaction of Indole

All the reactions were carried out according to the general procedure (GP-1) and C2- and C3-alkylation products of indole were isolated by column chromatography. Increasing amounts of methanol were added to the reaction mixture and total volume of the solvent were taken into consideration and kept constant at 1 mL.



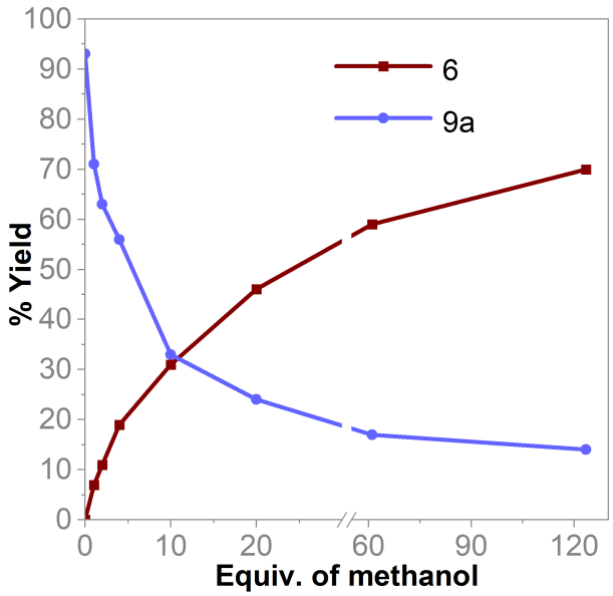


Figure S6. Solvent Dependency of Photocatalytic C-H Functionalization Reaction

Table S10. Solvent Dependency of Photocatalytic C-H Functionalization Reaction

Eq. of MeOH	MeOH (µL)	DCM (µL)	9a %	6 %
0	0	1000	0	93
1	4.05	996	7	71
2	8.1	992	11	63
4	16.2	984	19	56
10	40.5	959.5	31	33
20	81	919	46	24
61	247	753	59	17
123	498	502	70	14
246	1000	-	70	14

Fluorescence Quenching Studies

Fluorescence quenching experiments were performed on a Varian Cary Eclipse Fluorescence Spectrophotometer. All $Ir(ppy)_3$ solutions were excited at 377 nm and emission intensity at 515 nm were collected. All the measurements were carried out mixing a solution of 4.5×10^{-5} M solution of $Ir(ppy)_3$ in dry degassed DCM or degassed MeOH and appropriate amount of quencher in a screw top 1.0 cm quartz cuvette. Samples were degassed then the emission spectra of the samples were collected. I_0 is the intensity without quencher, and I is the intensity with quencher. Plots were drawn according to the Stern-Volmer equation and k_q were calculated.

Stern-Volmer equation: $I_0/I = 1+k_q[Q]$

Emission Quenching Studies of Ethyl Diazoacetate (4) and Indole (7)

Increasing amounts of quencher were added to a solution of $Ir(ppy)_3$ in DCM or methanol. After each addition the emission spectra was recorded.

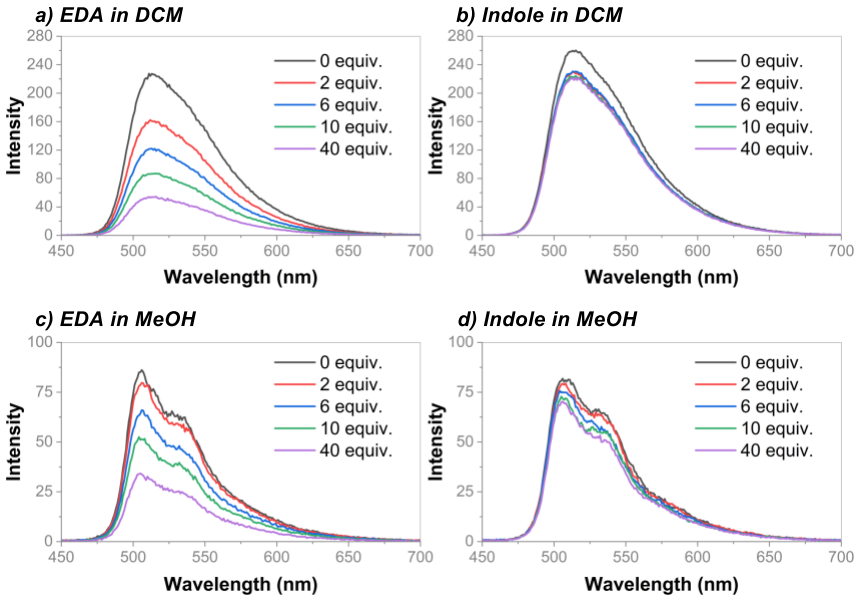


Figure S7. Fluorescence quenching of $Ir(ppy)_3$ with EDA **4** and indole **7** in DCM or methanol

Stern-Volmer Plots

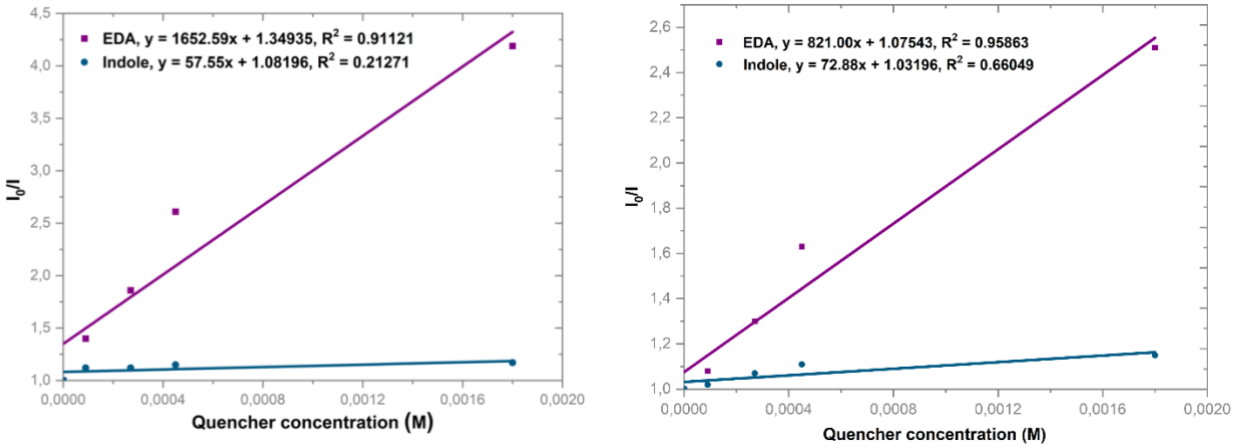


Figure S8. Stern-Volmer plot in DCM (left), Stern-Volmer plot in MeOH (right)

The reported long-lived excited state of $Ir(ppy)_3$ (τ = 1.9 µs) was used for k_q calculations.[2]

Table S11. Calculated k_q values in DCM and MeOH for ethyl diazoacetate and indole

Solvent	Quencher	k_q (M^{-1} s^{-1})
DCM	ethyl diazoacetate (**4**)	8.6×10^8
	indole (**7**)	3.0×10^7
MeOH	ethyl diazoacetate (**4**)	4.3×10^8
	indole (**7**)	3.8×10^7

Cyclic Voltammetry Measurements

Cyclic voltammetry was measured on a Metrohm Autolab analyzer using a standard three-electrode cell configuration. A platinum working electrode was employed alongside a platinum wire counter electrode and an Ag/AgCl reference electrode. All the solutions were degassed by bubbling N_2 prior to measurements. 10 mM solutions of the desired compounds were freshly prepared in dry SPS grade DCM along with 0.1 M of tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) as supporting electrolyte and were examined at a scan rate of 0.1 V s^{-1}. Solutions were kept under positive pressure of nitrogen during all the measurements. Ferrocene ($E_{1/2}$ = +0.43 V *vs* SCE)[3] was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the Ag/Ag^+ and converted to saturated calomel electrode (SCE) by adding 0.315.[3] Irreversible waves were obtained in all cases; therefore, the potentials were estimated at half the maximum current, as previously described by Nicewicz.[3a]

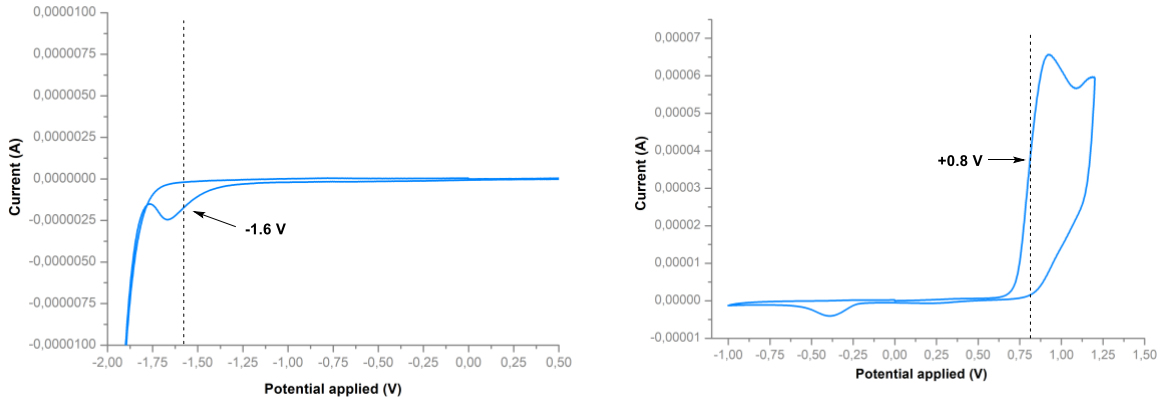


Figure S9. CV of ethyl diazoacetate **4** (left), CV of indole **7** (right)

Table S12. Redox potential of ethyl diazoacetate (xx) and indole (xx)

Compound	$E_{1/2}$ *vs* Ag/Ag^+	$E_{1/2}$ *vs* SCE
ethyl diazoacetate (**4**)	-1.60 V	-1.285 V
indole (**7**)	+0.80 V	+1.115 V

Control Experiments

On/Off Experiment

A reaction was setup according to the general procedure GP-1 in 0.6 mmol scale in 3 mL DCM, mesitylene was used as an internal standard under argon atmosphere. The reaction mixture was sequentially stirred under visible light irradiation and in the dark. Every two hours an aliquot of 50 µL was taken from the reaction mixture and analyzed by ^{1}H NMR spectroscopy. After a 12 h of reaction time the determined yields were plotted against the reaction time.

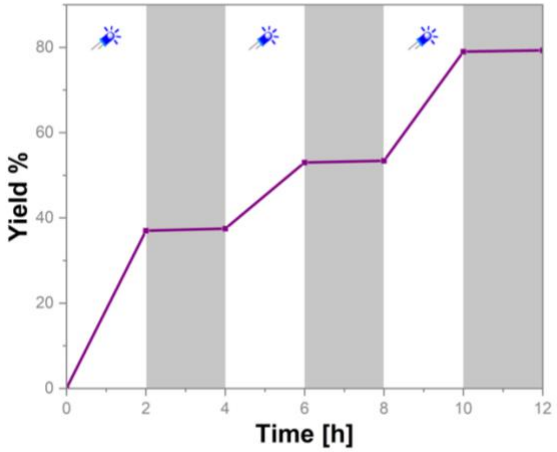
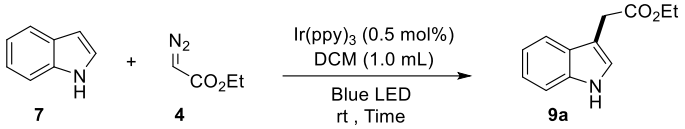


Figure S10. On/off experiment

Reaction Rate of Photocatalytic C-H Functionalization Reaction of Indole with Ethyl Diazoacetate



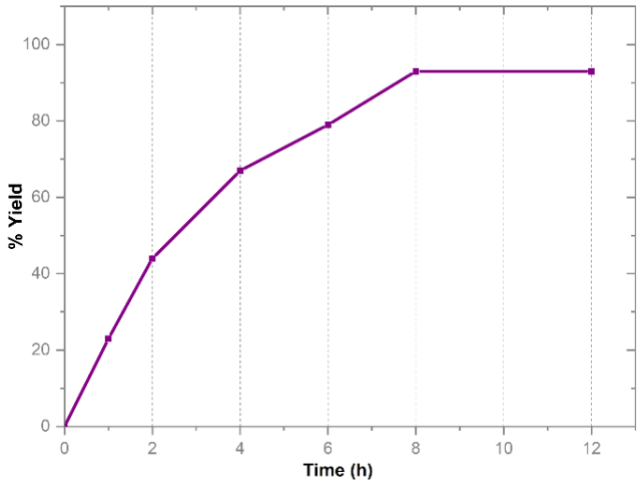
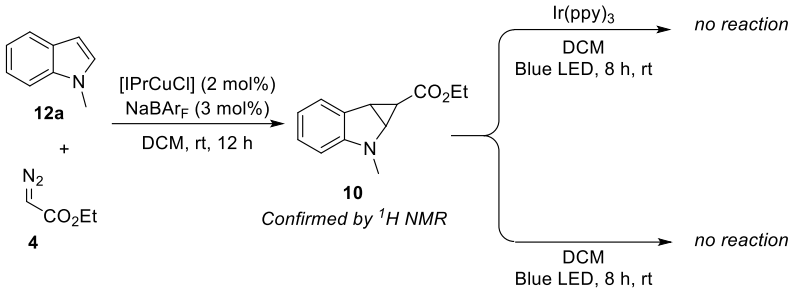


Figure S11. Yield *vs* reaction time

Excluding the Cyclopropane Intermediate



In an oven-dried reaction tube *N*-methyl indole (1.5 equiv., 0.3 mmol), 2 mol% [IPrCu(Cl)] and 3 mol% of $NaBAr_F$ were taken and dissolved in 1 mL of CD_2Cl_2. Then 0.2 mmol of EDA (1 equiv.) was dissolved in 1 mL of CD_2Cl_2 and added to the reaction mixture slowly over 60 mins and stirred 12 h at room temperature. Reaction mixture was analyzed by ^{1}H NMR and the cyclopropane xx could be detected. In a subsequent step the reaction mixture was divided into two portions, in one portion 0.5 mol% $Ir(ppy)_3$ was added and irradiated with 2 x 40 W blue LED (467 nm) under argon atmosphere for 8 h. The second portion was directly irradiated under blue LED at room temperature for 8 h. In neither cases cyclopropane ring opening to form the C3-alkylation product of indole was observed. In both portions the cyclopropane **10** remained untouched.

Radical Trapping Experiments

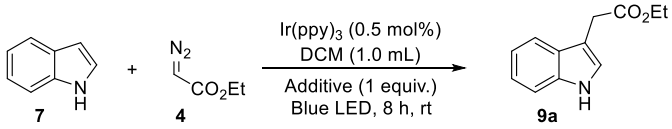


Table S13. Radical Trapping

Additive	Yield % 9a
TEMPO	trace, adduct observed in GC/MS
1,4-Cyclohexadiene	54
4-Nitrotoluene	17
Triethylamine	64
DMPO / DNP	trace, no adduct found in GC/MS or ^{1}H NMR

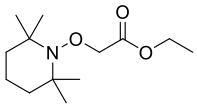
In an oven-dried reaction tube $Ir(ppy)_3$ (0.5 mol-%) and indole **7** (1.0 mmol, 3 equiv.) and additive (0.2 mmol, 1 equiv.) (if the additive is solid) were added. Then the tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) and additive (0.2 mmol, 1 equiv.) (if liquid) was dissolved in 1.0 mL of dry and degassed DCM and the solution was added via syringe to the reaction tube. Then the final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 8 h under irradiation with blue LEDs (2 × Kessil PR160L, 467 nm, 40 W at room temperature). After completion of the reaction, DCM was evaporated under reduced pressure and the crude reaction mixture was analyzed by ^{1}H NMR using mesitylene as internal standard.

GC/MS Analysis of Reaction with TEMPO as Additive

Method: 60 °C/5 min, 20 K/min, 300 °C/13 min

Compound below was detected in GC/MS at retention time range of 12.165 – 12.360 min.

MS: *m/z*: calcd for [M] = 243.1, found: 243, calcd for [M-CH_3] = 228.1, found: 228, calcd for [M-$C_4H_7O_2$] = 156.1, found: 156.



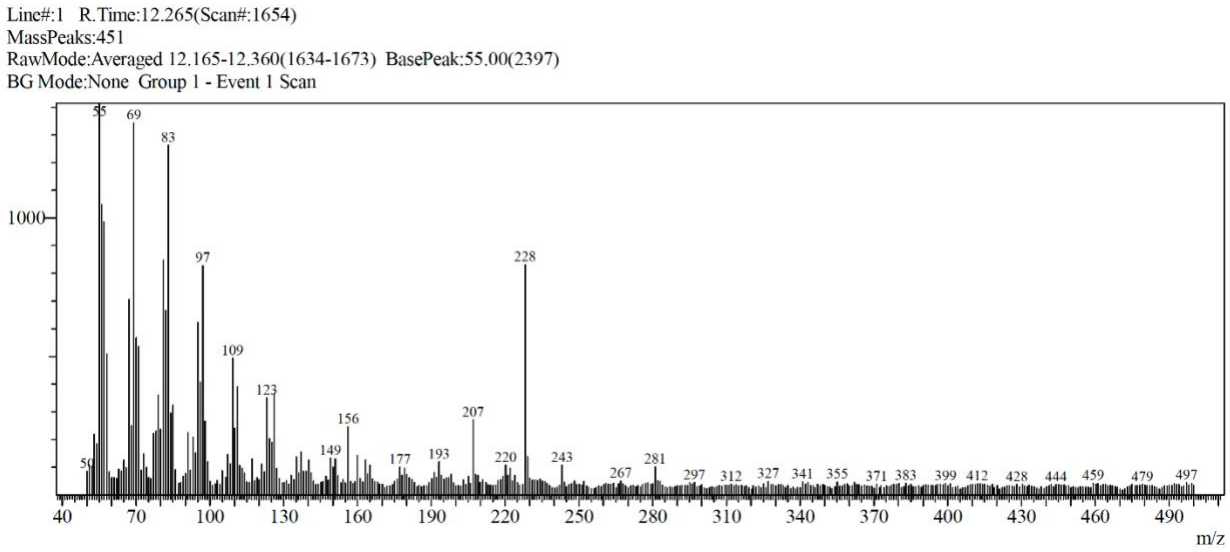
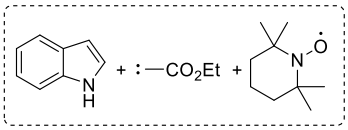


Figure S12. GC/MS analysis of crude reaction mixture of TEMPO additive

Addition of Trapping Agents after 2 h Reaction Time

In an oven-dried reaction tube $Ir(ppy)_3$ (0.5 mol-%) and indole **7** (1.0 mmol, 3 equiv.) were added. Then the tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1.0 mL of dry and degassed DCM and the solution was added via syringe to the reaction tube. Then the final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 2 h under irradiation with blue LED (2 × Kessil PR160L, 467 nm, 40 W, at room temperature). 1 equiv. of radical trap TEMPO or PBN was added to the reaction mixtures and immediately analyzed by ESI MS. We observe the three components adduct in each reaction mixture, although the exact structures of the adduct could not be identified.

ESI MS Analysis of Reaction with TEMPO as Additive



11

ESI: *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{31}N_2O_3Na^+$: 382.22, found: 382.6, $[M + K]^+$ calcd for $C_{21}H_{31}N_2O_3K^+$ = 398.19, found: 398.2.

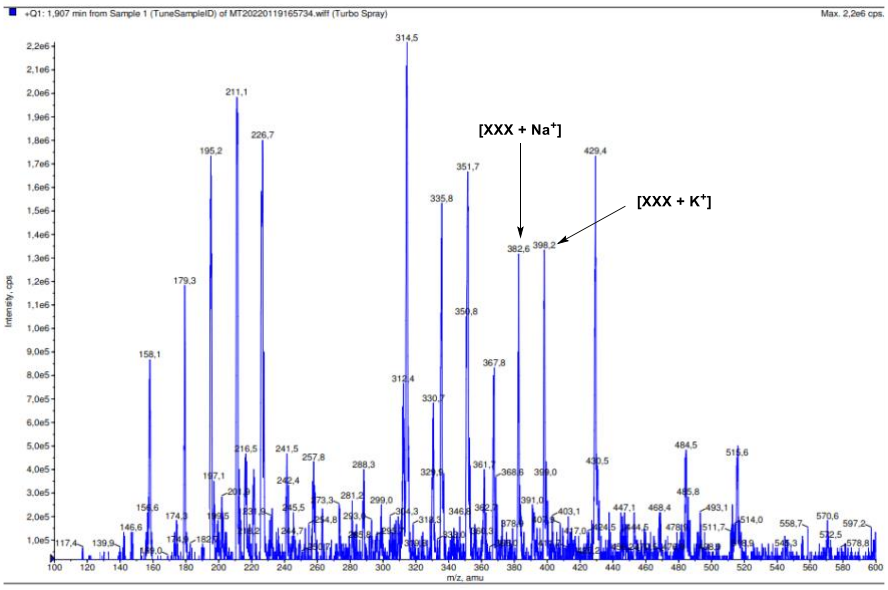
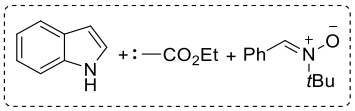


Figure S13. ESI mass analysis of crude reaction mixture of TEMPO additive

ESI MS Analysis of Reaction with PBN as Additive



ESI: *m/z*: $[M + Na]^+$ Calcd. for $C_{23}H_{28}N_2O_3Na^+$: 403.19; Found: 403.3.

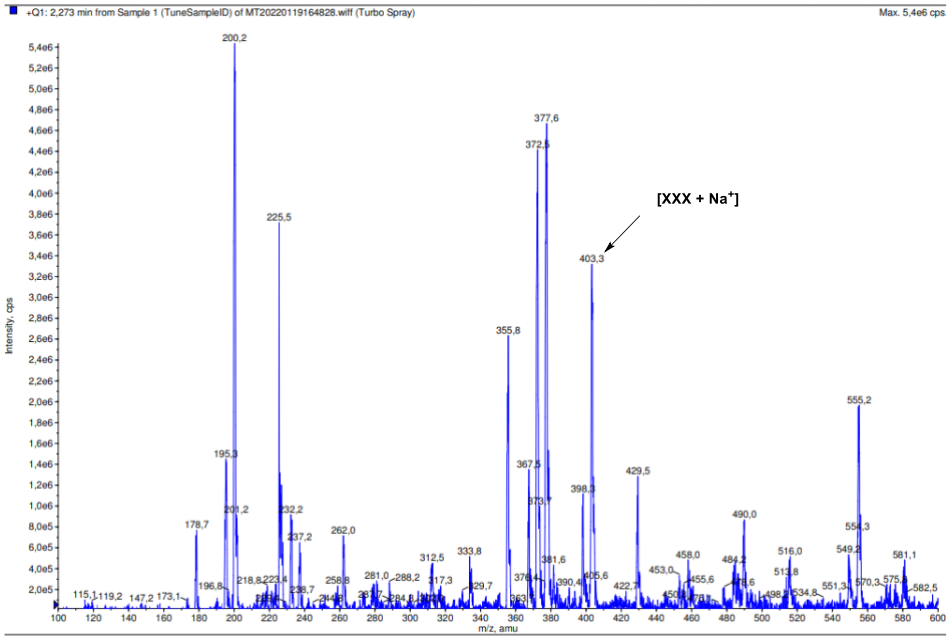
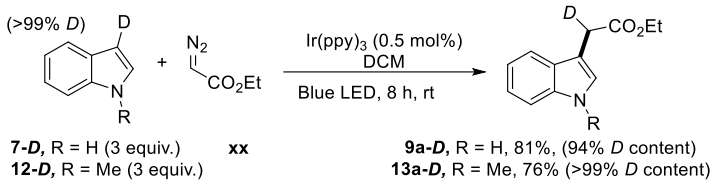


Figure S14. ESI mass analysis of crude reaction mixture of PBN additive

Deuterium Labelling Experiments



7-*D*, R = H (3 equiv.) **xx** **9a-*D*,** R = H, 81%, (94% *D* content)
12-*D*, R = Me (3 equiv.) **13a-*D*,** R = Me, 76% (>99% *D* content)

In an oven dried reaction tube $Ir(ppy)_3$ (0.5 mol%) and indole **7-*D*** or **12-*D*** (1 mmol, 3 equiv.) were added. Reaction tube was closed with septum and wrapped with parafilm. Then the tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1 mL of dry and degassed DCM and the solution was added via syringe to the reaction tube. The final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 8 h under irradiation with blue LED (2 × Kessil PR160L, 467 nm, 40 W, at room temperature). After the completion of the reaction, the product was purified by column chromatography on silica gel (*n*-Hexane : EtOAc) to afford the corresponding product **9a-*D*** or **13a-*D*** and the percentage of deuterium incorporation was analyzed by ^{1}H NMR.

Product **9a-*D*** was isolated in 81% yield, with 94% *D* incorporation.

Product **13a-*D*** was isolated in 76% yield. with 99% *D* incorporation.

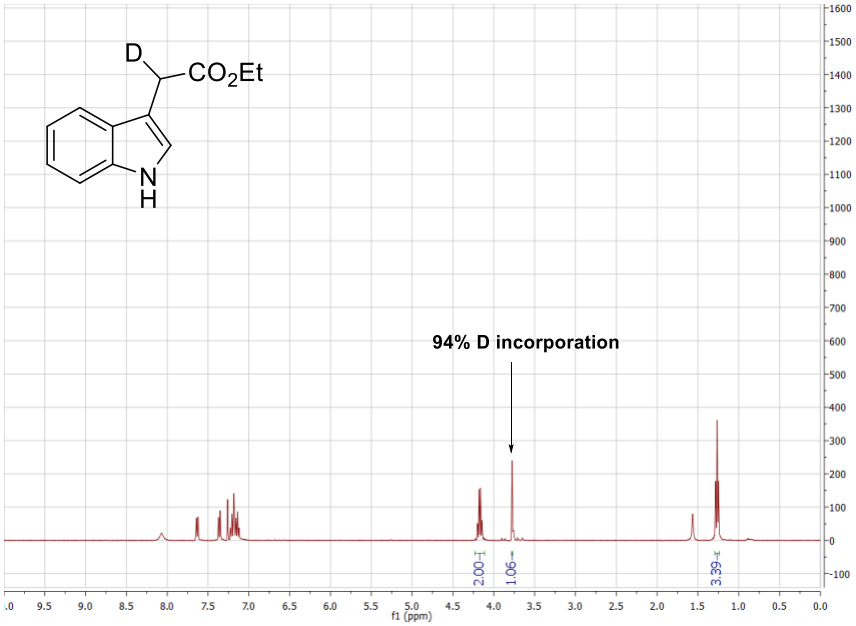


Figure S15. ^{1}H NMR (400 MHz, Chloroform-*d*) of **9a-*D***

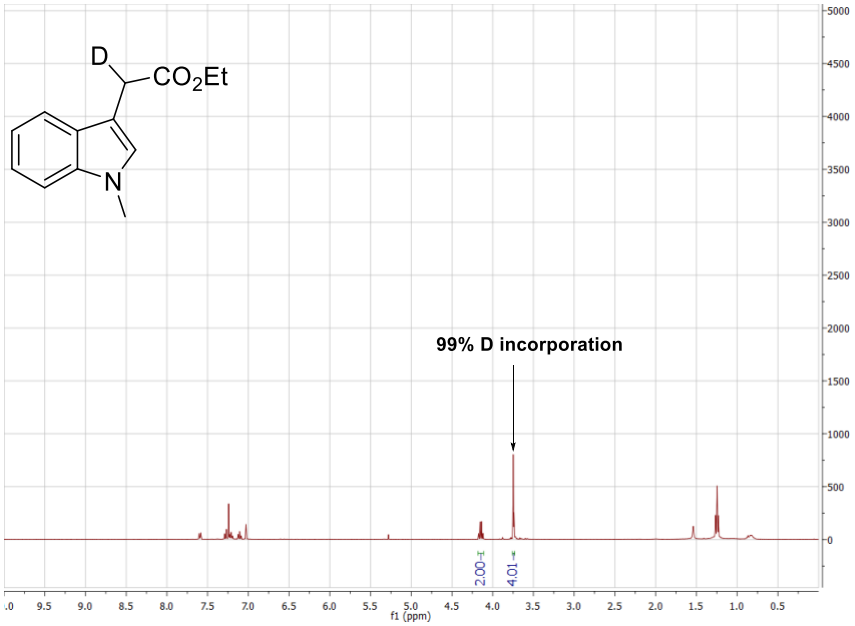
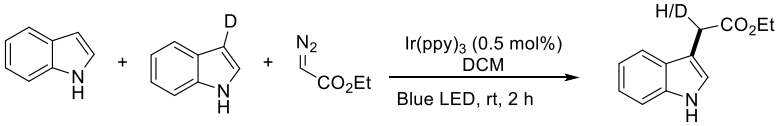


Figure S16. ^{1}H NMR (400 MHz, Chloroform-*d*) of **13a-*D***

KIE Determination by Intermolecular Competition Experiment



7 (1.5 equiv.) + **7-*D*** (1.5 equiv.) + **4** → **9a,** 36%, (46% *D* content), **KIE ~ 1**

In an oven-dried reaction tube $Ir(ppy)_3$ (0.5 mol%) and indole **7** (0.3 mmol, 1.5 eq.) and **7-*D*** (0.3 mmol, 1.5 equiv.) were added. Reaction tube was closed with septum and wrapped with parafilm. Then the tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1 mL of dry and degassed DCM and the solution was added via syringe to the reaction tube. The final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 2 h under irradiation with blue LED (2 × Kessil PR160L, 467 nm, 40 W, at room temperature). The crude reaction mixture was analyzed by ^{1}H NMR and purified by column chromatography on silica gel (*n*-Hexane : EtOAc) and analyzed by ^{1}H NMR, no decrease of deuterium was observed on column and the product was isolated in 36% yield with 46% *D* incorporation.

From this observation we can conclude that KIE ~ 1.

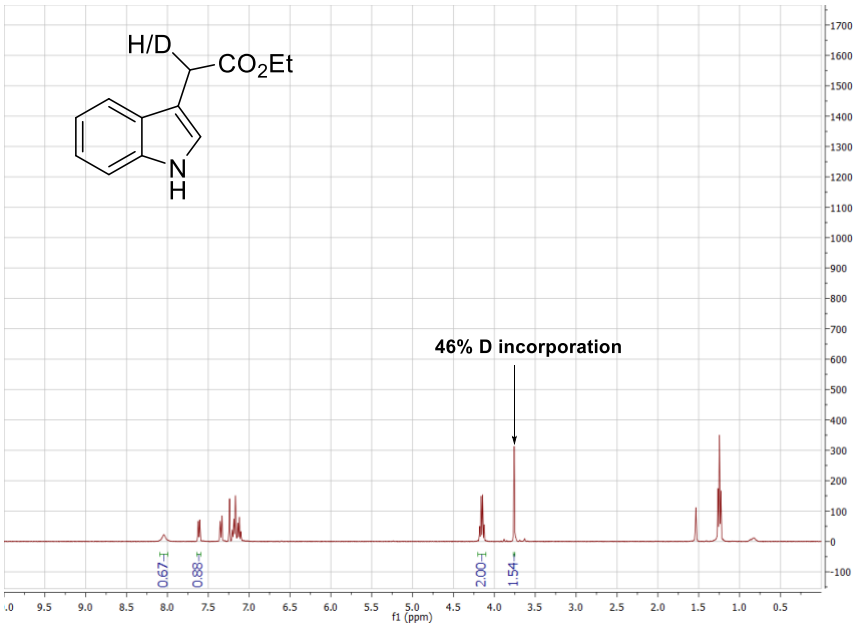


Figure S17. ^{1}H NMR (400 MHz, Chloroform-*d*) of **9a-*D***

Determination of K_H/K_D by Parallel Experiments

Total twelve separate reactions have been performed according to the general procedure (GP-1). In the first six reactions indole **7** (0.6 mmol, 3 equiv.), $Ir(ppy)_3$ (0.5 mol%) and ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) were taken in 1 mL of dry and degassed DCM in each reaction tube. In the other six reactions, indole **7-*D*** (0.6 mmol, 3 equiv.), $Ir(ppy)_3$ (0.5 mol%) and ethyl diazoacetate (0.2 mmol, 1 equiv.) were taken in 1 mL of dry and degassed DCM in each reaction tube. Then all twelve reactions were simultaneously placed under irradiation with blue LEDs. Then these reactions have been stopped consecutively at the time interval of 30 mins to 180 mins. After the corresponding reaction time, the solvent was removed under reduced pressure and the product was purified by flash column chromatography.

K_H/K_D = 0.30524/0.29333 ~ 1.04.

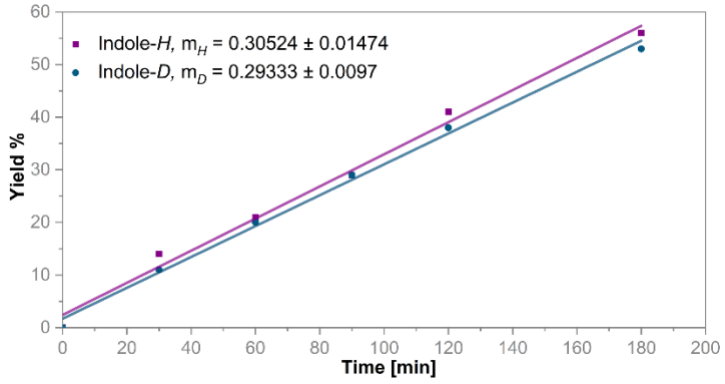


Figure S18. Yield *vs* Time plot for the determination of K_H/K_D

EPR Experiment

General Procedure for the EPR Experiment

In an oven-dried reaction tube $Ir(ppy)_3$ (0.5 mol-%) and indole **7** (0.6 mmol, 3 equiv.) were added. Then the tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1.0 mL of dry and degassed DCM and the solution was added via syringe to the reaction tube. Then the final reaction mixture was degassed for 30 seconds. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was stirred for 1 h under irradiation with blue LED (2 × Kessil PR160L, 467 nm, 40 W, at room temperature). 1 equiv. of radical trap DMPO or PBN was added to the reaction mixture and stirred for another 15mins under blue LED irradiations. Subsequently, small portion of the reaction mixture was loaded into a EPR sampler tube and measured the EPR spectra.

**For radical trap MNP the EPR spectra was measured immediately after the addition of MNP, as the mentioned radical trap decomposes under blue LED irradiation.*

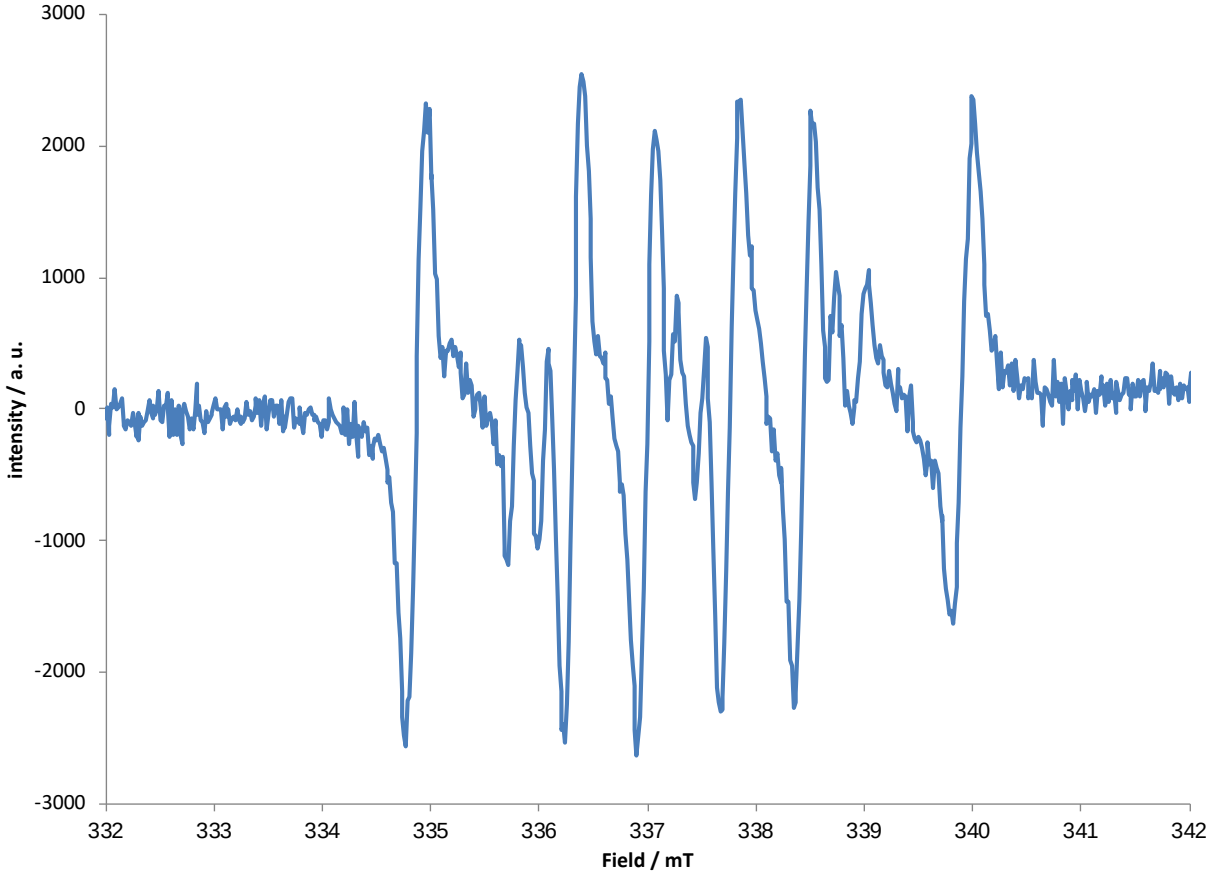
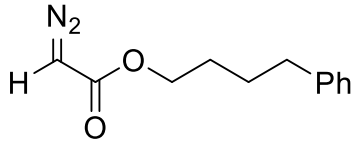


Figure S19. EPR Results

Physical data

4-Phenylbutyl 2-diazoacetate (4b)



The titled compound was synthesized according to the general procedure GP-D on a 1 mmol scale and was obtained after silica gel column chromatography (*n*-pentane : diethyl ether 40:1) as yellow oil (83%, 181 mg).

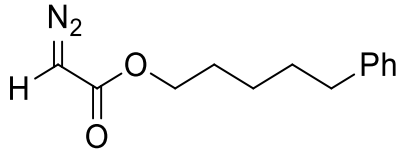
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.31 – 7.27 (m, 2H), 7.21 – 7.16 (m, 3H), 4.73 (brs, 1H), 4.21 – 4.17 (m, 2H), 2.67 – 2.63 (m, 2H), 1.72 – 1.67 (m, 4H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 142.0, 128.4, 128.3, 125.8, 64.7, 46.1, 35.4, 28.4, 27.6 ppm.

HRMS (ESI): mass found: 241.0945, calculated mass $C_{12}H_{14}N_2NaO_2^+$: 241.0947.

IR (KBr): 3377, 3109, 3027, 2938, 2860, 2330, 2108, 1916, 1689, 1603, 1494, 1454, 1395, 1355, 1239, 1183, 1032, 911, 740, 699 cm^{-1}.

5-Phenylpentyl 2-diazoacetate (4c)



The titled compound was synthesized according to the general procedure GP-D on a 1 mmol scale and was obtained after silica gel column chromatography (*n*-pentane : diethyl ether 40:1) as yellow oil (86%, 199 mg).

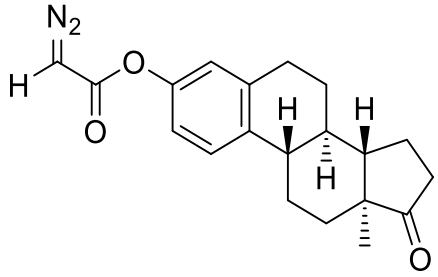
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 3H), 4.75 (brs, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.73 – 1.65 (m, 4H), 1.46 – 1.39 (m, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 142.3, 128.39, 128.31, 125.7, 64.8, 46.1, 35.7, 31.0, 28.6, 25.4 ppm.

HRMS (ESI): mass found: 255.1098, calculated mass $C_{13}H_{16}N_2NaO_2^+$: 255.1104.

IR (KBr): 3377, 3112, 3034, 2954, 2322, 2109, 1993, 1875, 1687, 1496, 1453, 1387, 1349, 1234, 1081, 1008, 910, 840, 697 cm^{-1}.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 2-diazoacetate (4d)



The titled compound was synthesized according to the general procedure GP-D on a 1 mmol scale but for the bromoacetylation step pyridine (2 equiv.) was used instead of $NaHCO_3$ in acetonitrile and the diazo compound was obtained after silica gel column chromatography (*n*-pentane : diethyl ether 4:1) as yellow gel (77%, 300 mg).

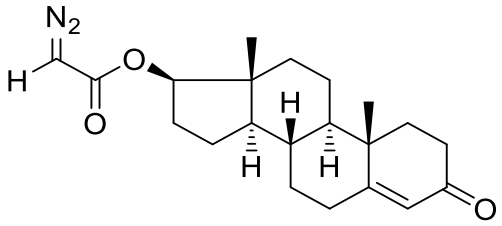
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.28 (d, *J* = 8.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 4.95 (brs, 1H), 2.94 – 2.89 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 – 2.37 (m, 1H), 2.29 (td, *J* = 11.2, 10.6, 3.8 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.09 – 1.93 (m, 3H), 1.65 – 1.42 (m, 6H), 0.91 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 220.7, 138.0, 137.4, 126.4, 121.6, 118.8, 115.3, 112.8, 50.4, 47.9, 46.7, 44.1, 38.0, 35.8, 31.5, 29.4, 26.3, 25.7, 21.6, 13.8 ppm.

HRMS (ESI): mass found: 361.1520, calculated mass $C_{20}H_{22}N_2NaO_3^+$: 361.1522.

IR (KBr): 3822, 3386, 3324, 3123, 2932, 2863, 2501, 2326, 2121, 1882, 1730, 1695, 1609, 1583, 1492, 1455, 1362, 1283, 1227, 1164, 1088, 1052, 1009, 976, 876, 786, 729 cm^{-1}.

(8*S*,9*R*,10*S*,13*R*,14*R*,17*R*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-diazoacetate (4e)



The titled compound was synthesized according to the general procedure GP-D on a 1 mmol scale and was obtained after silica gel column chromatography (*n*-pentane : diethyl ether 40:1) as yellow gel (64%, 230 mg).

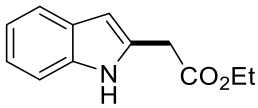
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 5.74 – 5.72 (m, 1H), 4.76 – 4.66 (m, 2H), 2.46 – 2.25 (m, 4H), 2.23 – 2.16 (m, 1H), 2.05 – 2.00 (m, 1H), 1.87 – 1.79 (m, 2H), 1.75 – 1.64 (m, 2H), 1.61 – 1.54 (m, 3H), 1.45 – 1.31 (m, 2H), 1.23 – 1.18 (m, 4H), 1.11 – 0.98 (m, 2H), 0.98 – 0.92 (m, 1H), 0.82 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 199.4, 170.8, 123.9, 82.9, 53.7, 50.1, 46.2, 42.6, 38.6, 36.6, 35.7, 35.4, 33.9, 32.7, 31.4, 27.6, 23.4, 20.5, 17.4, 11.9 ppm.

HRMS (ESI): mass found: 379.1988, calculated mass $C_{21}H_{28}N_2NaO_3^+$: 379.1992.

IR (KBr): 3328, 3115, 2939, 2910, 2850, 2468, 2300, 2195, 2029, 1998, 1949, 1667, 1613, 1441, 1366, 1327, 1238, 1184, 1147, 1048, 1022, 940, 862, 739, 693 cm^{-1}.

Ethyl 2-(1*H*-indol-2-yl)acetate (6)



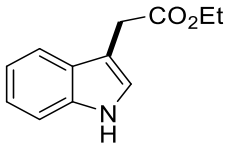
In an oven-dried reaction tube indole **7** (0.6 mmol, 3 equiv.), $Ir(ppy)_3$ (0.5 mol%) and one stirring bar were added. Then the tube was closed with septum and wrapped with parafilm. Reaction tube was evacuated and backfilled with argon for three times. Ethyl diazoacetate **4** (0.2 mmol, 1 equiv.) was dissolved in 1.0 mL of degassed MeOH in a separate tube under argon atmosphere and the resulting solution was added to the reaction tube via syringe. Finally, the puncture hole in the septum was sealed with parafilm. The reaction mixture was irradiated with blue LED (2 × Kessil PR160L, 467 nm, 40 W) for 8 h at a distance of ~ 3 cm from the LED, temperature was maintained at room temperature with a cooling fan. After completion of the reaction, the product was purified by column chromatography on silica gel (*n*-hexane : EtOAc 9:1) as a colorless oil (70%, 28 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.68 (s, 1H), 7.57 – 7.53 (m, 1H), 7.37 – 7.33 (m, 1H), 7.18 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 6.39 – 6.35 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.6, 136.3, 130.5, 128.2, 121.7, 120.1, 119.8, 110.8, 101.8, 61.4, 33.9, 14.1 ppm.

Physical data is in accordance with the previous literature.[4]

Ethyl 2-(1*H*-indol-3-yl)acetate (9a)



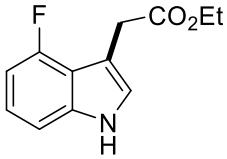
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (93%, 38 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.07 (brs, 1H), 7.63 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.3, 136.4, 127.6, 123.3, 122.5, 120.0, 119.3, 111.4, 109.0, 61.1, 31.7, 14.6 ppm.

Physical data is in accordance with the previous literature.[5]

Ethyl 2-(4-fluoro-1*H*-indol-3-yl)acetate (9b)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a brown oil (69%, 30 mg).

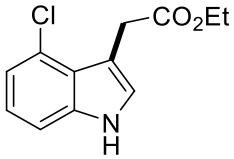
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.14 (brs, 1H), 7.14 – 7.05 (m, 3H), 6.77 – 6.72 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.90 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.3, 157.3 (d, *J* = 245.9 Hz), 138.8 (d, *J* = 11.0 Hz), 123.2, 122.75, 122.70, 116.4 (d, *J* = 20.1 Hz), 107.4 (d, *J* = 3.6 Hz), 104.9 (d, *J* = 19.4 Hz), 60.8, 32.1, 14.3 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -124.7 (m) ppm.

Physical data is in accordance with the previous literature.[6]

Ethyl 2-(4-chloro-1*H*-indol-3-yl)acetate (9c)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a brown oil (61%, 29 mg).

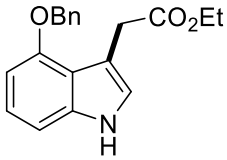
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.24 (brs, 1H), 7.20 (dd, *J* = 5.4, 3.6 Hz, 1H), 7.09 – 7.08 (m, 1H), 7.06 – 7.04 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.0, 138.0, 126.5, 125.0, 124.5, 123.0, 120.9, 110.4, 109.3, 61.1, 32.6, 14.6 ppm.

HRMS (ESI): mass found: 238.0621, calculated mass $C_{12}H_{13}ClNO_2^+$: 238.0629.

IR (KBr): 3347, 3031, 2982, 2920, 2491, 2229, 2165, 2077, 1889, 1729, 1611, 1552, 1521, 1441, 1351, 1247, 1073, 1021, 910, 838, 744, 690 cm^{-1}.

Ethyl 2-(4-(benzyloxy)-1*H*-indol-3-yl)acetate (9d)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (72%, 45 mg).

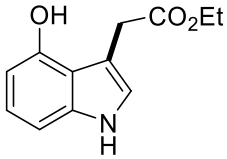
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.02 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.01 – 6.99 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 2H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.7, 153.6, 137.9, 137.5, 128.4, 127.6, 127.3, 123.0, 121.9, 117.5, 108.9, 104.7, 100.8, 69.8, 60.3, 32.5, 14.1 ppm.

HRMS (ESI): mass found: 332.1255, calculated mass $C_{19}H_{19}NNaO_3^+$: 332.1257.

IR (KBr): 3349, 3033, 2979, 2923, 2329, 2163, 2081, 1880, 1726, 1617, 1553, 1505, 1446, 1352, 1242, 1174, 1074, 1026, 983, 841, 730 cm^{-1}.

Ethyl 2-(4-hydroxy-1*H*-indol-3-yl)acetate (9ee)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 1:1) as a brown oil (49%, 21 mg).

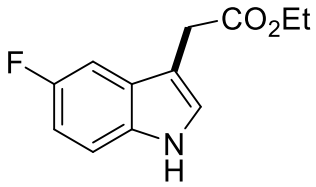
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.45 (s, 1H), 8.00 (brs, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 175.5, 150.4, 138.7, 123.8, 122.1, 117.4, 107.3, 106.7, 104.0, 62.0, 33.1, 14.0 ppm.

HRMS (ESI): mass found: 242.0784, calculated mass $C_{12}H_{13}NNaO_3^+$: 242.0787.

IR (KBr): 3399, 2982, 2927, 2855, 2539, 2329, 2162, 2078, 2035, 1965, 1881, 1696, 1626, 1587, 1506, 1456, 1314, 1250, 1186, 1086, 1028, 937, 734 cm^{-1}.

Ethyl 2-(5-fluoro-1*H*-indol-3-yl)acetate (9f)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (59%, 26 mg).

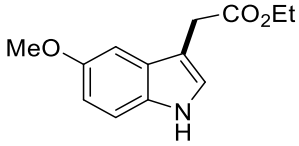
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.10 (brs, 1H), 7.28 – 7.23 (m, 2H), 7.20 (d, *J* = 2.3 Hz, 1H), 6.94 (td, *J* = 9.1, 2.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 2H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 157.9 (d, *J* = 234.9 Hz), 132.6, 127.7 (d, *J* = 9.7 Hz), 124.8, 111.7 (d, *J* = 9.8 Hz), 110.65 (d, *J* = 26.6 Hz), 108.8 (d, *J* = 3.8 Hz), 103.9 (d, *J* = 23.1 Hz), 60.8, 31.3, 14.2 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -124.4 (m) ppm.

Physical data is in accordance with the previous literature.[6]

Ethyl 2-(5-methoxy-1*H*-indol-3-yl)acetate (9g)



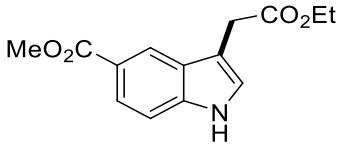
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (74%, 35 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.95 (brs, 1H), 7.25 (d, *J* = 10.1 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.73 (s, 2H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 154.2, 131.2, 127.7, 123.7, 112.5, 111.8, 108.4, 100.7, 60.7, 55.8, 31.5, 14.2 ppm.

Physical data is in accordance with the previous literature.[6]

Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-5-carboxylate (9h)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (72%, 37 mg).

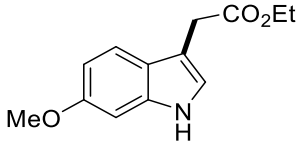
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.41 – 8.40 (m, 1H), 8.31 (brs, 1H), 7.91 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.25 – 7.23 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.80 (d, J = 0.9 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.7, 168.1, 138.7, 126.9, 124.3, 123.6, 122.0, 121.8, 110.8, 110.1, 60.9, 51.8, 31.1, 14.2 ppm.

HRMS (ESI): mass found: 262.1071, calculated mass $C_{14}H_{16}NO_4^+$: 262.1073.

IR (KBr): 3345, 2985, 2328, 2169, 2087, 1892, 1708, 1615, 1437, 1372, 1247, 1189, 1100, 1026, 980, 902, 861, 830, 760, 679 cm^{-1}.

Ethyl 2-(6-methoxy-1*H*-indol-3-yl)acetate (9i)



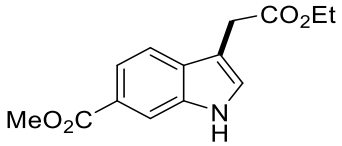
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (77%, 36 mg).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.92 (brs, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.11 – 7.02 (m, 1H), 6.89 – 6.76 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.73 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 156.6, 136.9, 121.74, 121.71, 119.6, 109.6, 108.7, 94.6, 60.7, 55.7, 31.5, 14.2 ppm.

Physical data is in accordance with the previous literature.[6]

Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-6-carboxylate (9j)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (77%, 40 mg).

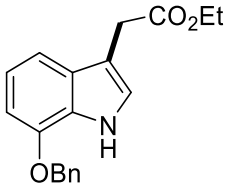
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.37 (brs, 1H), 8.13 – 8.10 (m, 1H), 7.82 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.36 – 7.33 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 3.78 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.7, 168.0, 135.4, 130.8, 126.4, 123.9, 120.7, 118.5, 113.5, 109.1, 60.9, 51.9, 31.2, 14.2 ppm.

HRMS (ESI): mass found: 262.1071, calculated mass $C_{14}H_{16}NO_4^+$: 262.1073.

IR (KBr): 3360, 2984, 2665, 2327, 2088, 1994, 1901, 1711, 1624, 1547, 1504, 1439, 1369, 1270, 1212, 1163, 1092, 1026, 980, 890, 860, 830, 774, 737 cm^{-1}.

Ethyl 2-(7-(benzyloxy)-1*H*-indol-3-yl)acetate (9k)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (84%, 52 mg).

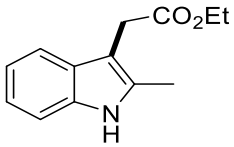
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.31 (brs, 1H), 7.47 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 7.25 (d, *J* = 10.5 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 5.21 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 145.3, 137.1, 128.7, 128.6, 128.1, 127.7, 127.3, 122.5, 120.0, 111.9, 109.1, 103.3, 70.2, 60.7, 31.5, 14.2 ppm.

HRMS (ESI): mass found: 332.1249, calculated mass $C_{19}H_{19}NNaO_3^+$: 332.1257.

IR (KBr): 3633, 3404, 3034, 2982, 2936, 2670, 2507, 2326, 2087, 1996, 1945, 1880, 1811, 1721, 1629, 1578, 1497, 1444, 1416, 1372, 1339, 1254, 1175, 1090, 1066, 972, 913, 854, 783, 727, 698 cm^{-1}.

Ethyl 2-(2-methyl-1*H*-indol-3-yl)acetate (9l)



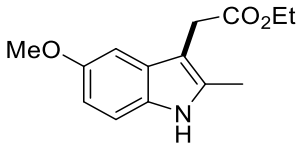
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (74%, 32 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.83 (brs, 1H), 7.55 – 7.52 (m, 1H), 7.27 – 7.25 (m, 1H), 7.14 – 7.07 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 2H), 2.42 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 135.1, 132.5, 128.5, 121.2, 119.5, 118.1, 110.2, 104.7, 60.6, 30.5, 14.2, 11.7 ppm.

Physical data is in accordance with the previous literature.[7]

Ethyl 2-(5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (9m)



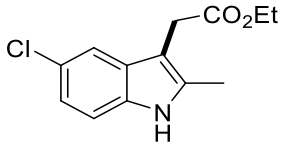
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1 – 2:1) as a yellow oil (64%, 32 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.72 – 7.62 (m, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.57 (s, 2H), 2.33 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 154.1, 133.4, 130.1, 129.0, 111.0, 110.8, 104.6, 100.5, 60.6, 55.9, 30.6, 14.2, 11.8 ppm.

Physical data is in accordance with the previous literature.[8]

Ethyl 2-(5-chloro-2-methyl-1*H*-indol-3-yl)acetate (9n)



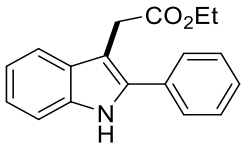
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1)as a yellow oil (63%, 32 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.86 (brs, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 2H), 2.41 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.6, 134.2, 133.4, 129.7, 125.3, 121.4, 117.8, 111.1, 104.7, 60.8, 30.3, 14.2, 11.8 ppm.

Physical data is in accordance with the previous literature.[9]

Ethyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (9o)



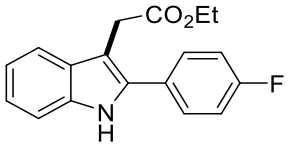
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (61%, 34 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.14 (brs, 1H), 7.68 (t, *J* = 7.4 Hz, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 15.7, 7.8 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 136.1, 135.6, 132.3, 129.0, 128.8, 128.2, 128.0, 122.5, 119.9, 119.3, 110.7, 105.7, 60.7, 31.1, 14.1 ppm.

Physical data is in accordance with the previous literature.[10]

Ethyl 2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)acetate (9p)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1) as a yellow oil (68%, 40 mg).

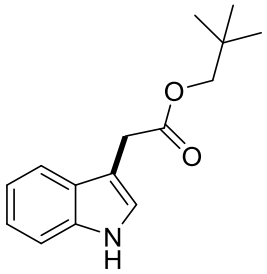
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.11 (brs, 1H), 7.74 – 7.64 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.17 (m, 4H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 162.6 (d, *J* = 248.3 Hz), 135.7, 135.2, 130.0 (d, *J* = 8.3 Hz), 128.9, 128.5 (d, *J* = 3.6 Hz), 122.6, 120.1, 119.3, 116.0 (d, *J* = 20.8 Hz), 110.8, 105.9, 60.9, 31.1, 14.2 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -113.3 (m) ppm.

Physical data is in accordance with the previous literature.[11]

Neopentyl 2-(1*H*-indol-3-yl)acetate (9q)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (72%, 35 mg).

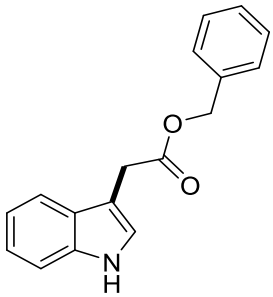
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.07 (brs, 1H), 7.65 – 7.62 (m, 1H), 7.37 – 7.35 (m, 1H), 7.22 – 7.18 (m, 2H), 7.16 – 7.12 (m, 1H), 3.81 (s, 4H), 0.90 (s, 9H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.2, 136.0, 127.3, 122.9, 122.2, 119.6, 118.9, 111.1, 108.8, 74.1, 31.3, 26.4 ppm.

HRMS (ESI): mass found: 268.1303, calculated mass $C_{15}H_{19}NNaO_2^+$: 268.1308.

IR (KBr): 3411, 3031, 2901, 2531, 2344, 2151, 2081, 1961, 1946, 1804, 1723, 1611, 1601, 1532, 1463, 1453, 1331, 1278, 1133, 1102, 1097, 1003, 906, 819, 778 cm^{-1}.

Benzyl 2-(1*H*-indol-3-yl)acetate (9r)



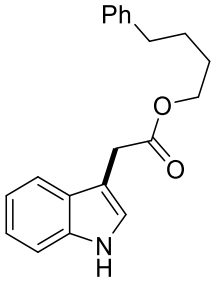
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 4:1) as a yellow oil (76%, 40 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.07 (brs, 1H), 7.61 (d, 1H), 7.39 – 7.31 (m, 6H), 7.22 – 7.19 (m, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.14 – 7.11 (m, 1H), 5.16 (s, 2H), 3.84 (d, *J* = 0.9 Hz, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 136.1, 135.9, 128.5, 128.23, 128.20, 127.2, 123.0, 122.2, 119.7, 118.9, 111.1, 108.4, 66.5, 31.3 ppm.

Physical data is in accordance with the previous literature.[17]

4-Phenylbutyl 2-(1*H*-indol-3-yl)acetate (9s)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 4:1) as a yellow oil (79%, 49 mg).

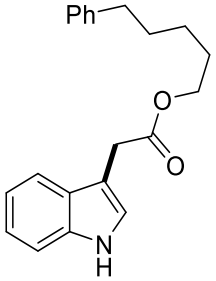
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.06 (brs, 1H), 7.64 – 7.62 (m, 1H), 7.36 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.11 (m, 4H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.78 (s, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.61 (m, 4H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 142.0, 136.1, 128.39, 128.33, 127.2, 125.8, 123.0, 122.2, 119.6, 118.9, 111.1, 108.6, 64.6, 35.4, 31.4, 28.2, 27.6 ppm.

HRMS (ESI): mass found: 330.1461, calculated mass $C_{20}H_{21}NNaO_2^+$: 330.1464.

IR (KBr): 3636, 3410, 3052, 2939, 2858, 1991, 1885, 1719, 1600, 1489, 1454, 1413, 1335, 1275, 1243, 1200, 1120, 1091, 1007, 895, 857 cm^{-1}.

5-Phenylpentyl 2-(1*H*-indol-3-yl)acetate (9t)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 4:1) as a yellow oil (74%, 47 mg).

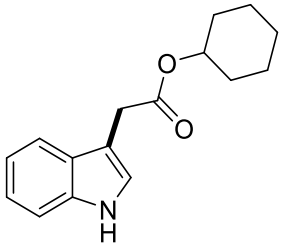
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.02 (brs, 1H), 7.62 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.12 (m, 6H), 4.10 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 2H), 2.61 – 2.52 (m, 2H), 1.68 – 1.57 (m, 4H), 1.38 – 1.31 (m, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 142.5, 136.1, 128.4, 128.2, 127.2, 125.6, 122.9, 122.2, 119.6, 118.9, 111.1, 108.7, 64.8, 35.7, 31.4, 31.0, 28.5, 25.5 ppm.

HRMS (ESI): mass found: 344.16259, calculated mass $C_{21}H_{23}NNaO_2^+$: 344.16210.

IR (KBr): 3646, 3410, 3051, 2951, 2670, 2495, 2335, 2098, 1992, 1723, 1610, 1490, 1454, 1413, 1335, 1273, 1244, 1161, 1091, 896, 850, 740 cm^{-1}.

Cyclohexyl 2-(1*H*-indol-3-yl)acetate (9u)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (73%, 37 mg).

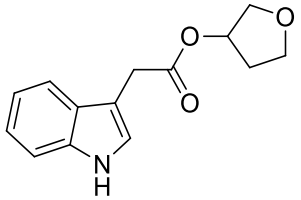
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.05 (brs, 1H), 7.67 – 7.61 (m, 1H), 7.37 – 7.35 (m, 1H), 7.22 – 7.17 (m, 2H), 7.15 – 7.11(m, 1H), 4.79 (tt, *J* = 9.1, 3.9 Hz, 1H), 3.75 (s, 2H), 1.86 – 1.81 (m, 2H), 1.73 – 1.66 (m, 2H), 1.55 – 1.48 (m, 1H), 1.46 – 1.39 (m, 2H), 1.38 – 1.30 (m, 2H), 1.28 – 1.21 (m, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.4, 136.1, 127.3, 122.8, 122.1, 119.5, 119.0, 111.0, 108.9, 73.0, 31.8, 31.6, 25.3, 23.7 ppm.

HRMS (ESI): mass found: 230.1304, calculated mass $C_{16}H_{19}NNaO_2^+$: 280.1308.

IR (KBr): 3407, 2934, 2858, 2664, 2512, 2327, 2178, 2092, 1993, 1946, 1806, 1716, 1620, 1552, 1491, 1453, 1337, 1295, 1258, 1163, 1122, 1095, 1013, 966, 899, 798 cm^{-1}.

Tetrahydrofuran-3-yl 2-(1*H*-indol-3-yl)acetate (9v)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (69%, 34 mg).

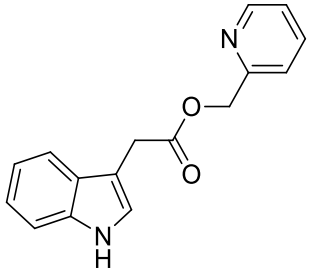
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.10 (brs, 1H), 7.65 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.18 – 7.15 (m, 1H), 5.36 – 5.33 (m, 1H), 3.94 – 3.89 (m, 2H), 3.88 – 3.83 (m, 2H), 3.81 (s, 2H), 2.21 – 2.13 (m, 1H), 2.05 – 1.97 (m, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.7, 136.1, 127.2, 122.9, 122.3, 119.7, 118.8, 111.1, 108.3, 75.1, 73.1, 67.0, 32.7, 31.4 ppm.

HRMS (ESI): mass found: 268.0951, calculated mass $C_{14}H_{15}NNaO_3^+$: 268.0944.

IR (KBr): 3402, 3055, 2950, 2869, 2683, 2160, 2034, 1722, 1623, 1554, 1489, 1457, 1431, 1338, 1296, 1260, 1159, 1080, 984, 908, 742, 662 cm^{-1}.

Pyridin-2-ylmethyl 2-(1*H*-indol-3-yl)acetate (9w)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a dark brown oil (54%, 29 mg).

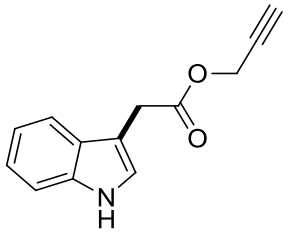
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.60 – 8.57 (m, 1H), 8.17 (brs, 1H), 7.64 – 7.60 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.18 (m, 3H), 7.15 – 7.11 (m, 1H), 5.27 (s, 2H), 3.90 (s, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.6, 155.8, 149.4, 136.7, 136.1, 127.2, 123.1, 122.8, 122.2, 121.7, 119.7, 118.9, 111.1, 108.2, 67.0, 31.2 ppm.

HRMS (ESI): mass found: 289.0945, calculated mass $C_{16}H_{14}N_2NaO_2^+$: 289.0947.

IR (KBr): 3402, 3187, 3057, 2920, 2851, 2161, 2115, 2030, 1890, 1733, 1594, 1437, 1341, 1266, 1236, 1150, 1004, 928, 893, 826, 742 cm^{-1}.

Prop-2-yn-1-yl 2-(1*H*-indol-3-yl)acetate (9x)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (73%, 31 mg).

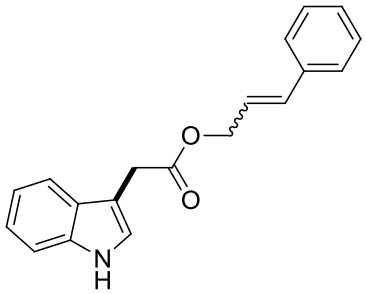
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.08 (s, 1H), 7.64 – 7.61 (m, 1H), 7.39 – 7.35 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 – 7.13 (m, 1H), 4.72 (d, *J* = 2.5 Hz, 2H), 3.84 (d, *J* = 0.9 Hz, 2H), 2.47 (t, *J* = 2.5 Hz, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.1, 136.0, 127.1, 123.1, 122.3, 119.8, 118.8, 111.1, 107.9, 77.6, 74.9, 52.2, 31.0 ppm.

HRMS (ESI): mass found: 236.0681, calculated mass $C_{13}H_{11}NNaO_2^+$: 236.0682.

IR (KBr): 3916, 3410, 3285, 3055, 2922, 2853, 2678, 2324, 2126, 1977, 1924, 1732, 1620, 1490, 1456, 1428, 1372, 1337, 1295, 1240, 1149, 1095, 999, 935, 875, 799, 687 cm^{-1}.

3-Phenylallyl 2-(1*H*-indol-3-yl)acetate (9y)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (78%, 45 mg).

The diazoalkane used for the synthesis of this compound is a 1 : 1 mixture of Z/E isomer.

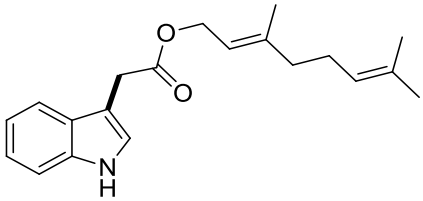
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.07 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.27 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 7.16 – 7.12 (m, 1H), 6.62 – 6.56 (m, 1H), 6.27 (dt, *J* = 16.0, 6.3 Hz, 1H), 4.78 (dd, *J* = 6.3, 1.4 Hz, 2H), 3.84 (s, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.6, 136.1, 136.0, 133.9, 128.5, 127.9, 127.2, 126.5, 123.1, 122.9, 122.2, 119.6, 118.8, 111.1, 108.4, 65.2, 31.3 ppm.

HRMS (ESI): mass found: 314.1152, calculated mass $C_{19}H_{17}NNaO_2^+$: 314.1151.

IR (KBr): 3410, 3054, 2927, 2677, 2496, 2331, 2156, 2081, 1994, 1880, 1725, 1620, 1579, 1492, 1453, 1377, 1336, 1298, 1246, 1154, 1096, 1067, 965, 841, 798, 740, 692 cm^{-1}.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 2-(1*H*-indol-3-yl)acetate (9z)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (67%, 42 mg).

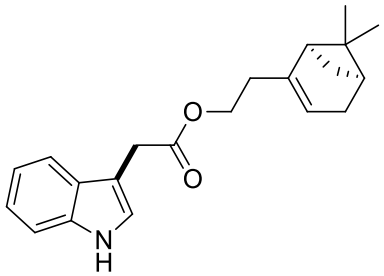
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.05 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.37 – 5.34 (m, 1H), 5.10 – 5.06 (m, 1H), 4.63 (d, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 2.11 – 2.07 (m, 2H), 2.05 – 2.01 (m, 2H), 1.69 – 1.68 (m, 6H), 1.60 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 142.3, 136.1, 131.8, 127.3, 123.7, 122.9, 122.2, 119.6, 118.9, 118.3, 111.1, 108.7, 61.7, 39.5, 31.4, 26.3, 25.6, 17.7, 16.4 ppm.

HRMS (ESI): mass found: 334.1779, calculated mass $C_{20}H_{25}NNaO_2^+$: 334.1777.

IR (KBr): 3407, 3055, 2920, 2856, 2675, 2329, 2191, 2086, 1999, 1955, 1724, 1620, 1552, 1490, 1453, 1378, 1344, 1295, 1242, 1157, 1096, 967, 832, 780, 740 cm^{-1}.

2-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 2-(1*H*-indol-3-yl)acetate (9aa)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (74%, 48 mg).

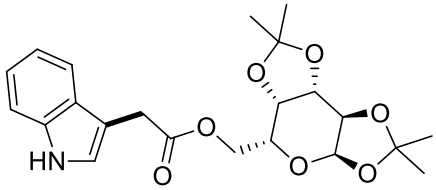
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.06 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.15 – 7.12 (m, 1H), 4.44 – 4.32 (m, 2H), 4.20 – 4.15 (m, 1H), 3.78 (s, 2H), 2.55 – 2.49 (m, 1H), 2.15 – 2.09 (m, 1H), 1.74 – 1.68 (m, 2H), 1.59 (t, *J* = 4.5 Hz, 1H), 1.52 (d, *J* = 4.1 Hz, 1H), 1.32 – 1.24 (m, 2H), 0.95 (s, 3H), 0.88 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 136.1, 127.3, 123.0, 122.2, 119.6, 118.9, 111.1, 108.6, 62.3, 60.2, 52.0, 48.5, 45.4, 41.6, 31.4, 29.3, 28.6, 27.9, 21.1, 19.1 ppm.

HRMS (ESI): mass found: 346.1774, calculated mass $C_{21}H_{25}NNaO_2^+$: 346.1777.

IR (KBr): 3407, 3054, 2954, 2325, 2162, 2097, 1916, 1723, 1621, 1457, 1425, 1335, 1299, 1244, 1161, 1095, 1000, 928, 865, 787, 740, 660 cm^{-1}.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)methyl 2-(1*H*-indol-3-yl)acetate (9ab)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (64%, 53 mg).

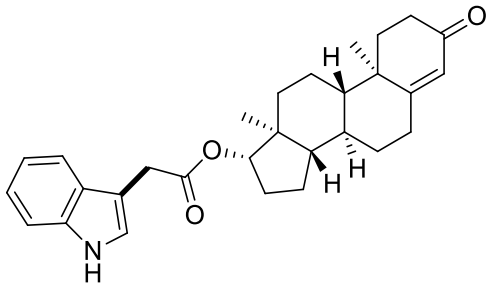
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 8.12 (brs, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.61 – 4.56 (m, 1H), 4.38 – 4.30 (m, 2H), 4.25 (dd, *J* = 11.6, 7.6 Hz, 1H), 4.17 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.07 – 4.02 (m, 1H), 3.82 (s, 2H), 1.45 (s, 6H), 1.32 (d, *J* = 5.5 Hz, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 136.0, 127.2, 123.2, 122.1, 119.6, 118.9, 111.1, 109.6, 108.8, 108.3, 96.3, 71.0, 70.6, 70.4, 66.0, 63.7, 31.2, 25.98, 25.97, 25.0, 24.4 ppm.

HRMS (ESI): mass found: 440.1686, calculated mass $C_{22}H_{27}NNaO_7^+$: 440.1679.

IR (KBr): 3391, 3056, 2986, 2930, 2159, 2029, 1731, 1622, 1457, 1377, 1252, 1210, 1164, 1112, 1065, 1002, 917, 892, 860, 742, 687 cm^{-1}.

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-17-yl 2-(1*H*-indol-3-yl)acetate (9ac)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (51%, 45 mg).

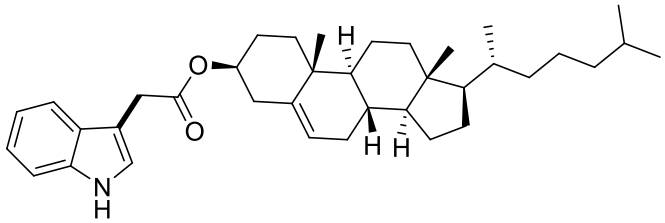
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.19 (brs, 1H), 7.61 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.14 – 7.11 (m, 1H), 5.73 (s, 1H), 4.63 (dd, *J* = 9.2, 7.8 Hz, 1H), 3.77 (s, 2H), 2.45 – 2.31 (m, 3H), 2.29 – 2.24 (m, 1H), 2.21 – 2.13 (m, 1H), 2.03 – 1.97 (m, 1H), 1.85 – 1.80 (m, 1H), 1.75 – 1.68 (m, 2H), 1.65 – 1.61 (m, 1H), 1.60 – 1.48 (m, 3H), 1.40 – 1.29 (m, 2H), 1.18 – 1.12 (m, 4H), 1.07 – 0.97 (m, 2H), 0.95 – 0.89 (m, 1H), 0.77 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 199.5, 172.1, 171.0, 136.1, 127.2, 123.9, 122.9, 122.1, 119.5, 118.9, 111.1, 108.7, 82.8, 53.6, 50.2, 42.5, 38.6, 36.6, 35.6, 35.4, 33.9, 32.7, 31.5, 31.4, 27.4, 23.4, 20.5, 17.4, 12.0 ppm.

HRMS (ESI): mass found: 468.2505, calculated mass $C_{29}H_{35}NNaO_3^+$: 468.2509.

IR (KBr): 3390, 3327, 3034, 2939, 2856, 2251, 2027, 1930, 1718, 1669, 1614, 1492, 1454, 1338, 1301, 1227, 1175, 1036, 1009, 907, 861, 730, 670 cm^{-1}.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-(1*H*-indol-3-yl)acetate (9ad)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (67%, 73 mg).

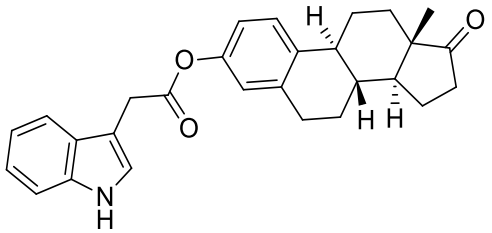
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.05 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.35 (d, *J* = 4.9 Hz, 1H), 4.68 – 4.62 (m, 1H), 3.75 (s, 2H), 2.33 (d, *J* = 6.7 Hz, 2H), 2.04 – 1.92 (m, 2H), 1.89 – 1.79 (m, 3H), 1.64 – 1.56 (m, 2H), 1.54 – 1.40 (m, 5H), 1.39 – 1.31 (m, 2H), 1.29 – 1.22 (m, 2H), 1.19 – 1.04 (m, 7H), 1.01 (s, 3H), 1.01 – 0.93 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.67 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.4, 139.6, 136.1, 127.3, 122.9, 122.6, 122.1, 119.6, 119.0, 111.1, 108.8, 74.4, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 31.7, 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8 ppm.

HRMS (ESI): mass found: 566.3970, calculated mass $C_{37}H_{53}NNaO_2^+$: 566.3968.

IR (KBr): 3904, 3406, 3052, 2937, 2323, 2179, 2099, 2015, 1975, 1914, 1727, 1621, 1459, 1375, 1321, 1236, 1172, 1121, 1087, 1005, 958, 924, 824, 803, 738 cm^{-1}.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl 2-(1*H*-indol-3-yl)acetate (9ae)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (49%, 42 mg).

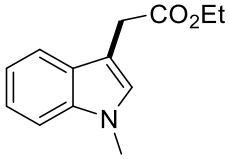
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.11 (brs, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.15 (m, 1H), 6.84 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 4.01 (s, 2H), 2.91 – 2.83 (m, 2H), 2.50 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.30 – 2.24 (m, 1H), 2.18 – 2.09 (m, 1H), 2.08 – 2.03 (m, 1H), 2.01 – 1.93 (m, 2H), 1.65 – 1.57 (m, 2H), 1.53 – 1.40 (m, 4H), 0.90 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 220.7, 170.6, 148.7, 137.9, 137.3, 136.1, 127.2, 126.3, 123.1, 122.3, 121.5, 119.8, 118.9, 118.7, 111.2, 108.1, 50.4, 47.9, 44.1, 38.0, 35.8, 31.5, 29.3, 26.3, 25.7, 21.5, 13.8 ppm.

HRMS (ESI): mass found: 428.2213, calculated mass $C_{28}H_{30}NO_3^+$: 428.2220.

IR (KBr): 3391, 3055, 2925, 2860, 2249, 2164, 2021, 1978, 1731, 1610, 1492, 1456, 1428, 1340, 1296, 1216, 1120, 1056, 1008, 907, 819, 732 cm^{-1}.

Ethyl 2-(1-methyl-1*H*-indol-3-yl)acetate (13a)



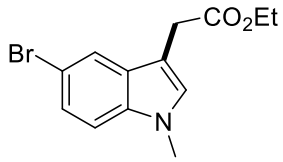
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (83%, 36 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.78 – 3.74 (m, 5H), 1.27 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 136.9, 127.7, 121.7, 119.1, 119.0, 109.2, 106.9, 60.7, 32.7, 31.3, 14.2 ppm.

Physical data is in accordance with the previous literature.[12]

Ethyl 2-(5-bromo-1-methyl-1*H*-indol-3-yl)acetate (13b)



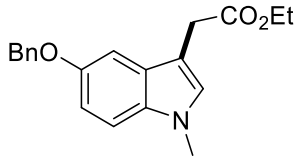
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (76%, 45 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.73 (d, *J* = 1.8 Hz, 1H), 7.30 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.04 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.70 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 135.6, 129.3, 128.9, 124.6, 121.7, 112.6, 110.7, 106.6, 60.9, 32.8, 31.1, 14.2 ppm.

Physical data is in accordance with the previous literature.[12]

Ethyl 2-(5-(benzyloxy)-1-methyl-1*H*-indol-3-yl)acetate (13c)



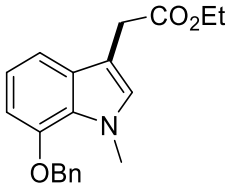
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (88%, 57 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.50 – 7.46 (m, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.30 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.02 (s, 1H), 6.97 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.12 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.70 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.4, 153.5, 138.0, 132.8, 128.8, 128.7, 128.3, 128.1, 127.9, 113.1, 110.3, 106.8, 102.8, 71.3, 61.0, 33.2, 31.7, 14.6 ppm.

Physical data is in accordance with the previous literature.[13]

Ethyl 2-(7-(benzyloxy)-1-methyl-1*H*-indol-3-yl)acetate (13d)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (85%, 55 mg).

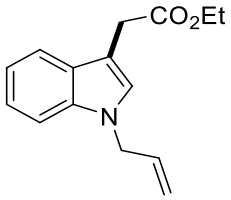
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.49 – 7.45 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.32 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.18 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 3.71 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 146.9, 137.2, 130.2, 128.9, 128.5, 127.9, 127.4, 126.6, 119.6, 112.1, 106.9, 103.7, 70.4, 60.7, 36.5, 31.3, 14.2 ppm.

HRMS (ESI): mass found: 346.1490, calculated mass $C_{20}H_{21}NNaO_3^+$: 346.1413.

IR (KBr): 3870, 3633, 3404, 3034, 2982, 2936, 2670, 2507, 2326, 2087, 1996, 1945, 1880, 1811, 1721, 1629, 1578, 1497, 1444, 1416, 1372, 1339, 1254, 1175, 1090, 1066, 1025, 972, 913, 854, 783, 727, 698 cm^{-1}.

Ethyl 2-(1-allyl-1*H*-indol-3-yl)acetate (13e)



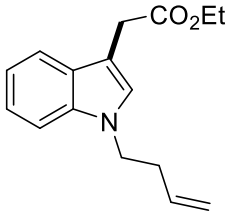
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (87%, 42 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.63 – 7.60 (m, 1H), 7.31 – 7.28 (m, 1H), 7.22 – 7.19 (m, 1H), 7.14 – 7.11 (m, 1H), 7.10 (s, 1H), 6.03 – 5.96 (m, 1H), 5.20 (dq, *J* = 10.2, 1.4 Hz, 1H), 5.11 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.70 (dt, *J* = 5.6, 1.7 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 136.3, 133.4, 127.9, 126.6, 121.7, 119.2, 119.1, 117.3, 109.6, 107.4, 60.7, 48.7, 31.3, 14.2 ppm.

Physical data is in accordance with the previous literature.[14]

Ethyl 2-(1-(but-3-en-1-yl)-1*H*-indol-3-yl)acetate (13f)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (76%, 39 mg).

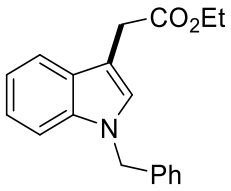
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.62 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.14 – 7.09 (m, 2H), 5.83 – 5.74 (m, 1H), 5.12 – 5.04 (m, 2H), 4.19 – 4.13 (m, 4H), 3.76 (s, 2H), 2.58 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 136.1, 134.6, 127.8, 126.6, 121.6, 119.1, 117.3, 109.3, 107.0, 60.7, 45.9, 34.5, 31.3, 14.2 ppm.

HRMS (ESI): mass found: 280.1305, calculated mass $C_{16}H_{19}NNaO_2^+$: 280.1308.

IR (KBr): 3453, 3054, 2979, 2932, 2670, 2331, 2188, 2079, 1730, 1642, 1614, 1552, 1516, 1465, 1365, 1305, 1254, 1148, 1029, 919 cm^{-1}.

Ethyl 2-(1-benzyl-1*H*-indol-3-yl)acetate (13g)



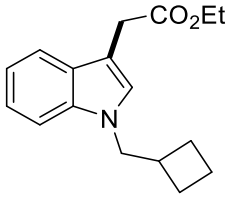
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (83%, 49 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.65 – 7.60 (m, 1H), 7.32 – 7.24 (m, 4H), 7.20 – 7.16 (m, 1H), 7.15 – 7.11 (m, 4H), 5.29 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 137.4, 136.5, 128.7, 128.0, 127.6, 127.1, 126.8, 121.9, 119.3, 119.1, 109.7, 107.7, 60.7, 50.0, 31.4, 14.2 ppm.

Physical data is in accordance with the previous literature.[15]

Ethyl 2-(1-(cyclobutylmethyl)-1*H*-indol-3-yl)acetate (13h)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (71%, 38 mg).

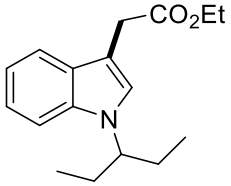
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.08 (d, *J* = 7.2 Hz, 2H), 3.75 (s, 2H), 2.87 – 2.78 (m, 1H), 2.10 – 2.03 (m, 2H), 1.93 – 1.85 (m, 2H), 1.84 – 1.77 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 136.4, 127.6, 126.6, 121.5, 119.0, 118.9, 109.4, 106.8, 60.7, 51.4, 35.9, 31.4, 26.3, 18.2, 14.2 ppm.

HRMS (ESI): mass found: 294.1463, calculated mass $C_{17}H_{21}NNaO_2^+$: 294.1464.

IR (KBr): 3454, 3050, 2932, 2864, 2664, 2328, 2190, 2090, 1994, 1874, 1732, 1612, 1550, 1522, 1465, 1367, 1249, 1146, 1030, 926, 848, 740 cm^{-1}.

Ethyl 2-(1-(pentan-3-yl)-1*H*-indol-3-yl)acetate (13i)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (59%, 32 mg).

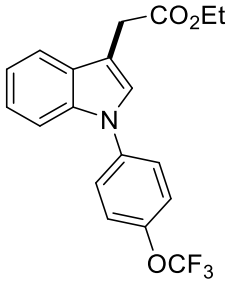
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.13 – 4.07 (m, 1H), 3.77 (s, 2H), 1.92 – 1.82 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 6H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.1, 137.0, 127.5, 123.3, 121.3, 118.9, 118.8, 109.6, 107.3, 60.6, 59.5, 31.5, 28.5, 14.2, 10.9 ppm.

HRMS (ESI): mass found: 296.1621, calculated mass $C_{17}H_{23}NNaO_2^+$: 296.1621.

IR (KBr): 3332, 2967, 2932, 2876, 2658, 2327, 2189, 2087, 2041, 1992, 1961, 1876, 1735, 1643, 1610, 1550, 1518, 1460, 1321, 1218, 1156, 1096, 1027, 926, 840, 740, 664 cm^{-1}.

Ethyl 2-(1-(4-(trifluoromethoxy)phenyl)-1*H*-indol-3-yl)acetate (13j)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (74%, 54 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 3H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.32 (s, 1H), 7.27 – 7.24 (m, 1H), 7.22 – 7.19 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

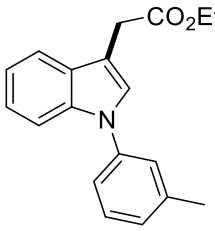
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.6, 147.1, 138.2, 135.9, 128.7, 126.5, 125.4, 122.9, 122.2, 120.57, 120.51 (q, *J* = 257.8 Hz), 119.4, 110.3, 110.2, 60.9, 31.2, 14.2 ppm.

^{19}F NMR (565 MHz, Chloroform-*d*): δ = -57.99 ppm.

HRMS (ESI): mass found: 364.1146, calculated mass $C_{19}H_{17}F_3NO_3^+$: 364.1155.

IR (KBr): 3450, 3057, 2984, 2666, 2326, 2089, 1994, 1898, 1732, 1604, 1511, 1457, 1373, 1334, 1255, 1205, 1162, 1024, 924, 854, 810, 742, 668 cm^{-1}.

Ethyl 2-(1-(*m*-tolyl)-1*H*-indol-3-yl)acetate (13k)



The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 20:1 – 9:1) as a yellow oil (81%, 47 mg).

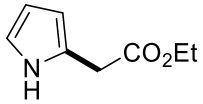
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.67 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.34 (s, 1H), 7.32 – 7.29 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.14 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.8, 139.64, 139.60, 136.0, 129.3, 128.6, 127.1, 126.8, 124.9, 122.5, 121.3, 120.1, 119.2, 110.6, 109.4, 60.8, 31.3, 21.4, 14.2 ppm.

HRMS (ESI): mass found: 316.1307, calculated mass $C_{19}H_{19}NNaO_2^+$: 316.1308.

IR (KBr): 3821, 3455, 3214, 3051, 2924, 2659, 2326, 2198, 2109, 2051, 1935, 1787, 1731, 1603, 1492, 1460, 1371, 1380, 1231, 1159, 1094, 1027, 936, 873, 840, 786, 698 cm^{-1}.

Ethyl 2-(1*H*-pyrrol-2-yl)acetate (14)



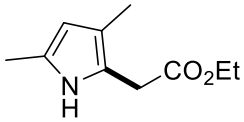
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 40:1 – 20:1) as a brown oil (81%, 25 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.73 (brs, 1H), 6.77 – 6.74 (m, 1H), 6.18 – 6.11 (m, 1H), 6.04 – 6.00 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.5, 123.6, 118.0, 108.5, 107.6, 61.4, 33.5, 14.5 ppm.

Physical data is in accordance with the previous literature.[16]

Ethyl 2-(3,5-dimethyl-1*H*-pyrrol-2-yl)acetate (15)



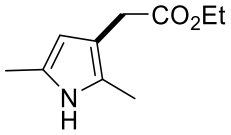
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 40:1 – 20:1) as a brown oil (72%, 26 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.15 (s, 1H), 5.68 – 5.66 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.54 (s, 2H), 2.22 (s, 3H), 1.99 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.5, 126.5, 117.7, 115.9, 107.7, 60.9, 31.2, 14.2, 12.9, 10.6 ppm.

Physical data is in accordance with the previous literature.[16]

Ethyl 2-(2,5-dimethyl-1*H*-pyrrol-3-yl)acetate (16)



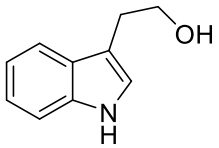
The titled compound was synthesized according to the general procedure GP-1 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 40:1 – 20:1) as a brown oil (64%, 23 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.51 – 7.42 (m, 1H), 5.76 – 5.74 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 2H), 2.20 (s, 3H), 2.17 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.6, 125.3, 123.3, 111.4, 107.2, 60.4, 32.2, 14.2, 12.9, 10.9 ppm.

Physical data is in accordance with the previous literature.[16]

2-(1*H*-Indol-3-yl)ethan-1-ol (17a)



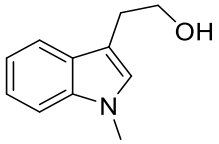
The titled compound was synthesized according to the general procedure GP-2 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 2:1 – 1:1) as a brown oil (81%, 91 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.06 (brs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.25 – 7.20 (m, 1H), 7.15 – 7.12 (m, 1H), 7.11 – 7.09 (m, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.3 Hz, 2H), 1.51 (brs, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 136.4, 127.4, 122.4, 122.2, 119.5, 118.8, 112.3, 111.2, 62.6, 28.7 ppm.

Physical data is in accordance with the previous literature.[18]

2-(1-Methyl-1*H*-indol-3-yl)ethan-1-ol (17b)



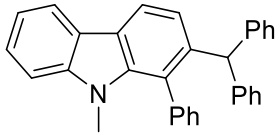
The titled compound was synthesized according to the general procedure GP-2 and was obtained after silica gel column chromatography (*n*-hexane : ethyl acetate 4:1) as a colorless oil (84%, 103 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 3.90 (t, *J* = 6.3 Hz, 2H), 3.77 (s, 3H), 3.03 (t, *J* = 6.3 Hz, 2H), 1.57 (bs, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 137.2, 127.8, 127.3, 121.7, 118.94, 118.92, 110.6, 109.3, 62.7, 32.6, 28.6 ppm.

Physical data is in accordance with the previous literature.[19]

2-Benzhydryl-9-methyl-1-phenyl-9*H*-carbazole (19)



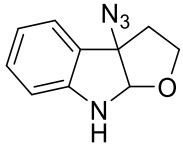
In an oven-dried reaction tube tryptophol **xx** (32.2 mg, 0.2 mmol, 1 equiv.), propargylic alcohol (62.6 mg, 0.22 mmol, 1.1 equiv.) and $BF_3 \cdot OEt_2$ (0.3 mmol, 1.5 equiv.) were dissolved in 2 mL of acetonitrile. Then the reaction mixture was stirred at 60 °C for 8 h. After cooling to room temperature, solvent was evaporated under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 40:1). Product xx was obtained as yellow oil (61%, 42 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.07 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.37 – 7.33 (m, 2H), 7.27 – 7.25 (m, 1H), 7.23 – 7.15 (m, 9H), 7.00 – 6.95 (m, 5H), 5.50 (s, 1H), 3.12 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 144.6, 142.1, 140.4, 138.8, 138.2, 131.1, 129.6, 128.0, 127.8, 127.5, 125.9, 125.5, 125.3, 122.4, 121.9, 121.1, 119.8, 119.0, 118.9, 108.6, 53.0, 31.7 ppm.

Physical data is in accordance with the previous literature.[20]

3a-Azido-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (20)



To an oven-dried reaction tube, 40 mol% $Cu(OAc)_2 \cdot H_2O$ (0.08 mmol), $PhI(OAc)_2$ (129 mg, 0.4 mmol), NaN_3 (78.8 mg, 1.2 mmol), acetic acid (28.8 mg, 0.48 mmol) and 4 mL of DMF were added. Stirred the mixture at room temperature for 30 min and then tryptophol **xx** (64.5 mg, 0.4 mmol) was added to the reaction mixture. The resulting reaction mixture was stirred at 60 °C for 10 h. After cooling to room temperature, the reaction mixture was quenched with water, extracted with ethyl acetate and dried over Na_2SO_4. The organic layer was evaporated under reduced pressure and the product was purified by silica gel column chromatography (*n*-hexane : ethyl acetate 9:1 – 4:1). Product xx was obtained as colorless oil (91%, 74 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.29 – 7.25 (m, 1H), 7.20 (td, *J* = 7.6, 1.3 Hz, 1H), 6.86 (td, *J* = 7.5, 1.0 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.54 (d, *J* = 2.1 Hz, 1H), 4.69 (s, 1H), 4.09 – 4.04 (m, 1H), 3.71 – 3.66 (m, 1H), 2.46 – 2.33 (m, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 149.7, 130.7, 125.9, 124.3, 119.7, 109.7, 98.0, 78.0, 67.4, 39.5 ppm.

Physical data is in accordance with the previous literature.[21]

Spectra

4-Phenylbutyl 2-diazoacetate (4b)

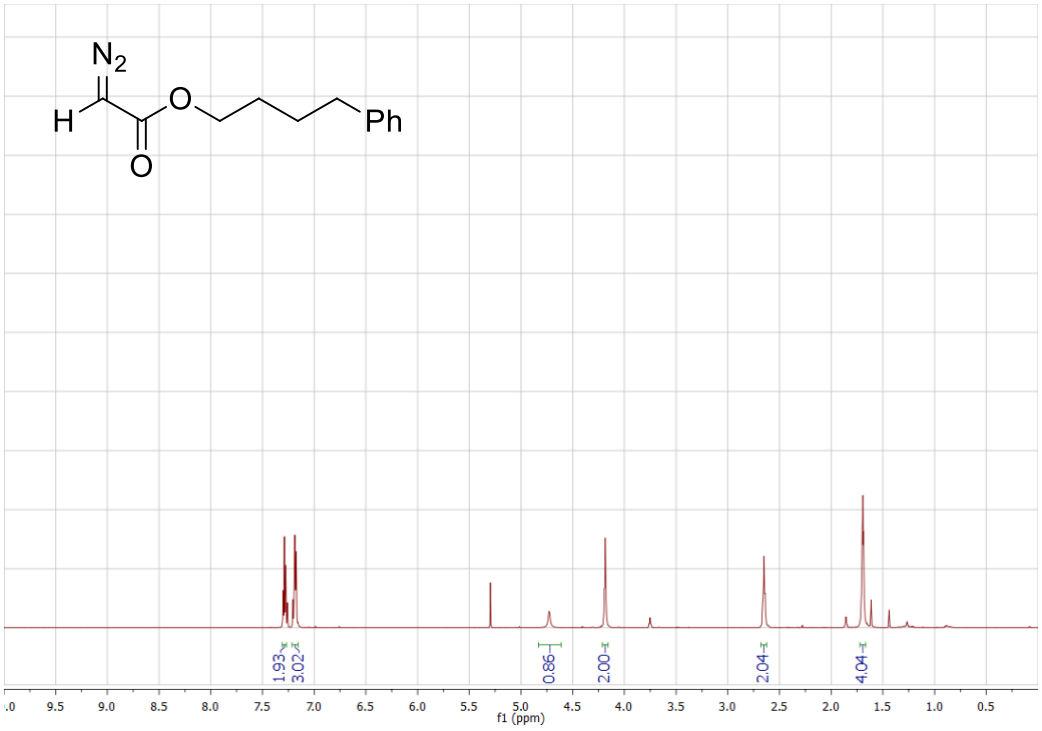


Figure S20. ^{1}H NMR (600 MHz, Chloroform-*d*) of **4b**

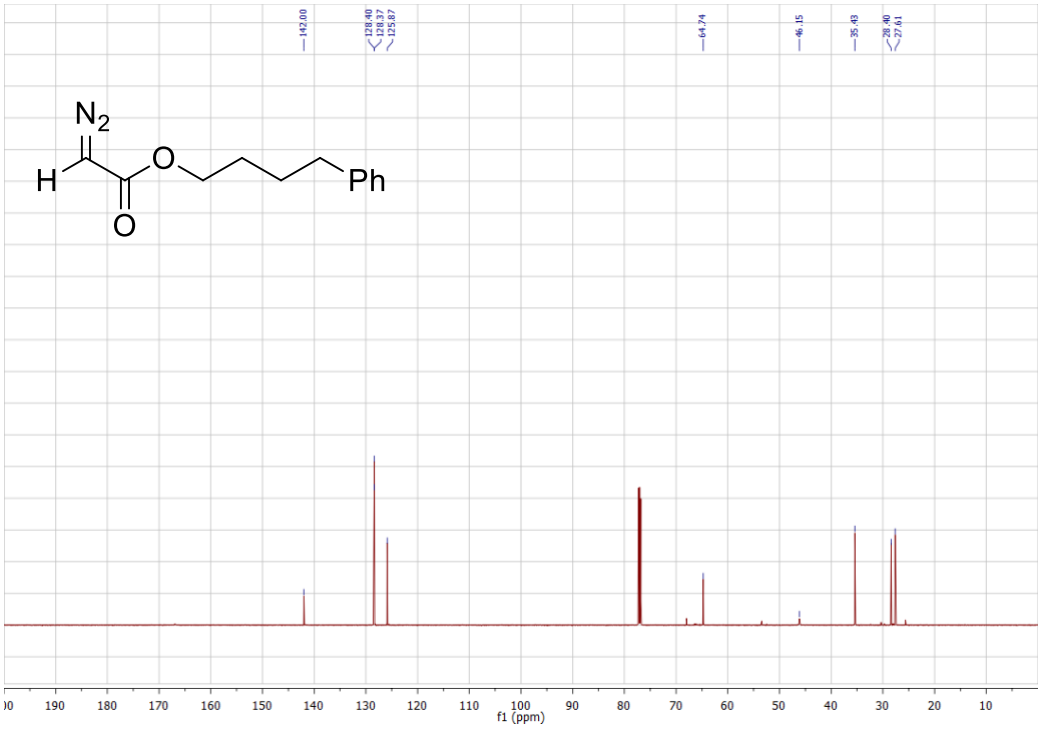


Figure S21. ^{13}C NMR (151 MHz, Chloroform-*d*) of **4b**

5-Phenylpentyl 2-diazoacetate (4c)

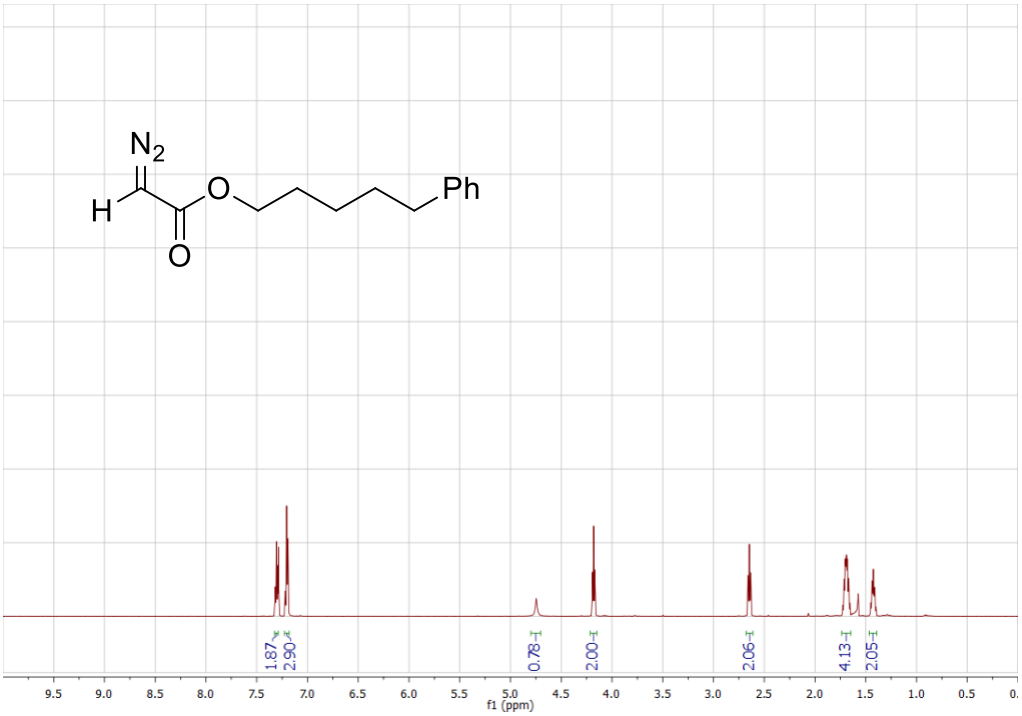


Figure S22. ^{1}H NMR (600 MHz, Chloroform-*d*) of **4c**

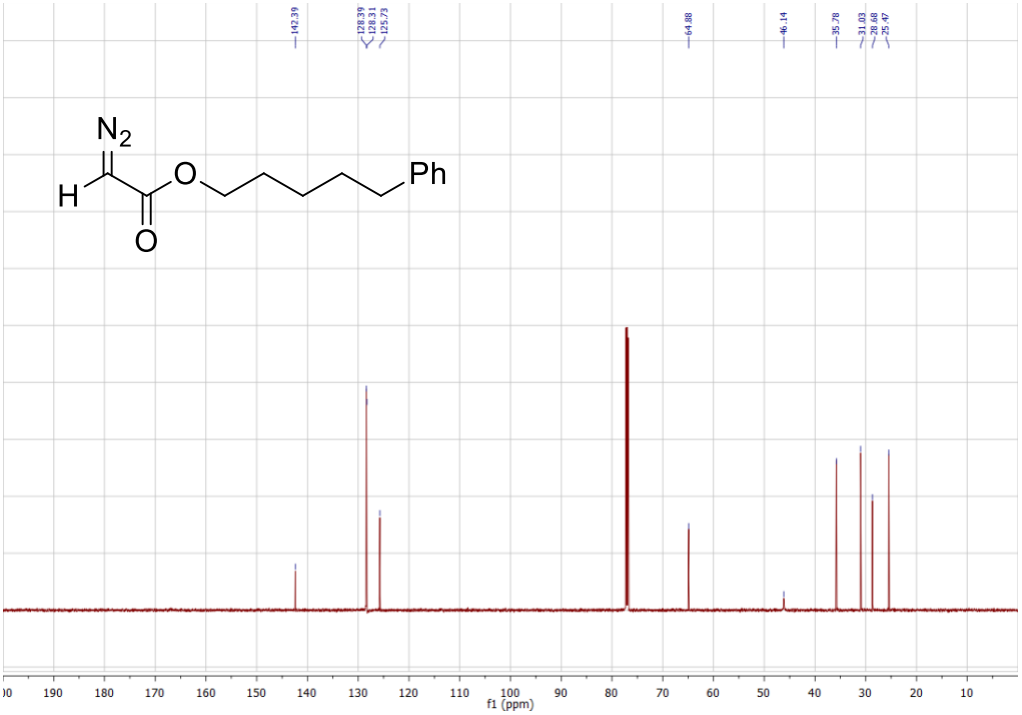


Figure S23. ^{13}C NMR (151 MHz, Chloroform-*d*) of **4c**

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 2-diazoacetate (4d)

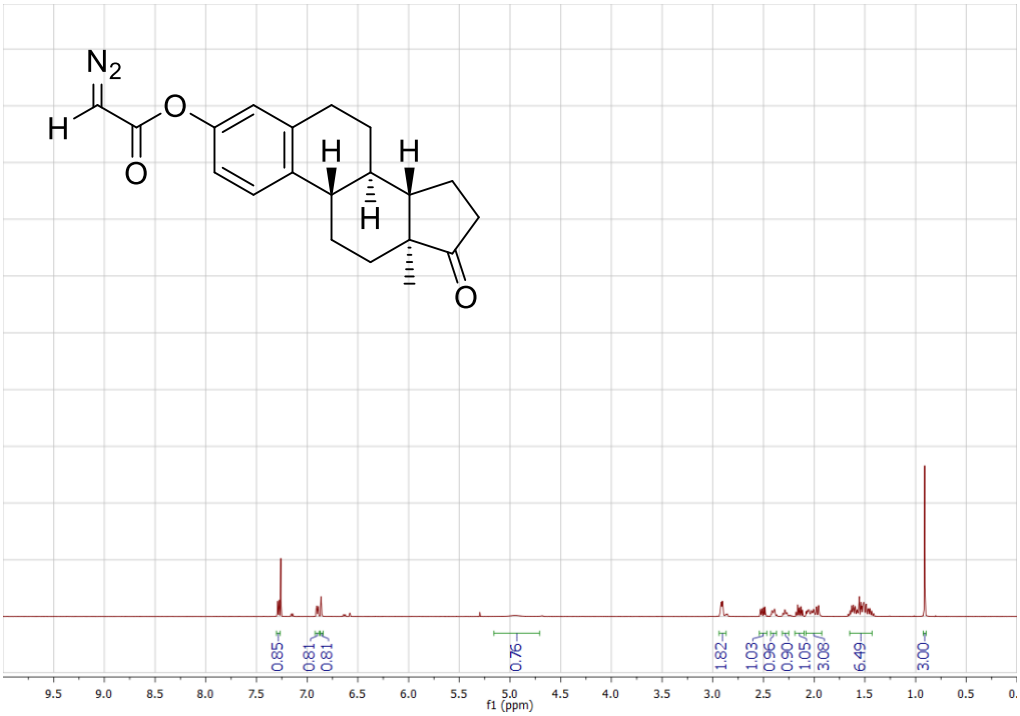


Figure S24. ^{1}H NMR (600 MHz, Chloroform-*d*) of **4d**

^{13}C NMR (151 MHz, Chloroform-*d*)

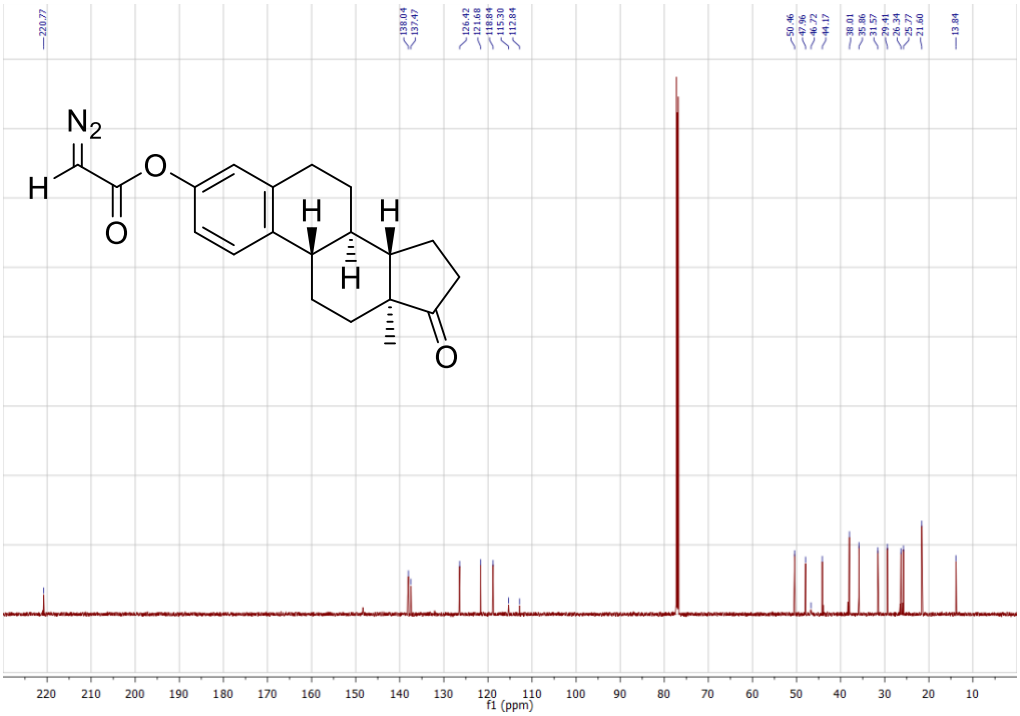


Figure S25. ^{13}C NMR (151 MHz, Chloroform-*d*) of **4d**

(8*S*,9*R*,10*S*,13*R*,14*R*,17*R*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-diazoacetate (4e)

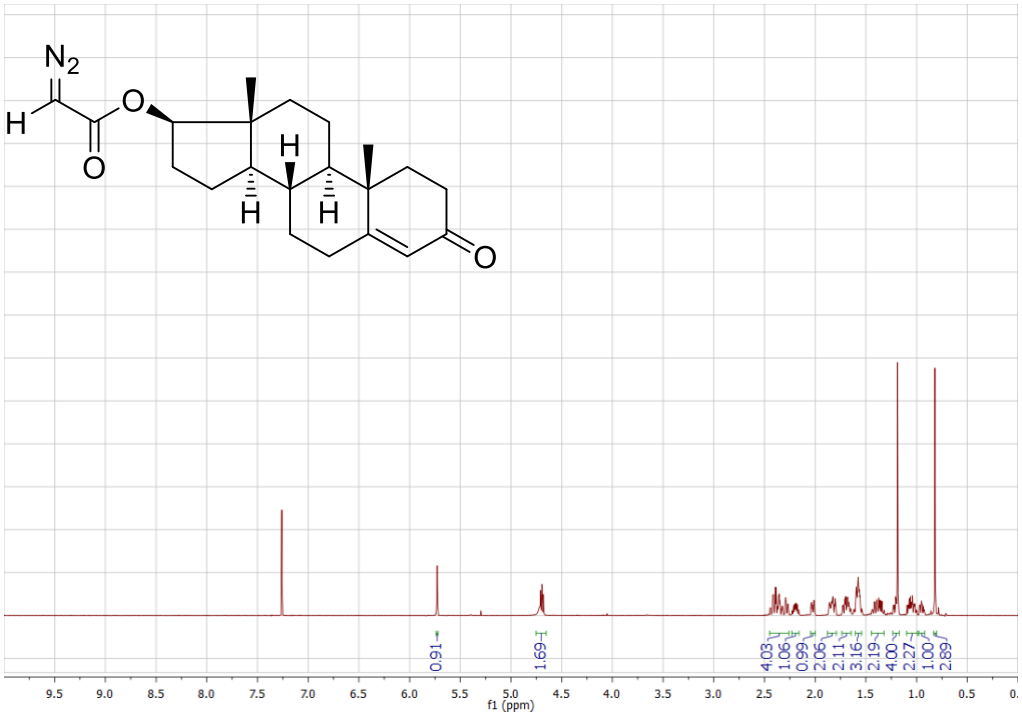


Figure S26. ^{1}H NMR (600 MHz, Chloroform-*d*) of **4e**

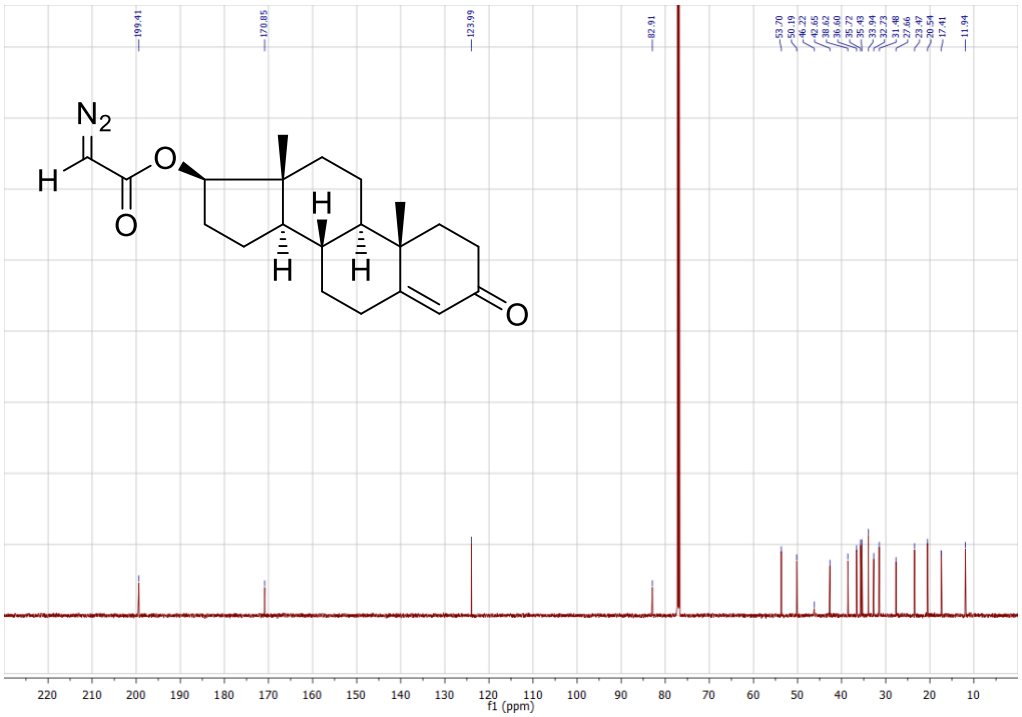


Figure S27. ^{13}C NMR (151 MHz, Chloroform-*d*) of **4e**

Ethyl 2-(1*H*-indol-2-yl)acetate (6)

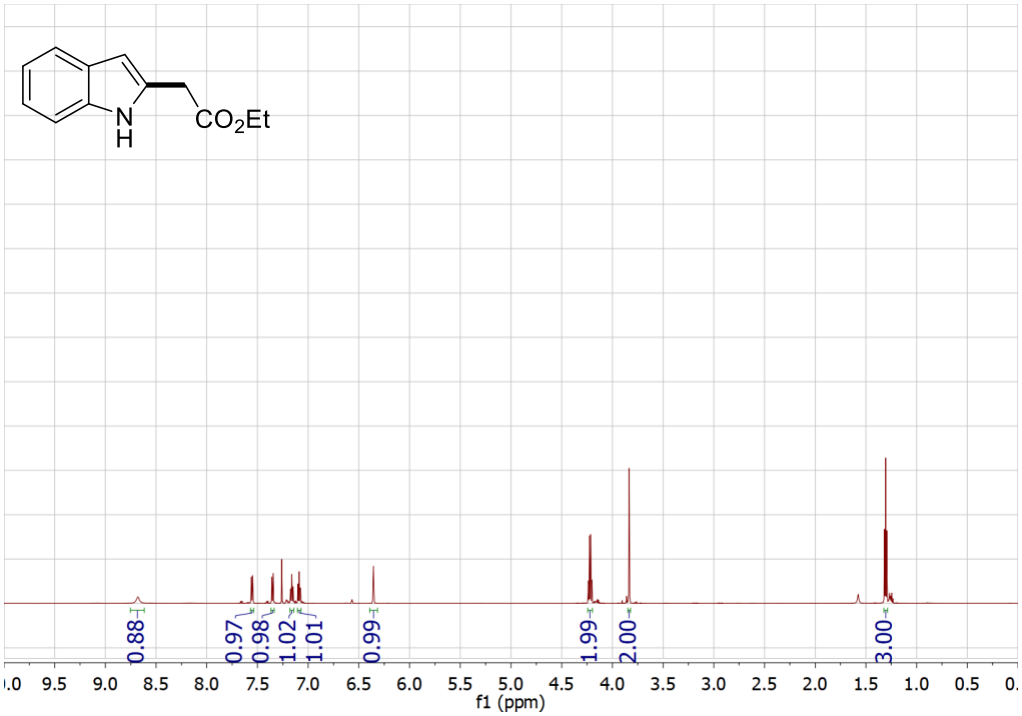


Figure S28. ^{1}H NMR (600 MHz, Chloroform-*d*) of **6**

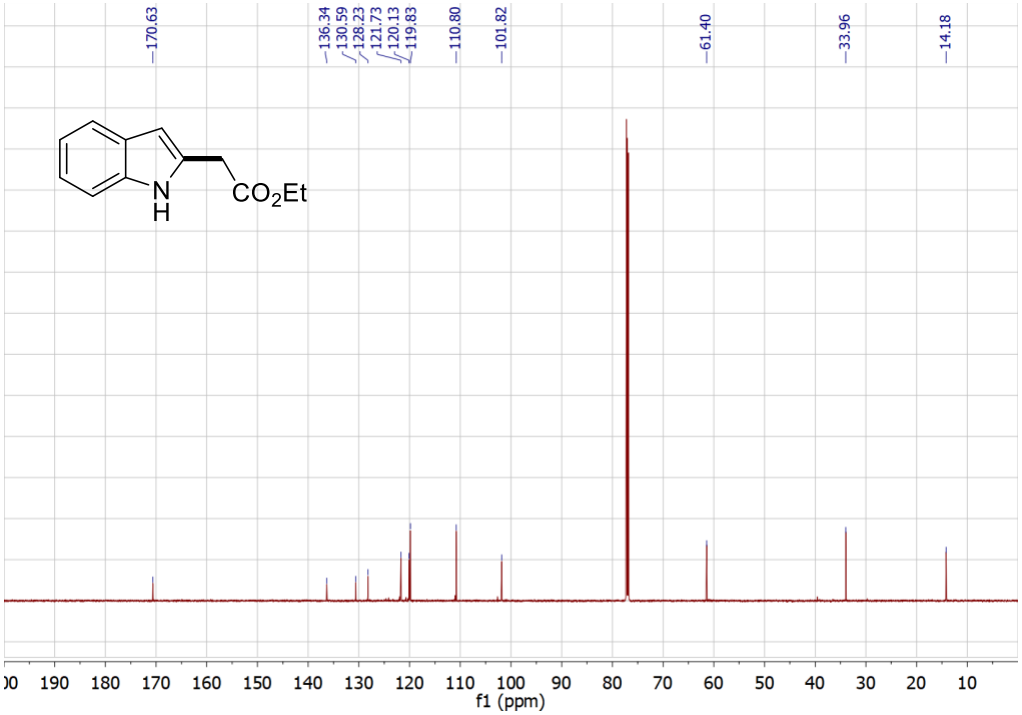


Figure S29. ^{13}C NMR (151 MHz, Chloroform-*d*) of **6**

Ethyl 2-(1*H*-indol-3-yl)acetate (9a)

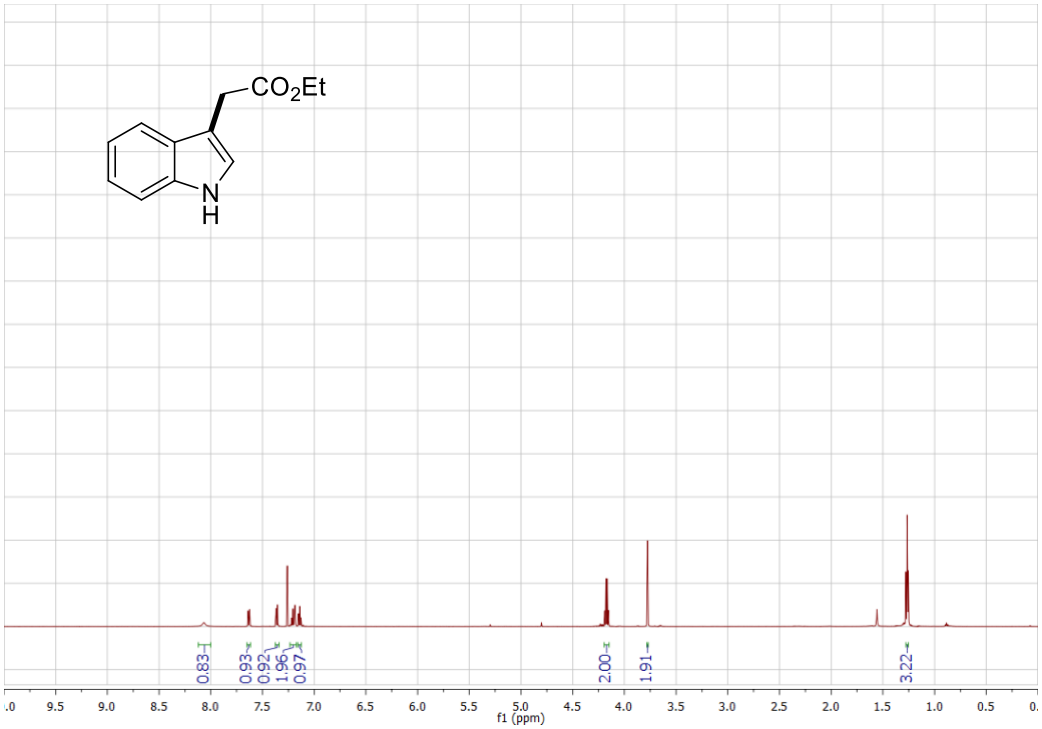


Figure S30. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9a**

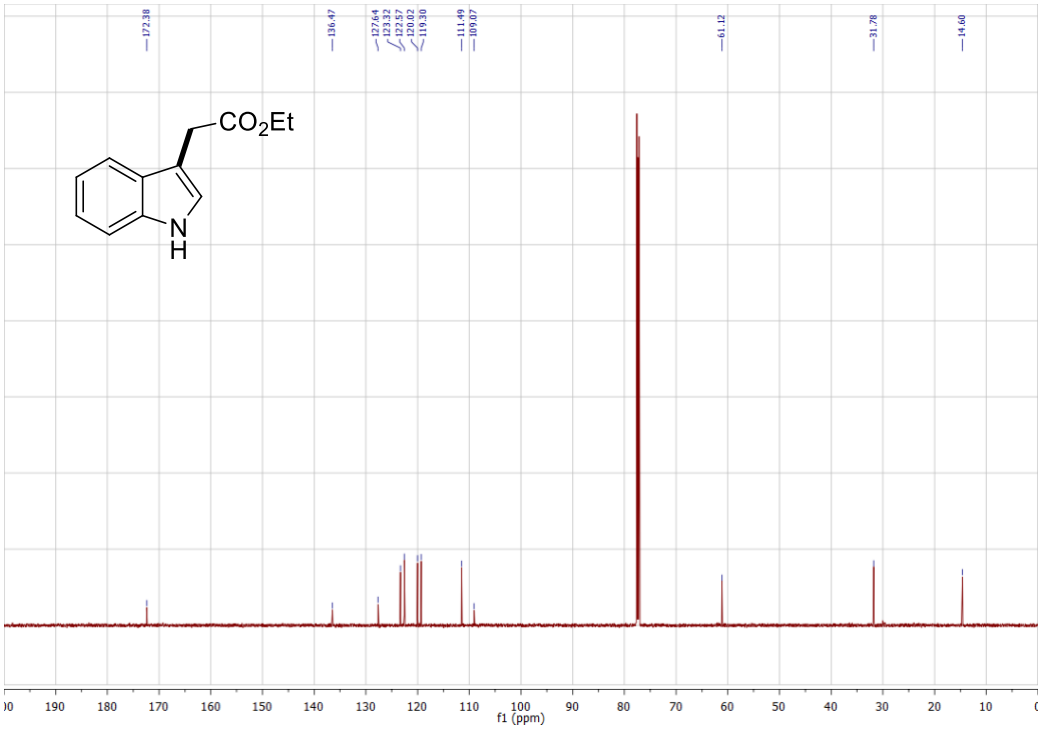


Figure S31. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9a**

Ethyl 2-(4-fluoro-1*H*-indol-3-yl)acetate (9b)

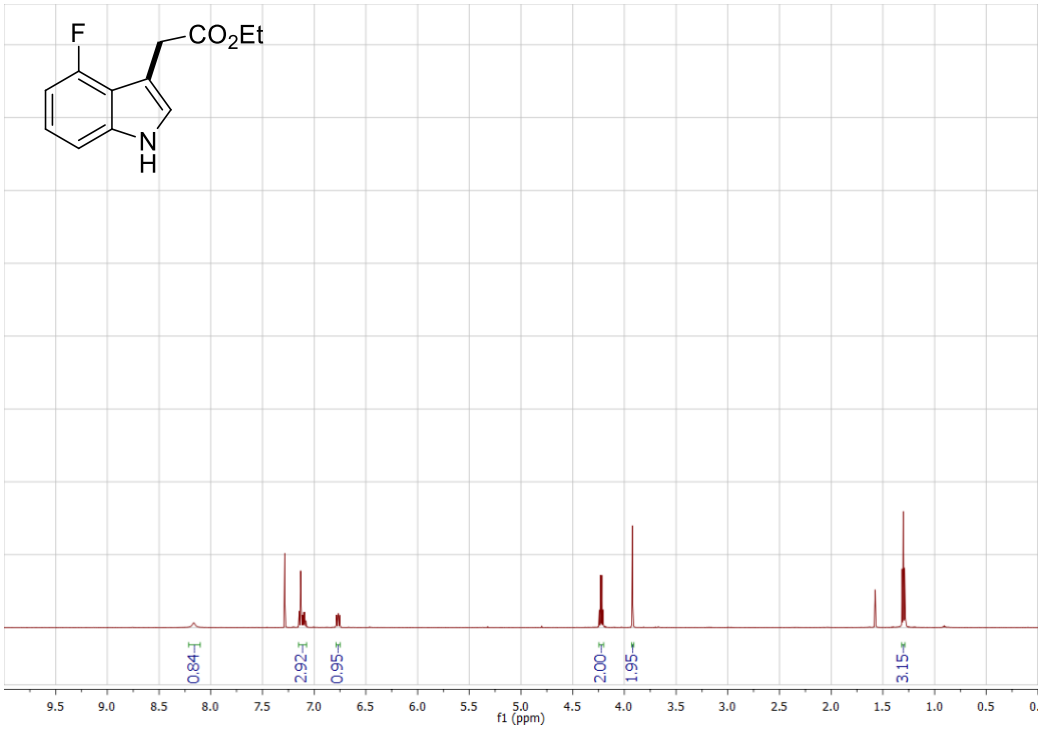


Figure S32. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9b**

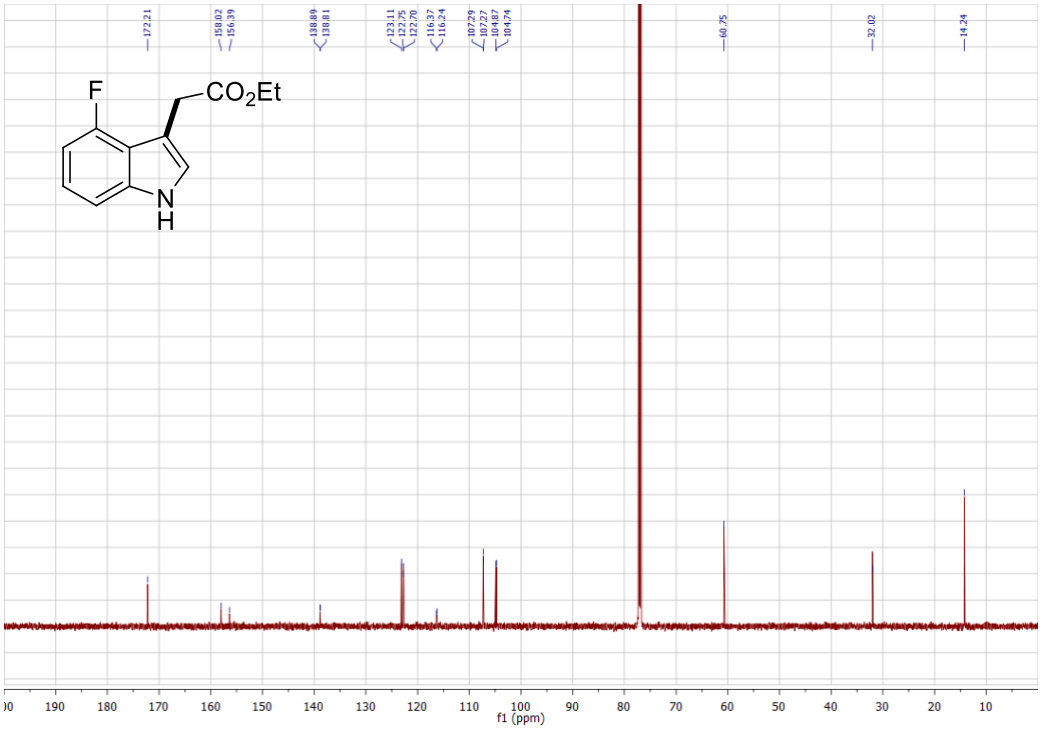


Figure S33. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9b**

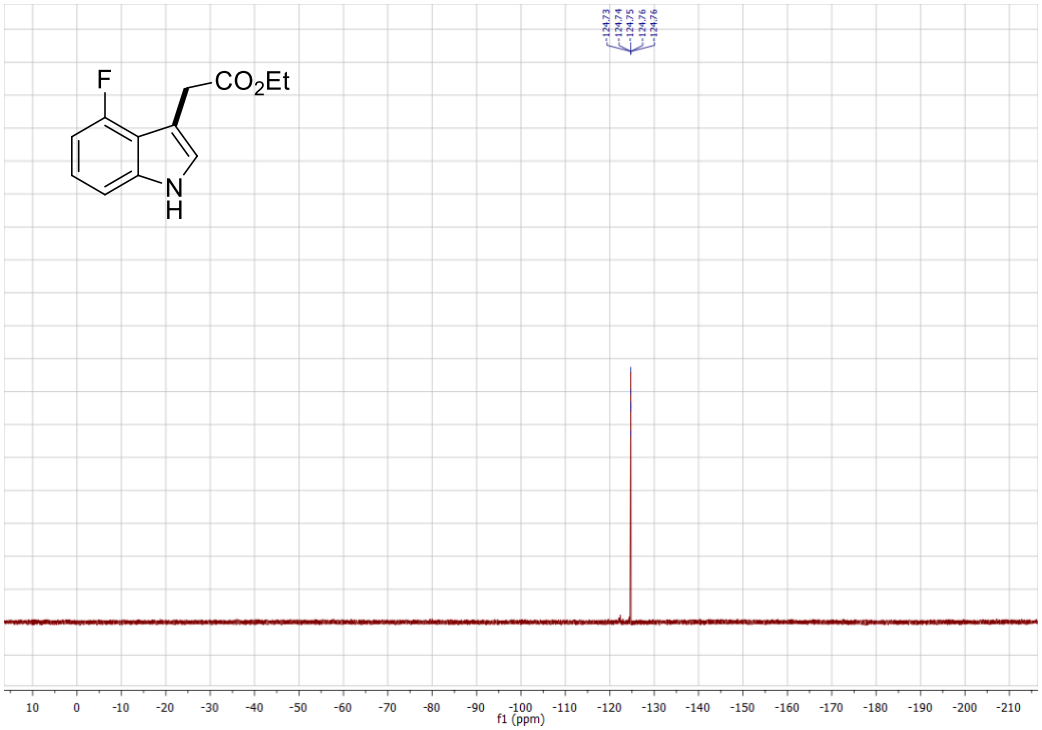


Figure S34. ^{19}F NMR (565 MHz, Chloroform-*d*) of **9b**

Ethyl 2-(4-chloro-1*H*-indol-3-yl)acetate (9c)

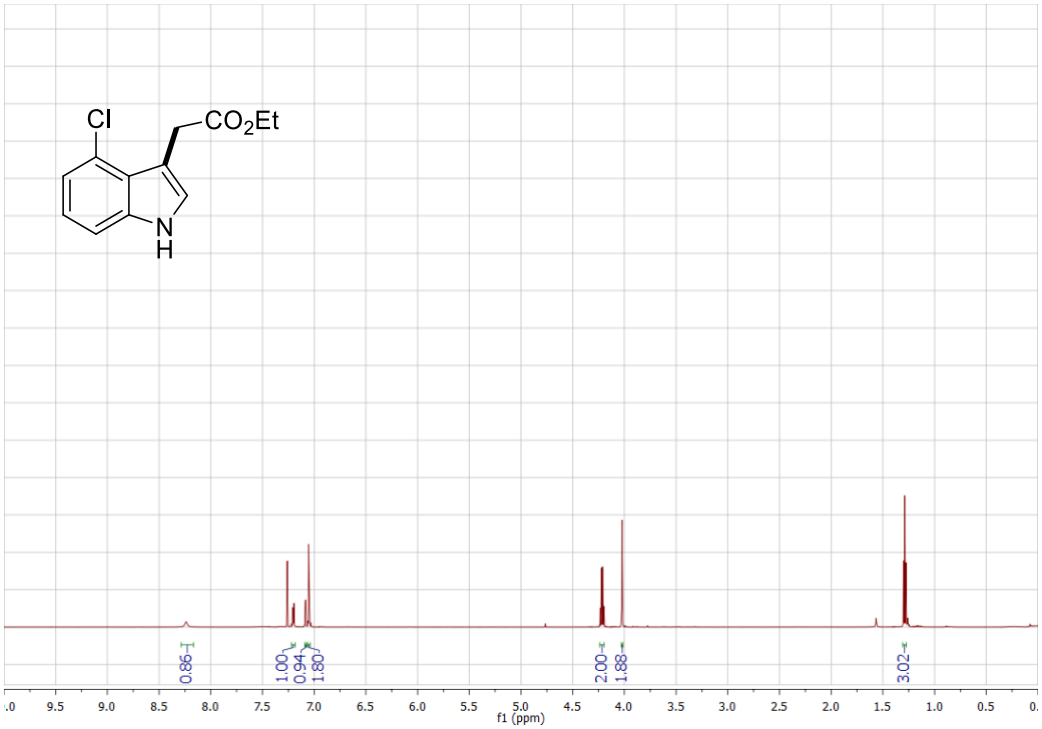


Figure S35. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9c**

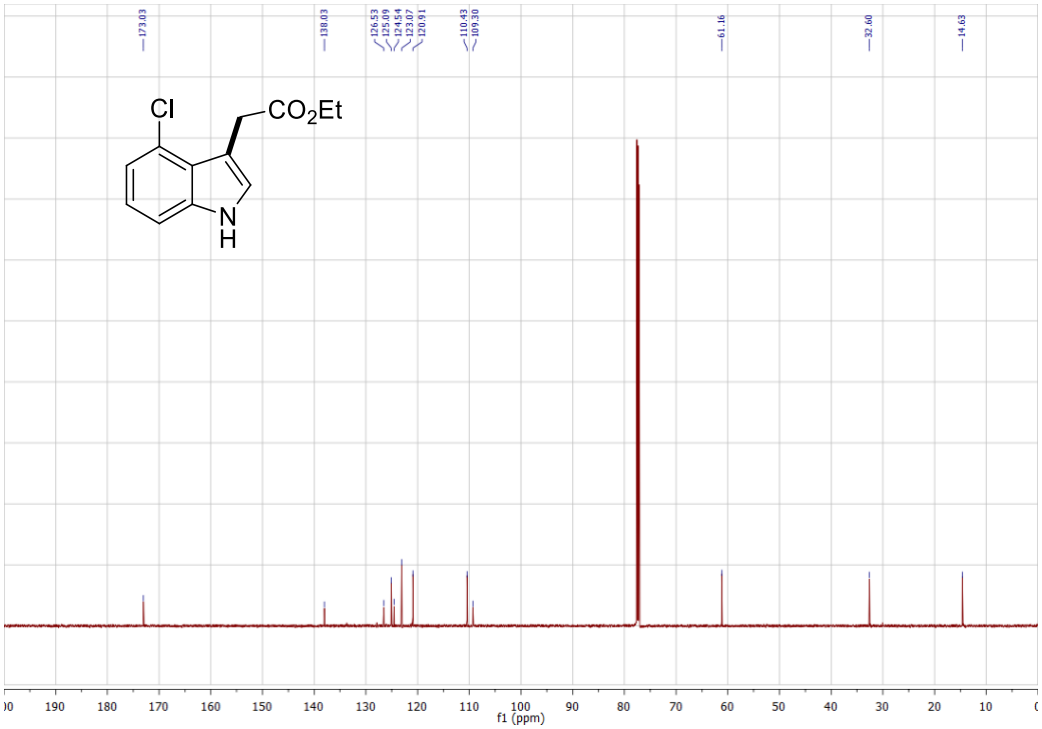


Figure S36. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9c**

Ethyl 2-(4-(benzyloxy)-1*H*-indol-3-yl)acetate (9d)

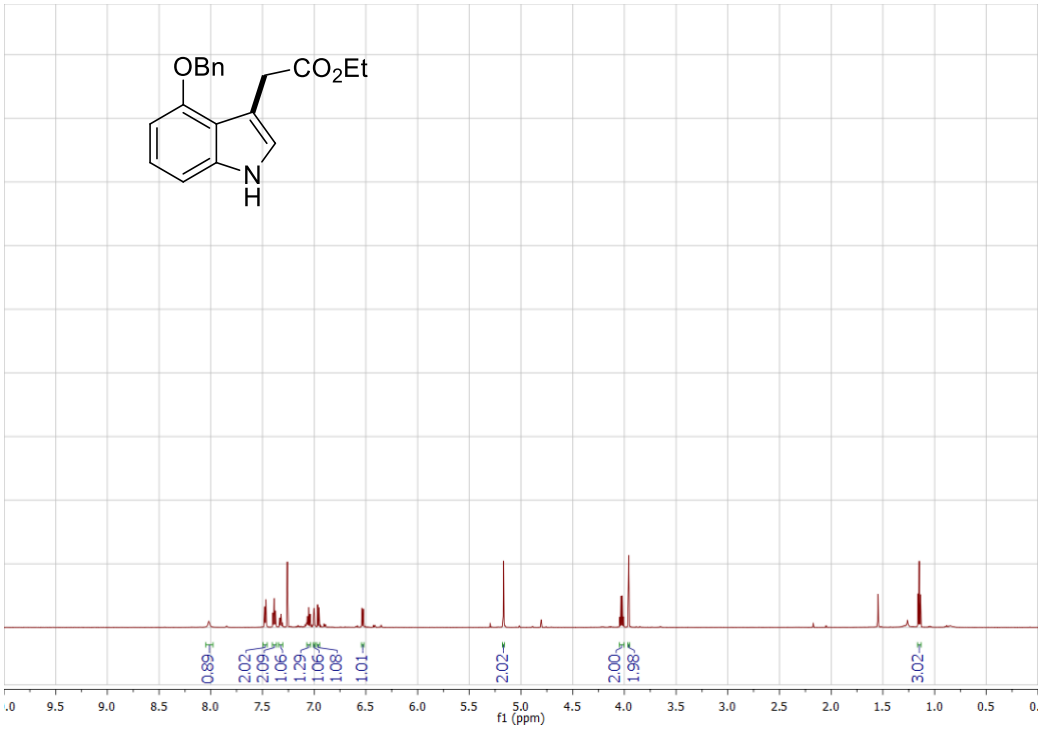


Figure S37. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9d**

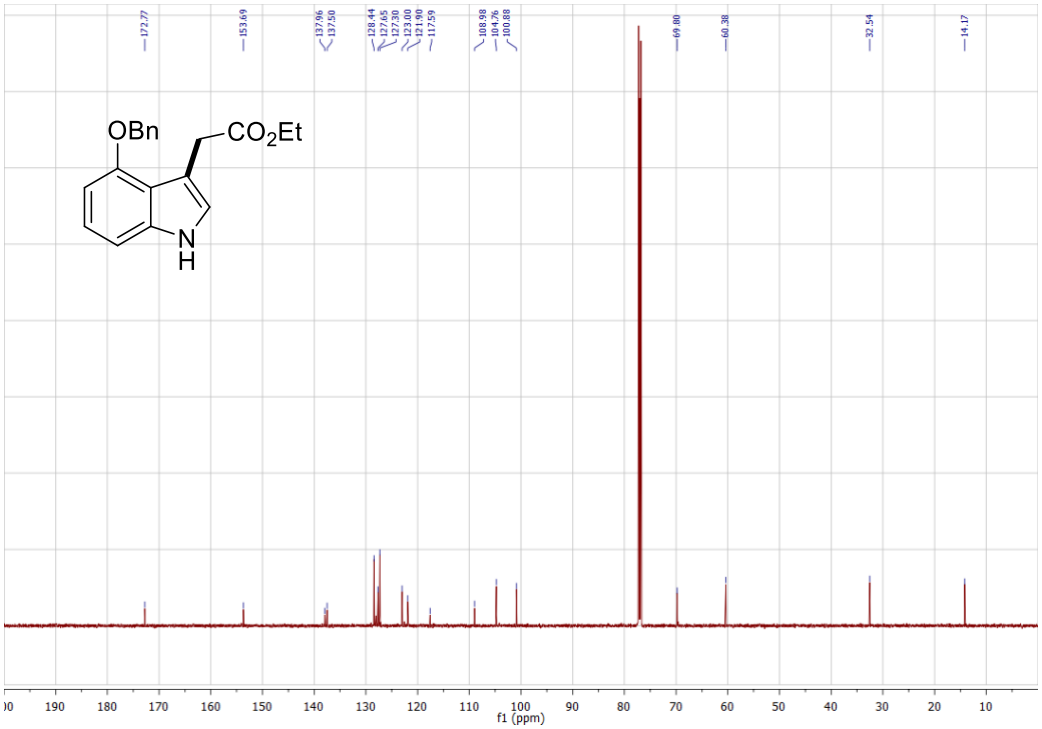


Figure S38. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9d**

Ethyl 2-(4-hydroxy-1*H*-indol-3-yl)acetate (9e)

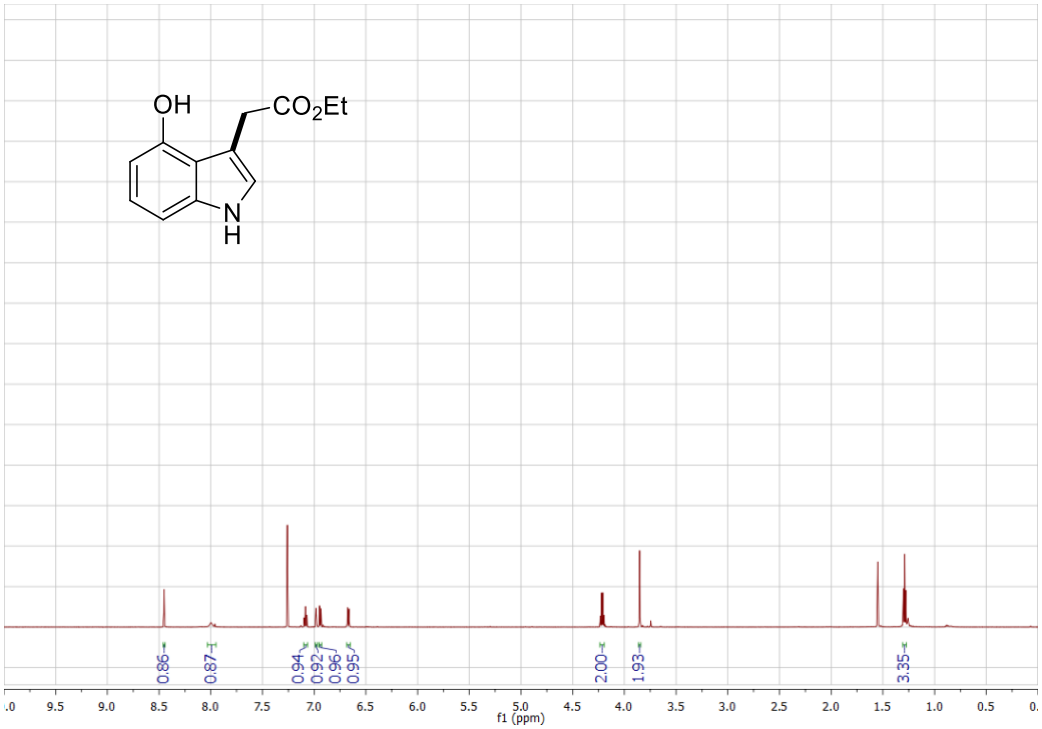


Figure S39. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9e**

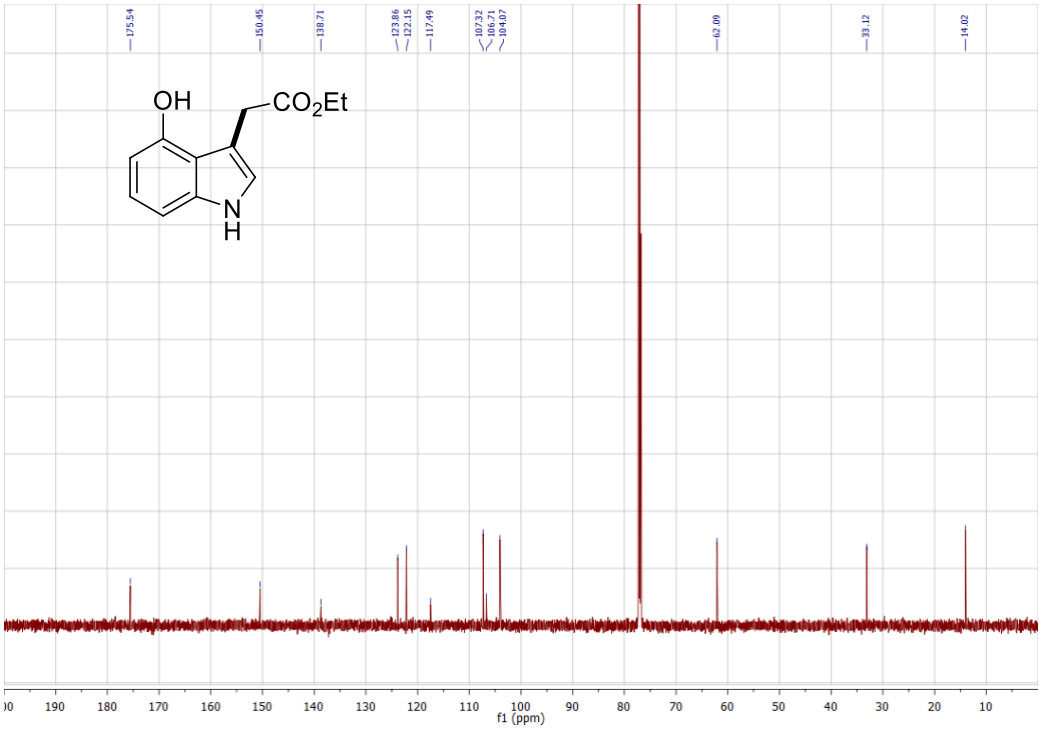


Figure S40. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9e**

Ethyl 2-(5-fluoro-1*H*-indol-3-yl)acetate (9f)

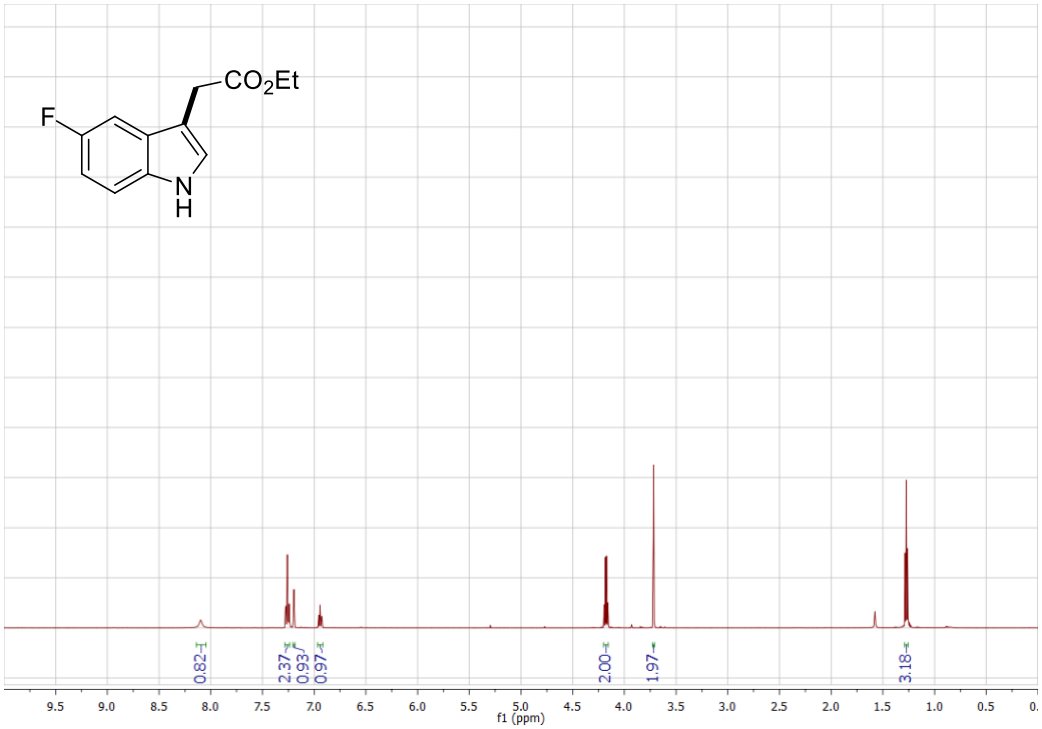


Figure S41. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9f**

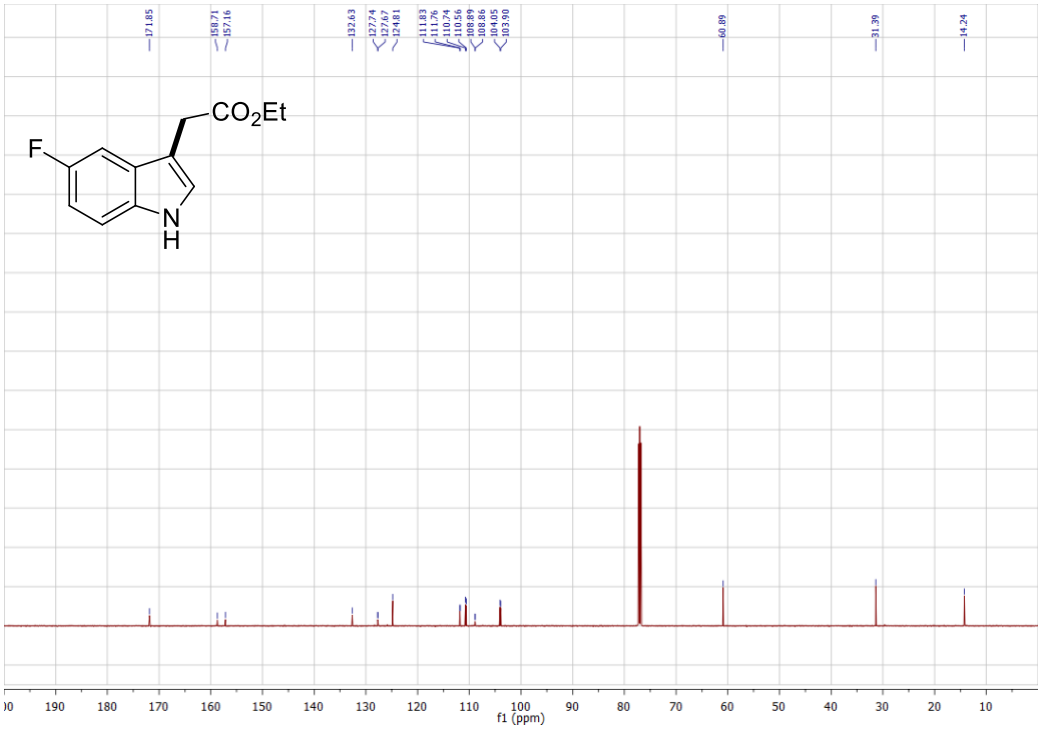


Figure S42. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9f**

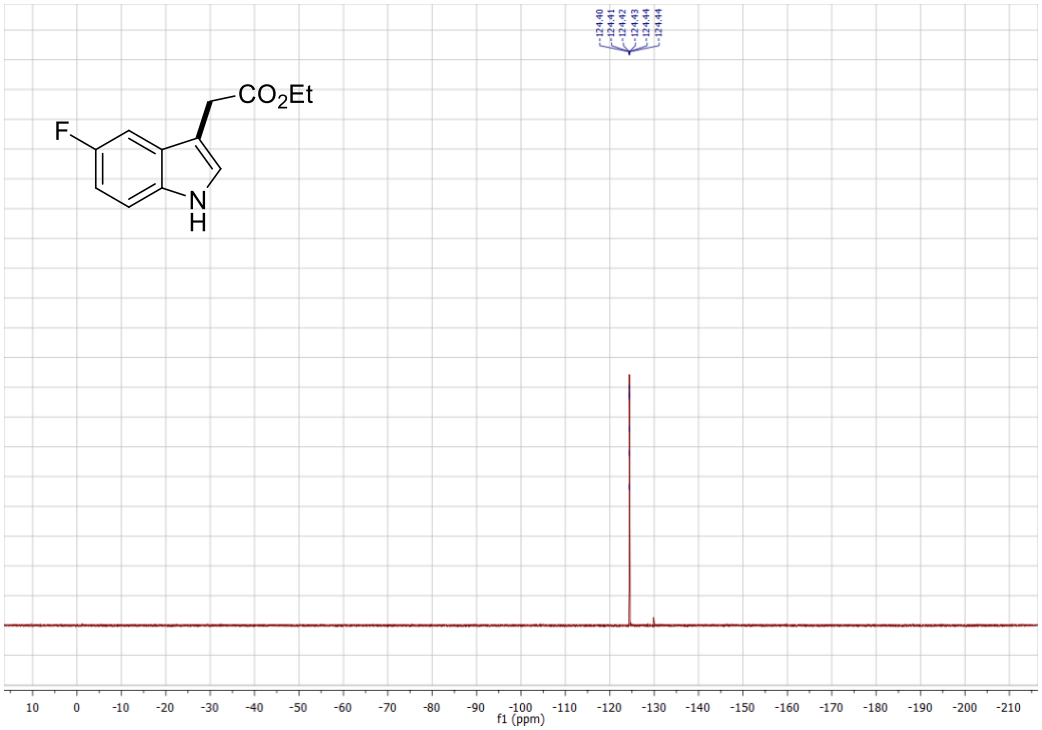


Figure S43. ^{19}F NMR (565 MHz, Chloroform-*d*) of **9f**

Ethyl 2-(5-methoxy-1*H*-indol-3-yl)acetate (9g)

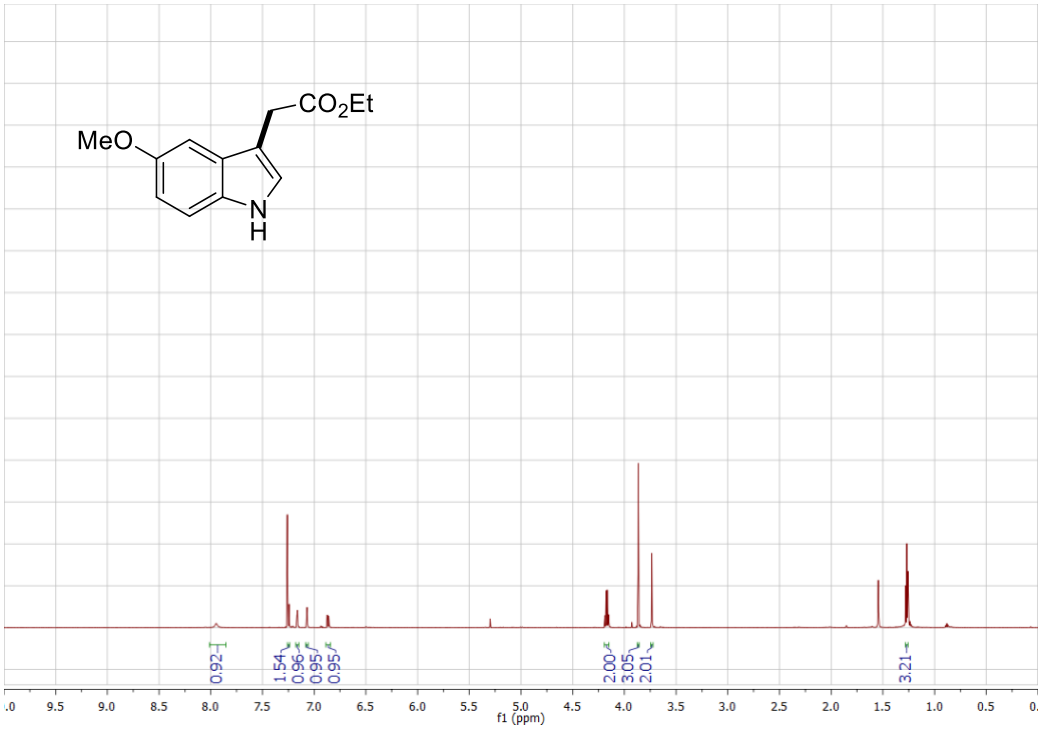


Figure S44. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9g**

Figure S45. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9g**

Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-5-carboxylate (9h)

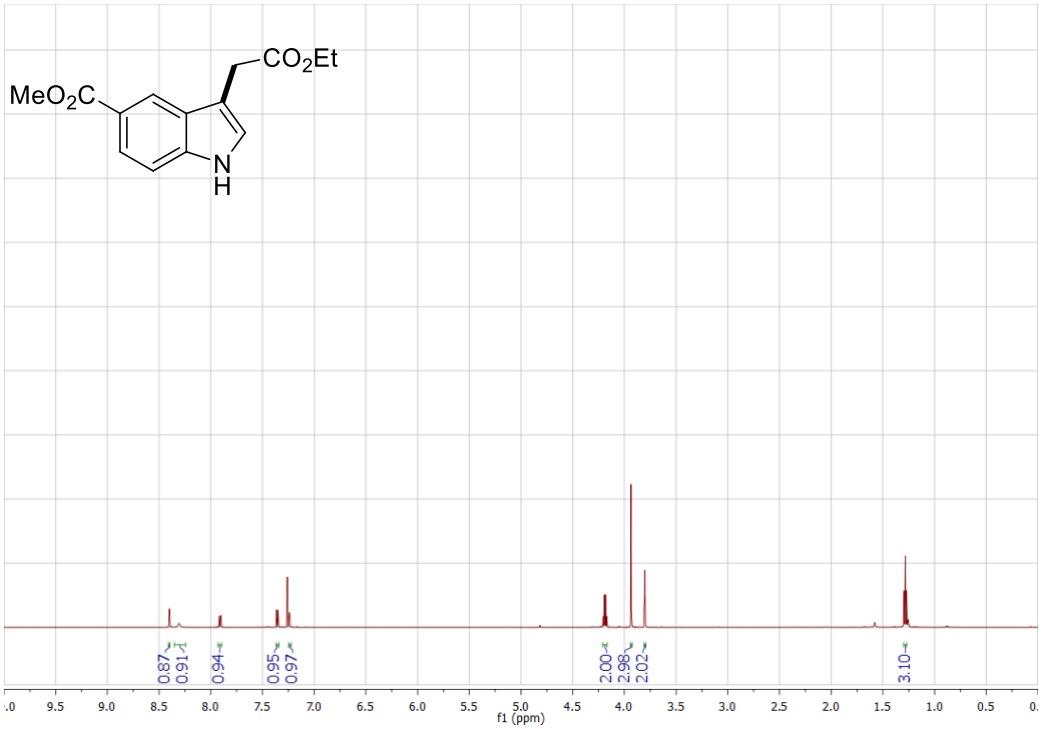


Figure S46. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9h**

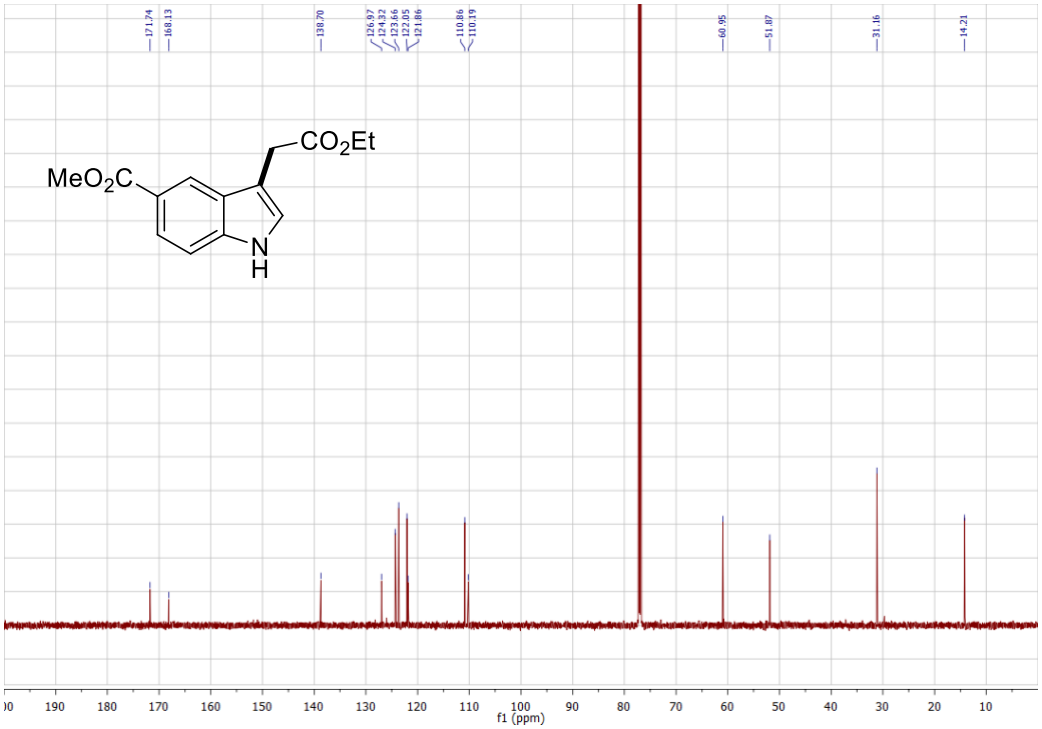


Figure S47. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9h**

Ethyl 2-(6-methoxy-1*H*-indol-3-yl)acetate (9i)

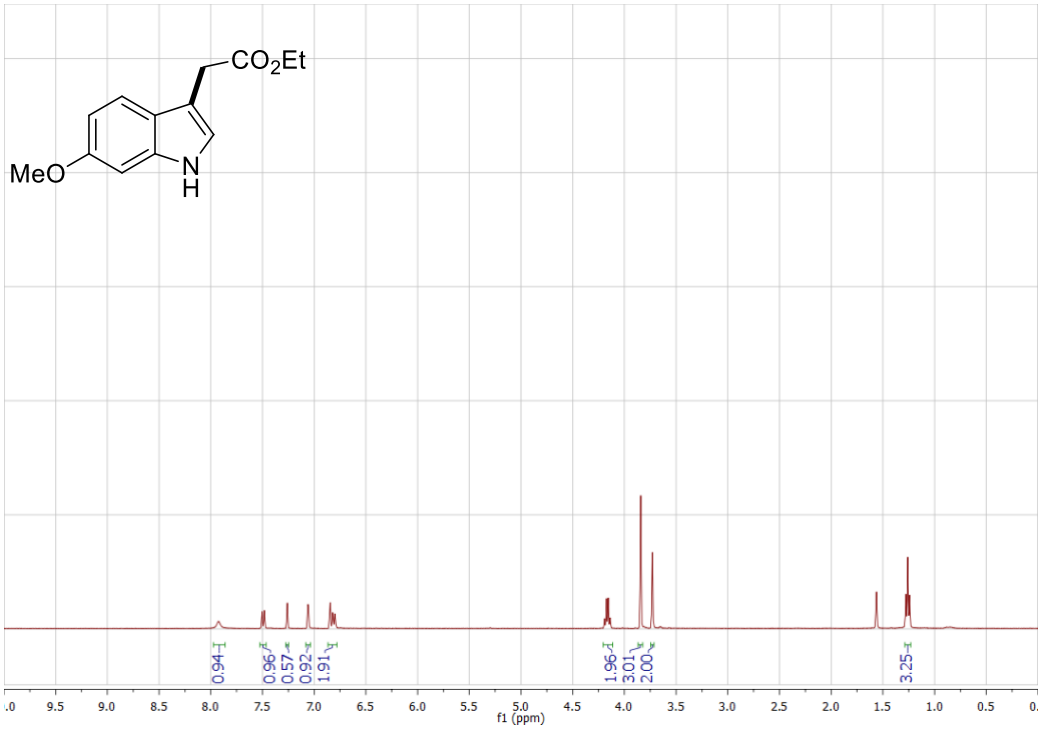


Figure S48. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9i**

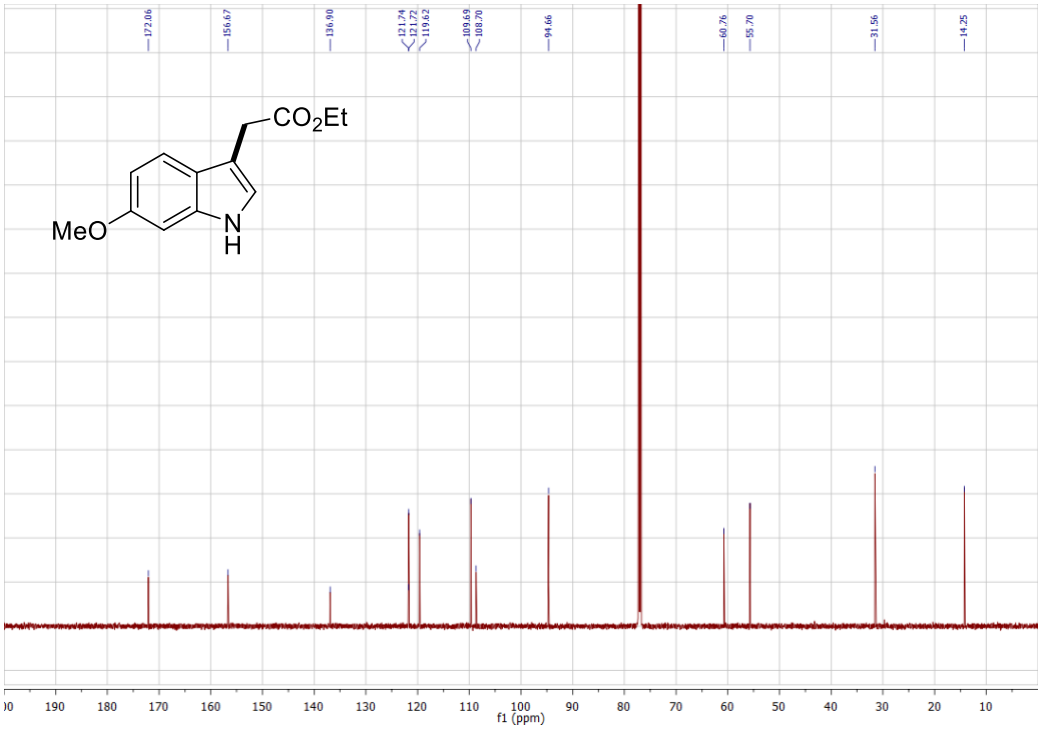


Figure S49. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9i**

Methyl 3-(2-ethoxy-2-oxoethyl)-1*H*-indole-6-carboxylate (9j)

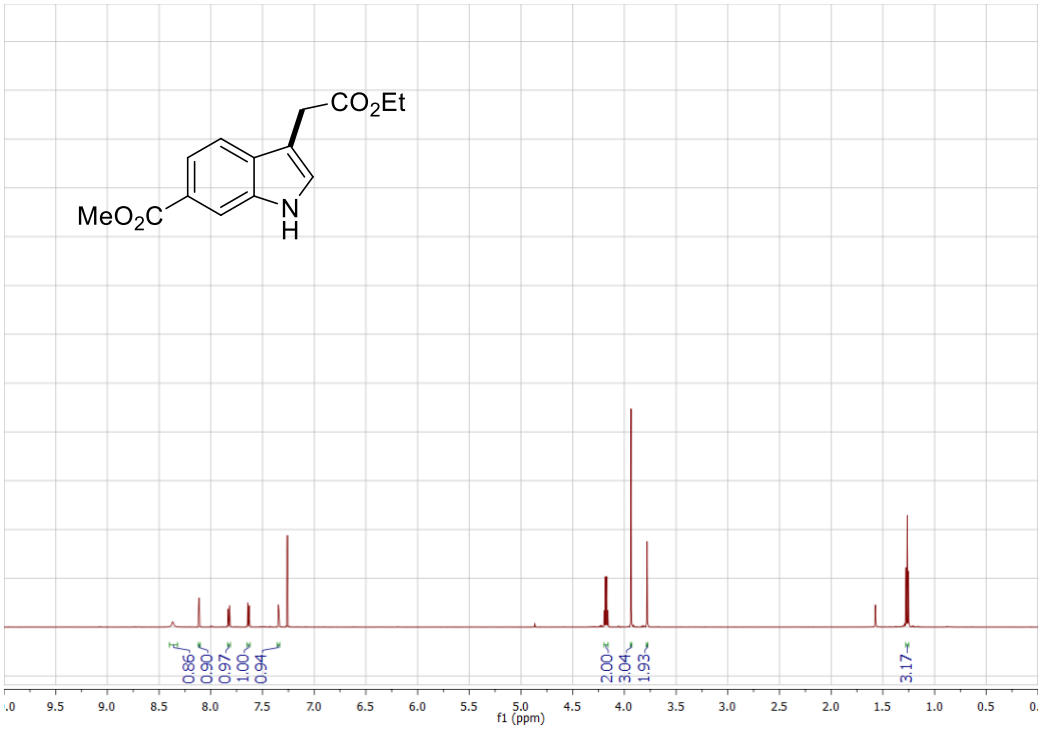


Figure S50. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9j**

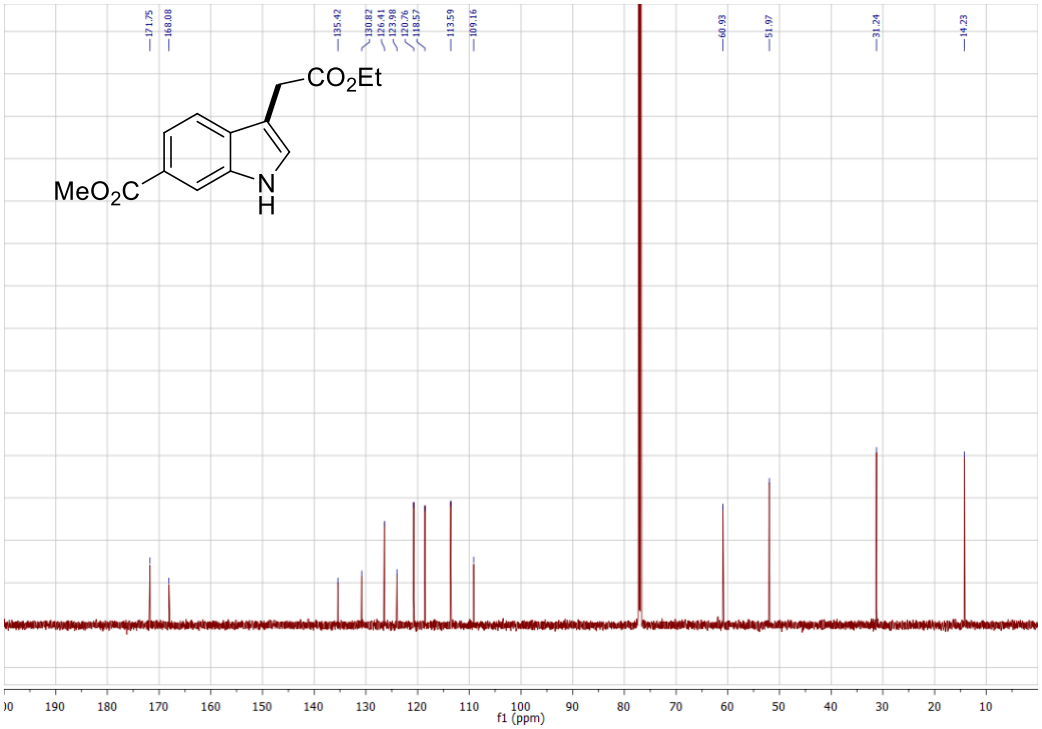


Figure S51. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9j**

Ethyl 2-(7-(benzyloxy)-1*H*-indol-3-yl)acetate (9k)

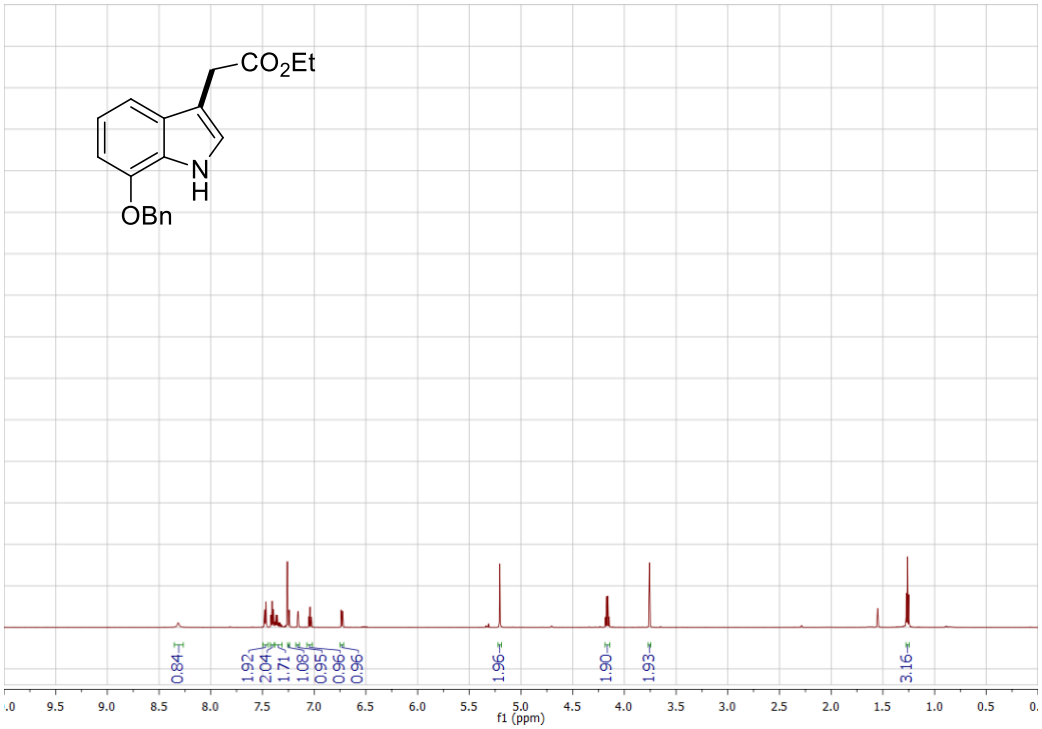


Figure S52. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9k**

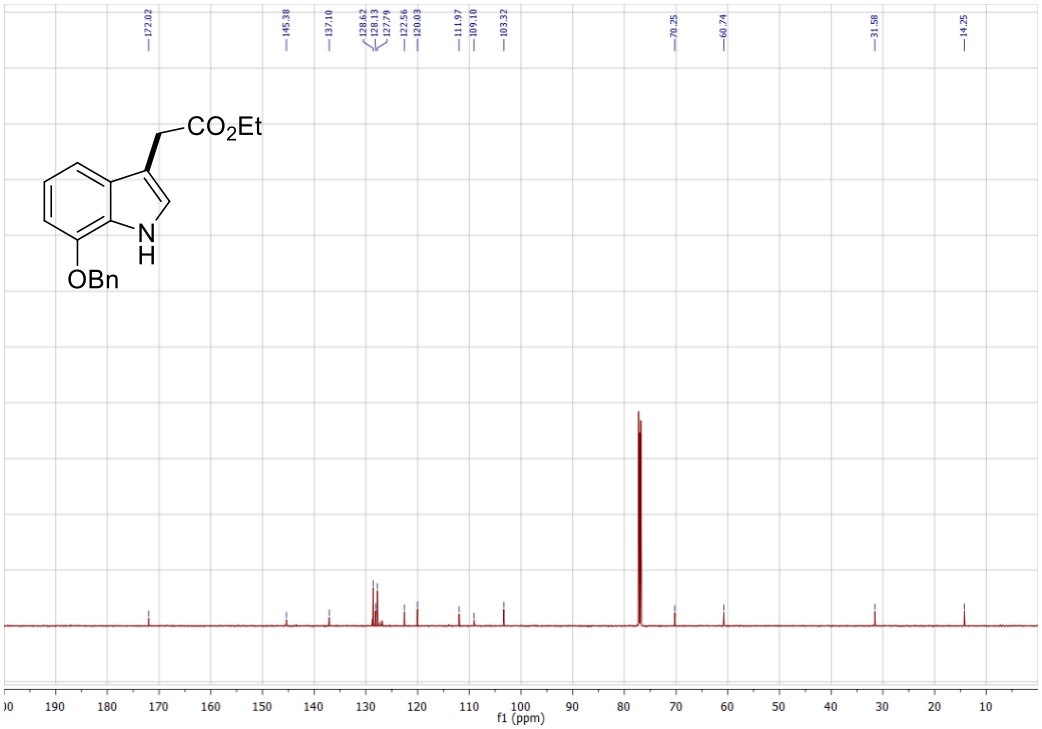


Figure S53. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9k**

Ethyl 2-(2-methyl-1*H*-indol-3-yl)acetate (9l)

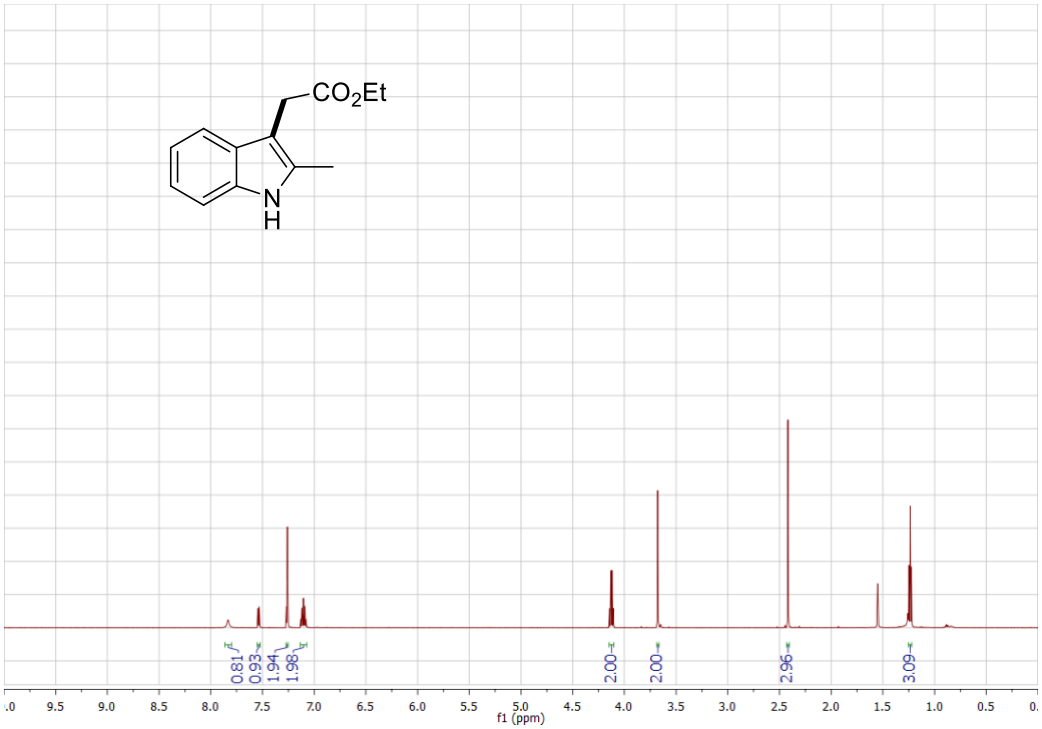


Figure S54. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9l**

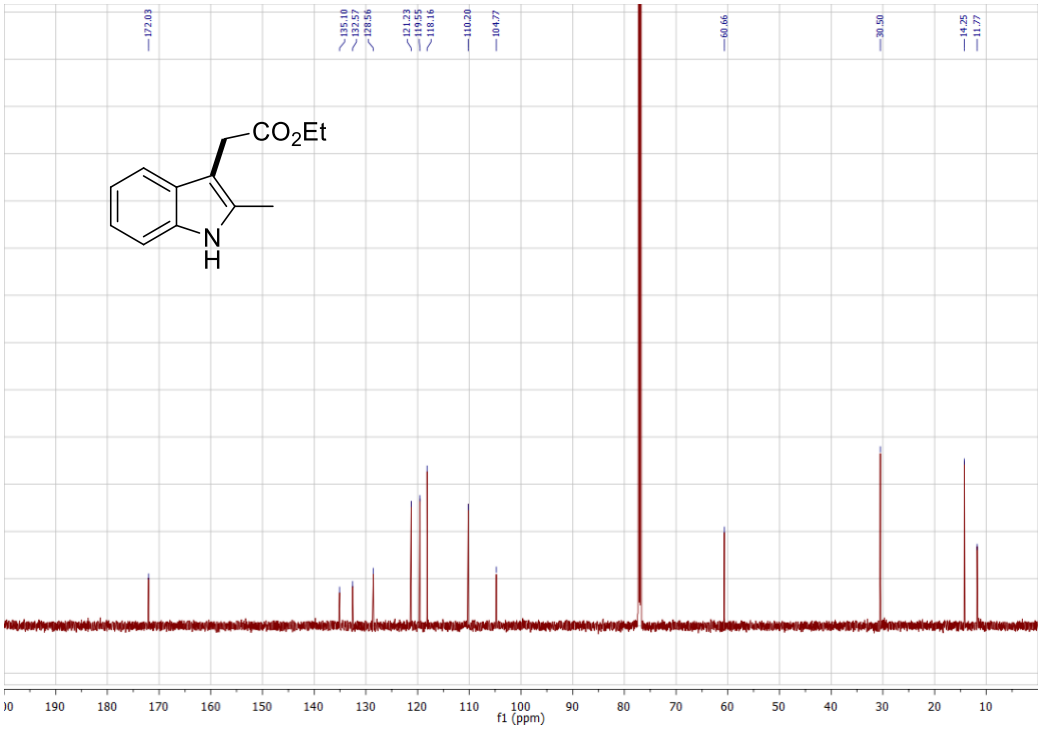


Figure S55. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9l**

Ethyl 2-(5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (9m)

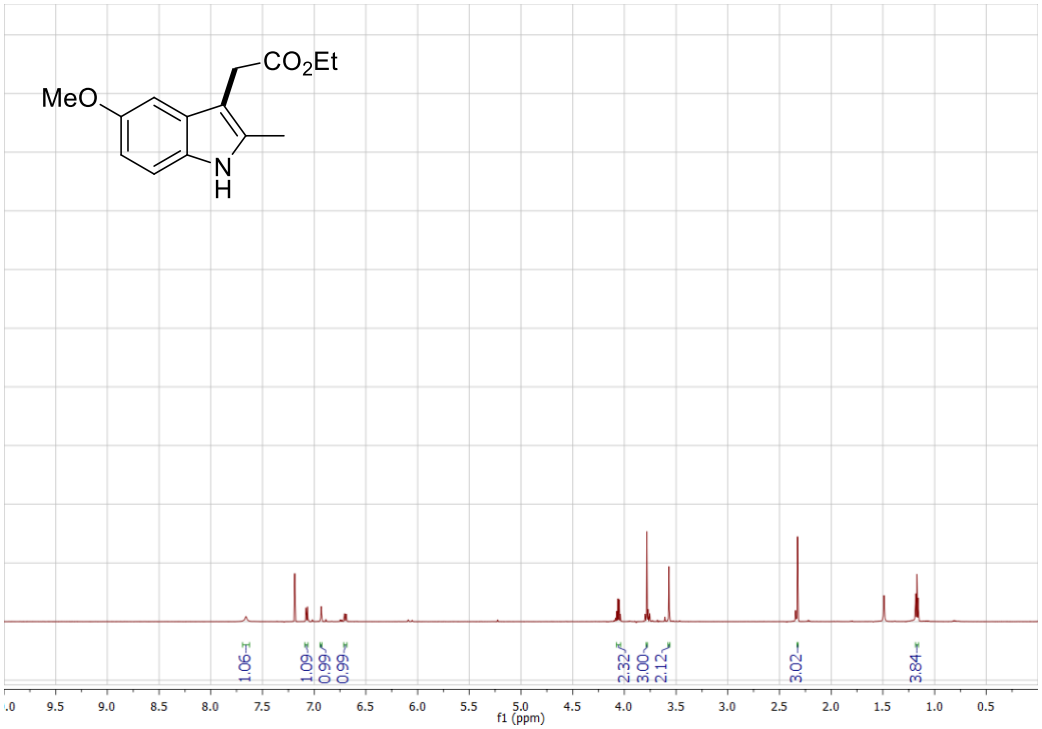


Figure S56. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9m**

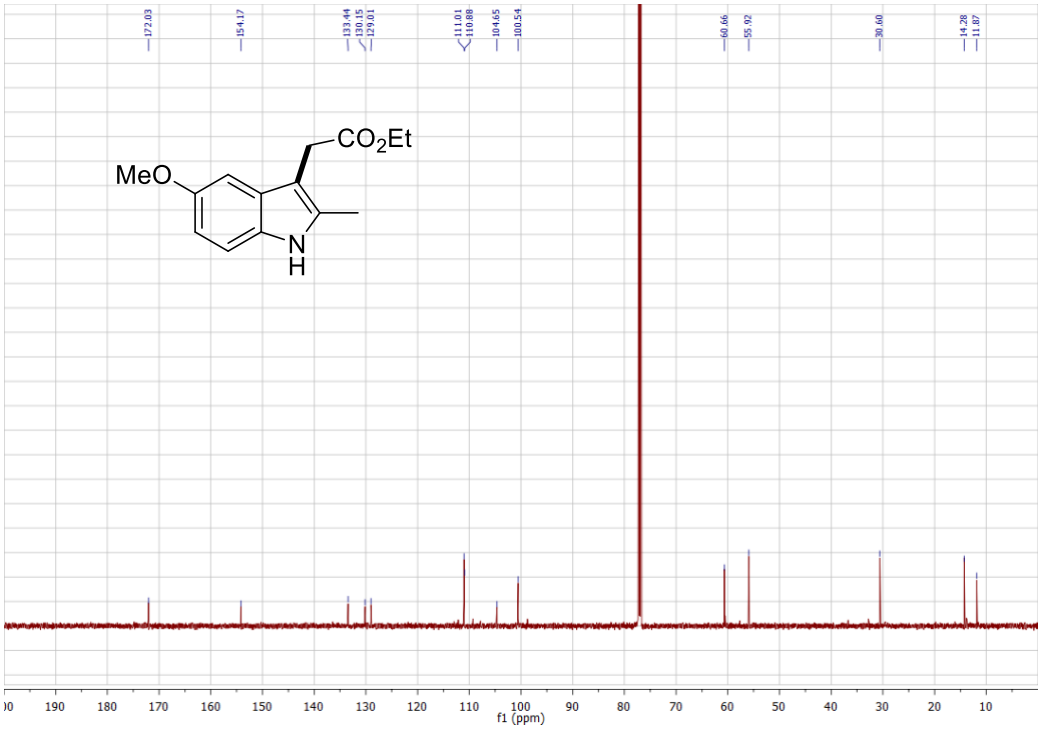


Figure S57. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9m**

Ethyl 2-(5-chloro-2-methyl-1*H*-indol-3-yl)acetate (9n)

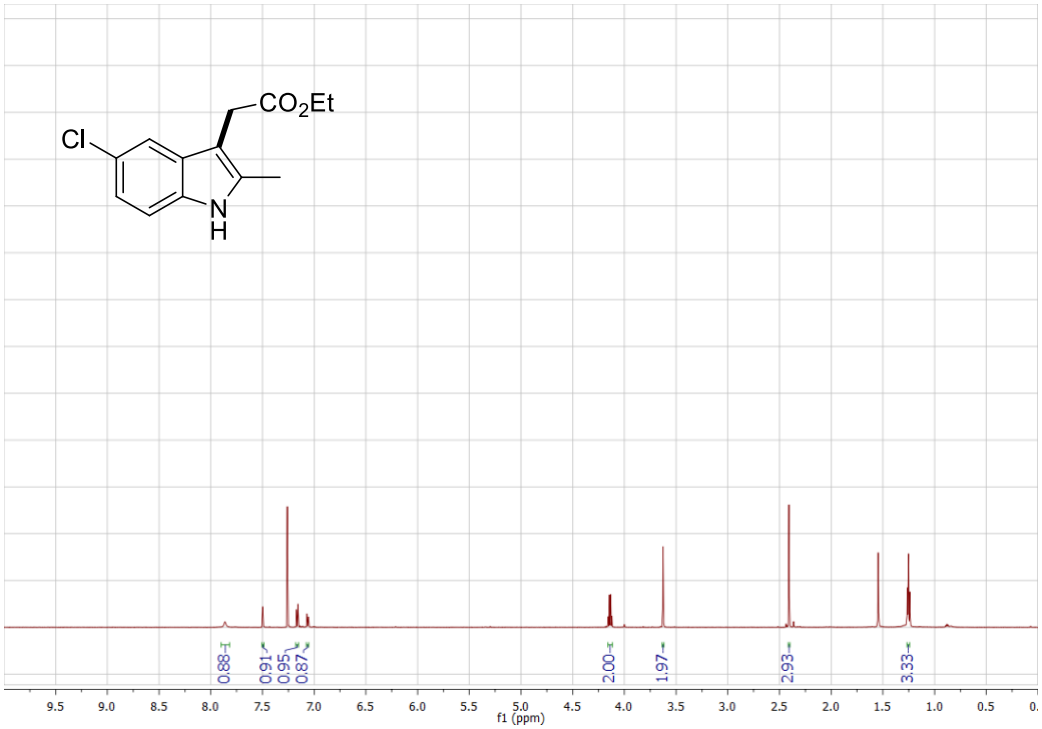


Figure S58. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9n**

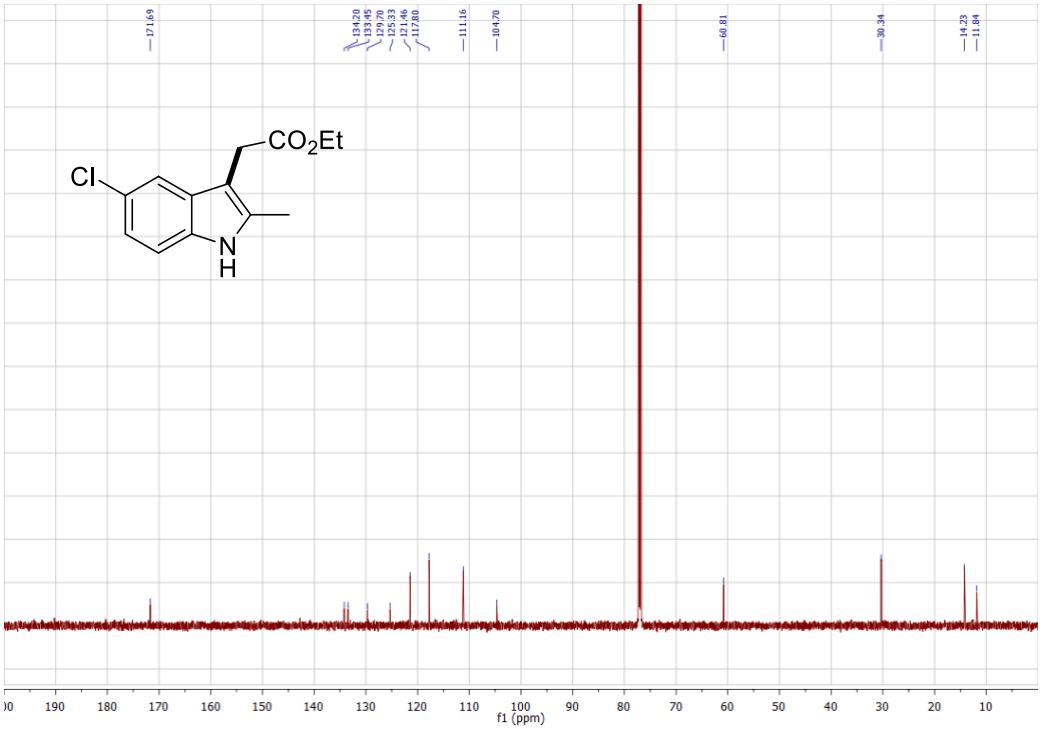


Figure S59. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9n**

Ethyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (9o)

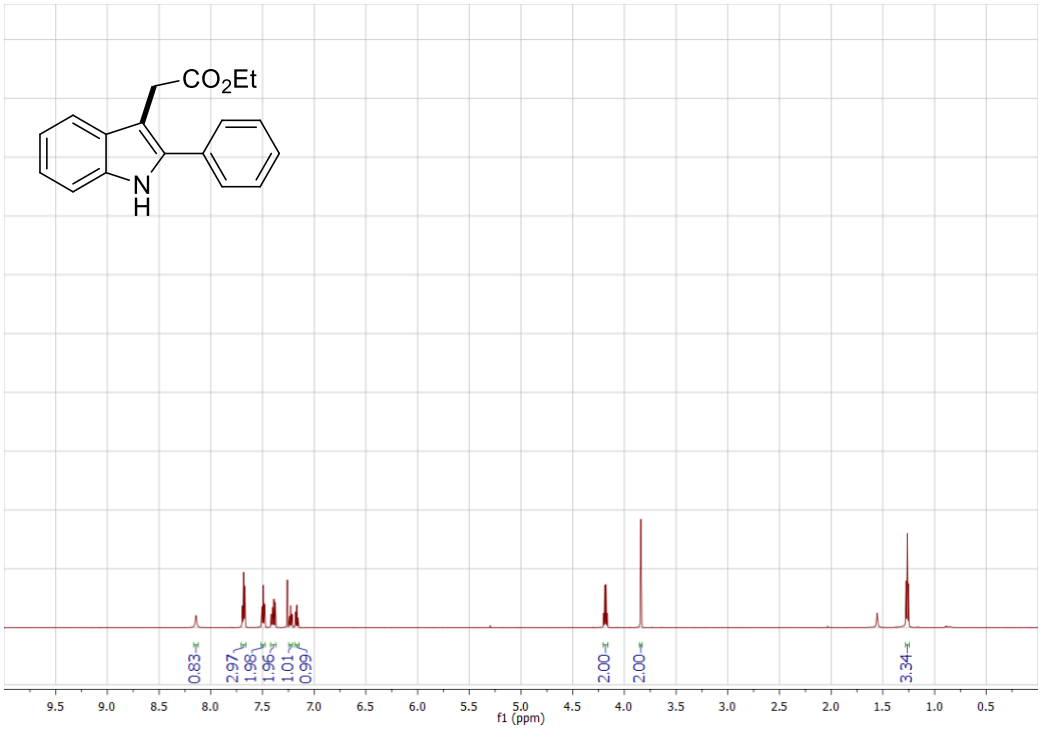


Figure S60. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9o**

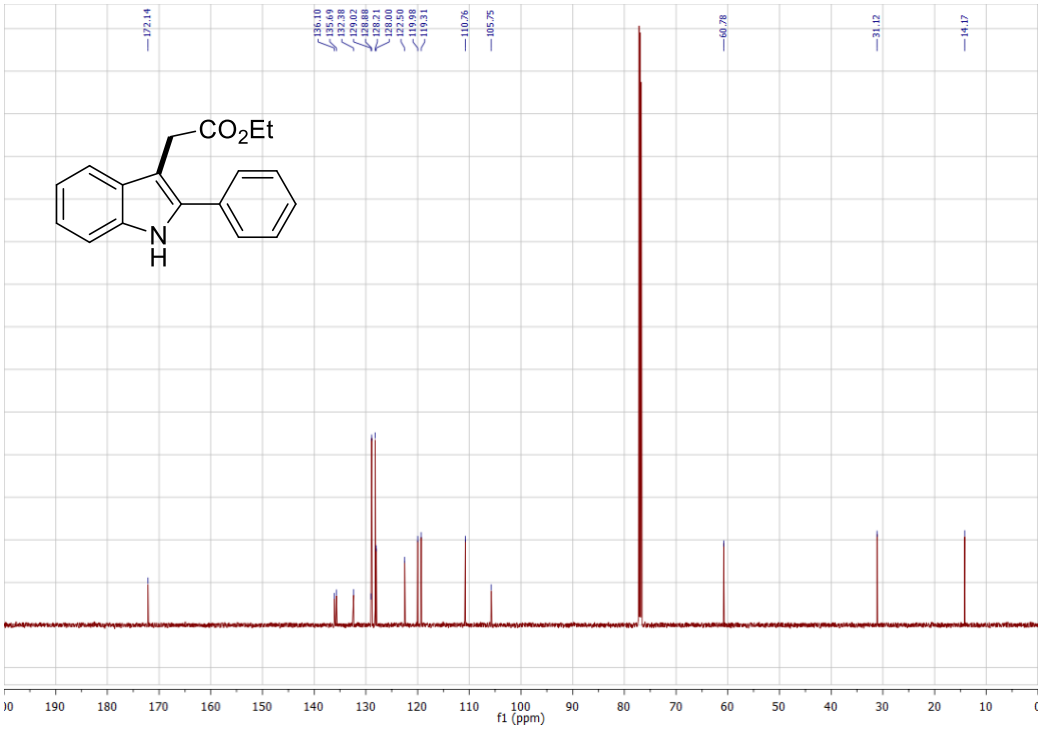


Figure S61. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9o**

Ethyl 2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)acetate (9p)

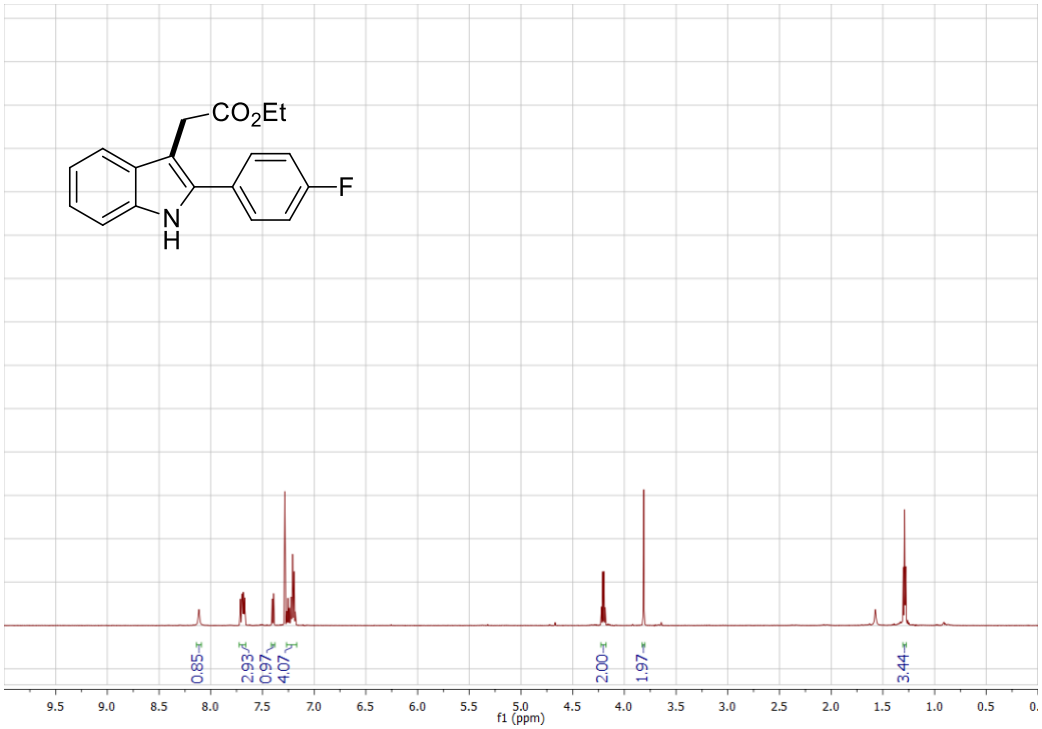


Figure S62. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9p**

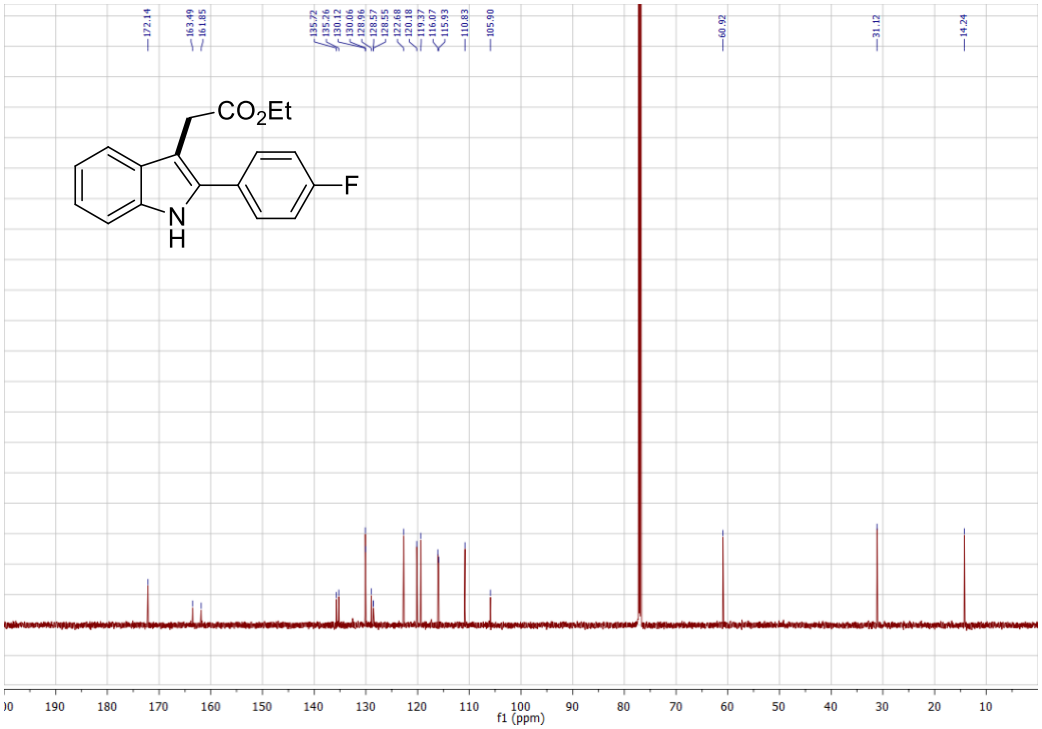


Figure S63. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9p**

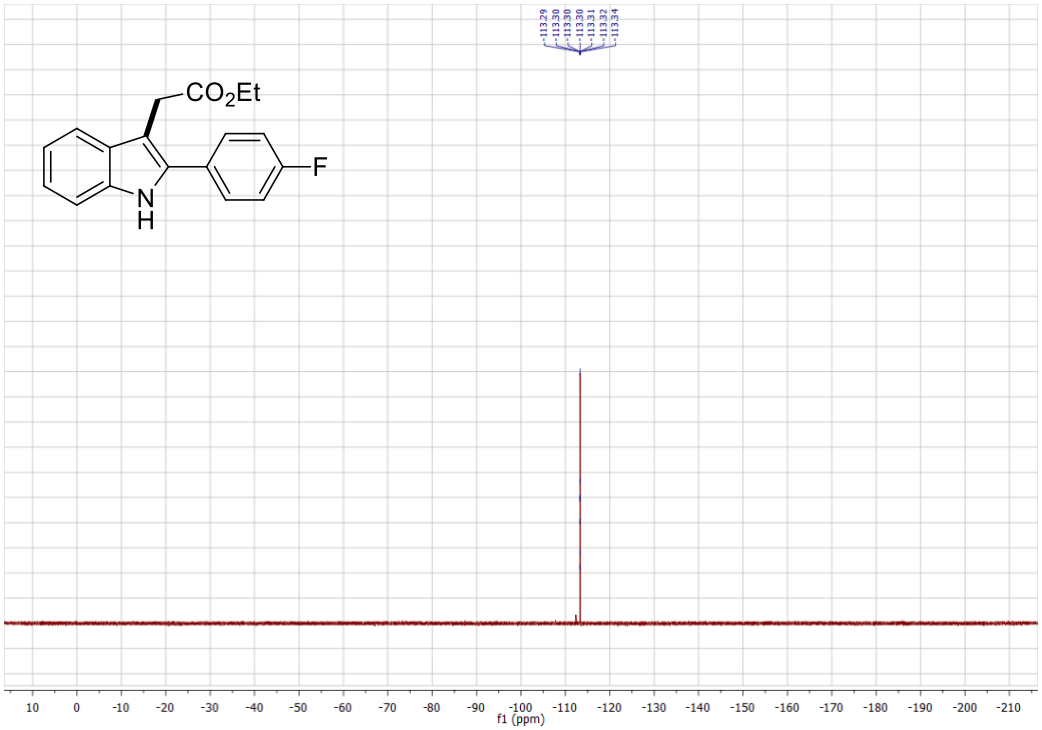


Figure S64. ^{19}F NMR (565 MHz, Chloroform-*d*) of **9p**

Neopentyl 2-(1*H*-indol-3-yl)acetate (9q)

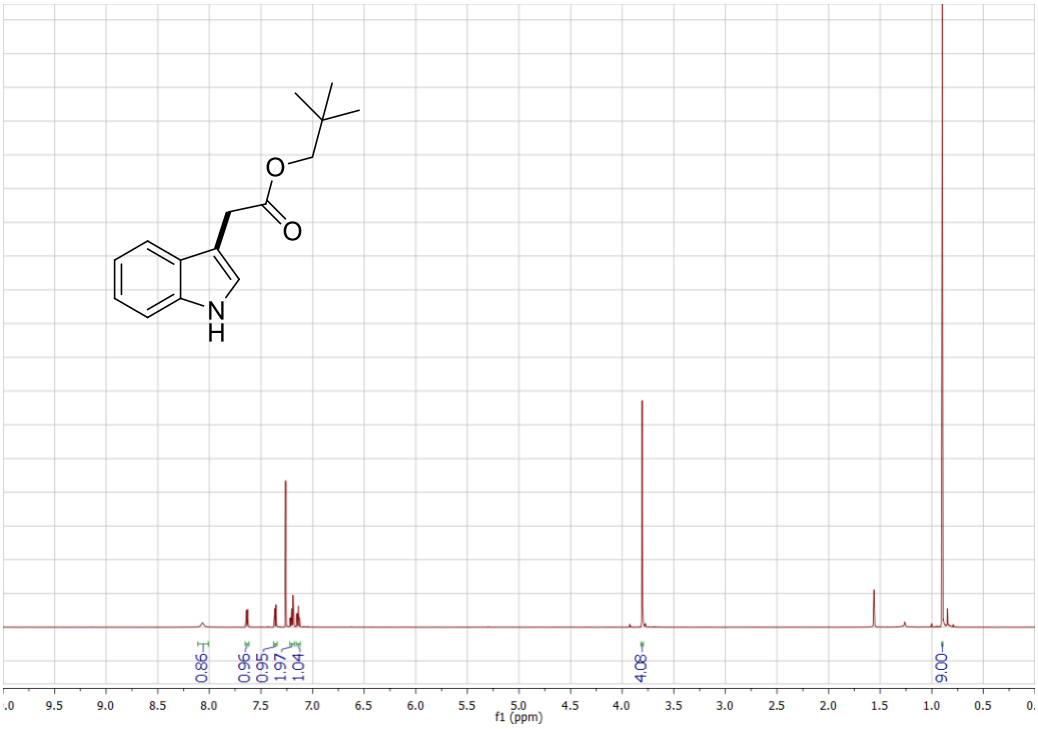


Figure S65. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9q**

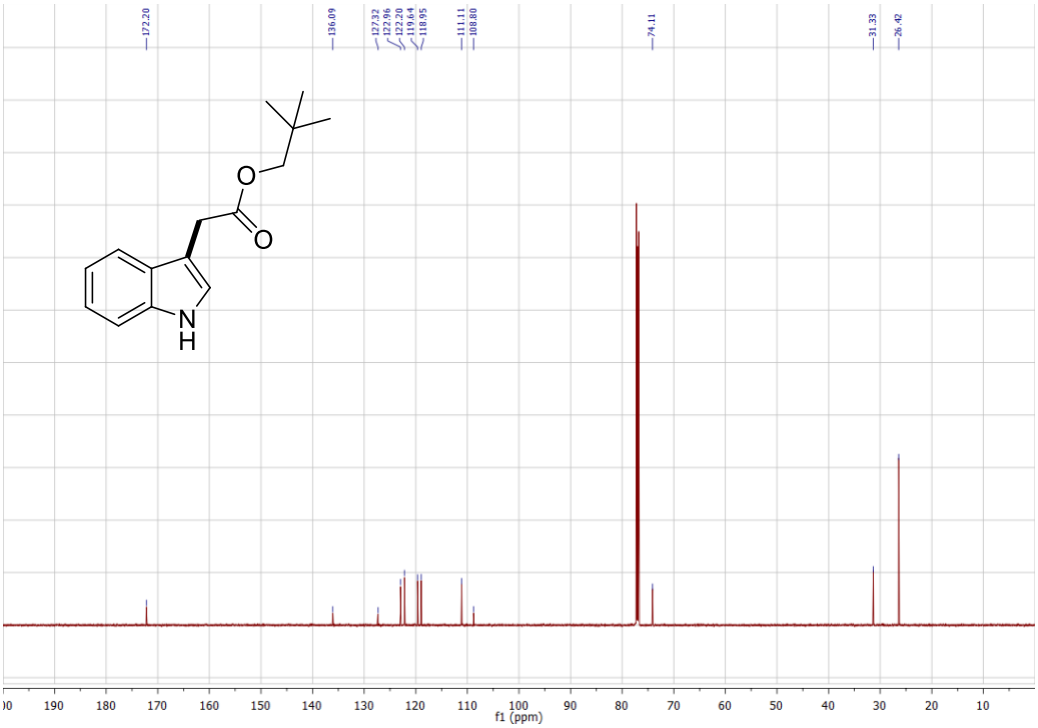


Figure S66. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9q**

Benzyl 2-(1*H*-indol-3-yl)acetate (9r)

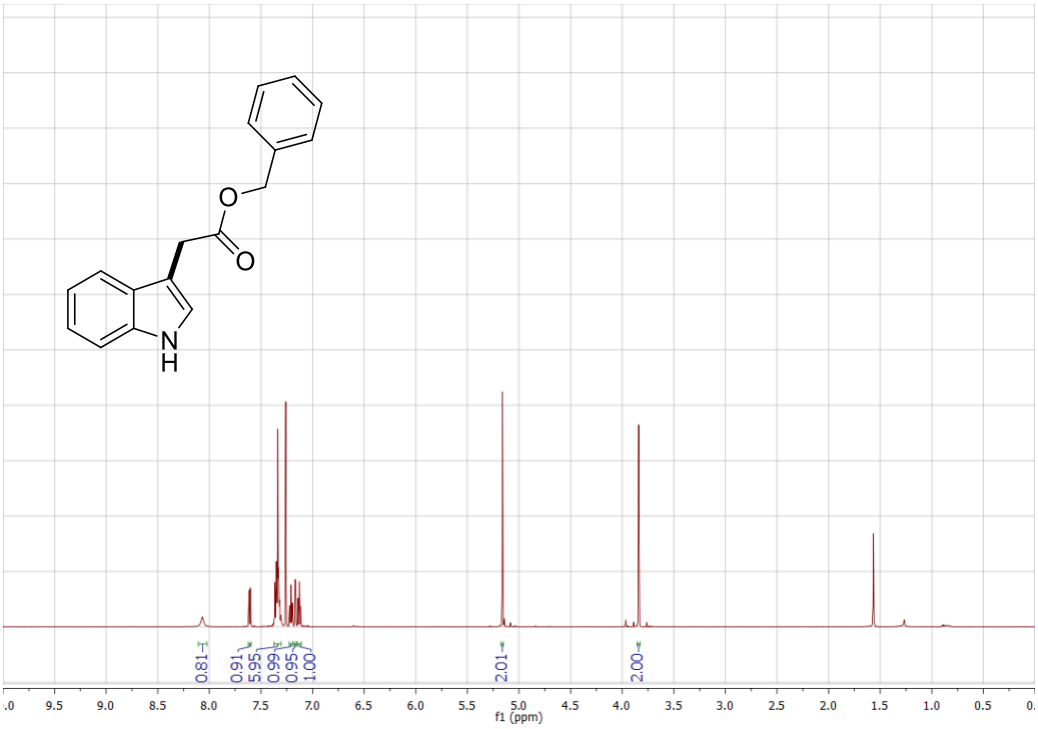


Figure S67. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9r**

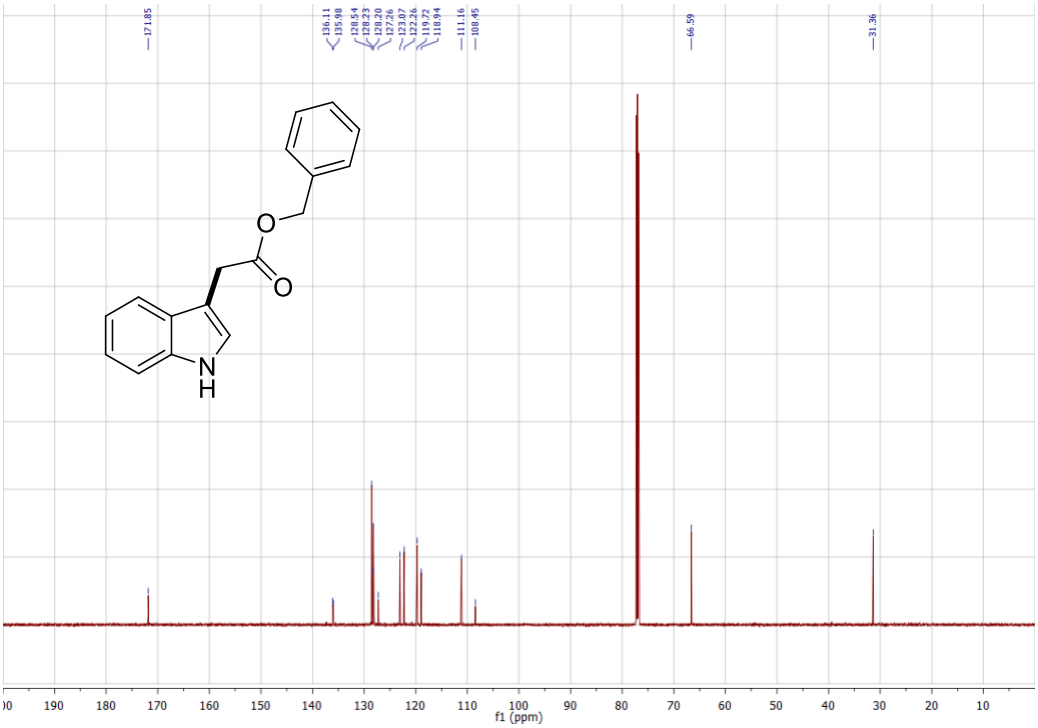


Figure S68. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9r**

4-Phenylbutyl 2-(1*H*-indol-3-yl)acetate (9s)

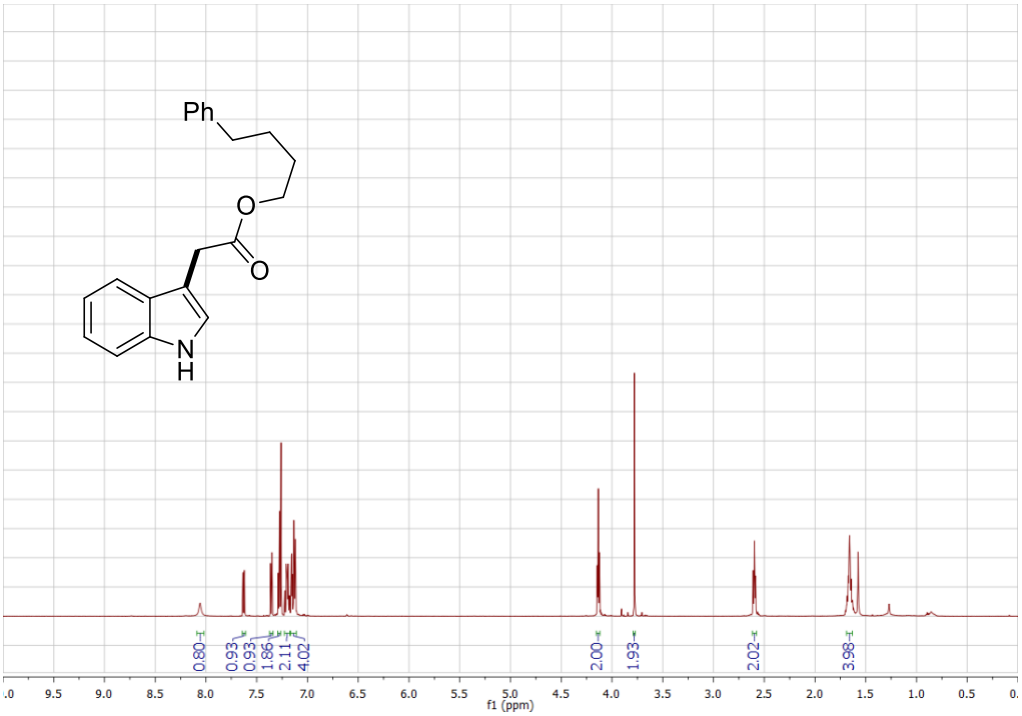


Figure S69. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9s**

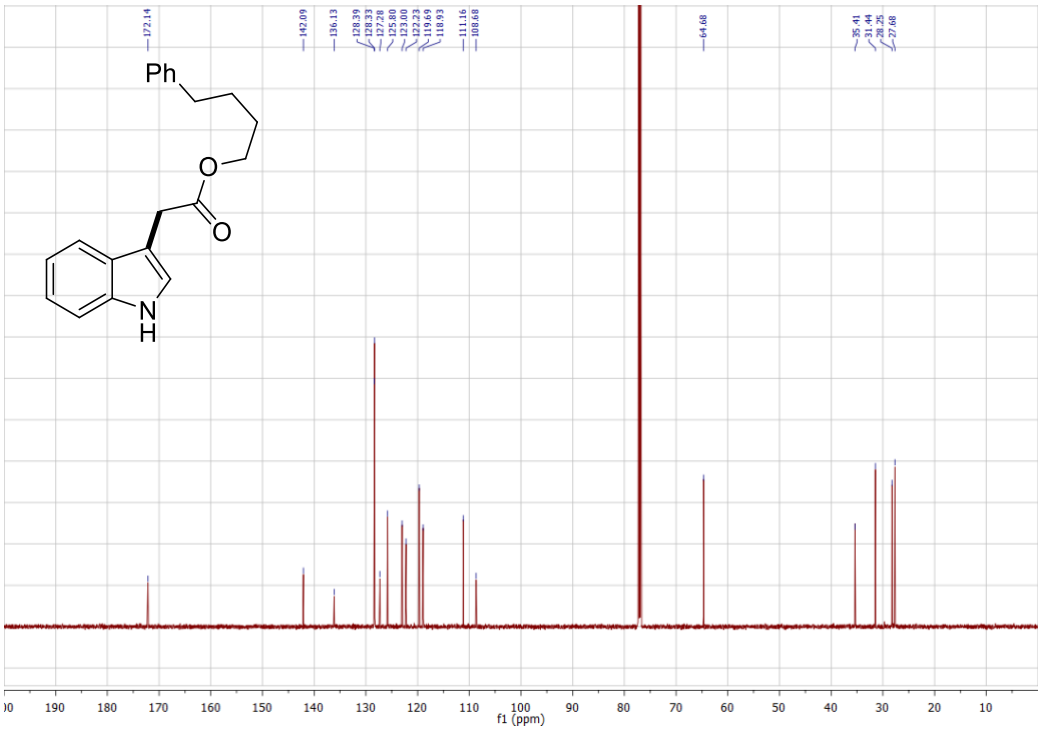


Figure S70. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9s**

5-Phenylpentyl 2-(1*H*-indol-3-yl)acetate (9t)

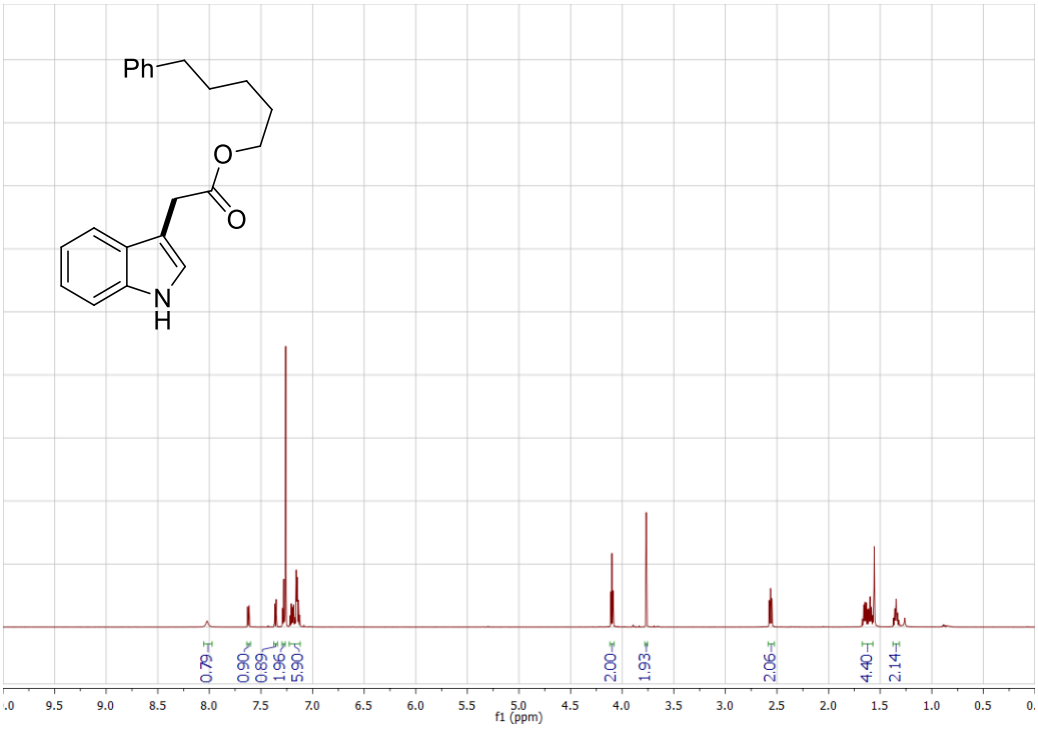


Figure S71. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9t**

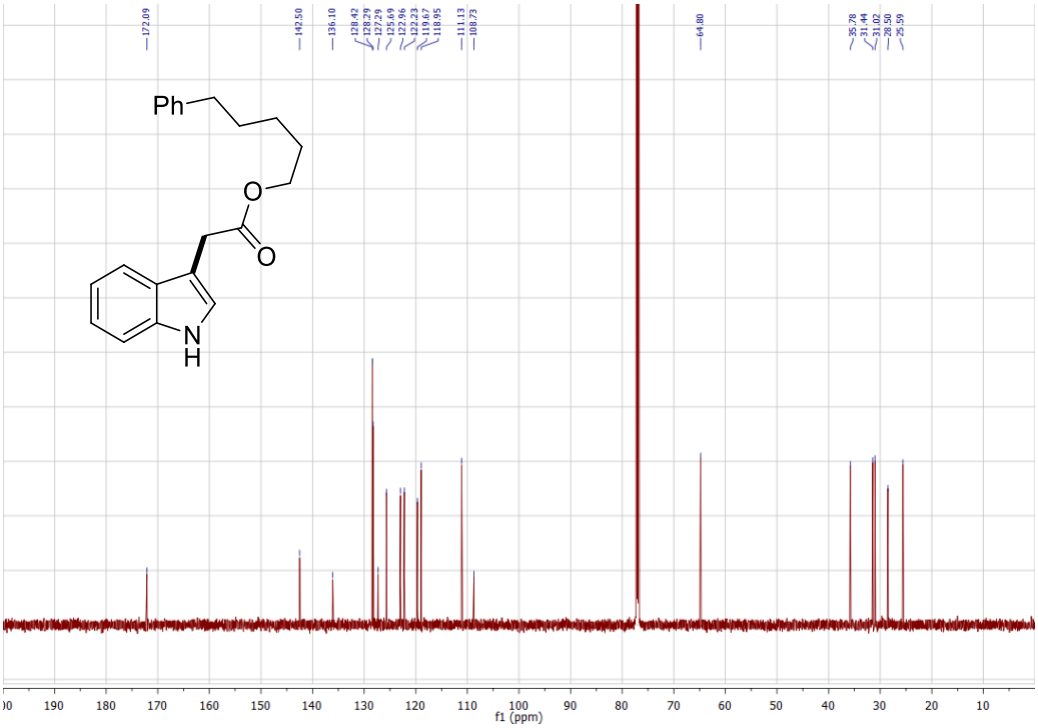


Figure S72. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9t**

Cyclohexyl 2-(1*H*-indol-3-yl)acetate (9u)

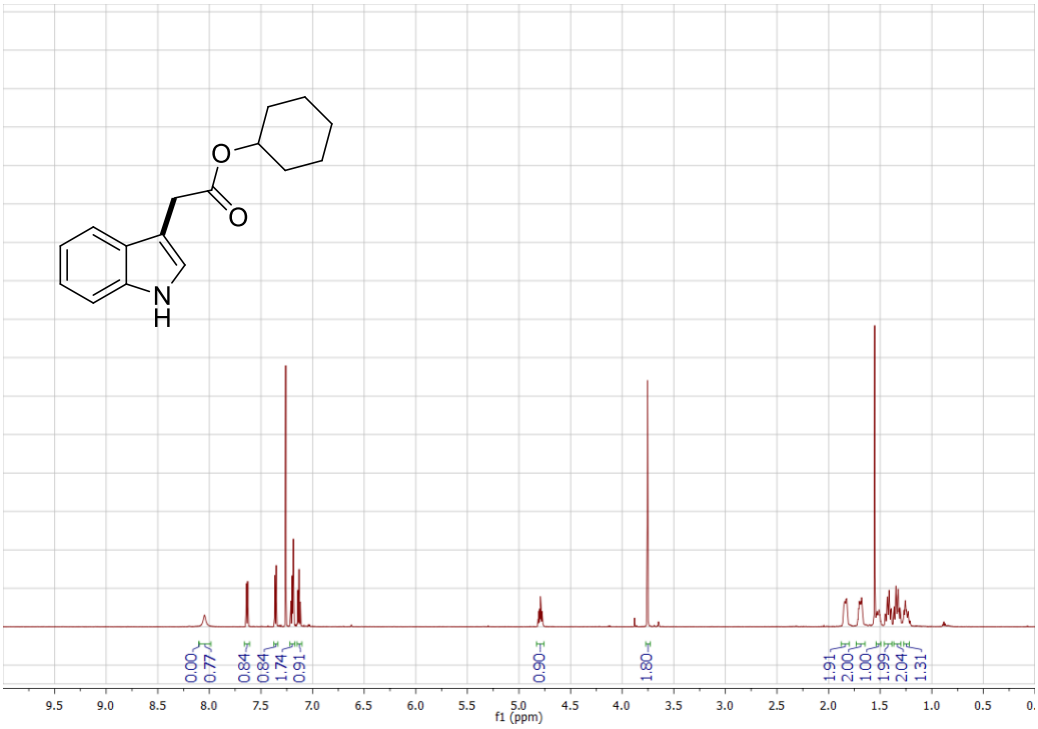


Figure S73. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9u**

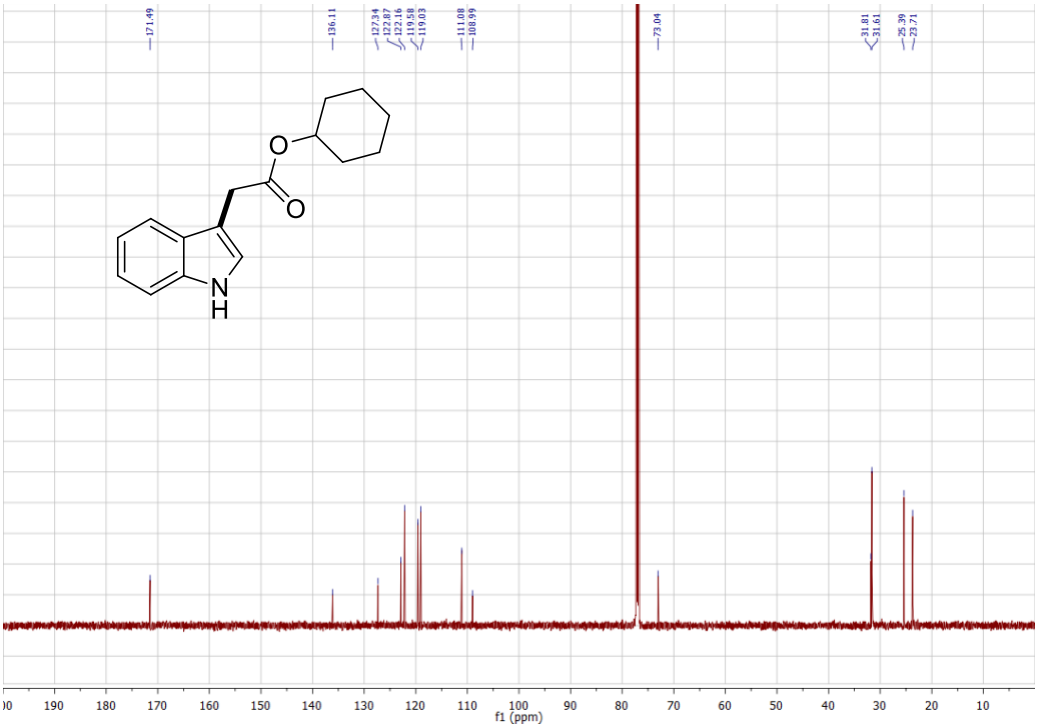


Figure S74. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9u**

Tetrahydrofuran-3-yl 2-(1*H*-indol-3-yl)acetate (9v)

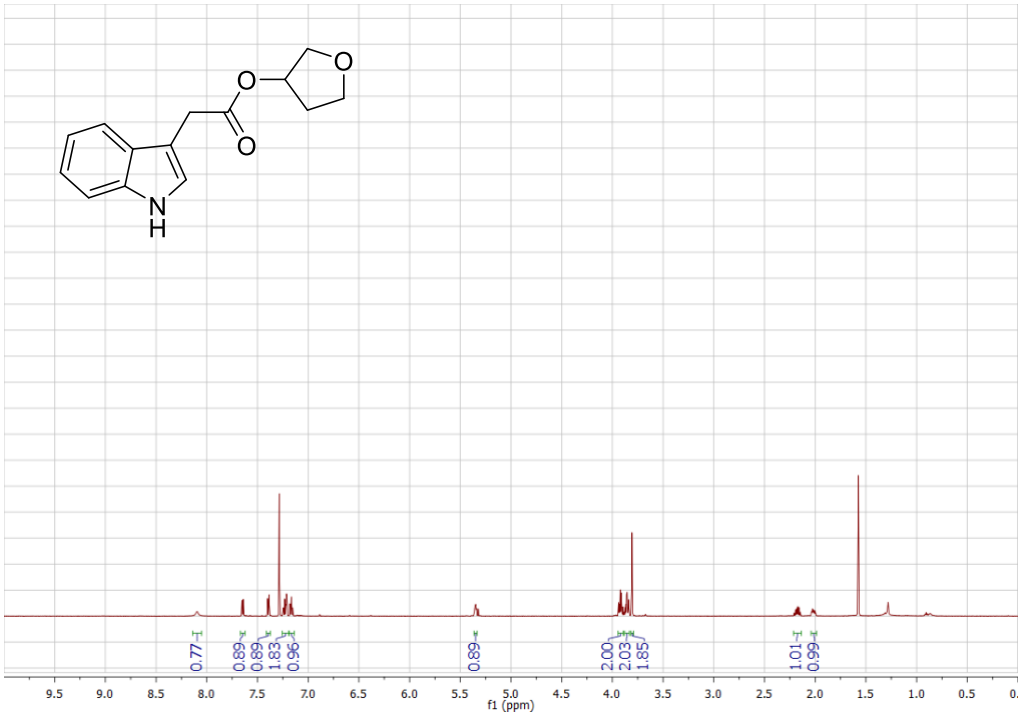


Figure S75. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9v**

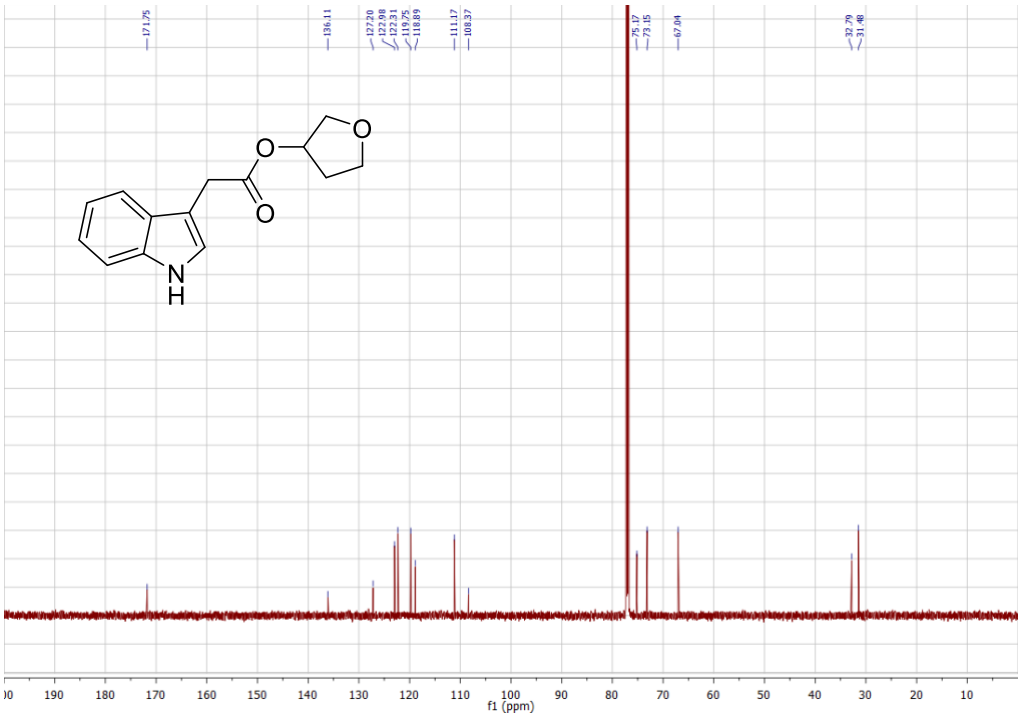


Figure S76. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9v**

Pyridin-2-ylmethyl 2-(1*H*-indol-3-yl)acetate (9w)

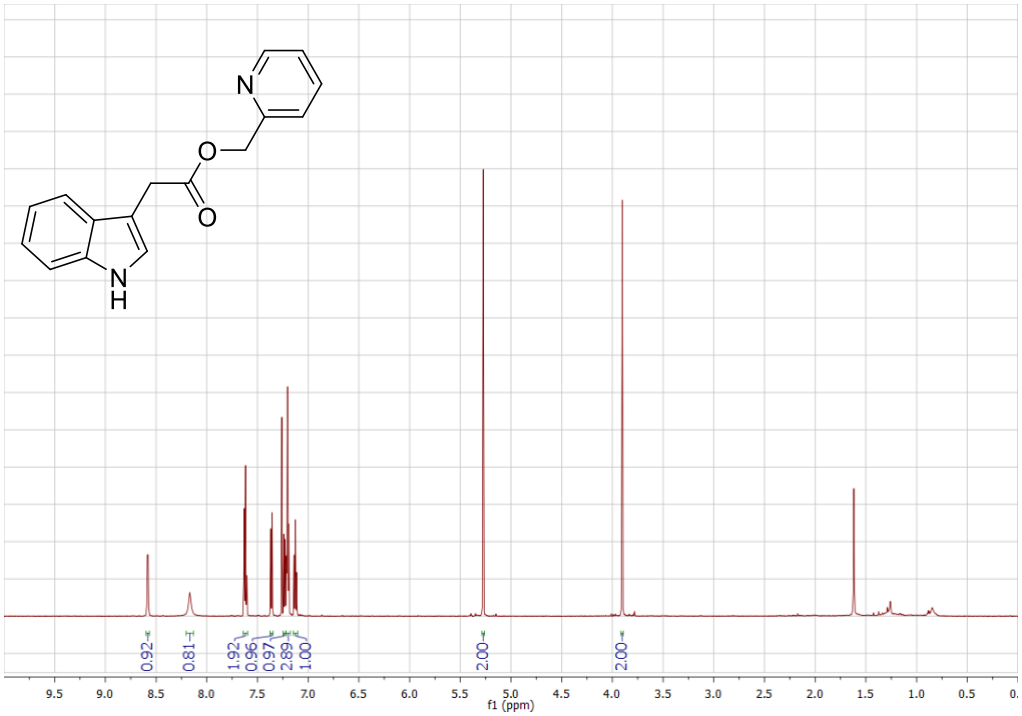


Figure S77. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9w**

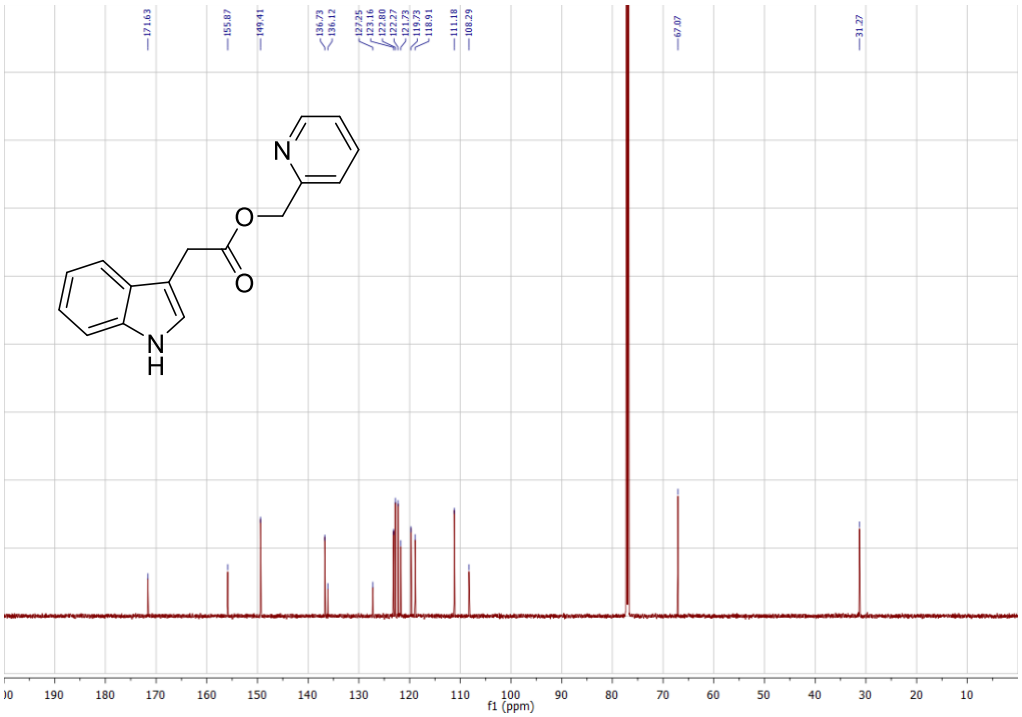


Figure S78. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9w**

Prop-2-yn-1-yl 2-(1*H*-indol-3-yl)acetate (9x)

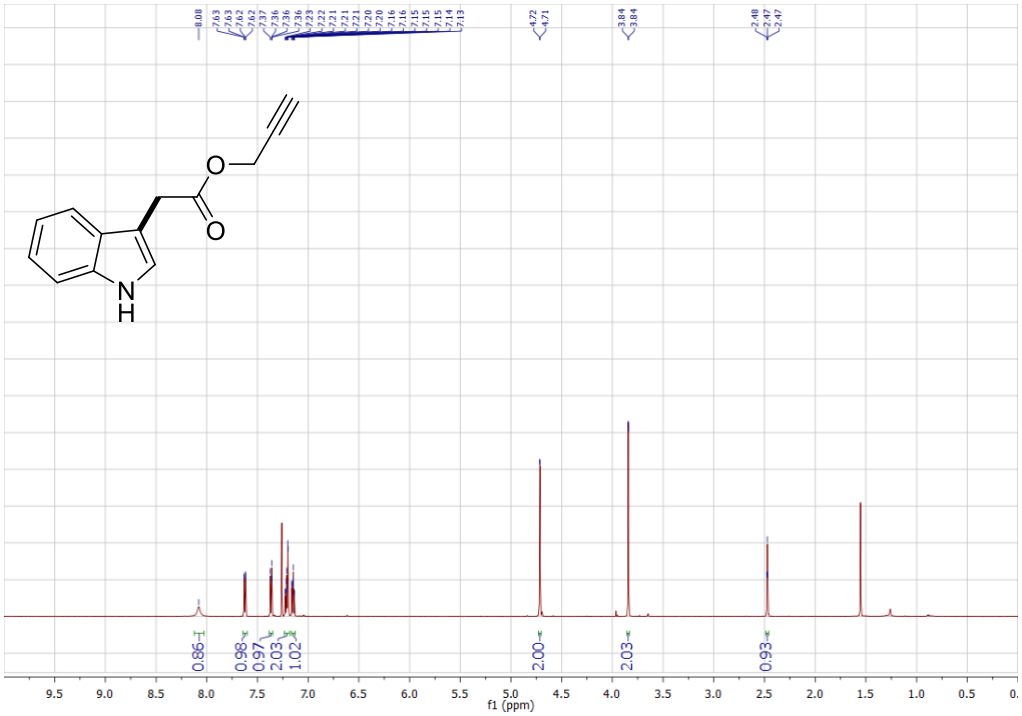


Figure S79. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9x**

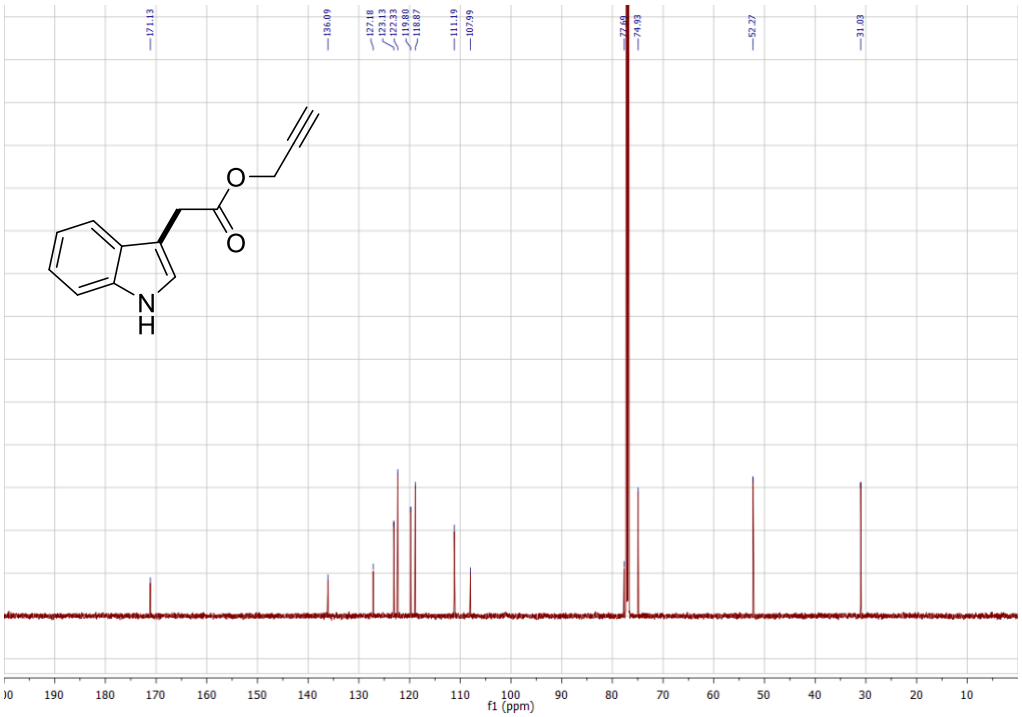


Figure S80. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9x**

3-Phenylallyl 2-(1*H*-indol-3-yl)acetate (9y)

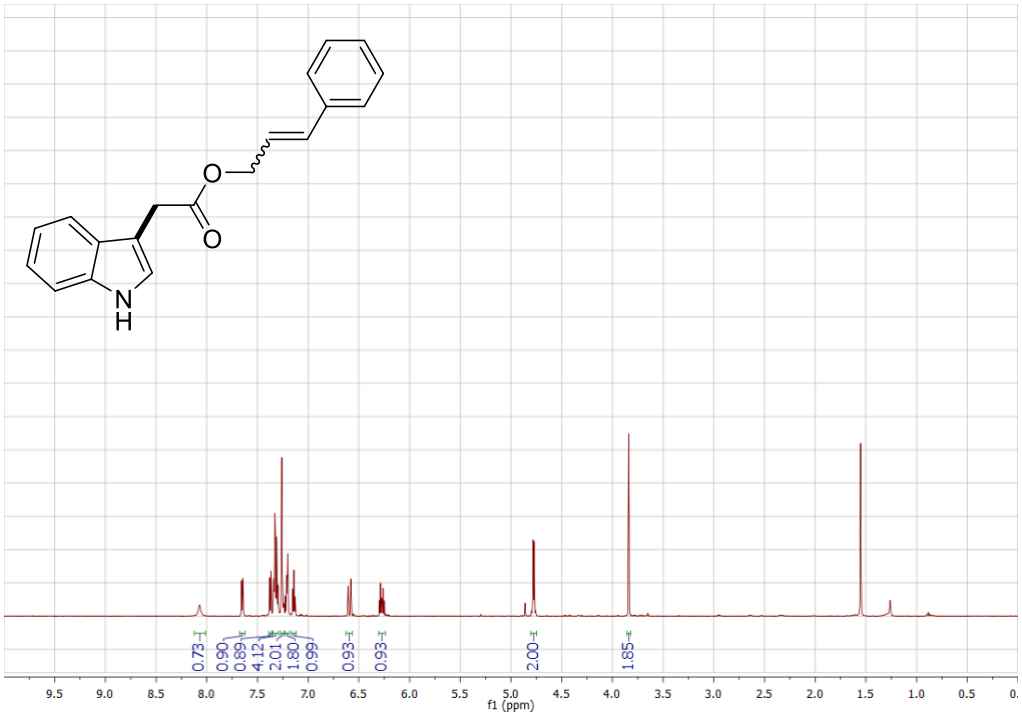


Figure S81. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9y**

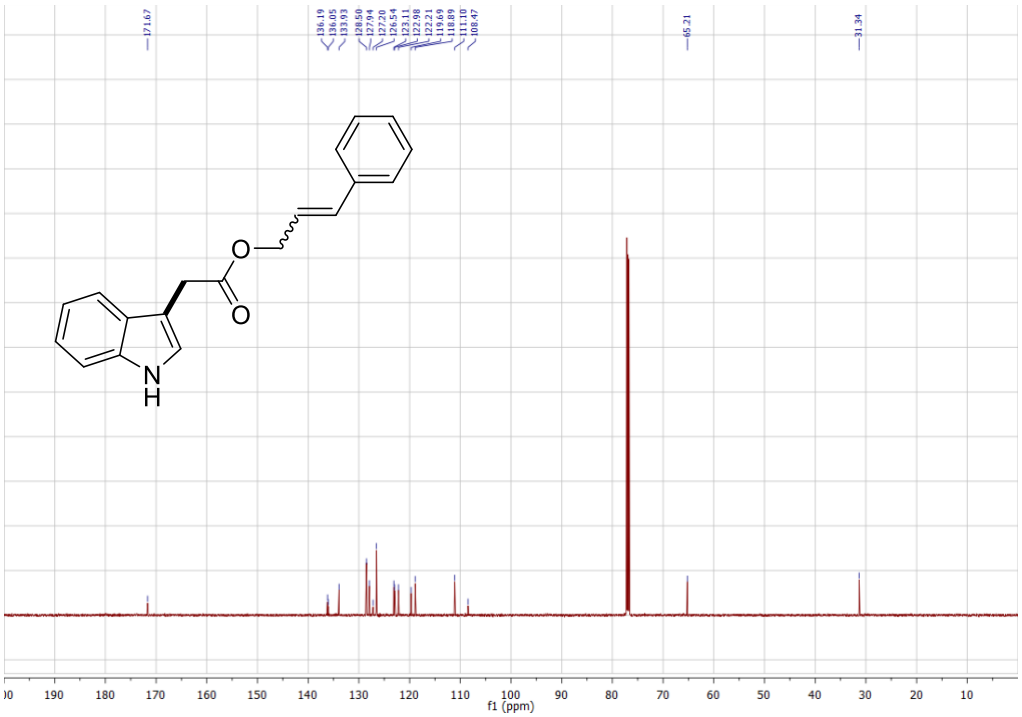


Figure S82. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9y**

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 2-(1*H*-indol-3-yl)acetate (9z)

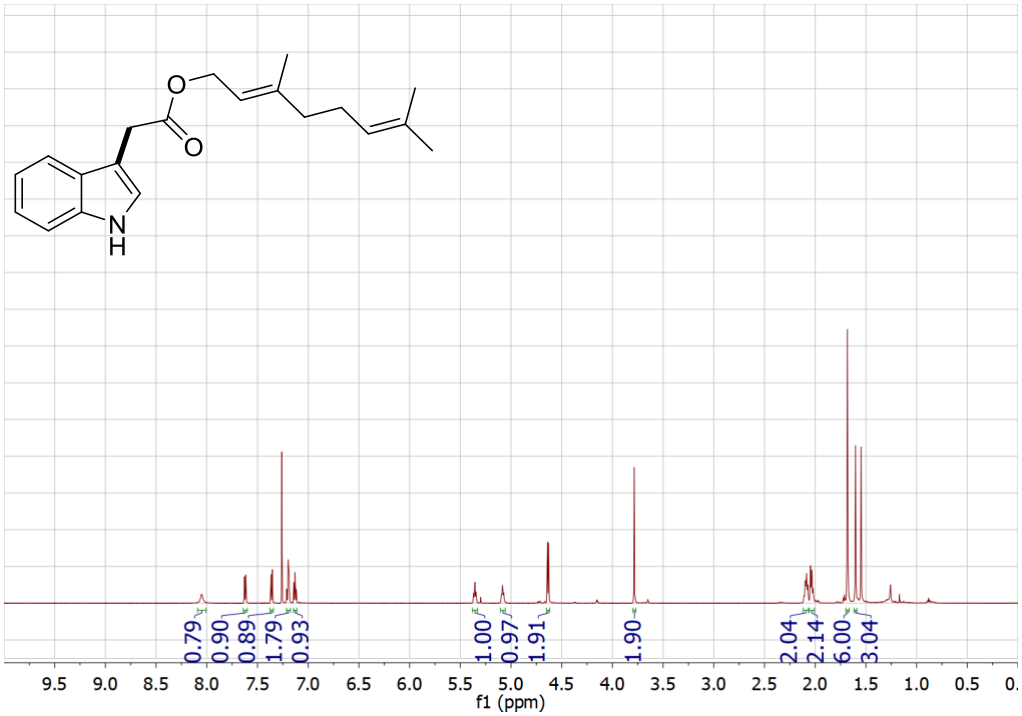


Figure S83. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9z**

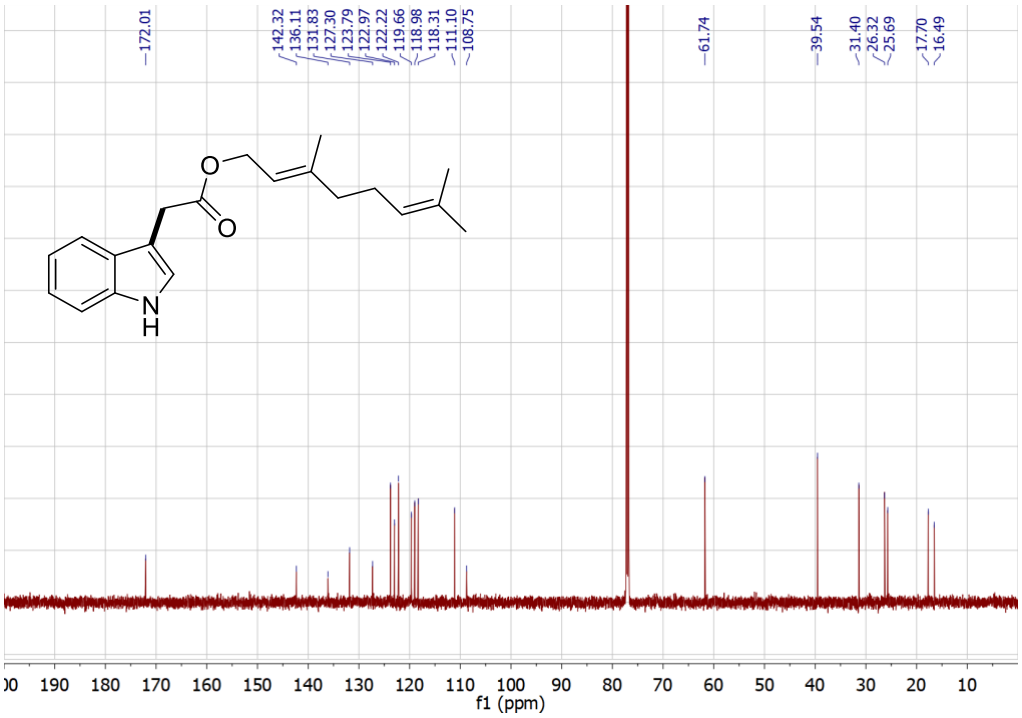


Figure S84. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9z**

2-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethyl 2-(1*H*-indol-3-yl)acetate (9aa)

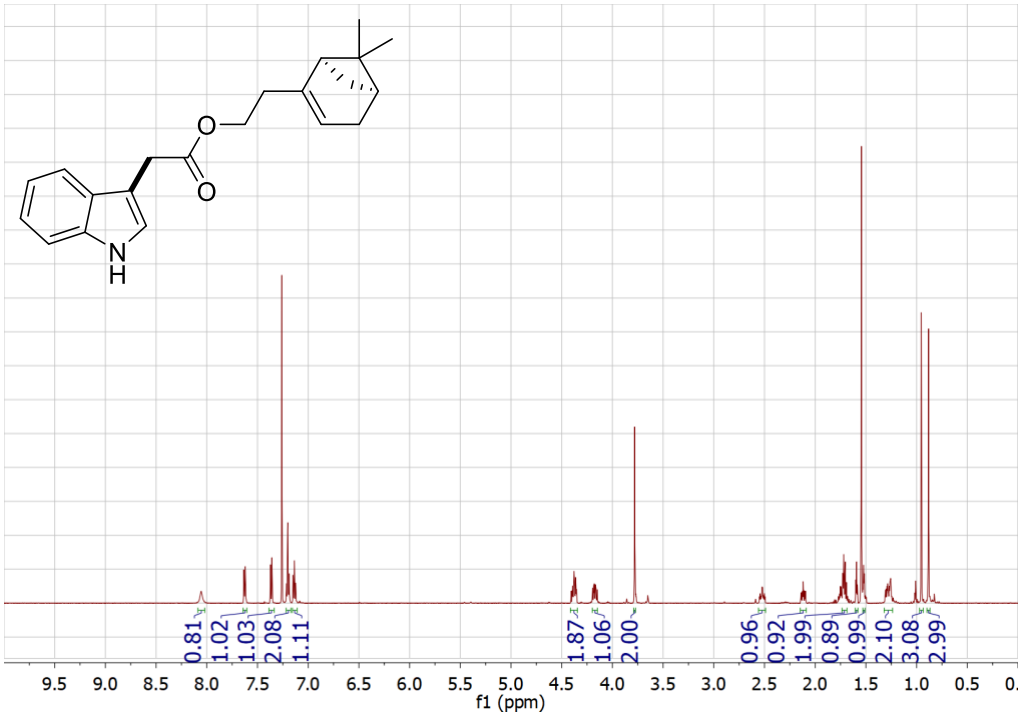


Figure S85. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9aa**

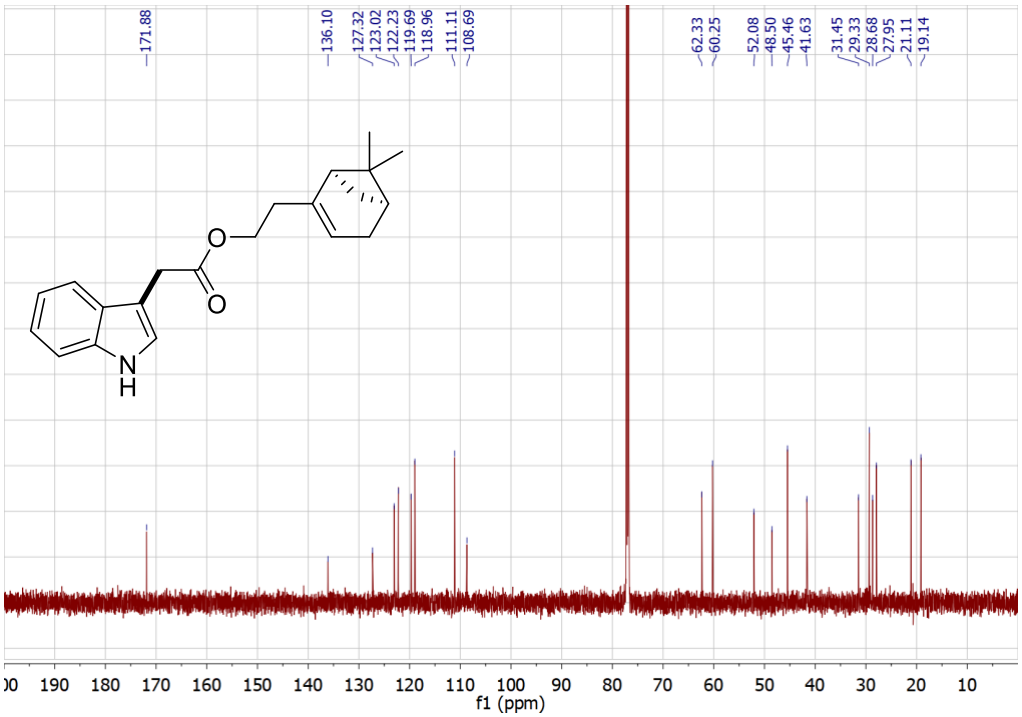


Figure S86. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9aa**

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)methyl 2-(1*H*-indol-3-yl)acetate (9ab)

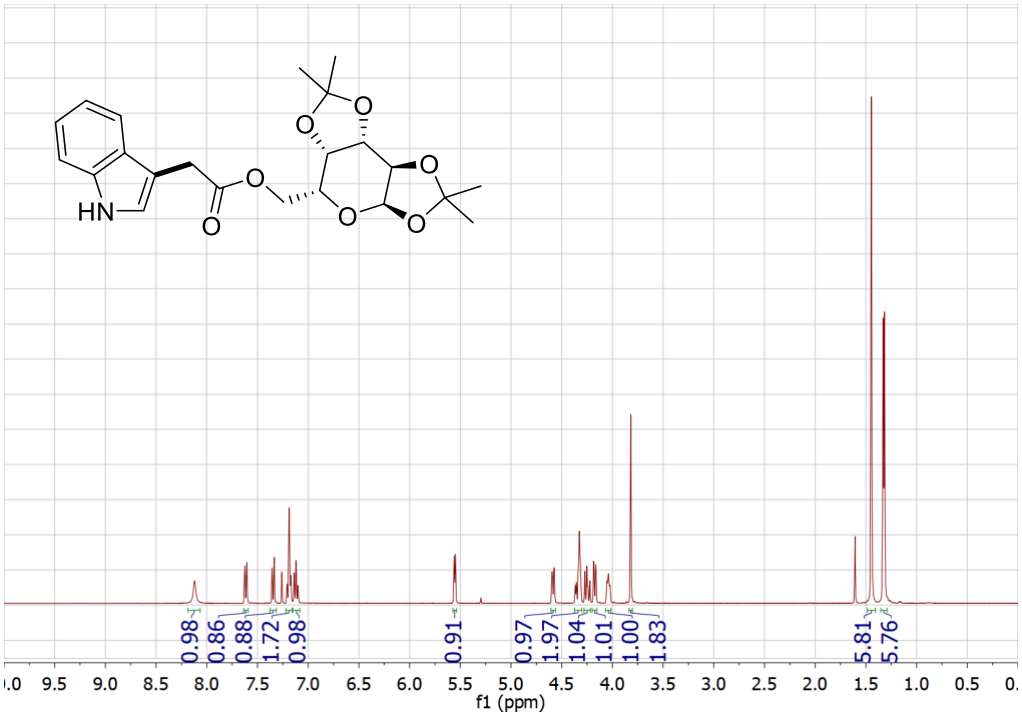


Figure S87. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9ab**

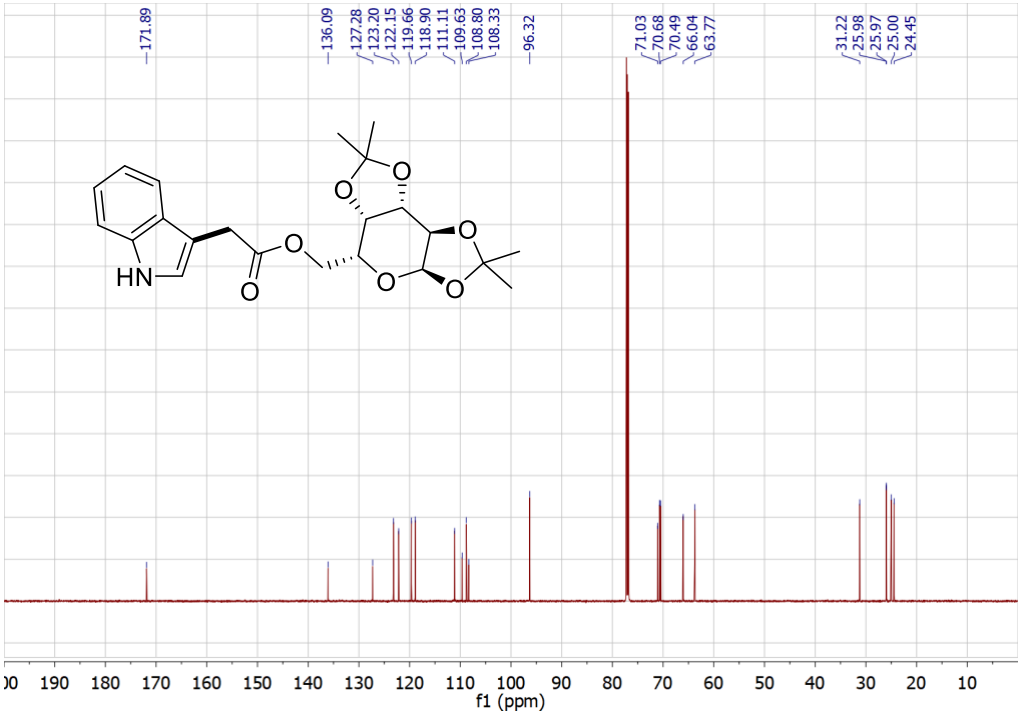


Figure S88. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9ab**

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl 2-(1H-indol-3-yl)acetate (9ac)

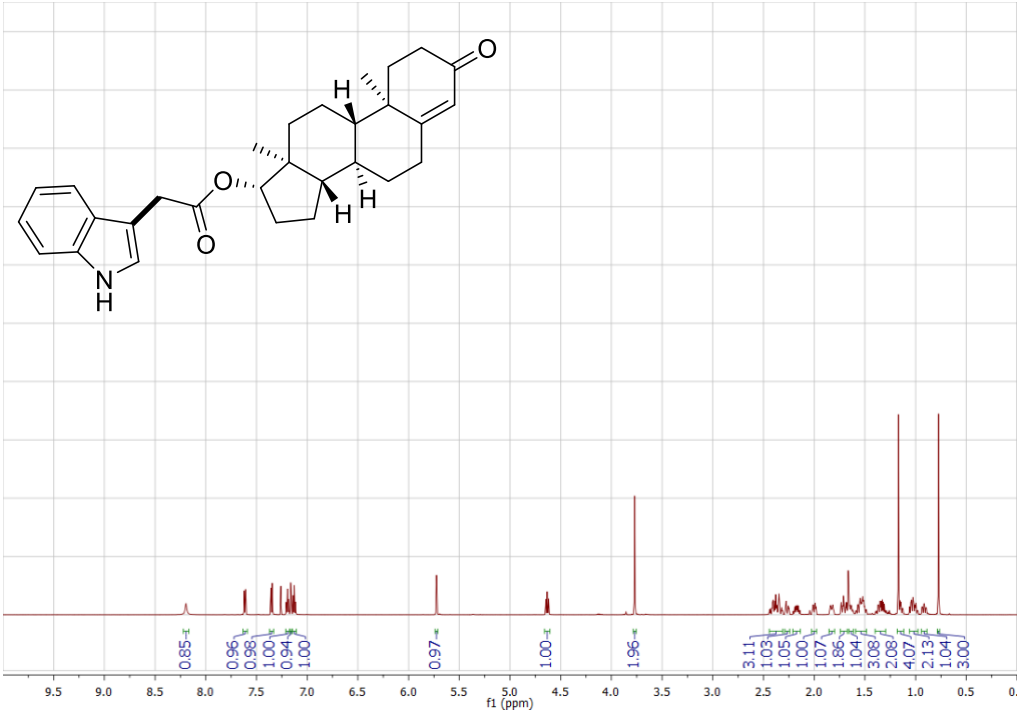


Figure S89. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9ac**

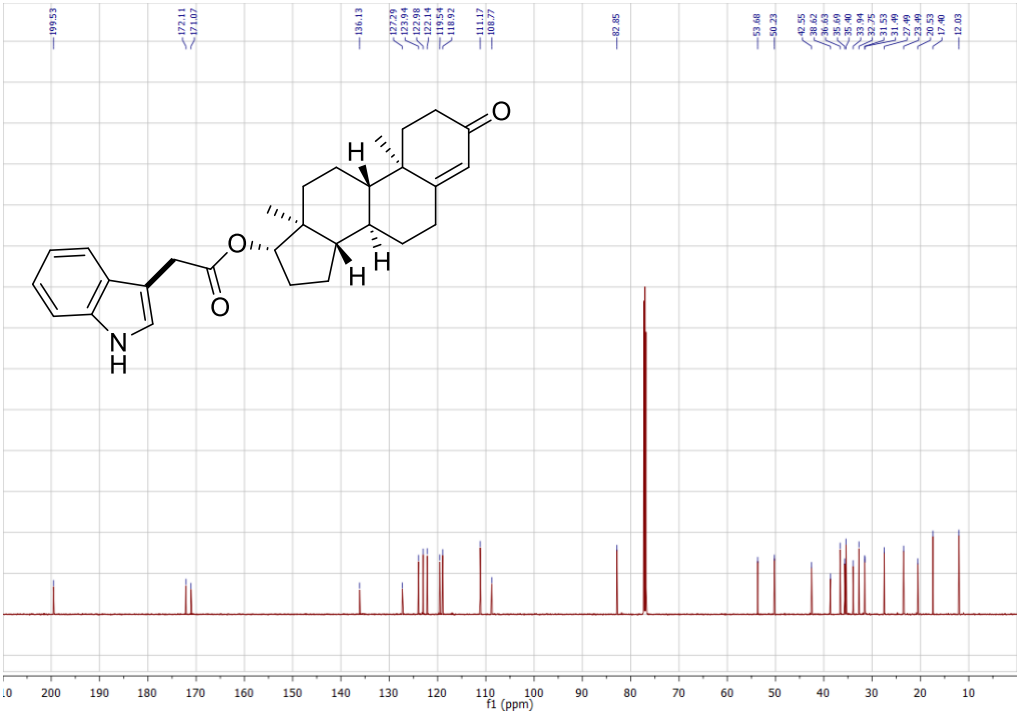


Figure S90. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9ac**

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl) 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-(1*H*-indol-3-yl)acetate (9ad)

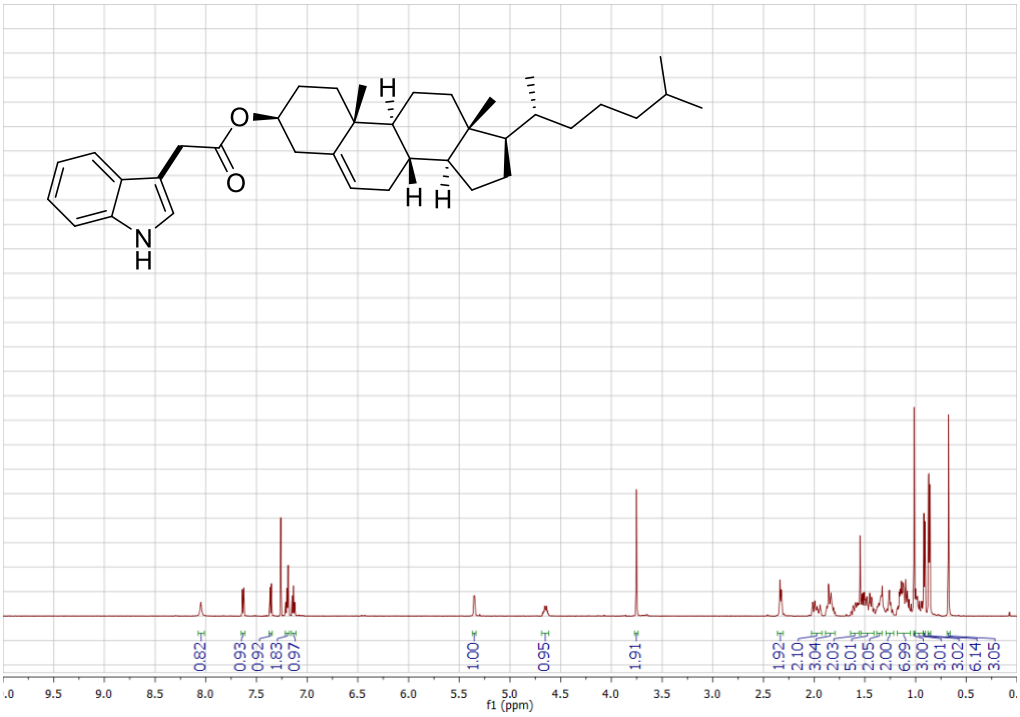


Figure S91. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9ad**

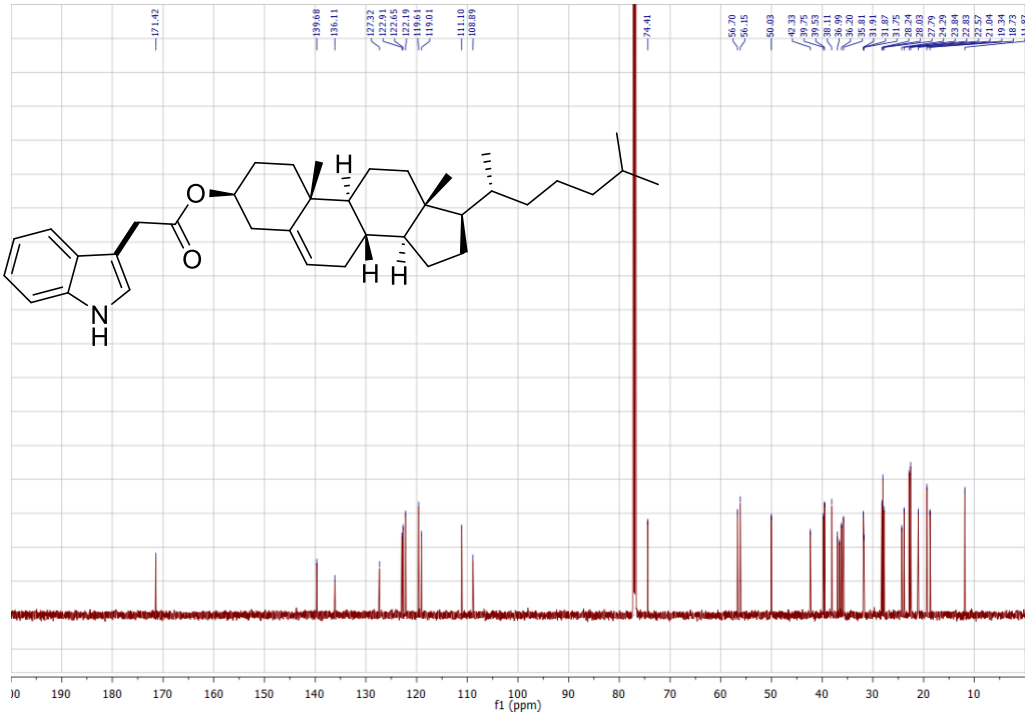


Figure S92. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9ad**

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl 2-(1*H*-indol-3-yl)acetate (9ae)

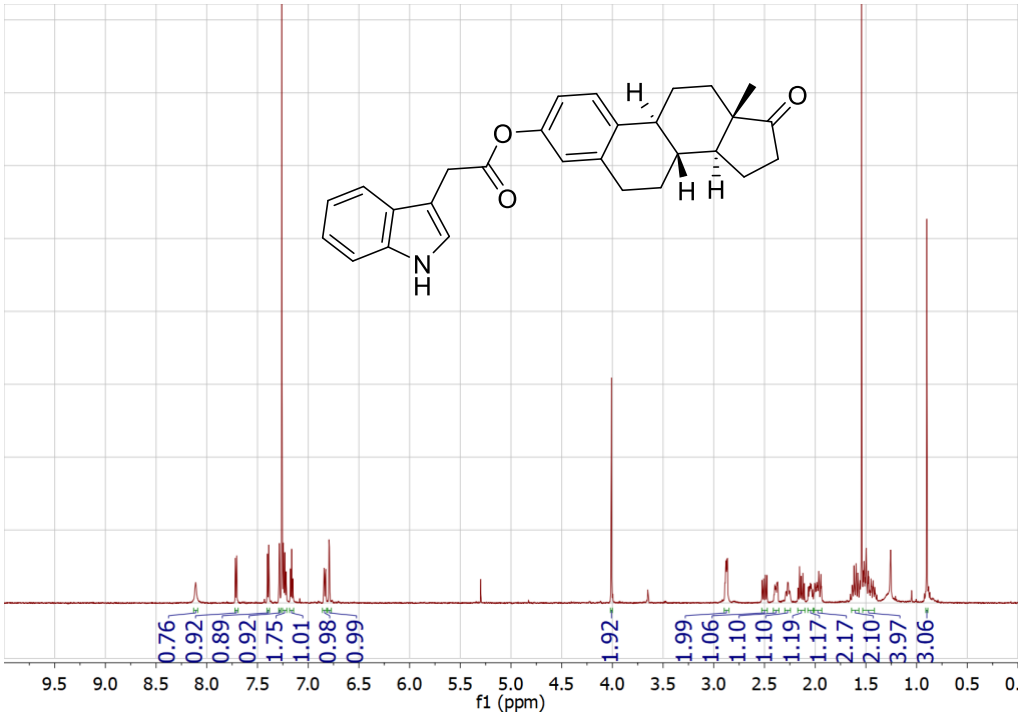


Figure S93. ^{1}H NMR (600 MHz, Chloroform-*d*) of **9ae**

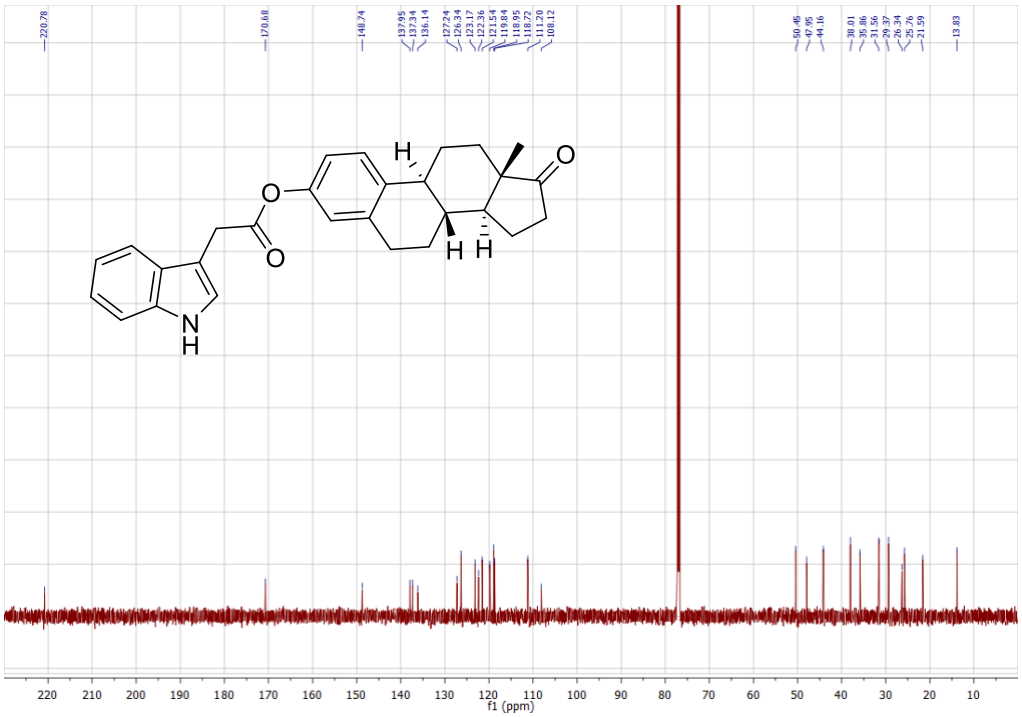


Figure S94. ^{13}C NMR (151 MHz, Chloroform-*d*) of **9ae**

Ethyl 2-(1-methyl-1*H*-indol-3-yl)acetate (13a)

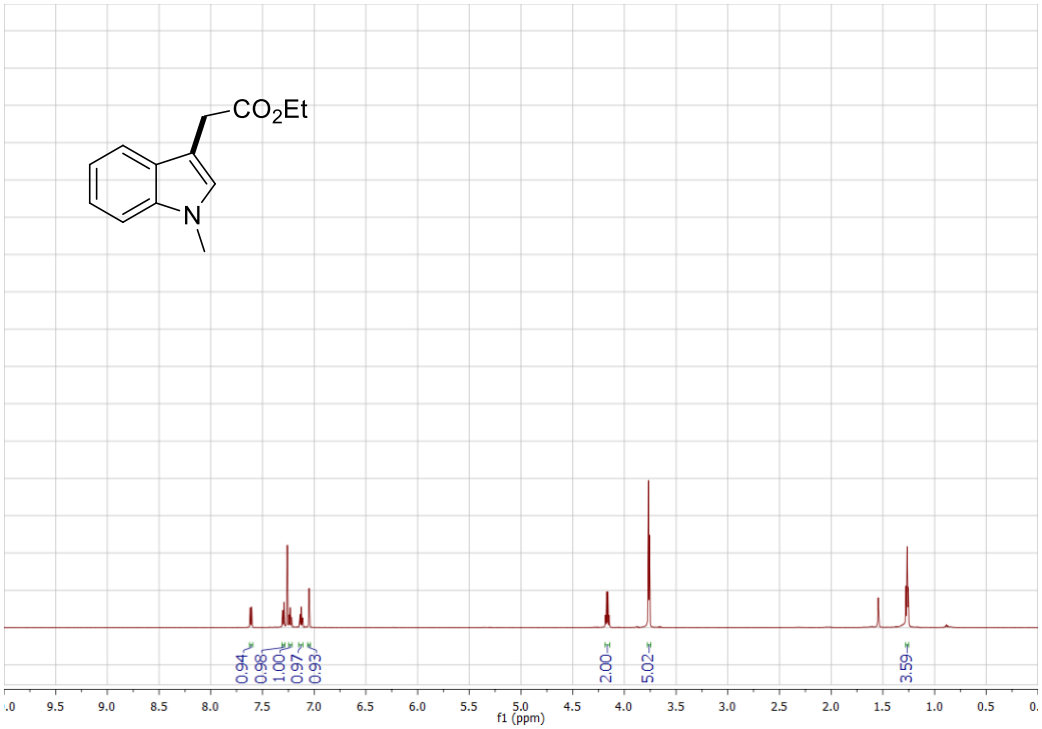


Figure S95. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13a**

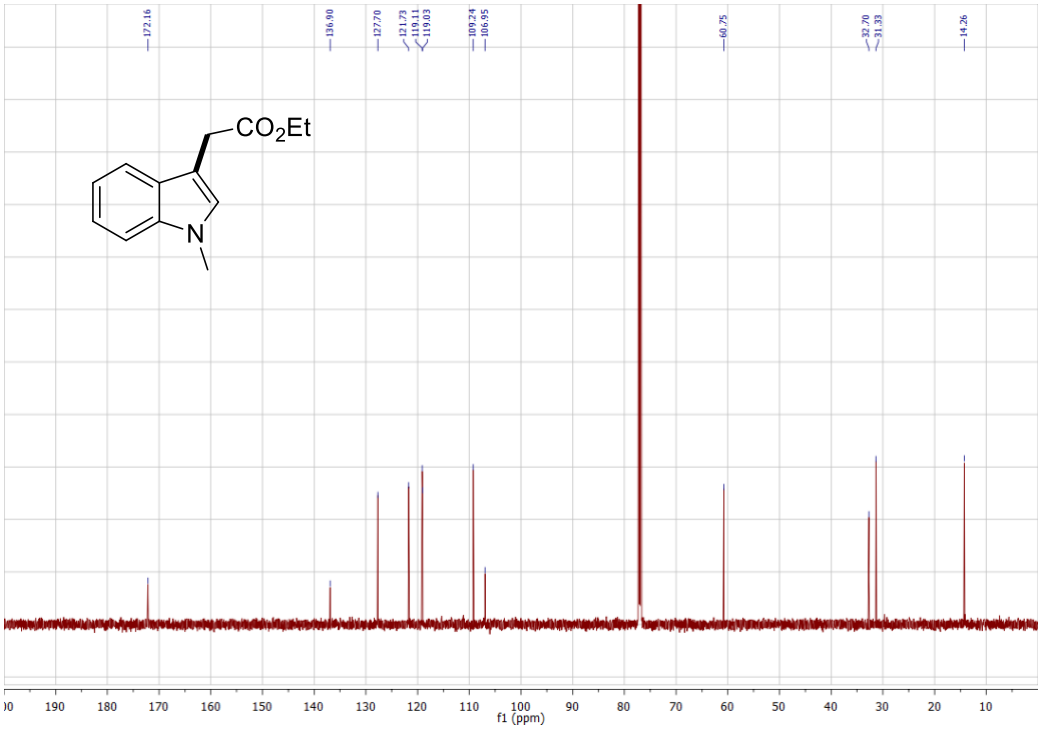


Figure S96. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13a**

Ethyl 2-(5-bromo-1-methyl-1*H*-indol-3-yl)acetate (13b)

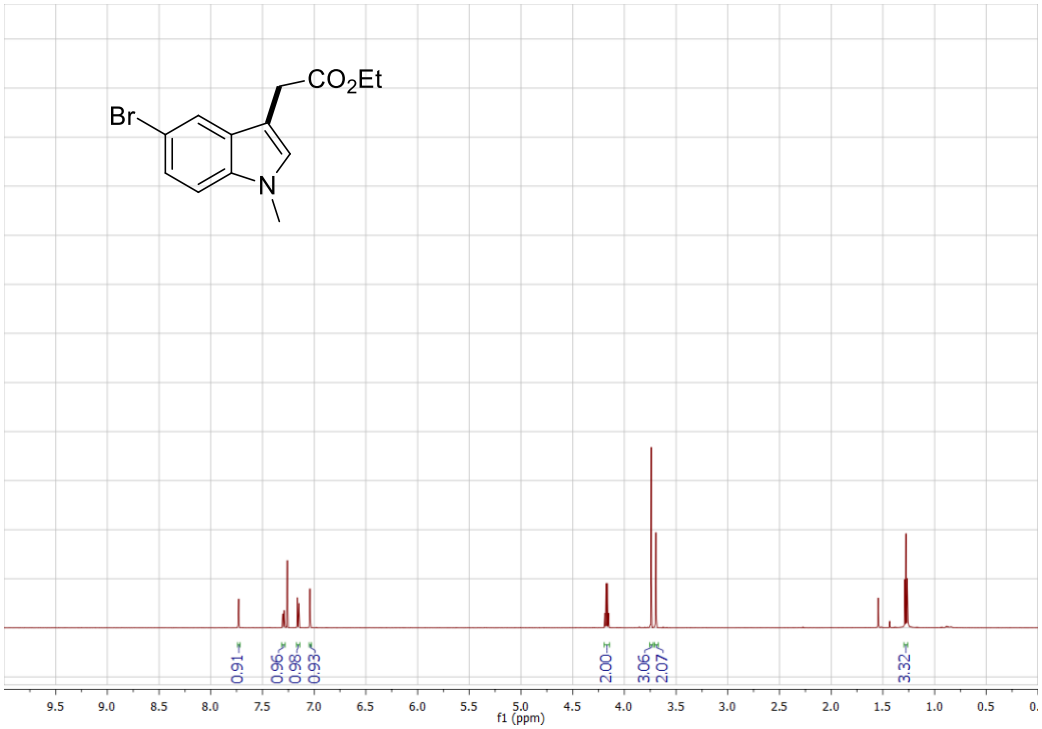


Figure S97. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13b**

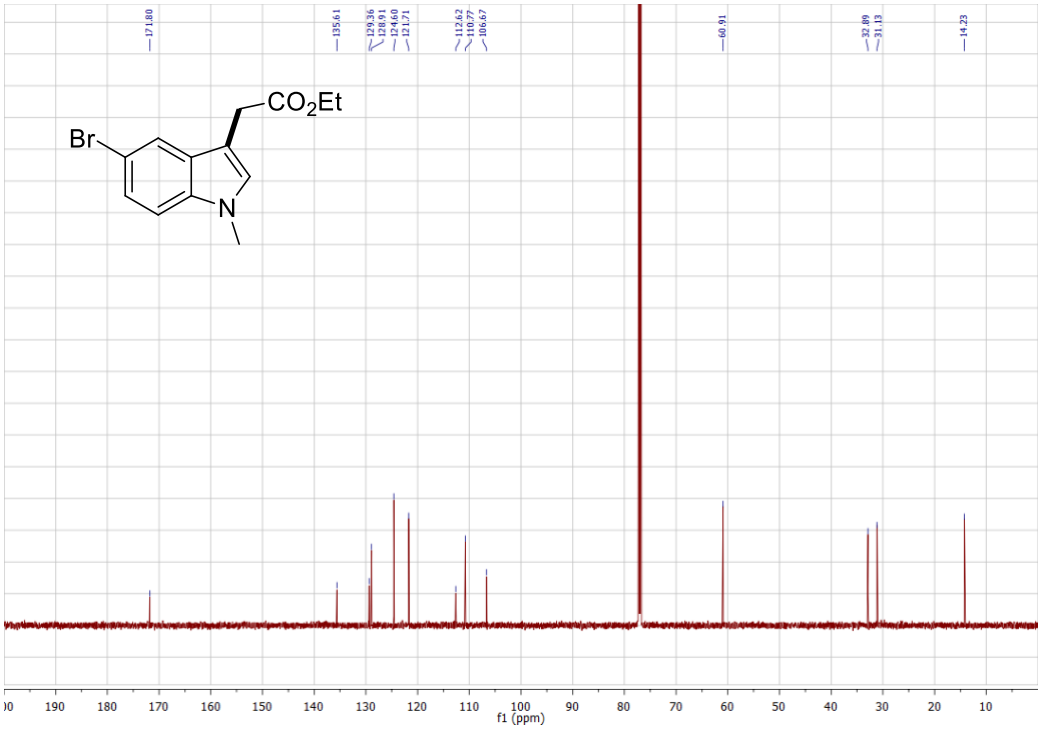


Figure S98. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13b**

Ethyl 2-(5-(benzyloxy)-1-methyl-1*H*-indol-3-yl)acetate (13c)

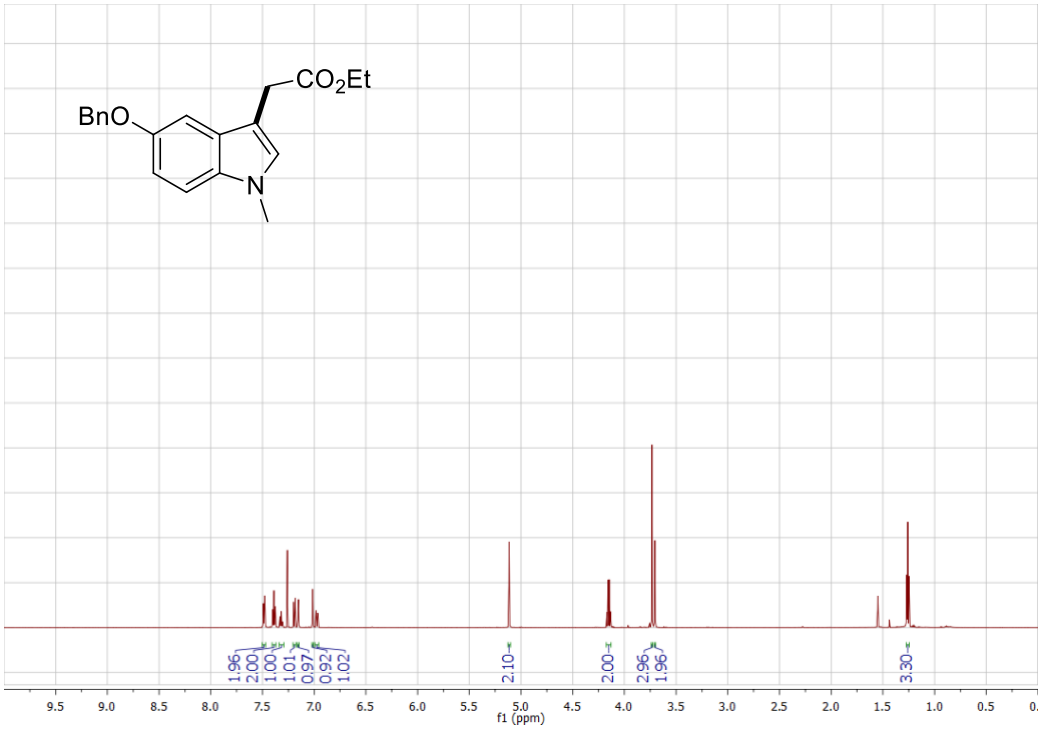


Figure S99. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13c**

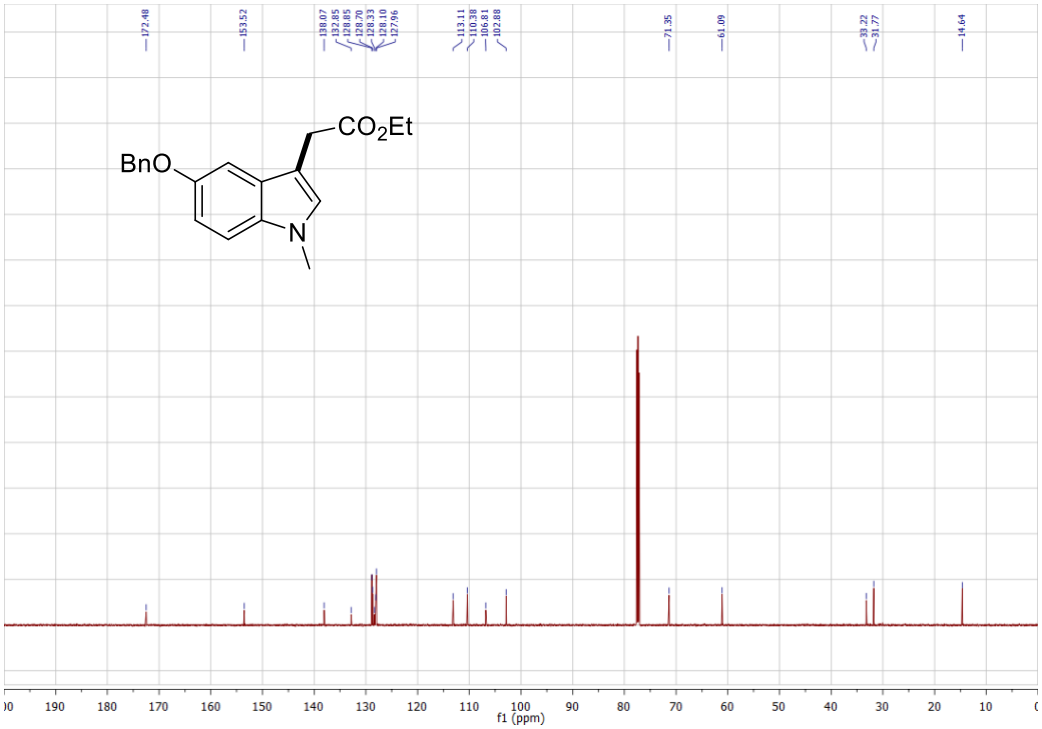


Figure S100. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13c**

Ethyl 2-(7-(benzyloxy)-1-methyl-1*H*-indol-3-yl)acetate (13d)

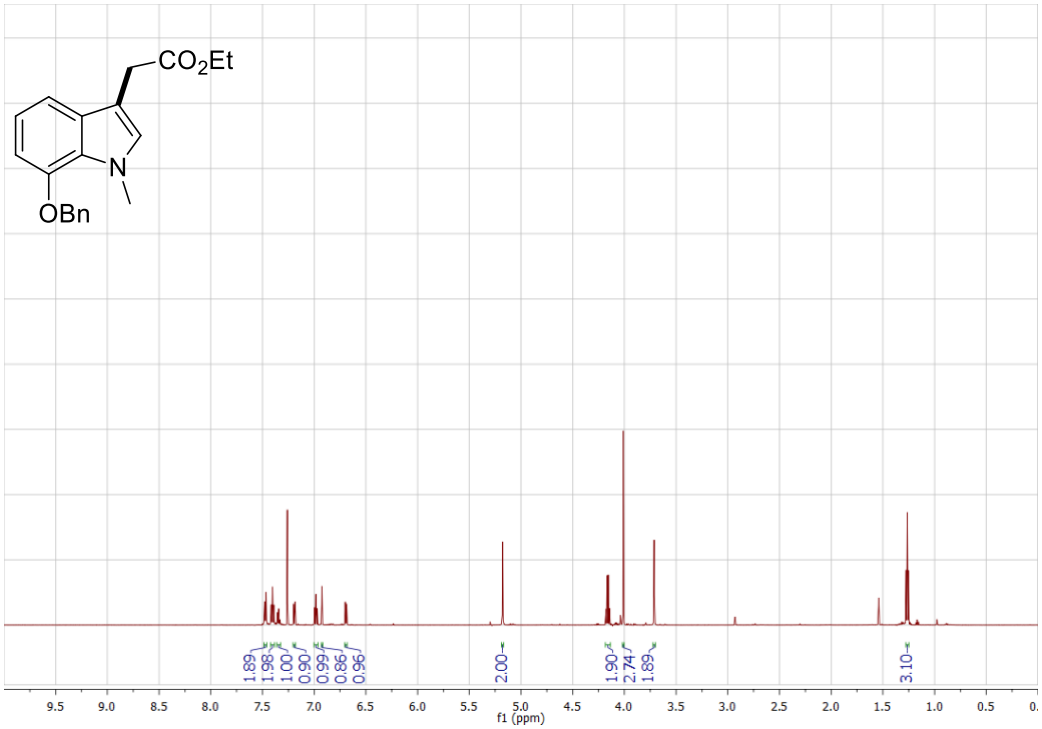


Figure S101. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13d**

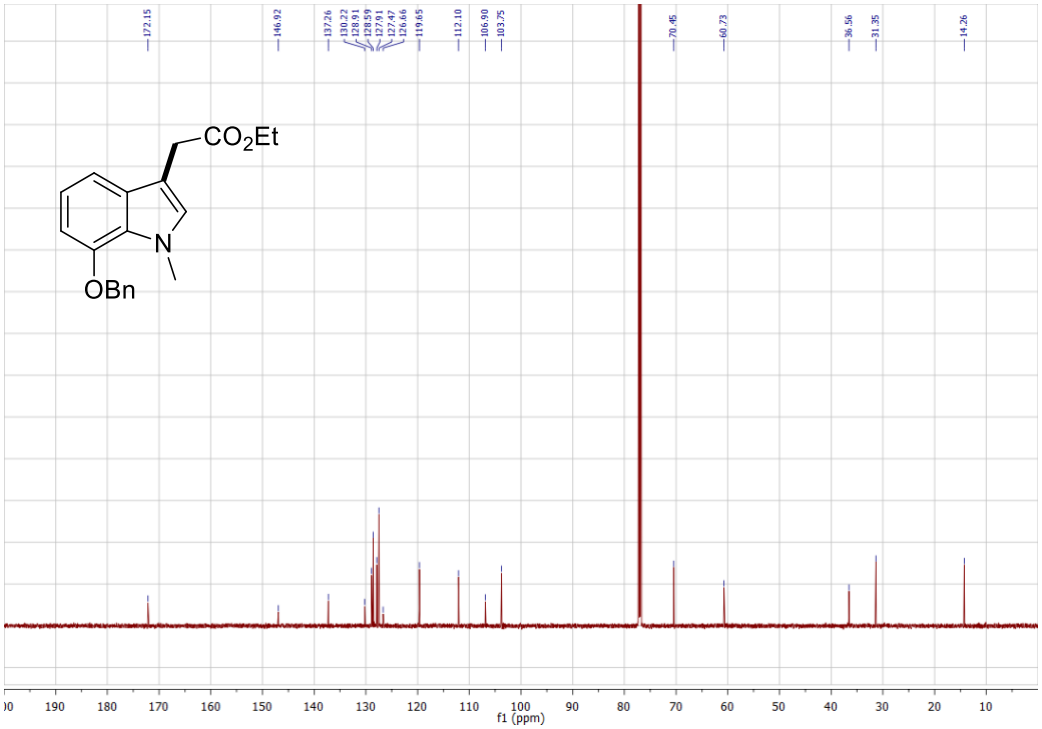


Figure S102. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13d**

Ethyl 2-(1-allyl-1*H*-indol-3-yl)acetate (13e)

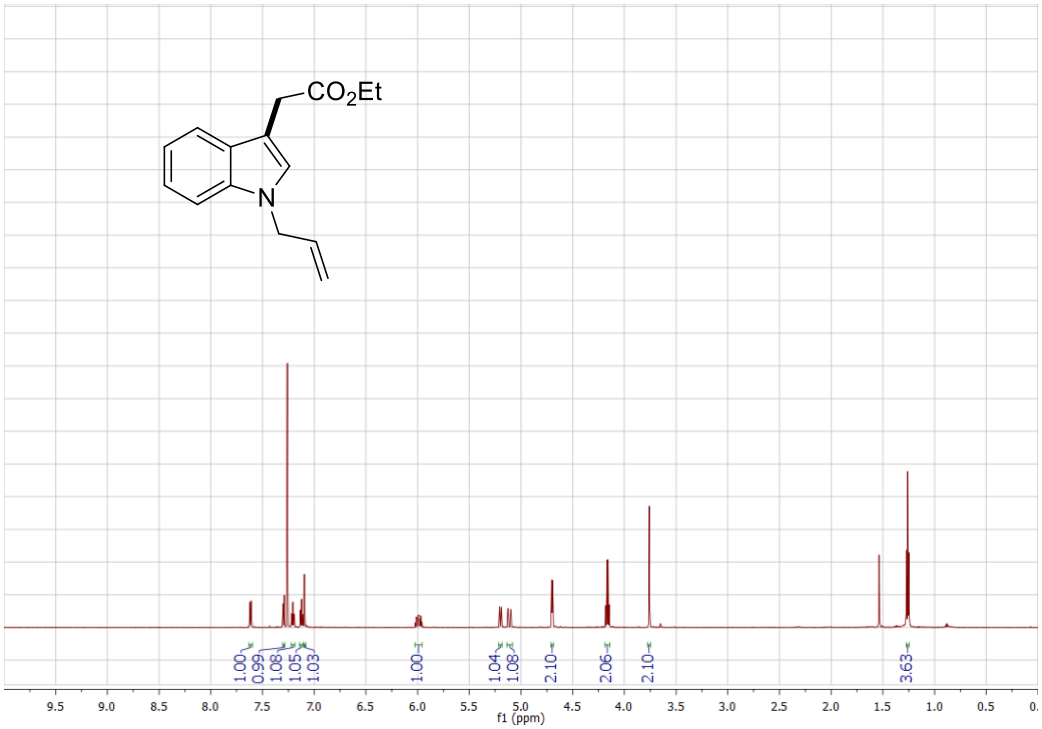


Figure S103. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13e**

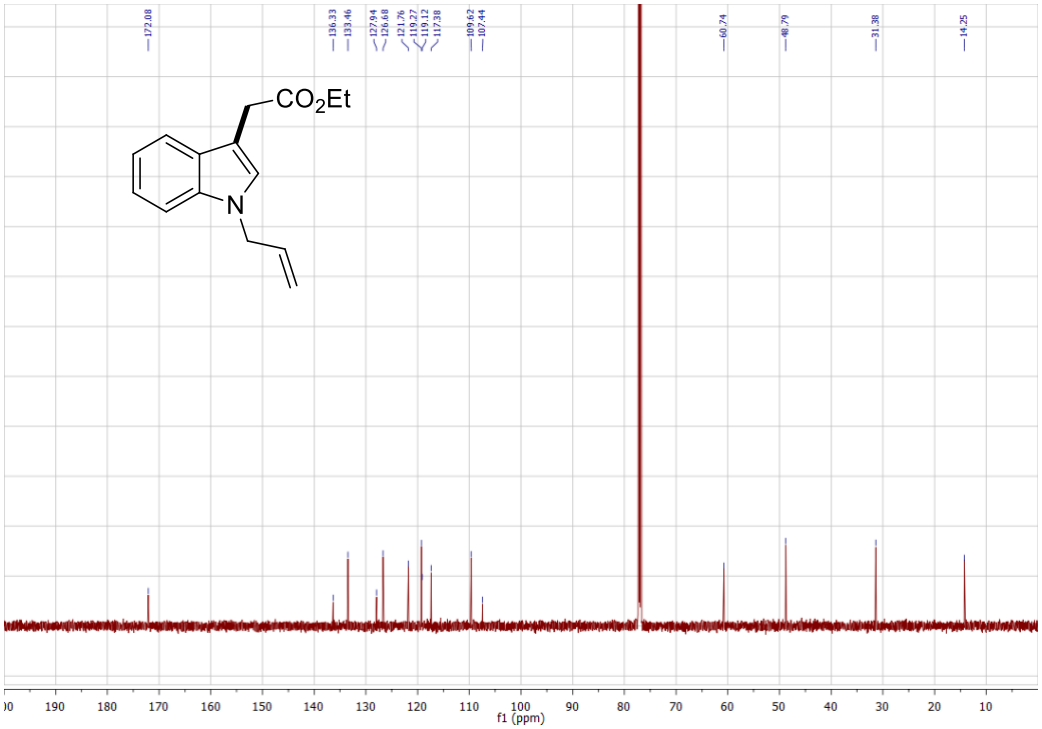


Figure S104. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13e**

Ethyl 2-(1-(but-3-en-1-yl)-1*H*-indol-3-yl)acetate (13f)

^{1}H NMR (600 MHz, Chloroform-*d*)

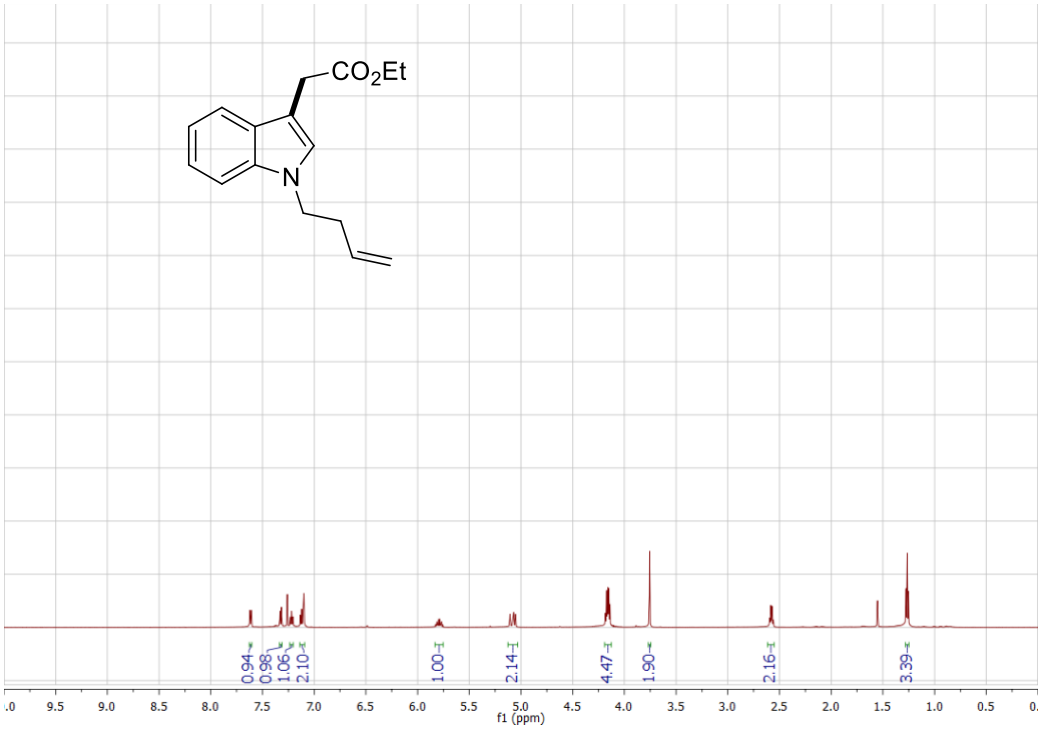


Figure S105. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13f**

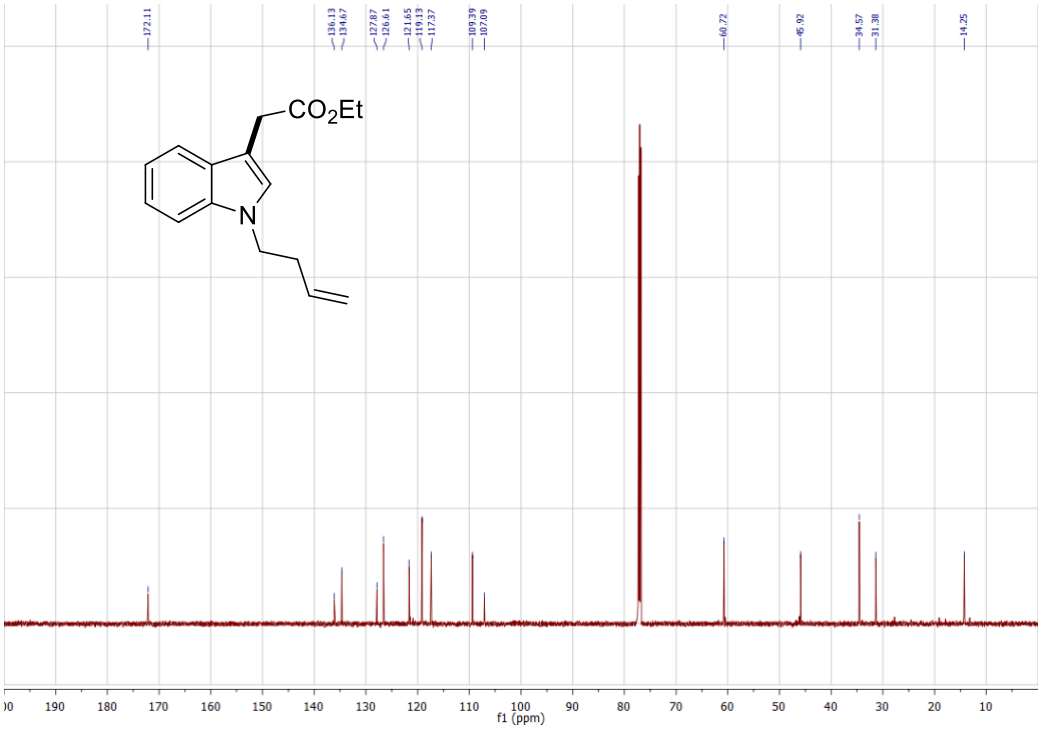


Figure S106. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13f**

Ethyl 2-(1-benzyl-1*H*-indol-3-yl)acetate (13g)

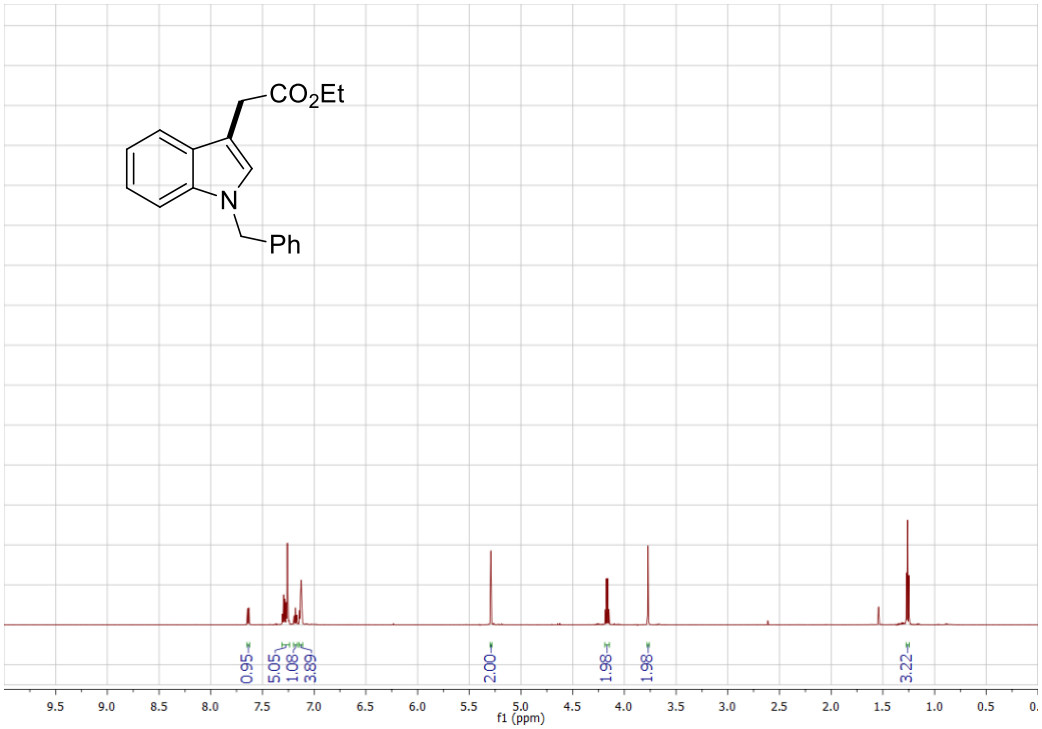


Figure S107. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13g**

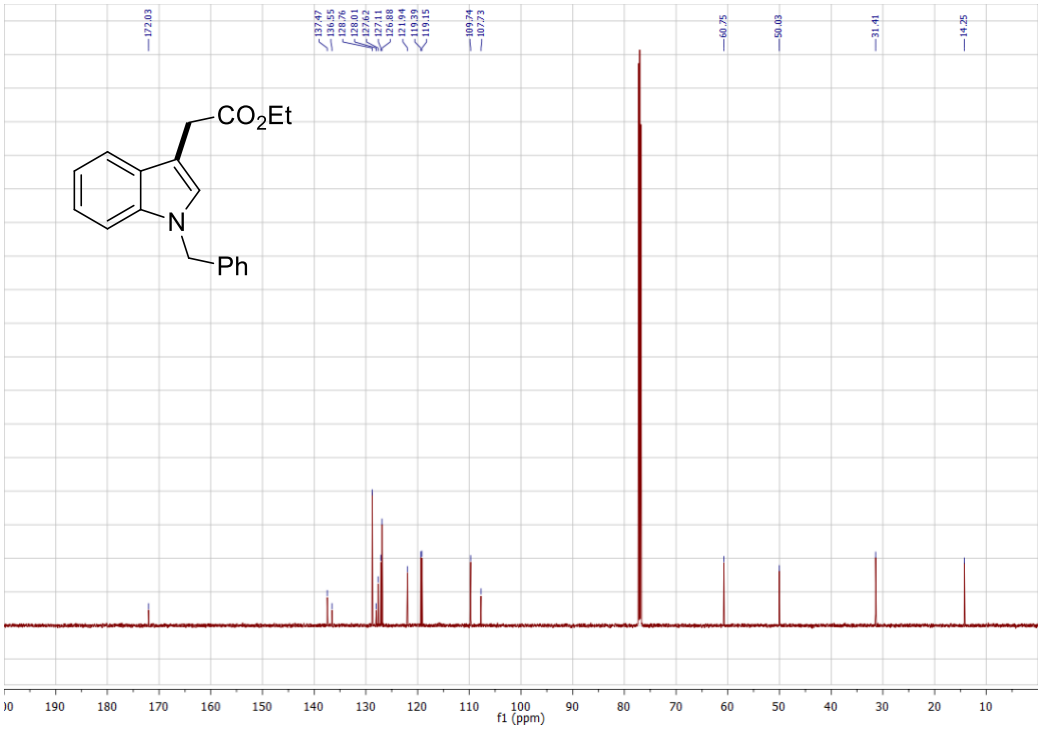


Figure S108. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13g**

Ethyl 2-(1-(cyclobutylmethyl)-1*H*-indol-3-yl)acetate (13h)

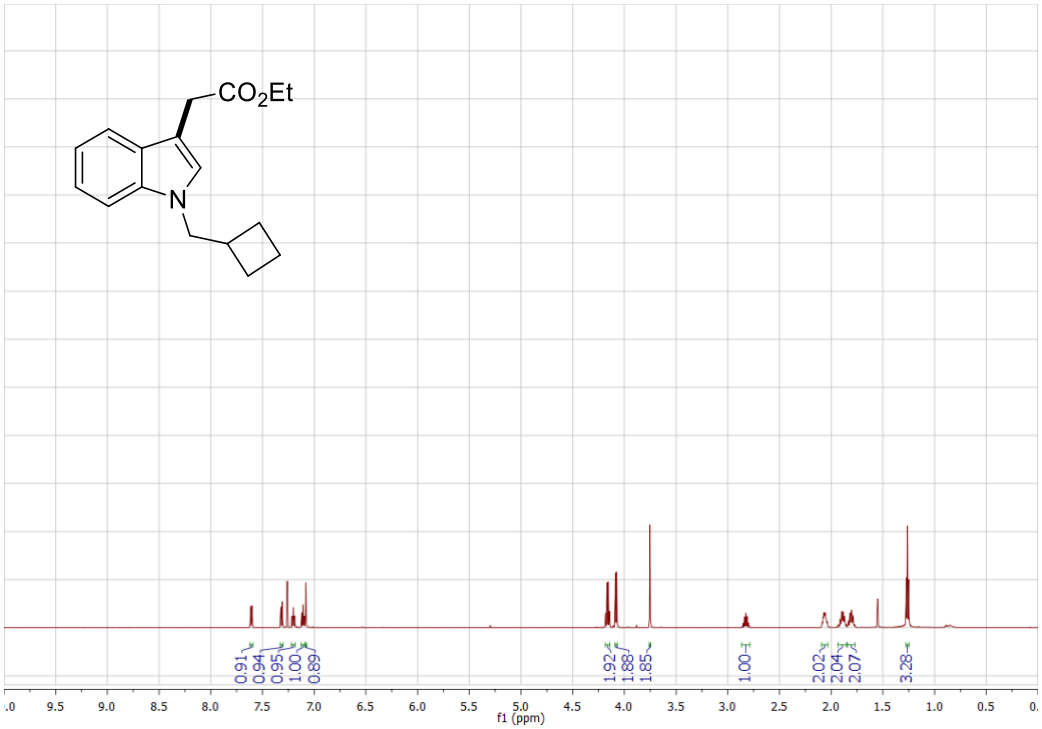


Figure S109. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13h**

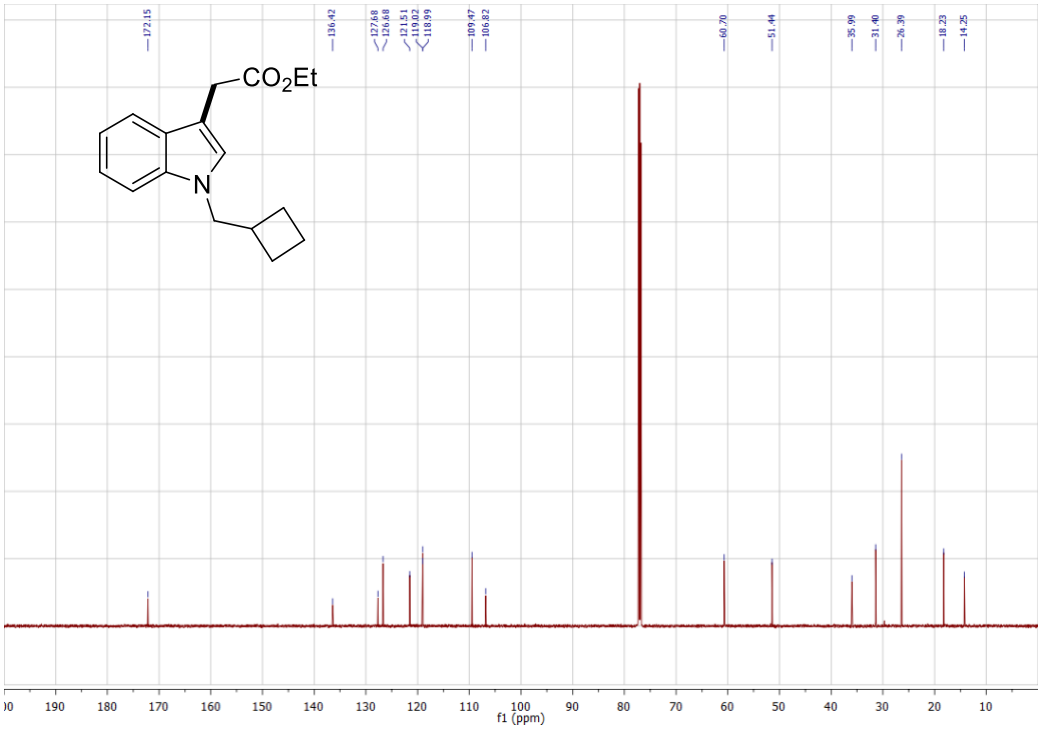


Figure S110. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13h**

Ethyl 2-(1-(pentan-3-yl)-1*H*-indol-3-yl)acetate (13i)

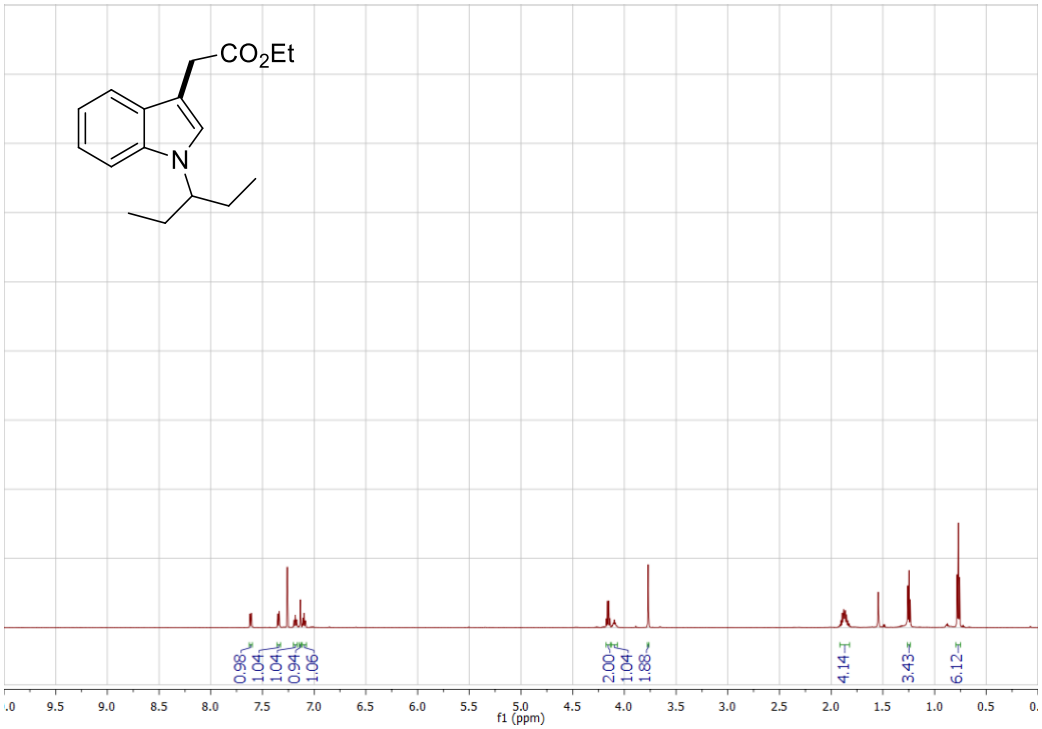


Figure S111. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13i**

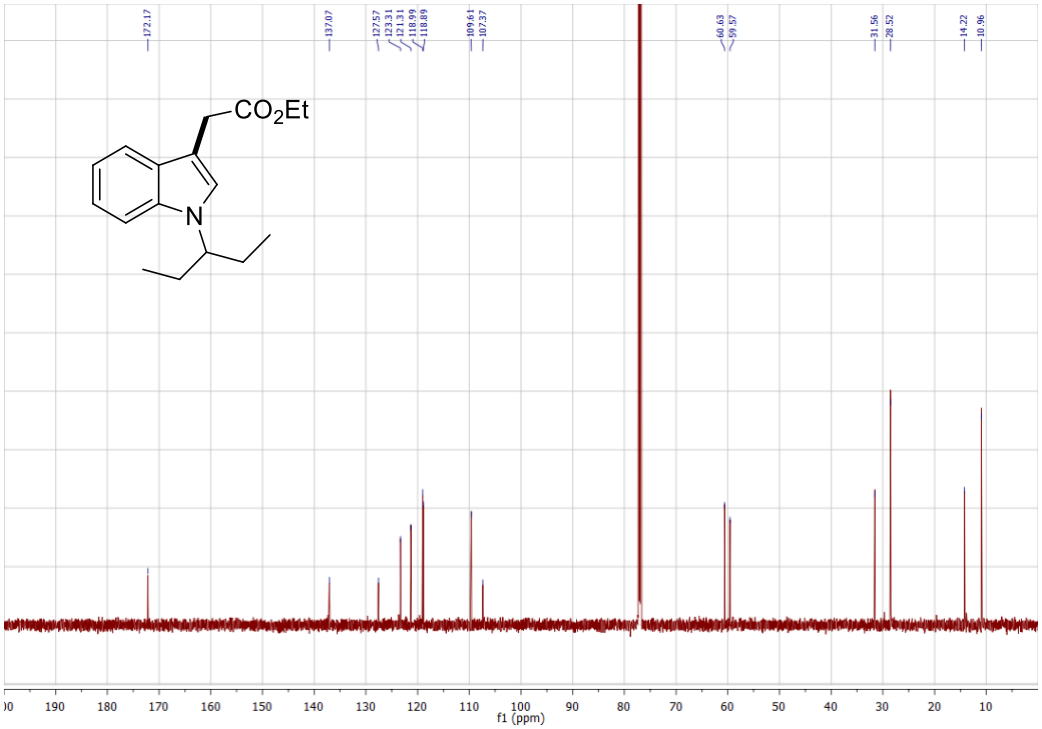


Figure S112. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13i**

Ethyl 2-(1-(4-(trifluoromethoxy)phenyl)-1*H*-indol-3-yl)acetate (13j)

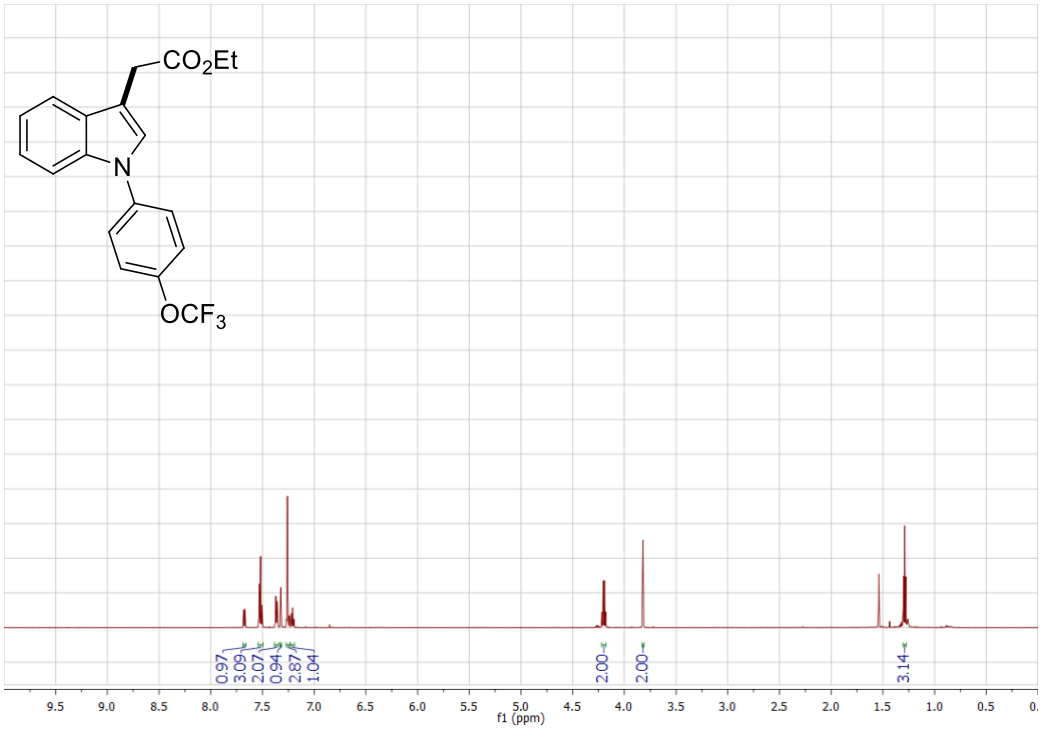


Figure S113. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13j**

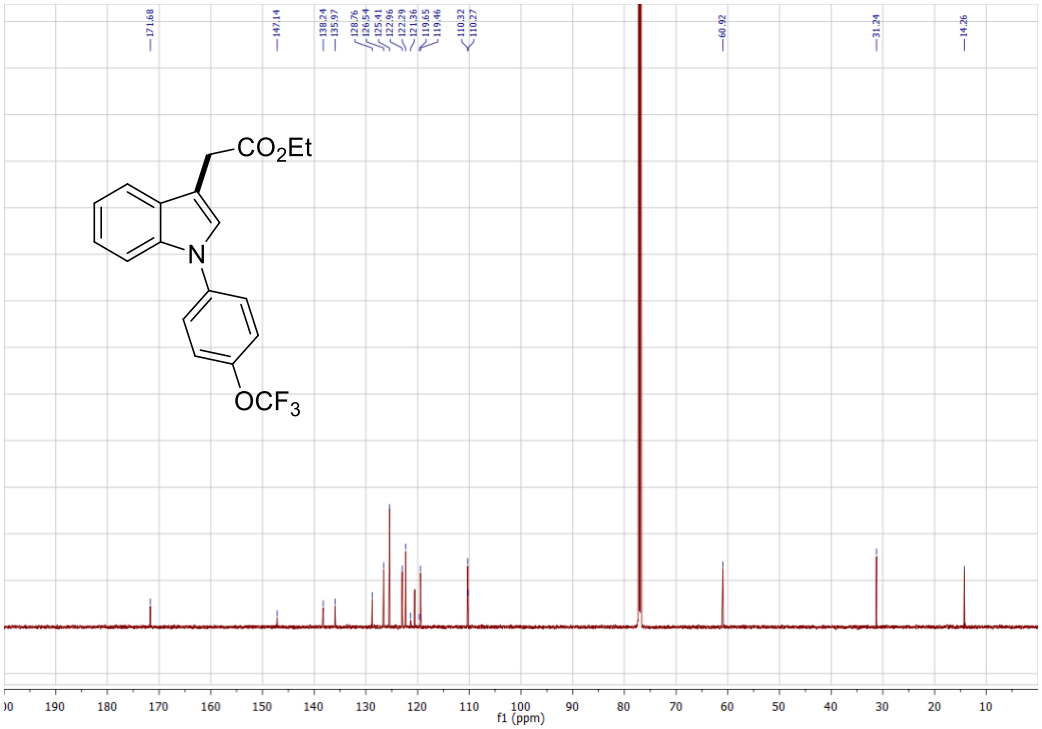


Figure S114. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13j**

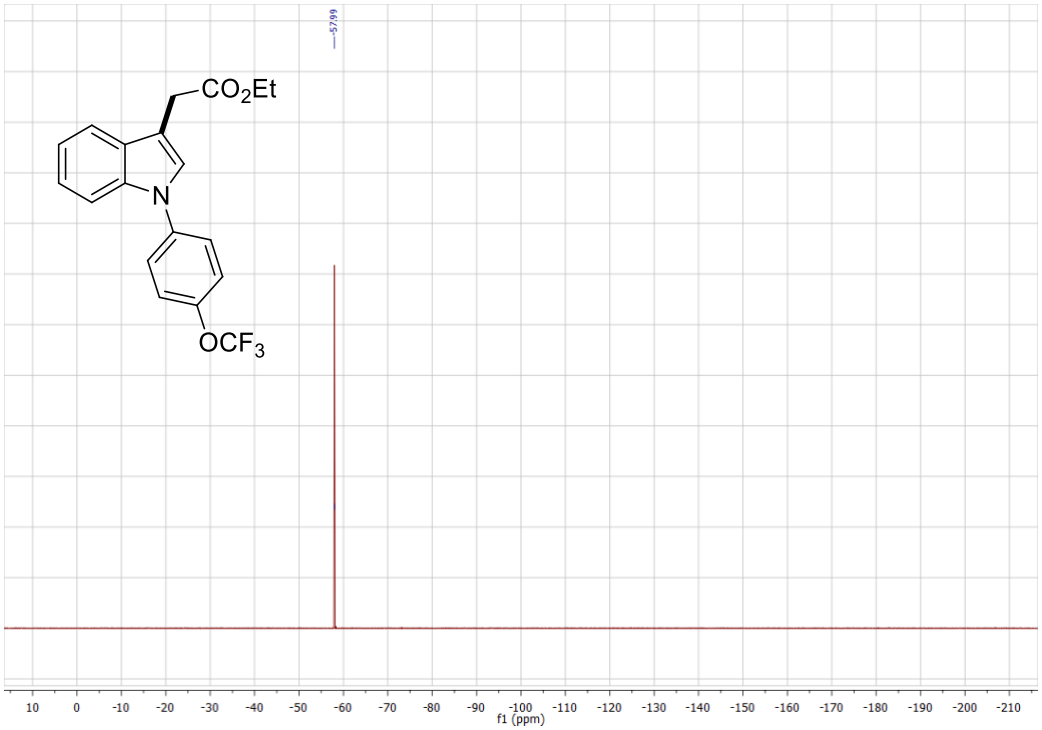


Figure S115. ^{19}F NMR (565 MHz, Chloroform-*d*) of **13j**

Ethyl 2-(1-(*m*-tolyl)-1*H*-indol-3-yl)acetate (13k)

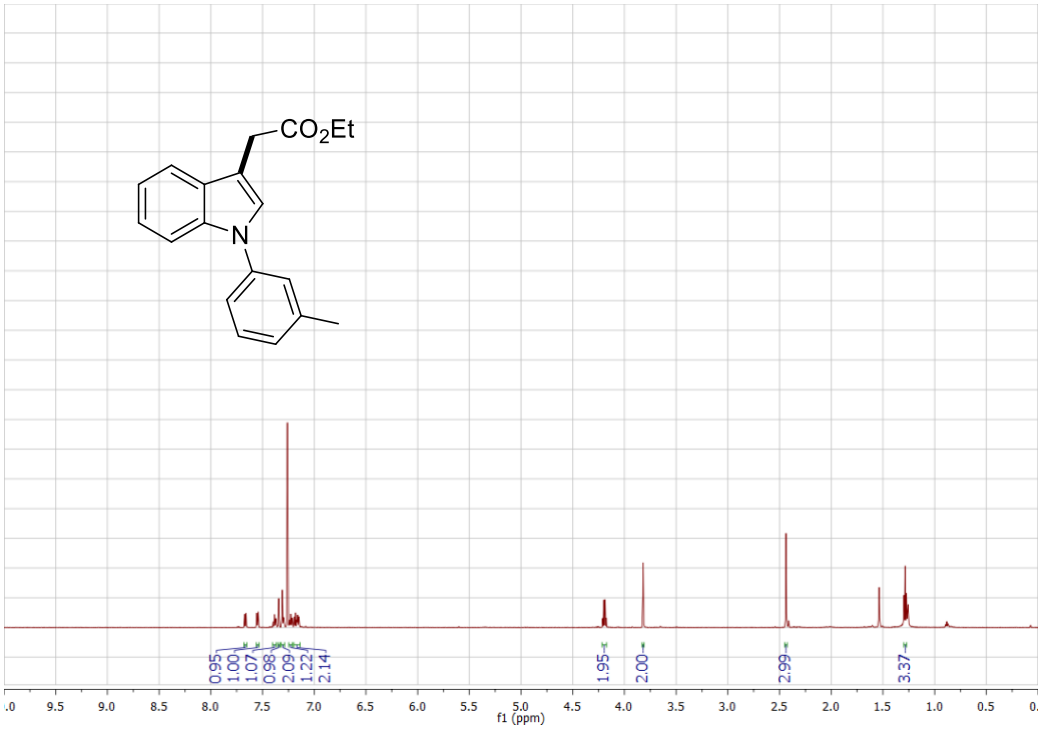


Figure S116. ^{1}H NMR (600 MHz, Chloroform-*d*) of **13k**

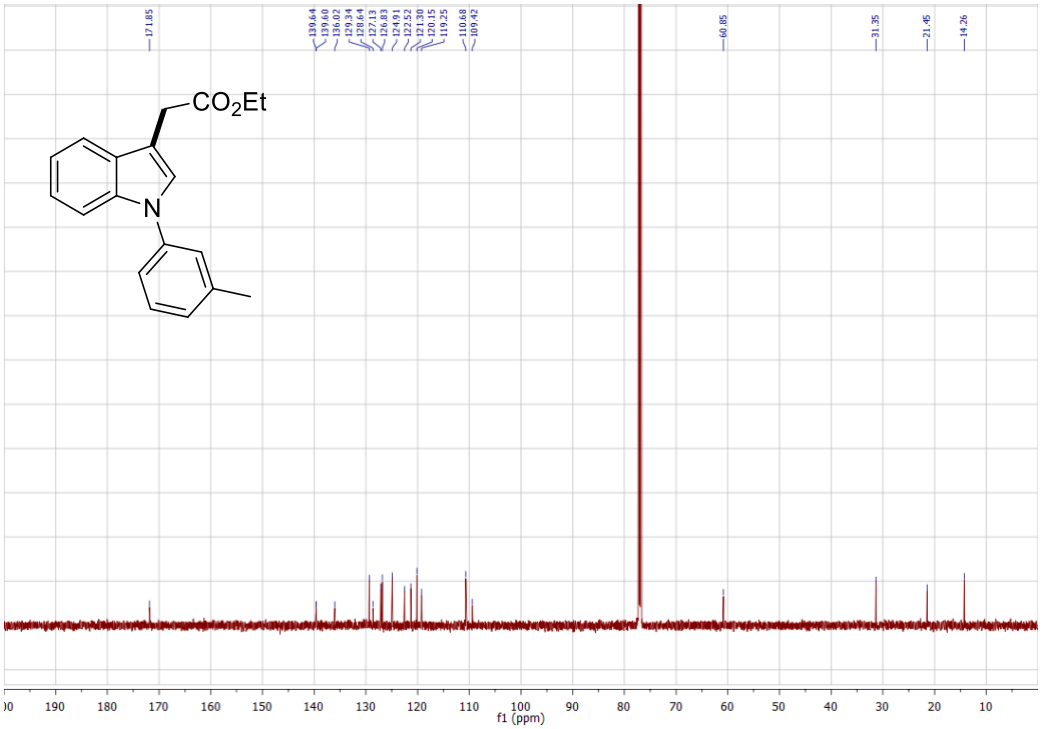


Figure S117. ^{13}C NMR (151 MHz, Chloroform-*d*) of **13k**

Ethyl 2-(1*H*-pyrrol-2-yl)acetate (14)

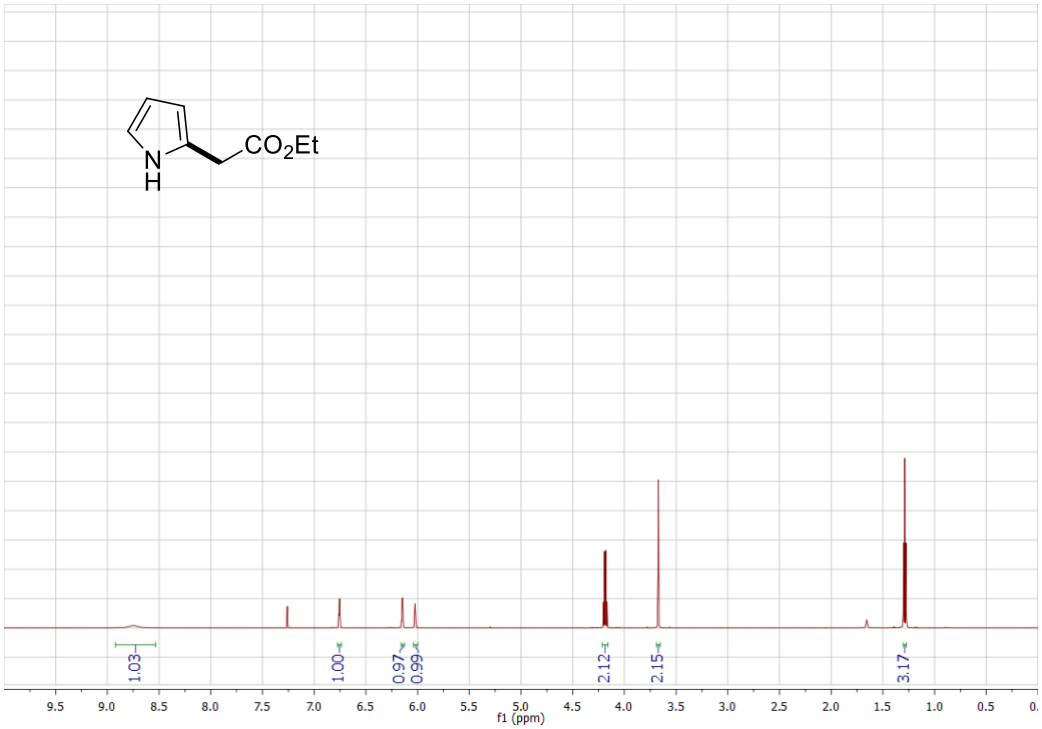


Figure S118. ^{1}H NMR (600 MHz, Chloroform-*d*) of **14**

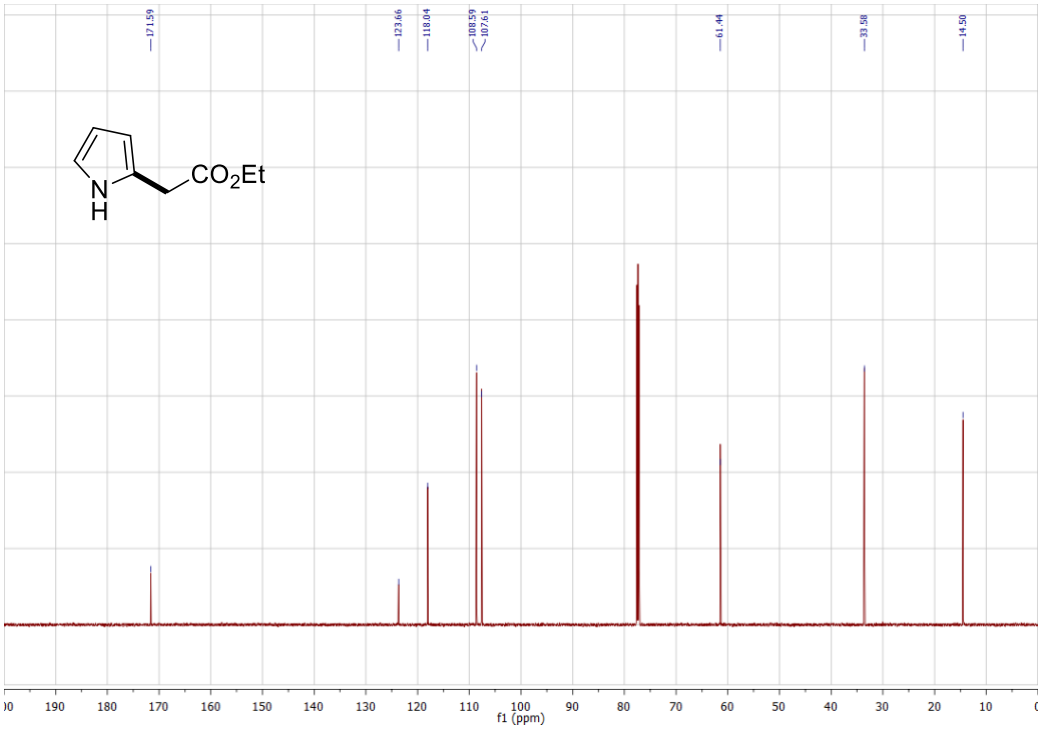


Figure S119. ^{13}C NMR (151 MHz, Chloroform-*d*) of **14**

Ethyl 2-(3,5-dimethyl-1*H*-pyrrol-2-yl)acetate (15)

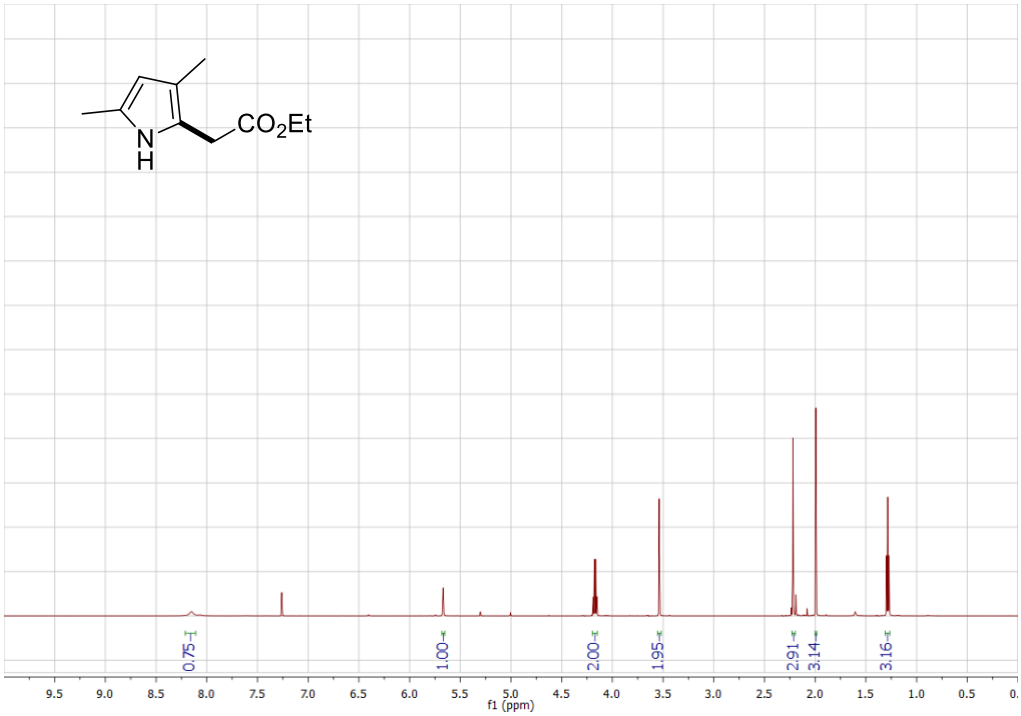


Figure S120. ^{1}H NMR (600 MHz, Chloroform-*d*) of **15**

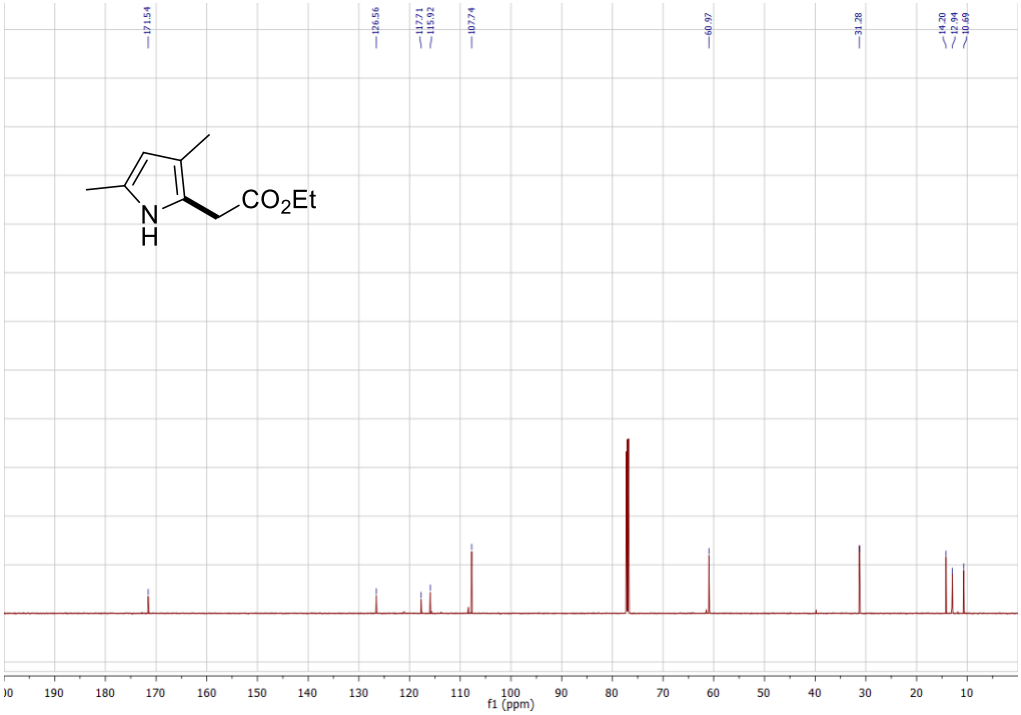


Figure S121. ^{13}C NMR (151 MHz, Chloroform-*d*) of **15**

Ethyl 2-(2,5-dimethyl-1*H*-pyrrol-3-yl)acetate (16)

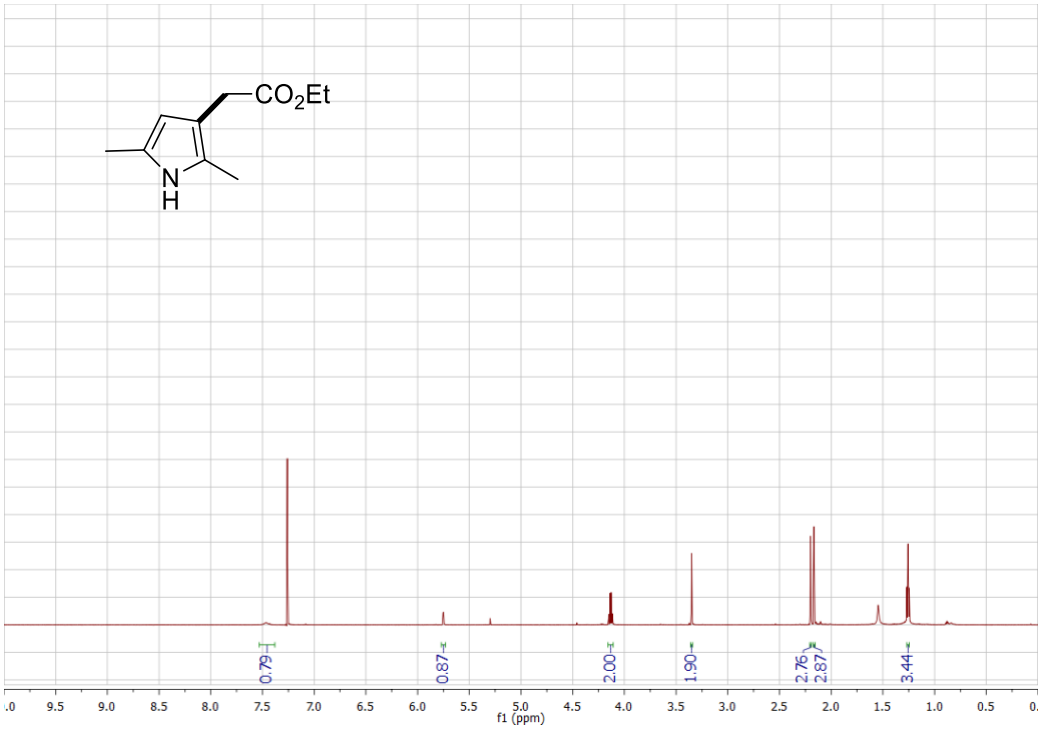


Figure S122. ^{1}H NMR (600 MHz, Chloroform-*d*) of **16**

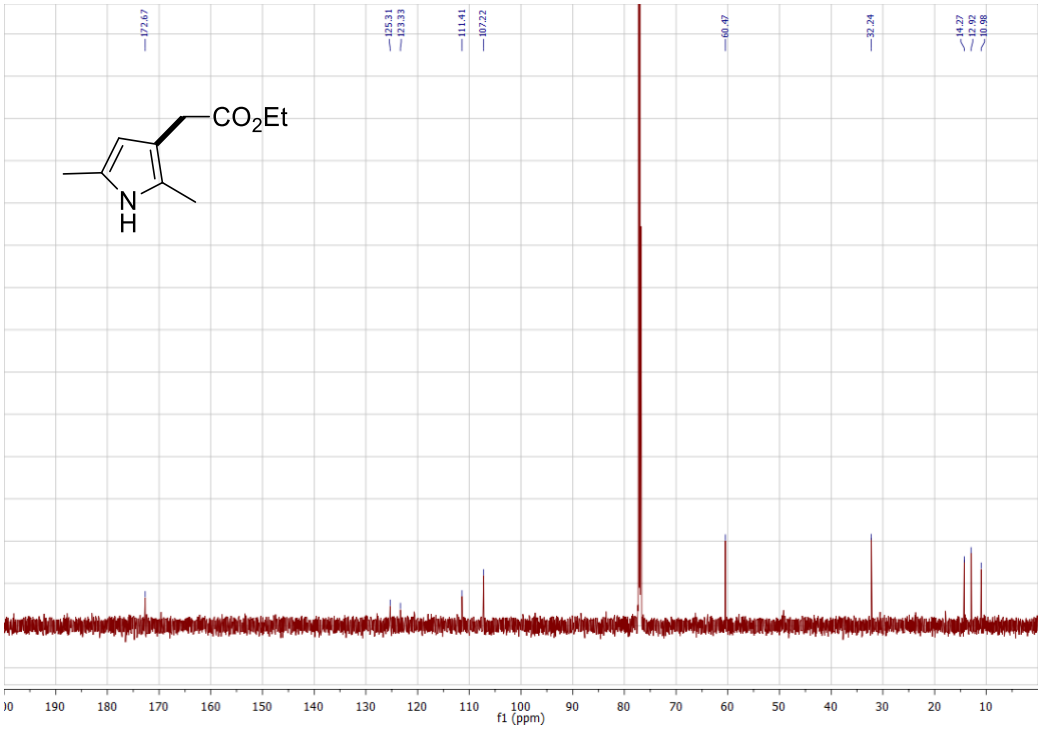


Figure S123. ^{13}C NMR (151 MHz, Chloroform-*d*) of **16**

2-(1*H*-Indol-3-yl)ethan-1-ol (17a)

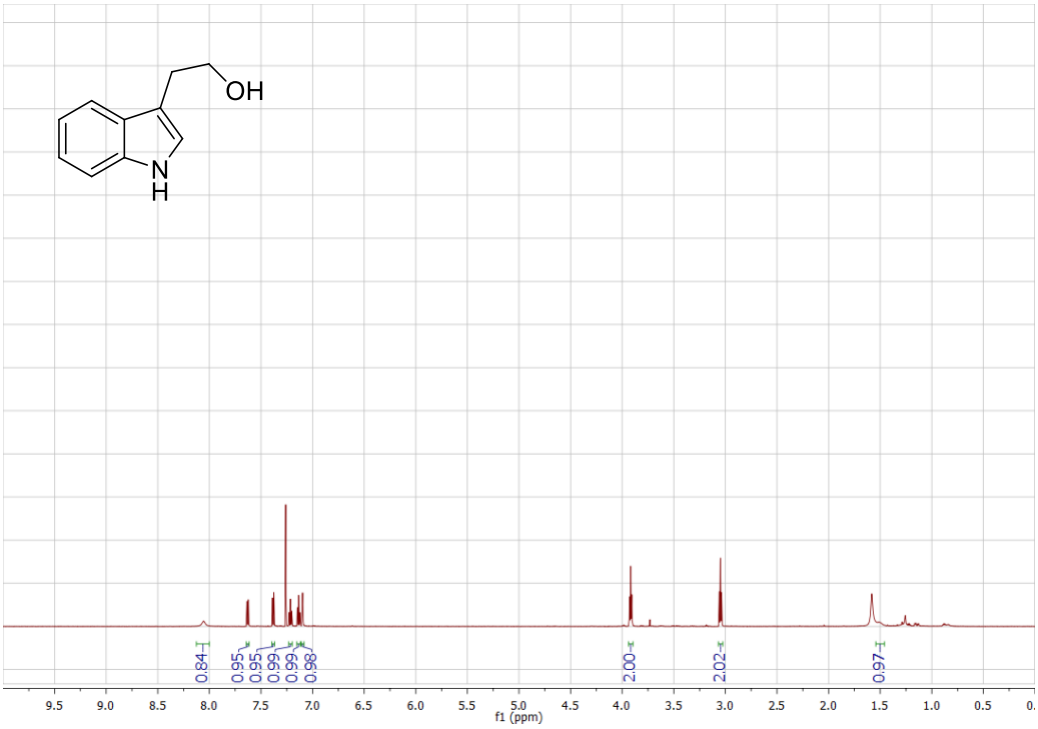


Figure S124. ^{1}H NMR (600 MHz, Chloroform-*d*) of **17a**

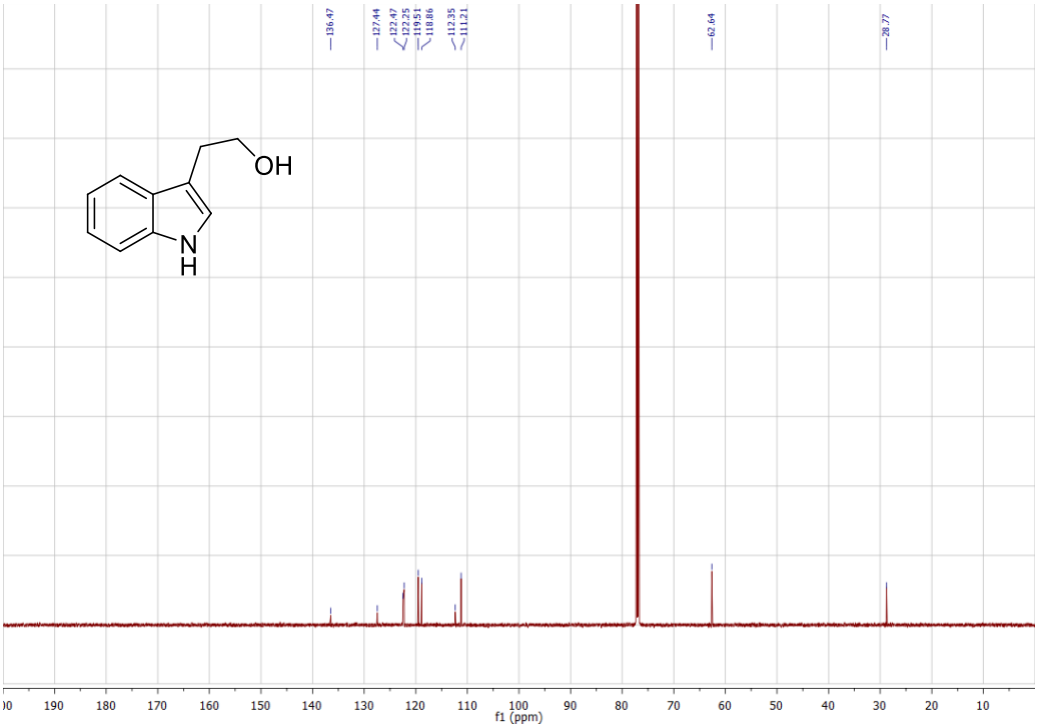


Figure S125. ^{13}C NMR (151 MHz, Chloroform-*d*) of **17a**

2-(1-Methyl-1*H*-indol-3-yl)ethan-1-ol (17b)

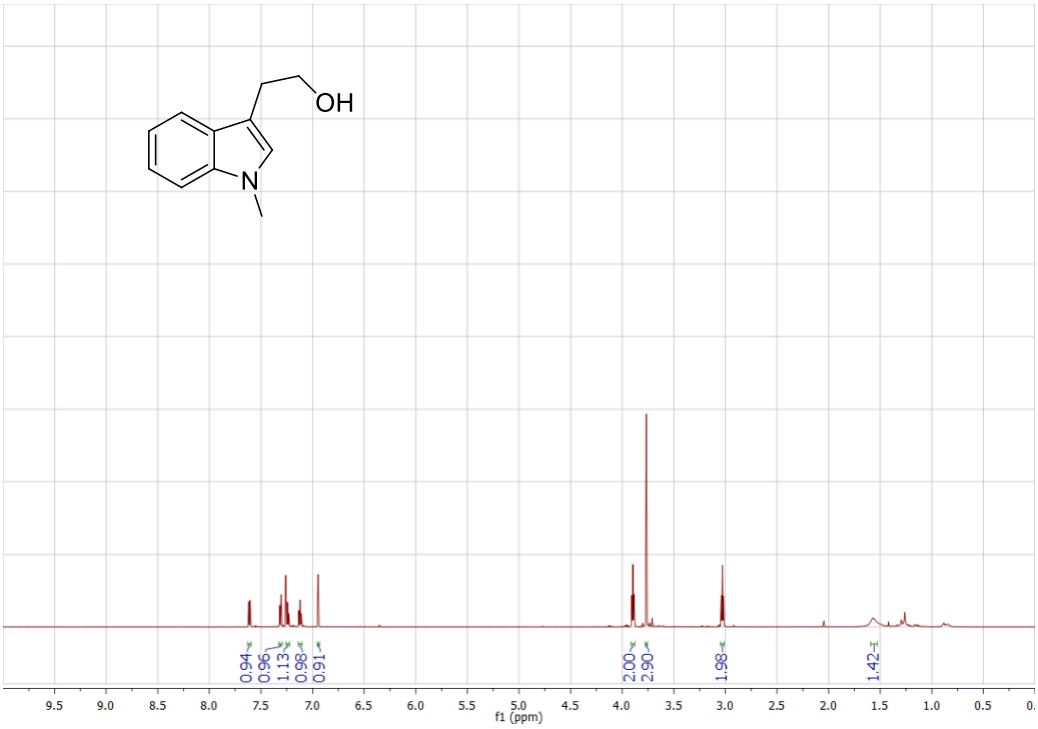


Figure S126. ^{1}H NMR (600 MHz, Chloroform-*d*) of **17b**

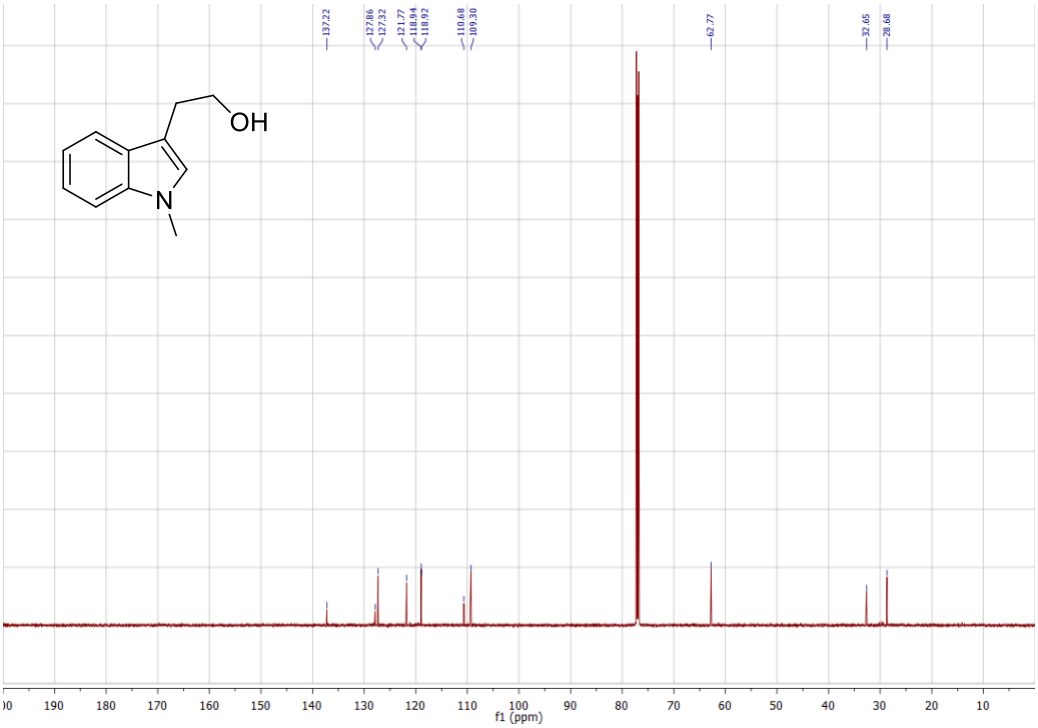


Figure S127. ^{1}H NMR (600 MHz, Chloroform-*d*) of **17b**

2-Benzhydryl-9-methyl-1-phenyl-9*H*-carbazole (19)

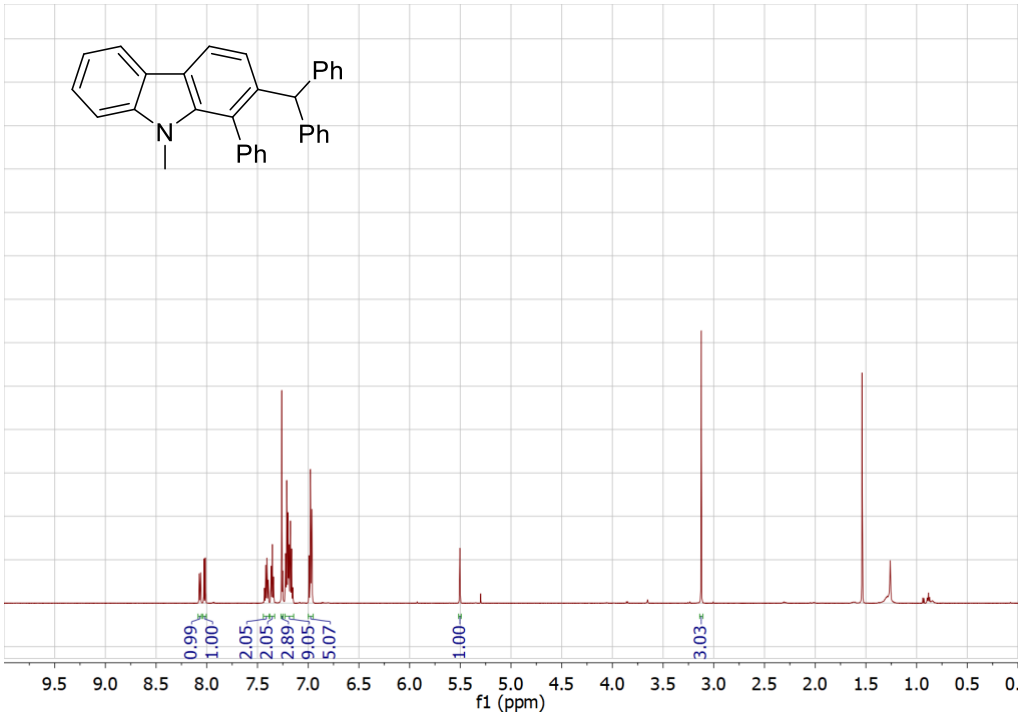


Figure S128. ^{1}H NMR (600 MHz, Chloroform-*d*) of **19**

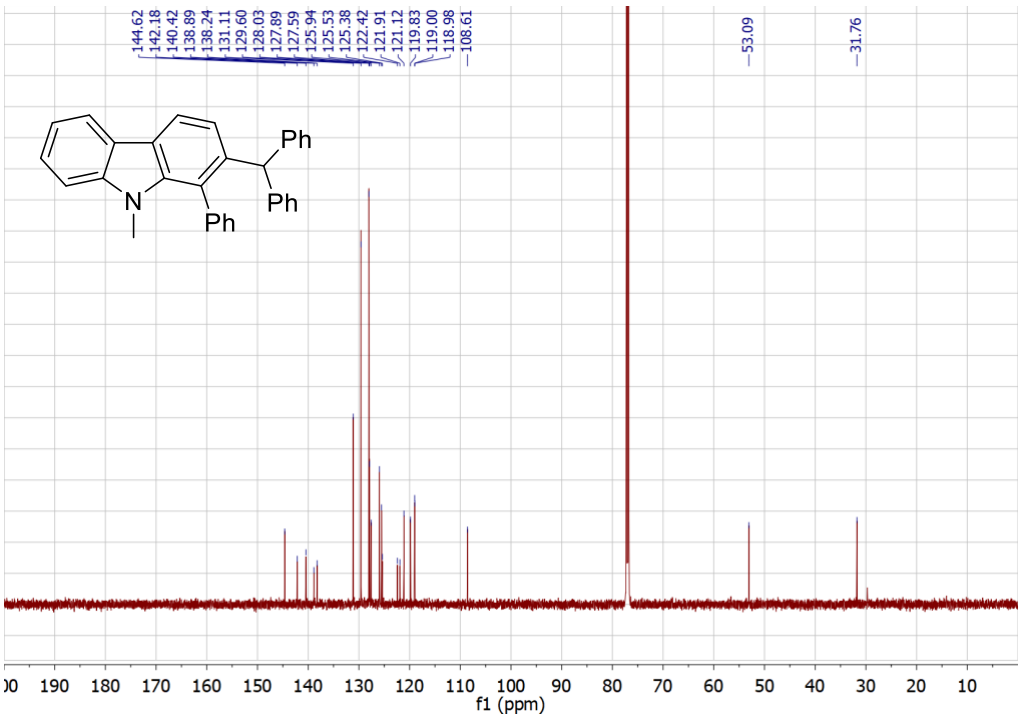


Figure S129. ^{1}H NMR (600 MHz, Chloroform-*d*) of **19**

3a-Azido-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (20)

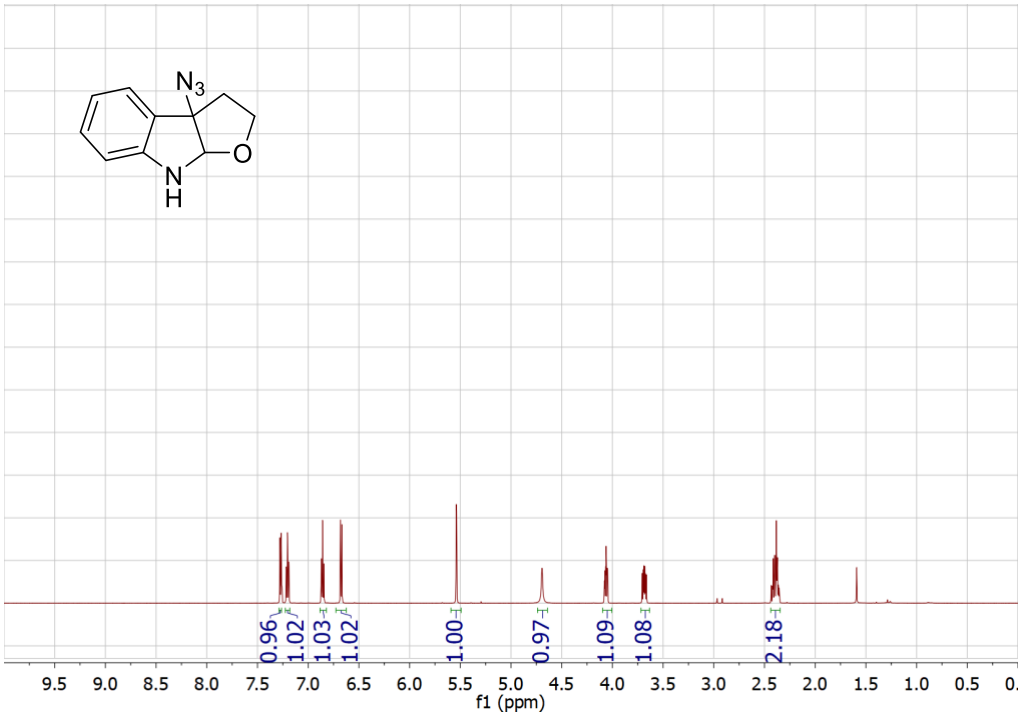


Figure S130. ^{1}H NMR (600 MHz, Chloroform-*d*) of **20**

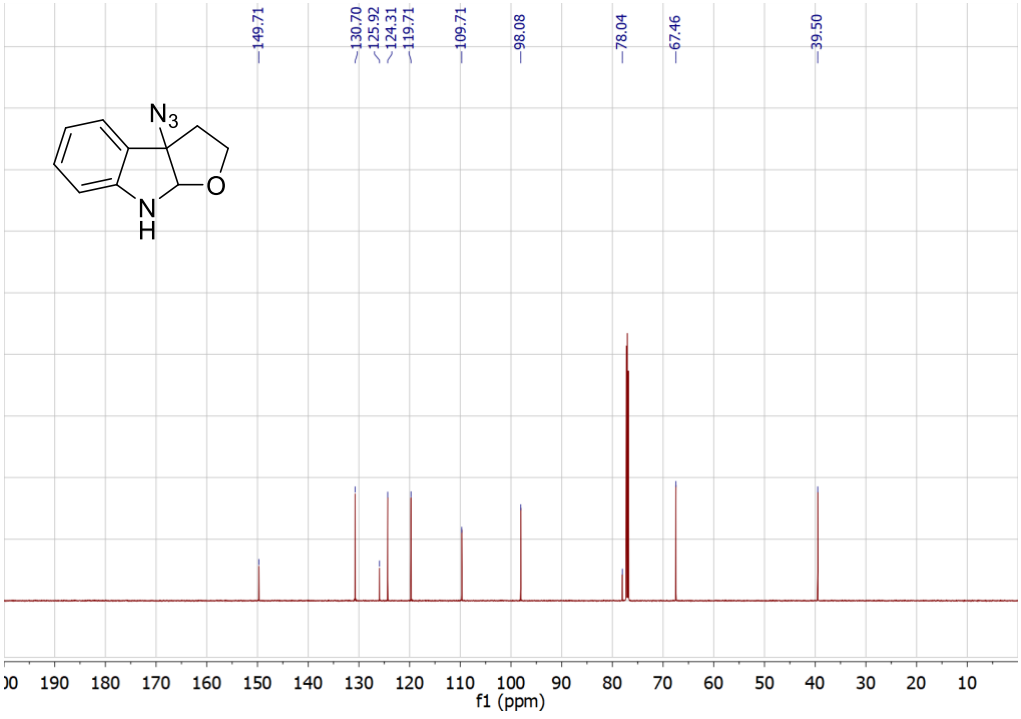


Figure S131. ^{1}H NMR (600 MHz, Chloroform-*d*) of **20**

References

1) Toma, T., Shimokawa, J., Fukuyama, T. (2007). *N,N'*-Ditosylhydrazine: a convenient reagent for facile synthesis of diazoacetates. Org. Lett. *9*, 3195-3197.
2) Shaw, M. H., Twilton, J., MacMillan, D. W. C. (2016). photoredox catalysis in organic chemistry. J. Org. Chem. *81*, 6898-6926.
3) a) Roth, H. G., Romero, N. A., Nicewicz, D. A. (2016). Experimental and calculated electrochemical potentials of common organic molecules for applications to single-electron redox chemistry. Synlett. *27*, 714-723. (b) Pavlishchuk, V. V., Addison, A. W. (2000). Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. Inorg. Chem. Acta. *298*, 97-102.
4) Ciszewski, Ł. W., Durka, J., Gryko, D. (2019). Photocatalytic alkylation of pyrroles and indoles with *α*-diazo esters. Org. Lett. *21*, 7028−7032.
5) Hoque, M. E., Hassan, M. M. M., Chattopadhyay, B. (2021). Remarkably efficient iridium catalysts for directed C(sp2)−H and C(sp3)−H borylation of diverse classes of substrates. J. Am. Chem. Soc. *143*, 5022-5037.
6) Maskeri, M. A., O'Connor, M. J., Jaworski, A. A., Bay, A. V., Scheidt, K. A. (2018). A cooperative hydrogen bond donor–brønsted acid system for the enantioselective synthesis of tetrahydropyrans. Angew. Chem. Int. Ed. *57*, 17225-17229.
7) Castro, L. C. M., Sultan, I., Nishi, K., Tsurugi, H., Mashima, K. (2021). Direct synthesis of indoles from azoarenes and ketones with bis(neopentylglycolato)diboron using 4,4′-bipyridyl as an organocatalyst. J. Org. Chem. *86*, 3287-3299.
8) Landstrom, E. B., Akporji, N., Lee, N. R., Gabriel, C. M., Braga, F. C., Lipshutz, B. H. (2020). One-pot synthesis of indoles and pyrazoles via Pd-catalyzed couplings/cyclizations enabled by aqueous micellar catalysis. Org. Lett. *22*, 6543-6546.
9) McKew, J. C., Foley, M. A., Thakker, P., Behnke, M. L., Lovering, F. E., Sum, F. -W., Tam, S., Wu, K., Shen, M. W. H., Zhang, W., Gonzalez, M., Liu, S., Mahadevan, A., Sard, H., Khor, S. P., Clark, J. D. (2006). Inhibition of Cytosolic Phospholipase A_2α: Hit to Lead Optimization. J. Med. Chem. *49*, 135-158.
10) Pagire, S. K., Reiser, O. (2017). Tandem cyclisation of vinyl radicals: a sustainable approach to indolines utilizing visible-light photoredox catalysis. Green Chem. *19*, 1721-1725.

11) Lee, S. J., Seo, H. -A., Cheon, C. -H. (2016). Synthesis of 2-aryl-substituted indole-3-acetic acid derivatives via intramolecular imino-stetter reaction of aldimines with cyanide. Adv. Synth. Catal. *358*, 1566–1570.

12) Nag, E., Gorantla, S. M. N. V. T., Arumugam, S., Kulkarni, A., Mondal, K. C., Roy, S. (2020). Tridentate nickel(II)-catalyzed chemodivergent C−H functionalization and cyclopropanation: regioselective and diastereoselective access to substituted aromatic heterocycles. Org. Lett. *22*, 6313−6318.

13) Chen, W., Gaisina, I. N., Gunosewoyo, H., Malekiani, S. A., Hanania, T., Kozikowski, A. P. (2011). Structure-guided design of a highly selective glycogen synthase kinase-3β inhibitor: a superior neuroprotective pyrazolone showing antimania effects. ChemMedChem *6*, 1587-1592.

14) Sarkar, M., Daw, P., Ghatak, T., Bera, J. K. (2014). Amide-functionalized naphthyridines on a Rh^{II}–Rh^{II} platform: effect of steric crowding, hemilability, and hydrogen-bonding interactions on the structural diversity and catalytic activity of dirhodium(II) complexes. Chem. Eur. J. *20*, 16537-16549.

15) DiPoto, M. C., Hughes, R. P., Wu, J. (2015). Dearomative indole (3 + 2) reactions with azaoxyallyl cations − new method for the synthesis of pyrroloindolines. J. Am. Chem. Soc. *137***,** 14861-14864.

16) Rodríguez, A. M., Molina, F., Díaz-Requejo, M. M., Pérez, P. J. (2020). Copper-catalyzed selective pyrrole functionalization by carbene transfer reaction. Adv. Synth. Catal. *362,* 1998-2004.

17) Levy, D. E., Wang, D. -X., Lu, Q., Chen, Z., Perumattam, J., Xu, Y. -J., Liclican, A., Higaki, J., Dong, H., Laney, M., Mavunkel, B., Dugar, S. (2008). Aryl–indolyl maleimides as inhibitors of CaMKIIδ. Part 1: SAR of the aryl region. Bioorg. Med. Chem. Lett. *18*, 2390-2394.

18) Bettoni, L., Gaillard, S., Renaud, J. -L. (2019). Iron-Catalyzed *β*-Alkylation of Alcohols. Org. Lett. *21*, 8404-8408.

19) Reddy, B. V. S., Babu, R. A., Reddy, B. J. M., Sridhar, B., Murthy, T. R., Pranathi, P., Kalivendic, S. V., Rao, T. P. (2015). A short and highly convergent approach for the synthesis of rutaecarpine derivatives. RSC Adv*. 5,* 27476-27480.

20) Huang, K., Sheng, G., Lu, P., Wang, Y. (2017). BF_3-promoted divergent reactions between tryptophols and propargylic alcohols. Org. Lett. *19*, 4114−4117.

21) Zhang, P., Sun, W., Li, G., Hong, L., Wang, R. (2015). Copper-catalyzed cascade azidation–cyclization of tryptophols and tryptamines. Chem. Commun. *51*, 12293-12296.